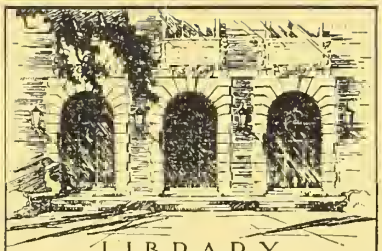


[redacted]

TABLE OF CONTENTS

1961-1962

THE BASICITY AND NUCLEOPHILICITY OF THE PHOSPHINES

D. P. Eyman September 19, 1961

I. INTRODUCTION

A base may be defined either as a proton acceptor or more generally in the Lewis concept as an electron-pair donor (1). Accordingly, a Lewis acid is an electron pair acceptor. Therefore, polar, ionic, or electron-sharing reaction may be regarded as acid-base processes.

By the convention of Swain and Scott (2), the terms nucleophilicity and electrophilicity are used in connection with the rates of polar reactions and the terms acidity and basicity are used with equilibria. For instance, the fact that the reaction

$$B^{1} + AB \rightarrow B^{1}A + B \qquad (1)$$

has a higher rate constant (in a given solvent at a given temperature) than the reaction

$$B^{11} + AB \rightarrow B^{11}A + B \qquad (2)$$

will be denoted by the statement that B^{1} is more nucleophilic than B^{11} toward AB in a given solvent at a given temperature. On the other hand, the fact that the equilibrium is further to the right in the latter reaction will be signified by stating that B^{11} is more basic that B^{1} toward AB in a given solvent at a given temperature.

II. METHODS OF INVESTIGATING ACID-BASE INTERACTIONS

To compare effectively the basicities of several Lewis bases, one must find a convenient parameter which can be correlated with the fundamental manifestation of basicity - the energy released when an acid and base combine. The strength of the acid-base bond is most satisfactorily defined as the enthalpy change, ΔH, accompanying the gas-phase dissociation of the complex (3). A knowledge of how the degree of dissociation varies with the temperature permits the calculation of this thermodynamic function, ΔH, and also ΔF and ΔS.

The gas-phase dissociation technique is limited because it cannot be used on complexes which are either too stable or too unstable. For these two classes of complexes it is possible to determine the stability by calorimetry.

Relative bond strengths have also been established by displacement reactions. However, since a displacement reaction depends on differences in free energy between products and reactants, entropy effects can conceivably determine the results.

Saturation pressures have been used to give a qualitative measure of the bond strength. As a general rule for two addition compounds of similar types and molecular weight the less stable exhibits the higher saturation pressure (4,5).

III. THE BASICITY OF THE PHOSPHINES

Studies of the non-aqueous tetrimetry of the amines and phosphine in nonprotolytic organic solvents have led to the conclusion that to a first approximation $pK_a(H_2O)$ values are a good index of the basicity of these compounds in other solvents. Furthermore, it was found that a correlation between $pK_a(H_2O)$ and HNP [half neutralization potential] in a given solvent permitted the calculation of $pKa(H_2O)$ without placing the bases into water (6,7,8). This correlation has been used to determine $pKa(H_2O)$ values for a large number of substituted phosphines. The results are presented in Table I. These $pKa(H_2O)$ values indicate that in general tertiary phosphines are stronger bases than secondary phosphines, which in turn are stronger bases than primary phosphines.

Several attempts have been made to develop a correlation between the structures of the phosphines and their basicities(9,10,11) but none has been as successful as the comprehensive correlation demonstrated by Hall (12) and Henderson and Streuli (13). These workers found the Hammet and Taft equations (14) [e.g. $\log k/ko = \sigma \rho$ or $\sigma^* \rho^*$] to be useful in correlating $pKa(H_2O)$ and structure for the substituted phosphines. A plot of $pKa(H_2O)$ vs. $\Sigma\sigma^*$ for a given phosphine gave three parallel lines representing tertiary, secondary, and primary phosphines. Attempts at explaining certain anomolies have involved consideration of rehybridization energies, steric requirements, and π bonding (13,15). However, probably the most consistent explanations involve applications of the solvation theory (12,16).

IV. THE NUCLEOPHILICITY OF THE PHOSPHINES

It has long been recognized that for a given nucleophilic atom nucleophilicity is fairly well correlated with the basicity of the nucleophilic agent (17). However, other factors such as steric effects and solvation energies must be considered.

Reaction rate is often discussed in terms of the increase in free energy required to reach the activated state, and in all cases the rate is governed by the free energy contents of the intermediate configuration through which the reactants must pass in their transformation to products. Hammond (18) has shown how one can predict qualitatively when a relationship between rate and overall free energy change should exist and how the effect of a substituent on the rate of a chemical reaction can be estimated.

Henderson and Buckler (19) conducted a broad investigation of the nucleophilicities of the substituted phosphines in an attempt to correlate structural properties and basicities with nucleophilicities. The rate of the SN2 attack on an alkyl halide by a substituted phosphine was used as the criterion for nucleophilicity. It was found that the effects of substituents in the phosphine on the rate of the quaternization reaction is best discussed in terms of a Taft plot [e.g. $\log k$ vs $\Sigma\sigma^*$]. The results [Table I] indicated that the rate is very sensitive to change in

phosphine substituents and that the Taft plot is indeed linear for those phosphines of low or moderate steric requirements. It was found that all phosphines containing the methyl group deviated greatly from the Taft plot line. Attempts at explaining the deviations from predicted values involved consideration of steric, conjugative, and rehybridization effects.

An increase in the rate of quaternization upon going to more polar solvents was attributed to a decrease in the activation energy resulting from the greater solvation of the relatively polar transition state.

V. CONCLUSIONS

The structures and basicities of the tertiary and secondary phosphines have been correlated successfully by the use of the Taft equation. Correlation between the structures and the nucleophilicities of the tertiary phosphines has been demonstrated also by the use of the Taft equation, but only for those tertiary phosphines having low or moderate steric requirements.

Table I (8,13,19)

pKa(H_2O) Values and Quaternization Rates For Substituted Phosphines

$$RR'R''P + C_2H_5I \xrightarrow[(CH_3)_2CO\ 35^\circ]{k_2} RR'R''C_2H_5P^{\oplus} + I^{\ominus}$$

Phosphine	△HNP	pKa(H_2O)calc.	$\sum\sigma^*$	k_2 (l.mole^{-1}sec.$^{-1}$)
$(CH_3)_3P$	114	8.65	0.000	$2.24 \pm 1.86 \times 10^{-3}$
$C_2H_5P(CH_3)_2$	117	8.61	-0.100	$8.05 \pm 0.30 \times 10^{-3}$
$(C_2H_5)_2PCH_3$	117	8.61	-0.200	$4.29 \pm 0.04 \times 10^{-3}$
$(C_2H_5)_3P$	111	8.69	-0.300	$1.54 \pm 0.05 \times 10^{-3}$
$(n-C_3H_7)_3P$	115	8.64	-0.345	$1.36 \pm 0.04 \times 10^{-3}$
$(n-C_4H_9)_3P$	131	8.43	-0.390	$1.62 \pm 0.05 \times 10^{-3}$
$(2-C_4H_9)_3P$	167	7.97	-0.375	$1.38 +\_ 0.01 \times 10^{-4}$
$(n-C_5H_{11})_3P$	139	8.33	-0.390	$1.58 \pm 0.04 \times 10^{-3}$
$(CNCH_3CH_2)_3P$	679	1.37	+2.400	$6.37 \pm 0.05 \times 10^{-6}$
$C_6H_5P(CH_3)_2$	281	6.50	+0.600	$7.60 \pm 0.11 \times 10^{-4}$
$C_6H_5P(C_2H_5)_4$	300	6.25	+0.400	$4.75 \pm 0.05 \times 10^{-4}$
$(C_6H_5)_3P$	573	2.73	+1.800	$3.78 \pm 0.02 \times 10^{-5}$
$(n-C_4H_9)_2PH$	435	4.51	+0.230	$8.75 \pm 0.08 \times 10^{-5}$
$(2-C_4H_9)_2PH$	466	4.11	+0.240	$3.83 \pm 0.07 \times 10^{-5}$

Bibliography

1. Lewis, G.N., *Valence and the Structure of Atoms and Molecules*, p. 142, The Chem. Catalog Co (1926).
2. Swain, C.G., and Scott, C. B., J. Am. Chem. Soc., 75, 141 (1953).
3. Stone, F. G. A., Chem. Revs., 58, 1 (1958).
4. Graham, W.G.A., and Stone, F.G.A., J. Inorg. Nuclear Chem., 3, 164(1956).
5. Amriano, S., Chatt, J., and Davies, N.R., Quart. Revs., 12, 265(19
6. Hall, M.K., J. Phys. Chem., 60, 63 (1956).
7. Streuli, C.A., Anal. Chem., 31, 1652 (1959).
8. *op. cit.*, 32, 985 (1960).
9. Brown, M. C., J. Am. Chem. Soc., 67, 503 (1945).
10. Brown, M. C., Record Chem. Progress, Kresge-Hooker Sci. Lib., 14, 83(1953).
11. Kaesz, M.D., and Stone, F.G.A., Abstracts of Papers, 135th Meeting American Chemical Society, p. G. 35, April 5, 1959.
12. Hall, M.K., Jr., J. Am. Chem. Soc., 79, 5441 (1957).
13. Henderson, W.A. Jr., and Streuli, C.A., J. Am.Chem.Soc., 82, 5791 (1960).
14. Taft, R.W., Jr., in Steric Effects in Organic Chemistry, John Wiley and Sons (1956), Ch. 13; M.S. Newman, Ed.
15. Gibbs, J. M., J. Chem. Phys., 22, 1460 (1954).
16. Trotman-Dickenson, A.F., J. Chem.Soc., 1293 (1949).
17. Hine, J., Physical Organic Chemistry, p. 138, McGraw-Hill Book Co. (1956).
18. Hammond, G.S., J. Am. Chem. Soc., 77, 339 (1958).
19. Henderson, W.A.Jr., and Buckler, S.A., J.Am.Chem.Soc., 82, 5794 (1960).

CHEMICAL ASPECTS OF SELECTED GEOLOGICAL AGE DETERMINATIONS

David L. Lydy September 26, 1961

All age measurements by radioactive methods depend upon the slow decay of a radioactive parent element to a stable daughter element either directly or in a radioactive chain. The age determined in this manner refers to the time that has elapsed since final solidification or crystallization of the rock or mineral containing the radioactive element. (1)

LEAD METHODS

A. Crude Uranium-lead Method

Early age determinations were made by the so-called "crude" uranium-lead method which utilized the ratio of total lead to uranium plus thorium in the mineral. With the introduction of mass spectrographic methods (2-4), several parent:daughter ratios became available which could be used for age determinations. These various ratios will be considered in the following sections of this seminar.

B. Isotopic-lead Method

There are three independent decay processes going on in a mineral containing uranium and thorium, namely those series involving decay of uranium-238 to lead-206, uranium-235 to lead-207, and thorium-232 to lead-208. The measurement of geologic time by the isotopic-lead method is based on the accumulation of these three radiogenic lead isotopes in the mineral to be dated. (5) The three decay series are in equilibrium after a period of 10^6 years for the uranium family, 10^5 years for the actinium family, and 10^2 years for the thorium family. (6-8) Uranium (9-11), thorium (9,11,12), and lead (9,11) concentrations may be determined by isotope dilution techniques.

The principal equation for the isotopic-lead method may be derived as follows: In general, the number of atoms, N_{Pb}, of a lead isotope accumulated in a time, t, is

$$N_{Pb} = N_0 - N_t$$

where N_0 and N_t are the numbers of atoms of the parent element present at a time $t = 0$ and t, respectively. Substitution into the fundamental equation of radioactive decay gives (13)

$$N_{Pb} = N_t(e^{\lambda t} - 1)$$

from which the standard isotopic-lead equation

$$t = \frac{1}{\lambda} \ln\left(\frac{N_{Pb}}{N_t} + 1\right)$$

can be derived.

When measuring ages by means of this equation, several basic requirements must be fulfilled: (12-17)

1. Established decay scheme and known rate of decay of parent element
2. Equilibrium established in mineral under investigation
3. Sampling representative of mineral or rock
4. Accurate analytical measurement
5. No lead present initially, unless an appropriate index is available to determine the concentration of initial lead
6. Parent element content changed only by its decay
7. No loss or gain of end products or intermediate precursors except by radioactive processes.

If all of these conditions are satisfied, the three independent isotopic ages which are determined by the ratios 206/238, 207/235, and 208/232 will agree within the limits of analytical errors. When any two of the isotopic ages fail to agree, it is obvious that at least one of these assumptions has been violated. We will now consider some of the possible causes of age discrepancies.

Almost all isotopic-lead age determinations must include a correction for the presence of common lead in the sample.(18) Common lead is a mixture of four stable isotopes having mass numbers 204, 206, 207, and 208. The last three of these are identical with the lead isotopes produced as the stable end products in the radioactive decays of uranium and thorium. (19,20) Lead-204, however, is not known to be produced by any natural process; so its abundance in a mineral can serve as an index for the amount of common lead present. (8,18-20)

Radioactive minerals are particularly susceptible to leaching and oxidation. Microscopic examination has shown that they are invariably intensely shattered. Ellsworth (21) observed that the degree of shattering increases with the uranium and thorium content, and that the rock matrix surrounding the radioactive minerals is likely to be penetrated by fractures which radiate in all directions from the radioactive source. These fractures afford openings through which solutions may enter and dissolve portions of the mineral.

Tilton (10,15,22) conducted leaching experiments on powdered samples for which the isotopic ages had been determined. He was able to show that there is a correlation between the isotopic composition of the lead removed by dilute acid treatment and the observed age of the mineral. Low thorium-lead ages were accompanied by excess solubilities of radiogenic lead-208 and thorium, whereas high uranium-lead ages were accompanied by excess solubilities of radiogenic lead-206 and uranium. The measured age was too low or too high depending upon whether the loss of the parent or daughter element predominated. These observations indicate that the transfers of material, which are the cause of lead age discrepancies, involve both parent and daughter elements.

Kuroda (23) presented evidence in his work on the isotopic composition of radium in uranium ores that fractionations of intermediate daughters may also occur in the uranium decay series.

All three of the decay chains which produce lead pass through an intermediate daughter product which is gaseous, chemically inert and capable of escape. The half-lives, and correspondingly the opportunity to escape, of these gaseous intermediates are very different. Radon, which comes from uranium-238, has a half-life of about 3.82 days; whereas thoron, from thorium-232, has a half-life of 51.5 seconds; and actinon, from uranium-235, has a half-life of only 3.92 seconds. (25) The longer half-life of radon results in a greater possibility of escape from the source mineral(20)

Radon leakage has been observed to increase with temperature, indicative of a gaseous diffusion process. The increase in leakage is largely due to the increase in the diffusion coefficient with temperature, although the partial pressure of radon may also contribute. (26)

Holmes (24) published an example of a monazite which appeared to have a low thorium-lead age and which gave no detectable radon leakage, but gave a one per cent thorium leakage.

In a strongly acidic environment, Phair and Levine (27) have shown that uranium is leached preferentially to lead.

All of these investigations illustrate the complex behavior of the various members of the uranium and thorium decay series with regard to alteration within the mineral.

C. Lead-lead Method

This method is time sensitive because of the differing half-lives of the respective parents. (28) The age equation for this method is

$$\frac{Pb^{207}}{Pb^{206}} = \frac{U^{235}}{U^{238}} \frac{(e^{\lambda_1 t} - 1)}{(e^{\lambda_2 t} - 1)}$$

where the chemical symbols indicate the number of atoms of each isotope, λ_1 and λ_2 are the decay constants for uranium-235 and uranium-238, respectively, and t is the age. (17) Wickman (29) has prepared graphs for determining the age from a known lead-lead ratio.

Age determinations based on this method are convenient because no chemical analyses are required. A correction for the presence of common lead may be made on the basis of the lead isotope 204.(5,18)

Leaching of lead or uranium from a mineral generally does not seriously affect the ages obtained by this method, but a small loss of radon makes this age very high. (5,7,26)

D. Lead-210 Method

Measurement of the ratio of the quantity of lead-206 to the quantity of lead-210 contained in a uranium mineral provides a method of determining the age. (17,30) Unfortunately, this method is subject to similar errors as the lead-uranium and lead-lead methods, owing to loss of constituents of the radioactive series by leaching or emanation. (7,8,26,31)

POTASSIUM-ARGON METHOD (32)

Potassium contains the naturally radioactive isotope potassium-40, which decays to calcium-40 and argon-40. To measure the age of a potassium containing mineral, it is necessary to determine either the amount of radiogenic calcium-40 or radiogenic argon-40 contained in the mineral. A potassium-calcium dating technique has not been perfected due to the prevalence of normal or non-radiogenic calcium-40 in virtually all potassium-bearing minerals. Owing to the inert nature of argon, the normal or nonradiogenic content of argon-40 in minerals is very low and therefore more easily determined. (33,34)

Potassium-argon ages are calculated from the formula (34-37)

$$t = \frac{1}{(1 + R)\lambda\beta} \ln\left[1 + \frac{A^{40}(R + 1)}{K^{40}\ (R)}\right]$$

where argon-40/ potassium-40 is the ratio of the number of radiogenic argon-40 atoms to the number of radiogenic potassium-40 atoms now present in the sample; R is the branching ratio, which is the ratio $\lambda e/\lambda\beta$; and t is the age. Because of the dual decay process, it is necessary to stipulate two decay constants in order to describe the decay scheme completely. The decay constant λe is for the decay of potassium-40 to argon-40 by electron capture, and $\lambda\beta$ is the decay constant for the decay of potassium-40 to calcium-40 by electron emission. (32,38)

In general, the gases present in the mineral, including argon, are extracted from it by fusion, with (11,39-42) or without (43,44) flux, in a high-vacuum system. The gas is then either purified (42,45) and the volume determined with a McLeod gauge (43), or a known volume of tracer argon-38 is added (11,39-42,44,46) to the unpurified gas, and the volume of radiogenic argon is calculated from mass spectrographic measurements. Recently, neutron activation analysis (47) has been used to determine the very small quantities of argon present in young minerals.

For the determination of potassium-40, either a gravimetric method (42,44,48,49), the use of isotope dilution (9,50), or flame photometry (41,46,51) may be used.

Several authors (41,44,48,52,53) have analyzed feldspars and micas from the same rock and have found that the micas showed significantly greater argon-40 to potassium-40 ratios than the feldspars. The possibility of incomplete recovery of the argon from the feldspars was disproven by the use of argon-37 (44,45,54) and X-ray (41) techniques. A second possible explanation, argon loss, has been advanced for the observed discrepancy. (34)

RUBIDIUM-STRONTIUM METHOD

The standard equation for radioactive decay may be expressed as

$$N = N_0 e^{-\lambda t}$$

where N_0 is the number of atoms originally present and N the number present after a time, t, has elapsed. Since the half-life of rubidium is very long in comparison to geologic time, only an insignificant proportion will have decayed even in the most ancient minerals. Consequently, one may regard the quantity of rubidium in a mineral as having remained constant throughout its lifetime. (55) The standard decay equation can then be simplified and written as(13)

$$N_0 - N = \lambda t N_0$$

where $(N_0 - N)$ equals the number of atoms of rubidium-87 that have decayed, which is equivalent to the number of strontium-87 atoms that have formed. The rubidium-strontium age equation then takes the form: (55,56)

$$t = \frac{\text{per cent radiogenic } Sr^{87}}{\text{per cent } Rb^{87}} \left(\frac{1}{\lambda}\right)$$

Rubidium forms no minerals of its own, but tends to substitute for potassium in its minerals, especially lepidolite. (17) It is also found in the cesium mineral, pollucite. (56)

Rubidium-87 and strontium-87 may be determined either by spectrochemical methods (56) or by isotopic dilution techniques (51,57-59). The spectrochemical method depends essentially on rendering strontium and rubidium volatile in the arc by pretreatment with hydrofluoric acid. Isotope dilution analysis involves equilibration with appropriate tracers, chemical and ion-exchange separation of the rubidium and strontium, and mass spectrographic analysis.

A recent publication "Bibliography of Geochronology" may be consulted for additional references concerning geological dating. This bibliography is available from Geochron Laboratories, Inc., 24 Blackstone Street, Cambridge 39, Massachusetts, upon request.

BIBLIOGRAPHY

1. Goodman, C., and Evans, R. D., Bull. Geol. Soc. Am., 52, 491(1941).
2. Nier, A. O., Phys. Rev., 55, 153 (1939).
3. Niew, A. O., Thompson, R. W., and Murphey, B. F., ibid., 60, 112 (1941).
4. Nier, A. O., ibid., 55, 150 (1939).
5. Collins, C. B., Farquhar, R. M., and Russell, R. D., Bull. Geol. Soc. Am., 65, 1 (1954).
6. Picciotto, E. E., Bull. soc. belge geol. palenontol. et hydrol., 59, 102 (1950).
7. Kulp, J. L., Bate, G. L., and Broecker, W. S., Am. J. Sci., 252, 345 (1954).
8. Kulp, J. L., Geol. Soc. Am. Spec. Paper No. 62, 609 (1955).
9. Aldrich, L. T., Wetherill, G. W., Davis, G. L., and Tilton, G.R., Trans. Am. Geophys. Union, 39, 1124 (1958).
10. Tilton, G. R., and Nicolaysen, L. O., Geochim. et Cosmochim. Acta, 11, 28 (1957).
11. Tilton, G. R., Patterson, C., Brown, H., Inghram, M., Hayden, R., Hess, D., and Larsen, Jr., E., Bull. Geol. Soc. Am., 66, 1131 (1955).
12. Aldrich, L. T., Science 123, 871 (1956).
13. Rankama, K., "Isotope Geology," Pergamon Press, Ltd., London(1954).
14. Wetherill, G. W., Trans. Am. Geophys. Union, 37, 320 (1956).
15. Tilton, G. R., ibid. 37, 224 (1956).
16. Aldrich, L. T., and Wetherill, G. W., Ann. Rev. Nuclear Sci., 8, 257 (1958).
17. Faul, H., ed., "Nuclear Geology," John Wiley and Sons, Inc., New York (1954).
18. Stieff, L. R., Stern, T. W., and Milkey, R. G., U. S. Geol. Survey Cir. 271 (1953).
19. Russell, R. D., and Farquhar, R. M., Mining Eng., 9, 556 (1957).
20. McCrady, E., Trans. Am. Geophys. Union, 33, 156 (1952).
21. Ellsworth, H. V., Geol. Survey Can., Econ. Geol. Ser., No. 11, 1 (1932).
22. Tilton, G. R., Nat. Acad. Sci.-Nat. Research Council, Publ. No. 400, 79 (1956).
23. Kuroda, P. K., Ann. N. Y. Acad. Sci., 62, 177 (1955).
24. Holmes, A., Proc. Geol. Assoc. Can., 7, 81 (1955).
25. Strominger, D., Hollander, J. M., and Seaborg, G. T., Revs. Mod. Phys., 30, 585 (1958).
26. Giletti, B. J., and Kulp, J. L., Am. Mineralogist, 40, 481(1955).
27. Phair, G., and Levine, H., Econ. Geol., 48, 358 (1953).
28. Ahrens, L. H., Rankama, K., and Runcorn, S. K., "Physics and Chemistry of the Earth," Vol. I, 44, Pergamon Press, London (1956).
29. Wickman, F. E., Sveriges Geol. Undersökn, Ser. C. Avhandl. och Uppsat., No. 427 (1939).
30. Kulp, J. L., Broecker, W. S., and Eckelmann, W. R., Nucleonics, 11, 19 (1953).
31. Kulp, J. L., Bate, G. L., and Giletti, B. J., Proc. Geol. Soc. Can., 7, 11, 15 (1955).
32. Shillibeer, H. A., and Watson, K., Science, 121, 33 (1955).
33. Curtis, G. H., Evernden, J. F., and Lipson, T., Calif. Div. Mines, Spec. Rep. No. 54 (1958).
34. Shillibeer, H. A., and Russell, R. D., Can. J. Phys., 32, 681 (1954).

35. Holmes, A., Shillibeer, H. A., and Wilson, J. T., Nature, 176, 390 (1955).
36. Shillibeer, H. A., and Burwash, R. A., Science, 123, 938 (1956).
37. Wasserburg, G. J., Pettijohn, F. J., and Lipson, J., ibid., 126, 355 (1957).
38. Lipson, J., Bull. Geol. Soc. Am., 69, 137 (1958).
39. Wasserburg, G. J., and Hayden, R. J., Phys. Rev., 98, 250(1955).
40. Wasserburg, G. J., and Hayden, R. J., Trans. Am. Geophys. Union, 35, 381 (1954).
41. Folinsbee, R. E., Lipson, J., and Reynolds, J. H., Geochim. et Cosmochim. Acta, 10, 60 (1956).
42. Wasserburg, G. J., and Hayden, R. J., ibid., 7, 51 (1955).
43. Polkanov. A. A., and Gerling, E. K., Trans. Am. Geophys. Union, 39, 713 (1958).
44. Carr, D. R., and Kulp, J. L., Bull. Geol. Soc. Am., 68, 763(1957).
45. Carr, D. R., and Kulp, J. L., Rev. Sci. Instr., 26, 379 (1955).
46. Hurley, P. M., Fairbairn, H. W., Pinson, W. H., and Faure, G., Geochim. et Cosmochim. Acta, 18, 247 (1960).
47. Moljk, A., Drever, R. W. P., and Curran, S. C., Nucleonica, 13, 44 (1955).
48. Wasserburg, G. J., Hayden, R. J., and Jensen, K. J., Geochim. et Cosmochim. Acta, 10, 153 (1956).
49. Baadsgaard, H., Goldich, S. S., Nier, A. O., and Hoffman, J.H., Trans. Am. Geophys. Union, 38, 539 (1957).
50. Wasserburg, G. J., and Hayden, R. J., Nat. Acad. Sci.-Nat. Research Council, Publ. No. 400, 131 (1956).
51. Hurley, P. M., Fisher, N. H., Pinson, Jr., W. H., and Fairbairn, H. W., Bull. Geol. Soc. Am., 72, 653 (1961).
52. Wetherill, G. W., Aldrich, L. T., and Davis, G. L., Geochim. et Cosmochim. Acta, 8, 171 (1955).
53. Goldich, S. S., Baadsgaard, H., and Nier, A. O., Trans. Am. Geophys. Union, 38, 547 (1957).
54. Carr, D. R., Damon, P. E., Broecker, W. S., and Kulp, J. L., Nat. Acad. Sci.-Nat. Research Council, Publ. No. 400, 109 (1956).
55. Ahrens, L., Bull. Geol. Soc. Am., 60, 217 (1949).
56. Ahrens, L. H., Trans. Geol. Soc. S. Africa, 50, 23 (1947).
57. Tomlinson, R. H., and Das Gupta, A. K., Can. J. Chem., 31, 909 (1953).
58. Herzog, L. F., Pinson, Jr., W. H., and Cormier, R. F., Bull. Am. Assoc. Petrol. Geologists, 42, 717 (1958).
59. Davis, G. L., and Aldrich, L. T., Bull. Geol. Soc. Am., 64, 379 (1953).

GRAPHITE INTERCALATION COMPOUNDS

R. C. Burrows October 3, 1961

I. INTRODUCTION

Graphite possesses unique spatial and electronic characteristics which allow it to bind a variety of substances within its structure quite apart from any physical occulsion. Three particularly comprehensive reviews (1-3) published within the last few years have effectively summarized the extensive literature on this subject. They have not altogether dispelled the confusion which has plagued the field, however, because in many instances the reviewers are themselves responsible for the conflicting experimental evidence. It is the purpose here to consider some of the properties of the various graphite intercalation compounds and to relate them to the structures thought to exist.

Evidence of compound formation is usually based on changes in the properties of the host substance which result from intercalation. In a recent review on the properties of graphite, Blackman (4) pointed out that they are unusually sensitive to the purity and the crystalline nature of the specimen. Since single crystals of very pure graphite are exceedingly rare and most work must be performed on variously prepared specimens, some of the conflicting reports concerning graphite intercalation compounds may be explained in terms of different starting materials.

Ideal macrocrystalline graphite consists of parallel layers of triply bound carbon atoms, which lie in a massive network of fused hexagonal rings. The planar layers, held by only weak van der Waals forces, are separated by 3.35 Å. The in-plane carbon-carbon distance (1.42 Å) is intermediate between the normal single and double bond distances; it is usually said to arise from $\underline{sp}^2$ hybridization which imparts to each bond at about 1/3 double bond character and to each plane a resonating quinoid-like structure (5). The presence of the single electron in the $2\underline{p}_z$ orbital of each carbon atom is apparently largely responsible for the reactivity of graphite compared to diamond. Carbon atoms at the edge of the layer planes and those at claw and hole defects are presumably covalently bound to hydrogen or oxygen and act essentially as impurities in the graphite structure. The stacking arrangement in the common hexagonal modification of graphite is ABA... in which alternating layers are superimposable.

II. COVALENT INTERCALATION COMPOUNDS

A. Graphite Oxide

Graphite oxide was the first graphite intercalation compound to be prepared (7). Riley$^{(8)}$ has reviewed its many interesting properties particularly thoroughly. Although graphite oxide has been studied extensively, neither its structure nor its composition is yet completely defined. The usual preparations involve treating a suspension of graphite in concentrated acid with a strong oxidizing agent (7,9-13). Large particles of graphite afford better yields of graphite oxide than do small ones, which tend to be consumed by the reaction mixture (13,14). Purification is especially difficult

because graphite oxide tenaciously retains water, oxidant and acid. Even thoroughly washed and dried samples are, nevertheless, strongly acidic.

Well-oxidized samples of graphite oxide are bright yellow, although they immediately turn black on contact with alkali and darken slowly on aging, heating, or exposure to light. These changes occur, however, with no detectable change in the C:O ratio, which is frequently used to characterize the products (11). Although early workers dried their specimens at 110° in the belief that graphite oxide is stable to much higher temperatures (1), careful work by de Boer and van Doorn (15) recently showed that gradual breakdown commences near 70°. These workers also discovered that the gases released at the lower decomposition temperatures are rich in oxygen (15,16). In a still more recent counter-investigation (17), however, no oxygen was detected by vapor-phase chromatography during slow decomposition of graphite oxide between 70 and 120°. The disposition of this question bears strongly on the liklihood of a peroxide structure. Quite unlike graphite, graphite oxide has a high electrical resistance (18) and a strong affinity for polar liquids. The colloidal nature of aqueous dispersions of graphite oxide has been studied extensively by Thiele (19-23). The material also undergoes swelling with certain organic liquids and in some cases forms interlamellar sorption complexes with them (24,25).

X-ray diffraction has had limited success in elucidating the structure of graphite oxide because only a few reflections appear (26,27). They show that the layer structure of graphite is retained but with interlayer spacings increased to 6.2 - 9.0 Å, depending on the extent of oxidation and dryness of the sample. The X-ray diagrams are consistent either with a planar layer structure with bond distances as in graphite or with puckered layers of carbon atoms joined by single covalent bonds. Chemical and spectroscopic (28,29) evidences strongly favor the latter disposition.

The nature of the functional groups in graphite oxide has been the subject of many investigations by Hofmann and his coworkers (11,17,18,26,27). A number of ideal empirical formulas have been suggested, $C_{6-8}H_2O_4$ being common (11,16,29). Methylation of graphite oxide with methanol and hydrochloric acid reduces the acid content only slightly, and because it does not affect the interplanar spacing, reaction is assumed to take place only with the carboxyl groups which lie on the periphery of the layer planes and which are insufficient to affect the composition (11). Acetylation accounts for about one hydroxyl group in the empirical formula, but reaction with KI releases two equivalents of iodine as if the reactive oxygen were present as carbonyl (16). A keto-enol tautomerization is therefore proposed and is said to be confirmed by infra-red measurements (16), although other workers (28,29) have failed to obtain good spectroscopic evidence for such an equilibrium. The nature of the other three oxygen atoms and the one hydrogen atom has been determined with even less certainty; proposals (11,16,27,30,31) have included combinations of peroxide, carboxyl, oxetane, and tertiary hydroxy groupings, each of which seems to have some justification.

B. Carbon Monofluoride

Graphite is inert towards fluorine below 400° and explosively reactive above 700°. At intermediate temperatures absorption takes place with the formation of compounds of the composition $CF_{0.68-0.99}$ (32,33). The reaction is strongly catalyzed by hydrogen fluoride so that it may be effected at much lower temperatures (34). Color and electrical conductance of these products decrease with increasing fluorine content until those substances near CF are white and non-conducting. Carbon monofluoride is hydrophobic like graphite and is unreactive, even towards warm concentrated acids and bases. Although it is wet by acetic acid and various hydrocarbons, no swelling occurs. Careful heating results in gradual loss of fluorine, but more vigorous treatment causes deflagration with the formation of soot and a mixture of fluorocarbons.

X-ray diffraction measurements on CF (33) meet with the same fate as those on graphite oxide, viz., only the interplanar spacing can be determined with certainty. In the most nearly fully fluorinated specimens, this distance corresponds closely to layers separated by two covalent carbon-fluorine bonds and two van der Waals fluorine radii. For decreasing fluorine content, the layer spacing increases from 6.6Å for $CF_{0.99}$ to 8.8 Å for $CF_{0.68}$. The pycnometric density of carbon monofluoride in hydrocarbons increases with decreasing fluorine content. In order to reconcile this phenomenon with the X-ray results, it is postulated that the specimens absorb the liquids by which they are wetted and that the density does, in fact, decrease with fluorine content. No explanation has been proffered for this apparent anomaly. During both formation and show degradation of CF only diffraction lines characteristic of graphite and of CF appear; homogeneous intermediate phases apparently do not exist(35).

All available chemical and electrical data indicate that bonding in carbon monofluoride is covalent with the carbon atoms exhibiting sp³ hybridization and the layer planes a puckered structure. Infra-red measurements show a single strong, broad band at 1215 $cm.^{-1}$, which is in the range for perfluorinated hydrocarbons (36).

C. Tetracarbon Monofluoride

W. and G. Rüdorff (37) found that when graphite is treated with a mixture of HF and F_2 at room temperature, only fluorine is consumed and that a product of the composition $C_{4.0-3.6}F$ is formed. Tetracarbon monofluoride is resistant to acids, bases, and strong reducing and oxidizing agents, but all compositions decompose above 100° even in the presence of HF and F_2 and thus cannot be converted to CF by further fluorination. Although C_4F does conduct electricity somewhat, its electrical resistance is about 100 times that of graphite (38).

The indications are that C_4F has a mostly planar structure similar to that of graphite with layers separated by 5.34Å and every fourth in-plane carbon bound covalently to fluorine. This unusual configuration places a great deal of strain on the layer planes and probably results in the low thermal stability of C_4F relative to CF. The composition $CF_{0.28}$ - i.e. $C_{3.6}F$, apparently represents the maximum fluorine content, and therefore the maximum strain, consistent with the planar structure. More fluorine is added to graphite only when conditions for the formation of $CF_{0.68}$ and a mostly puckered layer structure are satisfied.

III. LAMELLAR COMPOUNDS

Although the lammelar compounds of graphite result from the inclusion of a variety of species, they exhibit some remarkably similar properties (2). With the exception of the graphite salts they may be prepared by allowing graphite to react in a closed system with the liquid or vapor of the material to be intercalated. All of the formation reactions are so easily reversed, however, that most of the compounds are only stable in the presence of excess reactant. A large increase in conductance parallel to the crystallographic a-axis is invariably associated with compound formation. In all of those cases in which x-ray studies have been conducted, the planar graphite structure is retained with interplanar distances increased just sufficiently to accomodate one layer of the included species. The usual assumption is that electrons are transferred either to or from the singly occupied $2p_z$ orbitals of carbon in the graphite structure. The extent of this electron transfer is contested, however. On the basis of electrical measurements, Hennig (2,39-43) believes that it is never complete and that the nonionized fraction, usually 2/3 to 3/4 and constant for all compositions of a given compound, acts as a dielectric. Ubbelohde and his coworkers (38,44,45) contend that the properties reflect partial ionization only in some cases, particularly with potassium and the concentrated compounds. This group proposes "quasi-metallic" bonds between carbon and the intercalated species in these cases to account for the increased conductance parallel to the c-axis(44).

The lamellar compounds characteristically form in a series of discontinuous stages which correspond to the number of layers of graphite structure which separate layers of the intercalated material. Each stage varies homogeneously only over a narrow composition range before passing into another stage; intermediate compositions are mixtures of these two stages (3). The stacking arrangement of graphite is also somewhat modified in the lamellar compounds. The carbon layers which are adjacent to the same foreign layer are exactly superimposable with each other; those which are in juxtaposition have the same separation and hexagonal arrangement as in graphite. It is thus possible for each intercalated particle to occupy a position above and below the center of a hexagonal ring of carbon atoms. This disposition appears to exist regardless of the stage (3).

A. Alkali-Metal Compounds

Whereas K, Rb, and Cs enter the graphite structure readily, Li and Na exhibit a pronounced reluctance to do so under any conditions (46-48). A Na-Cs alloy has been used to incorporate very small amounts of Na (47), and a stage 8 compound has been produced by heating graphite with 3% Na, although other composition could not be found under a variety of conditions (49). A non-carbide Li product was reported (47), which changed from black to white as the Li content increased to C_4Li. Structural studies have not been made on any of these compounds. Theoretical evidence against the probable existence of the normal C_8M compounds with Li and Na has been presented (2,48).

III. LATTICE CONSTANT

[illegible]

[illegible]

A. [illegible]

[illegible]

Compounds of the other alkali metals have been studied by X-ray diffraction (50,51). By this means Rüdorff obtained evidence for the first five stages of the K and Rb compounds. These stages correspond to the ideal compositions CxM, where x is 8,24,36,48 and 60. In stage 1 the metal atoms are disposed in a triangular network. The metal layers in the subsequent stages are less density packed and occur less frequently. The distance between the carbon planes which surround each metal layer is the same for all stages and, after correction is made for the normal graphite interplanar distance, is less even than the ionic radii of the metals. The explanation (2) for this discrepancy is that the metal ions resulting from electron donation to the graphite structure penetrate the π-electron cloud of the carbon layers. The concept of graphite as an electron acceptor in these compounds is confirmed by the fact that they are n-type semi-conductors (42).

Herold has recently initiated a systematic study of the reactions of the alkali metal-graphite compounds. Hydrogen is fixed rapidly at room temperature by the K compounds, whereby the spacer atoms seem to be converted to the hydride without the K ions involved with graphite being affected. The presumably more highly ionized Rb and Cs compounds did not react with hydrogen (52). The halogens convert the C_8M compounds to a mixture of alternating layers of graphite and the metal halide (53).

B. Halogen Compounds

Compound formation between graphite and chlorine has been demonstrated only recently (41,54-57). Changes in the electrical properties of graphite in the presence of chlorine at low temperatures and isobaric degradation studies suggest a composition C_8Cl, which decomposes above 0^o even under saturation pressure of chlorine. Graphite residue compounds are much more reactive toward chlorine than is pure graphite (57).

In contrast, bromine is readily absorbed by pure graphite, giving second and third-stage compounds (58,47). These products are p-type semi-conductors, the electrical resistance of which decreases with increasing bromine content, especially over the dilute stages (41,38,59). Calculations based on electrical measurements give $C_{56}^{+}Br^{-}.3Br_2$ as the probable constitution of stage 2 (41). The X-ray interplanar spacing, which is greater than that calculated for Br atoms but slightly less than that required for Br ions, also suggests partial ionization (58). Although graphite-bromine decomposes at room temperature on reduction of the external bromine pressure, some bromine is held tenaciously and cannot be completely expelled without rupturing the graphite network (40).

It is generally agreed that iodine does not react with pure graphite (41,47,57), but intercalation of iodine monochloride resembles that of bromine (41,60). That ICl molecules are not recovered when the compound is allowed to decompose indicates that the initial material is dissociated within the graphite structure(45). The reported inclusion of iodine tinchloride (61) has not been verified and is believed to occur only with coreactants or with impure graphite (2).

[illegible] many years ago by [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

C. Graphite Salts.

If graphite is oxidized in the presence of concentrated acids, either chemically or electrolytically, the acid anion and several acid molecules enter the graphite structure:

$$G + \frac{n}{2}[O] + n\,HX \rightleftarrows G^{n+}(nX^-) + \frac{n}{2}H_2O.$$

Since the reaction is reversible, the various compounds may be converted one into another by treatment with the appropriate concentrated acid. These graphite salts form only with strong acids and are normally stable only in highly acidic media. They are readily attacked by reducing agents and by polar liquids (62-65).

Both the formation and decomposition reactions of the graphite salts take place in the well-defined steps characteristic of lamellar compounds. The composition of the first stage of the bisulfate salt is approximately $C_{24}^{+}HSO_4^{-}\cdot 2H_2SO_4$. Its structure is identical with that of the alkali-metal compounds in all stages except that the charges are reversed and that the interlayer spacing is consistent with the size of the intercalated substance (3,66).

D. Molecular Compounds

For many years ferric chloride was the only molecule known to intercalate with graphite. Since 1950, primarily through the efforts of Croft (61,67-70), this category has been expanded to include most of the covalent metal chlorides and many oxyhalides, oxides, and sulfides. A rather convincing qualitative correlation between intercalation capacity and the electronic characteristics of the metal ion was advanced by Croft (71) to summarize his results. Much of this work has become suspect, however, because several independent investigations (42, 64,72,73) have failed to verify the results. Hennig (2) and Rüdorff (3) believe the discrepancies are due to the presence of free chlorine in Croft's reactions. This enters the graphite lattice preliminarily and acts as a spacer for the metal halide. Croft did succeed in demonstrating, however, that intercalation of molecules is not restricted to the more volatine halides and that multivalent cations in their highest oxidation state at least assist the process.

Graphite-ferric chloride is a *p*-type semi-conductor, which corresponds to $C_x^{+}Cl^{-}\cdot FeCl_2\cdot 3\,FeCl_3$ (42). The other compounds in this class are expected to be analogous in constitution (2). Some of them apparently show striking iresistance to polar solvents and even acids, whereas others are immediately attacked (61). The present consensus is that probably all the molecular compounds are decomposed by water but that the rate and extent of hydrolysis is largely determined by particle size, interlayer spacing, and mobility of the included species rather than by the type of bonding (3).

D. Ternary Compounds

Ternary compounds are those in which two species appear to be simultaneously held by the graphite structure. This classification is useful primarily in differentiating intercalation involving very pure materials and that occurring only in the presence of another

species which acts as a spacer. By use of these spacers it is possible to cause graphite to react with materials to which it is normally inert, e.g., I_2 (57), $AlCl_3$(42), $CdCl_2$(3), Li(48) and Na(47,48). It is particularly interesting that neither the substance which undergoes electron transfer nor the substance which is the spacer need itself be especially reactive toward graphite (1). This synergism may be related to the ability of the molecular species to form a complex ion with the coreactant in the presence of graphite.

An interesting series of ternary compounds was found by Rüdorff (3,74,75) when solutions of the alkali- or alkaline earth-metals in liquid ammonia or amines were treated with graphite. The electrical and chemical properties of these compounds indicate that they are similar in structure to the alkali-metal compounds except that ammonia rather than nonionized metal acts as the spacer (2).

IV. RESIDUE COMPOUNDS

When a graphite intercalation compound, either covalent or lamellar, is thermally decomposed or reduced, several percent of the intercalated substance is usually retained by the graphite. (40,41,76). Only the n- type semi-conductors, the alkali-metal compounds, and the ternary ammonia complexes, seem to be exceptions in that their formation is completely reversible (2). There is very little difference in the X-ray diagrams of pure graphite and those of the residue compounds; there is a great deal of difference in their electrical and chemical properties. Evidence has been presented to show that the residue is held either at crystal imperfections (41) or at hole defects in the carbon layers (76).

V. CONCLUSION

The formation of graphite intercalation compounds is invaribly accompanied by a change of the electron concentration in the graphite. The elements of the highest electron affinity, viz., fluorine and oxygen, associate with particular carbon atoms and form covalent bonds which destroy the graphitic character of the host. In the lamellar compounds graphite behaves amphoterically, accepting electrons from the very electropositive elements and donating them to electronegative species. This change , however, in always small compared to the total number of electrons ins the graphite structure. Although the structures of even the well-known compounds have not been completely elucidated, continuing research with more careful attention to relatively minor experimental details is beginning to evolve consistent explanations. The recent discovery of many new reactions of graphite and its intercalation compounds will undoubtedly promote even greater interest in this field.

Bibliography

1. R. C. Croft, Quarterly Revs. (London), 14, 1 (1960).
2. G. R. Hennig, "Interstitial Compounds of Graphite," Progress in Inorganic Chemistry, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, Vol. 1, 1959, p. 125.
3. W. Rüdorff, "Graphite Intercalation Compounds," Advances in Inorganic Chemistry and Radiochemistry, H. G. Emeléus and A. G. Sharpe, Eds., Academic Press, Inc., New York, Vol. 1, 1959, p. 223.
4. L. C. F. Blackman, Research (London), 13, 390, 441, 492 (1960).
5. T. Moeller, Inorganic Chemistry, John Wiley and Sons, Inc., New York, 1952, p. 666.
6. A. R. Ubbelohde, Nature, 180, 380 (1957).
7. B. C. Brodie, Ann. chim. phys., [3], 45, 351 (1855); Ann. Chem. Pharm., 114, 6 (1860).
8. H. L. Riley, Fuel, 24, 8, 43 (1945).
9. L. Staudenmaier, Ber. 31, 1481 (1898); ibid., 32, 139 (899).
10. G. Charpy, Compt. rend., 148, 920 (1909).
11. A. Clauss, R. Plass, H. P. Boehm, and U. Hofmann, Z. anorg. u. allgem. Chem., 291, 205 (1957).
12. W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 80, 1339 (1958).
13. U. Hofmann and A. Frengel, Ber., 63B, 1248 (1930).
14. J. H. de Boer and A. B. C. van Doorn, Konink. Ned. akad. Wetenshap., Proc., 61B, 12 (1958); through C.A., 53, 956b (1959).
15. J. H. de Boer and A.B.C. van Doorn, Keninkl. Ned. Akad. Wetenshap., Proc., 61B, 17 (1958); through C.A., 53, 956d (1959).
16. J. H. de Boer and A.B. C. van Doorn, Kenink. Ned. Akad. Wetenshap., Proc., 61B, 160 (1958); through C.A., 53, 956c (1959) and reference 17.
17. H. P. Boehm, A. Clauss, and U. Hofmann, J. chim. phys., 58, 141 (1961).
18. U. Hofmann and R. Holst, Ber. 72, 754 (1939).
19. H. Thiele, Kolloid-Z., 56, 129 (1931).
20. H. Thiele and H. Lück, Z. Naturforsch., 3b, 393 (1948).
21. H. Thiele, Kolloid-Z., 111, 15 (1948).
22. H. Thiele, Trans. Faraday Soc., 34, 1033 (1938).
23. H. Thiele and H. Micke, Kolloid-Z., 116, 1 (1950).
24. D.M.C. Mac Ewan and J. C. Ruiz, Nature, 176, 1222(1955).
25. F. Aragon, J. C. Ruiz, and D.M.C. Mac Ewan, Nature, 183, 740(1959).
26. H. Hofmann and E. König, Z. anorg. u. allgem. Chem., 234, 311 (1937).
27. G. Ruess, Monatsh. Chem., 76, 381 (1947).
28. D. Hadzi and A. Novak, Trans. Faraday Soc., 51, 1614 (1955).
29. C. Alexanian, J. chim. phys., 58, 133 (1961).
30. A. E. Balfour, H. L. Riley, and R. M. Robinson, J. Chem. Soc., 1936, 456.
31. A. H. Carter, L. de V. Moulds, and H. L. Riley, J. Chem. Soc., 1937, 1305.
32. O. Ruff and O. Bretschneider, Z. anorg. u. allgem. Chem., 217, 1 (1934).
33. W. Rüdorff and G. Rüdorff, Z. anorg. Chem., 253, 281 (1947).
34. W. Rüdorff and G. Rüdorff, Chem. Ber., 80, 413 (1947).
35. W. Rüdorff, Angew. Chem., 60, 74 (1948).

36. W. Rüdorff and K. Brodersen, Z. Naturforsch., 12b, 595 (1957).
37. W. Rüdorff and G. Rüdorff, Chem. Ber., 80, 417 (1947).
38. F. R. M. McDonnell, R. C. Pink and A. R. Ubbelohde, J. Chem. Soc., 1951, 191.
39. G. R. Hennig, J. Chem. Phys., 19, 922 (1951).
40. G. R. Hennig, J. Chem. Phys., 20, 1438 (1952).
41. G. R. Hennig, J. Chem. Phys., 20, 1443 (1952).
42. M. L. Dzurus and G. R. Hennig, J. Am. Chem. Soc., 79, 1051 (1957).
43. M. L. Dzurus and G. R. Hennig, J. Chem. Phys., 27, 275 (1957).
44. L. C. F. Blackman, J. F. Mathews, and A. R. Ubbelohde, Proc. Roy. Soc. (London), A256, 15 (1960).
45. A. R. Ubbelohde, J. chim. phys., 58, 107 (1961).
46. K. Fredenhagen and G. Cadenbach, Z. anorg. u. allgem. Chem., 158, 249 (1926).
47. A. Hérold, Bull. soc. chim. France, 1955, 999.
48. M. L. Dzurus, G. R. Hennig, and G. L. Montet, Proc. Confs. Carbon, Buffalo, 4th, 1959, 165.
49. R. C. Asher and S. A. Wilson, Nature, 181, 409 (1958).
50. A. Schlude and M. Willmann, Z. physik. Chem. (Leipzig), B18, 1 (1932).
51. W. Rüdorff and E. Schulze, Z. anorg. u. allgem. Chem., 277, 156 (1954).
52. A. Hérold and D. Saehr, Compt. rend., 250, 545 (1960).
53. R. Diebold and A. Hérold, Compt. rend., 252, 1328 (1961).
54. R. Juza, P. Schmidt, A. Schmeckenbecher, and P. Jönck, Naturwissenschaften, 42, 124 (1955).
55. R. Juza and P. Schmidt, Chem. Ber., 89, 428 (1956).
56. R. Juza, P. Jönck and A. Schmeckenbecker, Z. anorg. u. allgem. Chem., 292, 34 (1957).
57. R. Juza and A. Schmeckenbecher, Z. anorg. u. allgem. Chem., 292, 46 (1957).
58. W. Rüdorff, Z. anorg. u. allgem. Chem., 245, 383 (1941).
59. M. Goldsmith, J. Chem. Phys., 18, 523 (1950).
60. W. Rüdorff, V. Sills, and R. Zeller, Z. anorg. u. allgem. Chem. 283, 299 (1956).
61. R. C. Croft, Australian J. Chem., 9, 184 (1956).
62. A. Frenzel and U. Hofmann, Z. Elecktrochem., 40, 511 (1934).
63. W. Rüdorff, Z. anorg. u. allgem. Chem., 254, 319 (1947).
64. W. Rüdorff and A. Landel, Z. anorg. u. allgem. Chem., 293, 327 (1958).
65. W. Rüdorff and W. F. Siecke, Chem. Ber., 91, 1348 (1958).
66. W. Rüdorff, Z. physik. Chem. (Lupzig), B45, 43 (1938).
67. R. C. Croft and R. G. Thomas, Nature, 168, 32 (1951).
68. R. C. Croft, J. Appl. Chem. (London), 2, 557 (1952).
69. R. C. Croft, Australian J. Chem., 9, 201 (1956).
70. Platzer and B. de la Martiniere, Bull. soc. chim. France, 1961, 177.
71. R. C. Croft, Australian J. Chem., 9, 194 (1956).
72. W. Rüdorff and R. Zeller, Z. anorg. u. allgem. Chem., 279, 182 (1955).
73. W. Rüdorff and E. Stumpp, Z. Naturforsch., 13b, 459 (1958).
74. W. Rüdorff and E. Schulze, Angew. Chem., 66, 305 (1954).
75. W. Rüdorff, E. Schulze, and O. Rubisch, Z. anorg. u. allgem. Chem., 282, 232 (1955).
76. E. A. Kmetko, J. Chem. Phys., 21, 2152 (1953).
77. A. R. Ubbelohde and F. A. Lewis, Graphite and Its Crystal Compounds, Clarenden Press, Oxford, 1960; through C.A., 54, 18054b (1960) and reference 45.
78. D. S. Smith, Inorganic Seminars, University of Illinois, Nov. 29, 1955.

SUBSTITUTION REACTIONS INVOLVING SILICON

Nicholas Matwiyoff October 10, 1961

I. INTRODUCTION

The chemistry of silicon compounds containing organic sutstituents has been a subject of much interest to both inorganic and organic chemists and, since the extensive investigations by Kipping (1) in the early part of this century, a wealth of literature which is devoted to studies of the synthesis and properties of organo-silicon compounds and the inorganic polymers of silicon has been accumulated (2,3,4,5). It has been only recently that a systematic study of the mechanisms of the reactions of silicon compounds has been initiated. Of these reactions, the most extensivly investigated have been those involving substitution at silicon in a derivative R_3SiX, in which R- is an organic and -X is a functional group. This seminar will be concerned with the interpretation of the mechanisms of those nucleophilic substitution reactions of the derivatives, R_3Si-X, which have been the object of detailed kinetic and stereochemical studies.

II. PRELIMINARY CONSIDERATIONS

For many years, the primary force motivating research in organosilicon chemistry was the desire to demonstrate the similarity between the organic chemistry of carbon and that of silicon. It is now generally recognized that, although some formal analogies can be drawn between the two fields of chemistry, the assumption that the reactions of silicon compounds can be predicted by analogy with those of carbon is not justified (1).

In its chemical behavior, silicon, like carbon, is usually tetracovalent; however, unlike carbon, its coordination number is not restricted to four. The six-coordinate species $[SiF_6]^=$ is well known (6), and many addition compounds of the silicon halides with Lewis bases have been described (7). Recently it has been reported that phthalocyanine forms six-coordinate complexes with the silicon halides (8). The fact that the acetylacetone (AcAcH) complex of silicon, $[Si(AcAc)_3]^{\oplus}$, has been resolved into its optical antipodes (9) is in agreement with the octahedral structure which has been proposed for the complex on the basis of infra-red studies (10). (It is interesting, however, that although methyl trichloro silane appears to form a similar octahedral complex, neither dimethyl dichloro- nor trimethylchloro-silane do (10)). Thus, it is possible that in some reactions of silicon compounds, five- or six-coordinate species can be formed as intermediates, the existence of which might cause significant departures of the behavior of silicon compounds from those of carbon.

There has been much speculation concerning the ability of the non-transition elements of the second and third row of the Periodic Table to participate in π bonds through the use of d-orbitals (11). The existence of this π-bonding has been used to rationalize the structures and properties of the silylamines (3), silanols (12), and siloxanes (13). Additional factors to be considered in comparing the

eactivity of silicon compounds with those of carbon are: (a) the lower lectronegativity of silicon (14); and (b) the larger atomic radius of ilicon (14), which results in a decrease of the steric inhibition to olvation and attack by nucleophic reagents.

II. THE SOLVOLYSIS OF ORGANO-SILICON HYDRIDES

The solvolysis of the organo-silicon hydrides, represented by quation 1 below, has been more intensively investigated than any other eaction involving substitution at silicon.

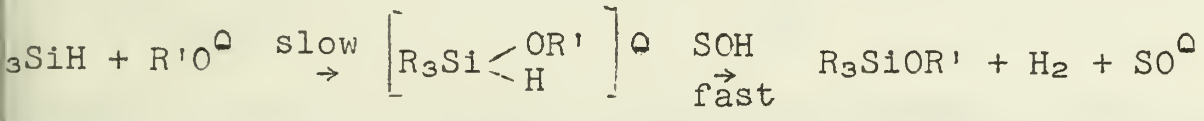
$$R_3SiH + R'O^{\ominus} + SOH \rightarrow R_3SiOR' + H_2 + SO^{\ominus} \qquad (1)$$

(R represents an alkyl or aryl group, R' and S represent hydrogen or an alkyl group.)

Price (15) determined the rates and free energies of activation Table I) of the solvolysis of a series of organo-silanes in aqueous thanolic potassium hydroxide and found that the rate of the reaction, $_2$, is of the first order in silane and hydroxide. Because of the inear variation (except for small deviations which have been attributed o salt effects (16)) of k_2 with respect to the concentration of water n the ethanol, he concluded that a solvent molecule is present in the ctivated complex and that the rate, k_2, is determined by the equation

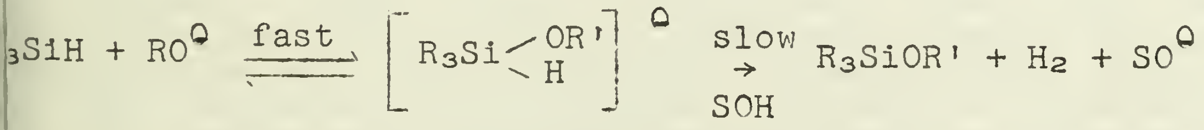
$$k_2 - k'[EtoH] + k''[H_2O] \qquad (2)$$

The results from a study of the effects of substituents on the ydrolysis of triaryl silanes (Table II) in wet piperidine (17) and hose from a study of the solvolysis of fluoroalkyl silanes (18) Table III), indicate that electron-release to the silicon decreases he rate of the reaction whereas electron withdrawal increases it. hese results, in conjunction with those from a study of steric effects 16) on the reaction rate (Table IV)),can be interpreted in terms of hree mechanisms, represented by A, B, and C below.



$$_3SiH + R'O^{\ominus} \xrightarrow{slow} \left[R_3Si{<}\begin{smallmatrix}OR'\\H\end{smallmatrix}\right]^{\ominus} \xrightarrow[fast]{SOH} R_3SiOR' + H_2 + SO^{\ominus} \qquad A.$$

$$_3SiH + R'O^{\ominus} + SOH \xrightarrow[concerted]{slow,} R_3SiOR' + H_2 + SO^{\ominus} \qquad B.$$



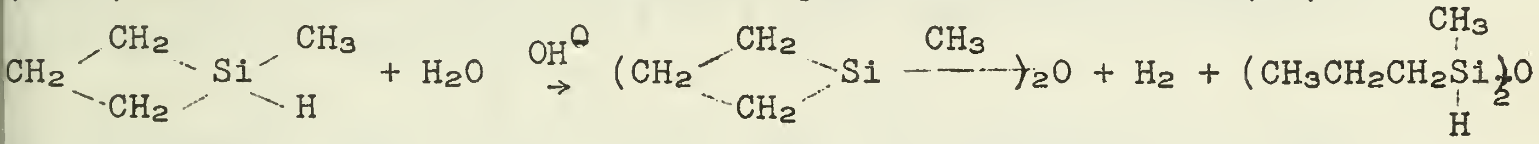
$$_3SiH + RO^{\ominus} \underset{}{\overset{fast}{\rightleftharpoons}} \left[R_3Si{<}\begin{smallmatrix}OR'\\H\end{smallmatrix}\right]^{\ominus} \xrightarrow[SOH]{slow} R_3SiOR' + H_2 + SO^{\ominus} \qquad C.$$

The mechanism represented by A cannot be excluded on the basis of rice's data (15) due to the effect of water on the equilibrium: $^{\ominus}$ + EtOH ⇄ HOH + EtO$^{\ominus}$. Kaplan and Wilzbach have excluded mechanism A the basis of a study of the isotope effects on the reaction rate by competition technique, the results of which are given in Table V (19). e small isotope effect observed for the cleavage of the silicon-drogen bond can be rationalized by using any of the three mechanisms stulated; likewise, the isotope effect observed for the solvent can

be interpreted on the basis of each of the mechanisms, since the effect observed only indicates that for the slowest step involving the solvent a solvent hydrogen bond is cleaved. Mechanism A was excluded because of the isotope effect that was observed in the hydrolysis of tri-*n*-propyl silane in the solvents, ethanol-water and ethanol-deuterium oxide. However, since the two media in which the reaction was studied, are different (20), the results of these experiments cannot be considered an unequivocal exclusion of A.

Studies (21,22,23,24) of the reactivity of cyclic and bicyclic organo silicon hydrides, the results of which are summarized in Table IV, haveprovided a valuable insight concerning the structure of the transition state or intermediate involved in the rate-determining step of the solvolysis reactions. The relative reactivities of II, III, and IV (see Table VI) are attributed to the release of internal strain accompanying the formation of a five-coordinate intermediate. The data for the compounds V, VI, and VII indicate that, in nucleophilic substitution reactions involving silicon, back-attack and inversion of configuration at the silicon center is not necessary--the entering group can attack the silicon at a site neighboring the leaving group (22). Additional justification for this conclusion, which provides an interesting contrast to carbon chemistry, has been obtained from the observation that some substitution reactions at silicon proceed with retention of configuration (25,26,27)--an attack by the nucleophile *trans* to the leaving group would result exclusively in inversion of configuration (if the solvent does not enter the primary coordination sphere of silicon).

The assumption that a five-coordinate intermediate occurs in the solvolysis of the cyclic organo-silanes was tested by performing a competition study of the solvolysis of 1-methyl-1-silabucyclobutane (VIII) which follows the two reaction paths outlined below (28).



VIII IX X

Product IX results from the ordinary solvolysis of the silicon-hydrogen bond (the silanol is formed initially but immediately condenses to the siloxane) and product X results from the base-catalyzed cleavage of the strained ring (X does not evolve hydrogen under the conditions of the experiment). Since the substitution of deuterium for hydrogen (Si-H) in I caused a larger change in the product ratio (IX/X) than in the rate of solvolysis, it was concluded that a common five-coordinate intermediate is formed in the rate determining step and is destroyed in rapid product-controlling ones. The data can also be interpreted, however, by assuming that VIII passes through a different transition state to form IX than to form X (without the intervention of an intermediate in either reaction path).

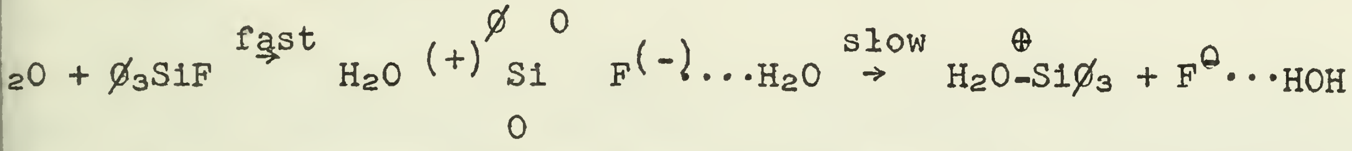
Thus, at present, there is no unequivocal choice that can be made among the mechanisms postulated for the base-catalyzed solvolysis of organo-silanes in hydroxylic solvents. It is interesting that, in a recent publication (29), there is presented the possibility that a gradual transition from mechanism *A* to mechanism *C* occurs in the solvolysis of silanes which vary widely in steric requirements and "electron-donating" properties.

IV. THE SOLVOLYSIS OF ORGANO-SILICON HALIDES

In the early studies of silicon chemistry, the reactions of many derivatives of the organo-silanes had been thought to proceed through siliconium ion intermediates (30). This interpretation seemed reasonable from ground-state considerations of chemical reactivity since, in the chemistry of carbon (which is less electropositive than silicon) limiting ionic mechanisms were known for many reactions and some carbonium ions were known to be stable under special conditions.

In recent studies it has been shown that the silicon analogues of carbonium are not detectable in some systems in which the latter do exist (31, 32). Although these studies do not exclude the possibility that siliconium ions can be formed as reactive intermediates, the data available from kinetic studies can best be interpreted on the basis of a concerted mechanism or the intervention of a five-coordinate intermediate even in the substitution reactions of the organo-silyl halides. It must be emphasized, however, that the absence of siliconium ion intermediates in systems in which carbonium ion intermediates can be produced does not necessitate the conclusion that the former are less stable than the latter--it may merely signify that the silicon compound can react via a lower energy path than that involving an ionic intermediate in the particular reaction (Sommer and Boughman, in a recent communication (33), have reported that under the proper conditions a limiting siliconium ion mechanism is isolable).

Swain, Esteve, and Jones (34) have studied the hydrolysis of triphenylsilyl fluoride (XI) and that of tris (p-methylphenyl) silylfluoride (XII) in 50% aqueous acetone. It was found that the rate of olvolysis of (XI) was greater than that of (XII) and that the rate in oth cases was subject to positive salt and solvent effects. On the asis of these considerations and the observation that triphenylsilyl hloride appeared to solvolyze more rapidly than XI, the mechanism hown below was postulated.



$$_2O + \emptyset_3SiF \xrightarrow{fast} H_2O\ ^{(+)}\overset{\emptyset\quad O}{\underset{O}{Si}}\ \ F^{(-)}\cdots H_2O \xrightarrow{slow} H_2O\text{-}\overset{\oplus}{Si}\emptyset_3 + F^{\ominus}\cdots HOH$$

he data cited above can also be interpreted in terms of an Sn2 mechnism in which the electronic requirements depend on the relative ontributions of bond-making and bond-breaking in the transition tate (35).

Allen and Modena (36) have studied the solvolysis of a series of ilyl chlorides in both inert and hydroxylic solvents. It was shown hat the rates of hydrolysis and alcoholysis of the silyl chlorides n inert solvents are of the first order in silyl chloride and of ultiple order with respect to the water or methanol, and are subject o positive salt and solvent effects and to catalysis by chloride ion. owever, when the reactions were carried out in iso-propanol (which id not react with the silyl chlorides in the time necessary to complete he studies), the rate was found to be of the first order in water or ethanol and not subject to catalysis by the chloride ion. The relative ffectiveness of the nucleophiles in inert solvents was shown to be:

[illegible]

[illegible]

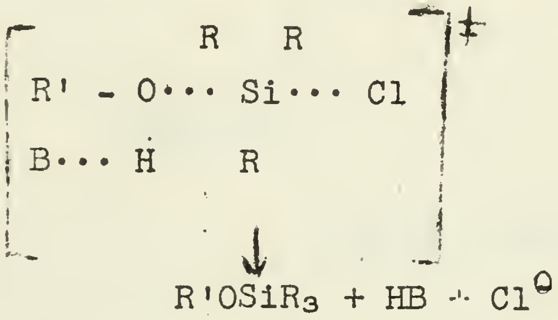
[illegible]

[illegible]

water methanol 1-hexanol iso-propanol (these "nucleophilicities" are however not independent of medium effects, for they were determined in a large excess of the reagent, viz., 10-25% of the total solvent composition). The rate of chloride exchange between $Et_4N^{\oplus}Cl^{36\ominus}$ and various silyl chlorides in dioxane-nitromethane mixtures was found to be of the second order and relatively insensitive to changes in the dielectric constant of the medium. The order of reactivity of the various silyl chlorides toward chloride ion was: triphenyl > tri-1-naphthyl > triisopropyl (for hydrolysis the order was: triphenyl > triisopropyl > tri-1-naphthyl). On the basis of these data, the mechanism shown below was proposed.

$R'-O-H\cdots B + R_3SiCl \rightarrow$

B represents R'OH or $Cl^{\ominus}$
for the reaction in inert
olvents and a molecule
solvent in the
ydroxyl solvents.)



$$\left[\begin{array}{cccc} & & R & R \\ R' - & O\cdots & Si\cdots & Cl \\ B\cdots & H & R & \end{array}\right]^{\ddagger} \rightarrow R'OSiR_3 + HB + Cl^{\ominus}$$

The data cited above are, however, also consistent with either a echanism involving a five-coordinate intermediate or with one involving transition state in which the entering group is in a cis position elative to the leaving group (Sommer has reported (23) that this must e the case for the solvolysis of 1-chloro-1-silabicycloheptane). The esults of Ackerman's studies (37,38) of the hydrolysis of trialkylyloxysilanes, in like manner, are consistent with more than one of he mechanisms postulated for the solvolysis of the silyl chlorides.

The exchange rates, though rapid, were not considered kinetically fast" by the authors who, partially on this basis, considered the echanism proposed by Swain, et al, unlikely. The interpretation of he exchange rate data is not straightforward and the conclusion eached by these authors concerning the intermediate proposed by wain, et al, is questionable.

TABLE I

Silane	$k_2^{45^\circ}$ l.mole.$^{-1}$sec.$^{-1}$	$\Delta H^{\ddagger} - \Delta H_0^{\ddagger}$ kcal. l mole	$\Delta S^{\ddagger} - \Delta S_0^{\ddagger}$ e.u.	$\Delta F^{\ddagger} - \Delta F_0^{\ddagger}$ kcal. l mole
Diethyl methyl	0.329	0.0	0	0.0
Dimethyl propyl	0.779	1.8	7	-0.4
Dipropyl methyl	0.241	1.7	4	0.5
Triethyl	0.219	2.4	6	0.5
Tripropyl	0.096	4.2	9	1.4

TABLE II

Silane $R(C_6H_5)_2SiH$ R	k x 10^4 sec.$^{-1}$
p-chlorophenyl	16.9
phenyl	3.22
m-tolyl	2.75
p-tolyl	1.08
m-dimethylaminophenyl	0.75
p-methoxyphenyl	0.89

TABLE III

Silane: $RR'CH_3SiH$ R	R'	Relative Rate
n-propyl-	methyl-	1.0
$CF_3CH_2CH_2$-	methyl-	5.9
$CF_3CH_2CH_2CH_2$-	methyl-	8.3
$CF_3CF_2CH_2CH_2$-	methyl-	83
$CF_3CH_2CH_2$-	$CF_2CH_2CH_2$-	2100

TABLE IV

Silane	Relative Rate
triethyl-	1
tri-*n*-propyl-	0.63
tri-*n*-butyl-	0.59
tri-*iso*-butyl-	0.17
tri-*iso*-propyl-	0.06
triphenyl-	3.0
tri(*p*-chlorophenyl)-	1.3
p-chlorophenyldimethyl-	2.2
phenyldimethyl	1.8
p-methylphenyldimethyl-	1.5

TABLE V

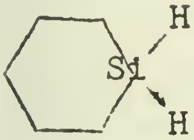
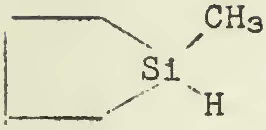
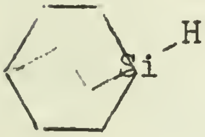
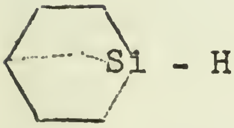
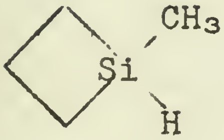
Temperature, °C	Silane	Solvent	
25	$(C_6H_5)_3Si\text{-}H\text{-}d$	Piperidine-1.0$\underline{M}H_2O$	$k_{Si\text{-}H}/k_{Si\text{-}D} = 1.152^b$
0	$(C_6H_5)_3Si\text{-}H\text{-}t$	Piperidine-1.0$\underline{M}H_2O$	$k_{Si\text{-}H}/k_{Si\text{-}T} = 1.288^b$
25	$(C_6H_5)_3Si\text{-}H\text{-}t$	Piperidine-1.0$\underline{M}H_2O$	$k_{Si\text{-}H}/k_{Si\text{-}T} = 1.257^b$
0	$(C_6H_5)_3Si\text{-}H$	Piperidine-1.0$\underline{M}H_2O^a$	$k_{S\text{-}H}/k_{S\text{-}T} = 3.32^c$
25	$(C_6H_5)_3Si\text{-}H$	Piperidine-1.0$\underline{M}H_2O^a$	$k_{S\text{-}H}/k_{S\text{-}T} = 3.05^c$
25	$(C_6H_5)_3Si\text{-}H\text{-}d$	Piperidine-1.0$\underline{M}H_2O^a$	$k_{S\text{-}H}/k_{S\text{-}T} = 3.00^c$
25	$(\underline{n}\text{-Propyl})_3SiH$	EtOH-3.47$\underline{M}H_2O$-0.53$\underline{M}KOH$	$k_2 - 1.74(10^{-4})$ l $mole^{-1}$ $sec.^{-1}$
25	$(\underline{n}\text{-Propyl})_3SiH$	EtOH-3.47$\underline{M}D_2O$-0.53$\underline{M}KOH$	$k_2 - 1.21(10^{-4})$ l $mole^{-1}$ $sec.^{-1}$

a, contains tracer amounts of tritium oxide

b, the silicon-hydrogen cleavage isotope effect

c, the solvent isotope effect

TABLE VI

Silane		Relative k_2 in 95% Ethanol with a fixed concentration of OH^-.
Et_3SiH	I	1
	II	10^{-1} (Solvolysis of the <u>first</u> hydrogen)
	III	1-10 (Solvolysis of the <u>first</u> hydrogen)
	IV	10
	V	10
	VI	10^3
	VII	10^4 - 10^5

Bibliography

1. H. Gilman and G. E. Dunn, Chem. Revs., 52, 77 (1953).
2. E. G. Rochow, "Chemistry of the Silicones," John Wiley and Sons, Inc., New York, 1951.
3. R. Fessenden and J. S. Fessenden, Chem. Revs., 61, 361 (1961).
4. P. D. George, M. Prober, and J. R. Elliot, ibid., 56, 1065 (1956).
5. E. G. Rochow, "Un-natural Products: New and Useful Materials from Silicon," 34th Annual Priestley Lectures at the Pennsylvania State University, April 25-29, 1960.
6. A. F. Wells,"Structural Inorganic Chemistry", Oxford at the Clarendon Press, London, 2nd Ed., 1950, p. 293.
7. F.G.A. Stone and D. Seyferth, J. Inorg. Nucl. Chem., 1, 112(1955).
8. R. D. Joyner, R. L. Linck, and M. E. Kenney, 139th Meeting of the American Chemical Society, St. Louis, Mo., March 21-30, 1961, Abstracts of Papers, pp. 16 M, 17 M.
9. S.K. Dahr, V. Doron, and S. Kirschner, J. Am. Chem. Soc., 81, 6372 (1959).
0. R. West, J. Am. Chem. Soc., 80, 3246 (1958).
1. D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, J. Chem. Soc., 1954, 332.
2. R. West and R. N. Baney, J. Am. Chem. Soc., 81, 6145 (1959).
3. R. West, R. H. Baney, and D. L. Powell, ibid., 82, 6269(1960).
4. L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca, 3rd Ed., 1960.
5. F. P. Price, J. Am. Chem. Soc., 69, 2600 (1947).
6. J. E. Baines and C. Eaborn, J. Chem. Soc., 1955, 4023.
7. H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 3404 (1951).
8. O. W. Steward and O. R. Pierce, ibid., 81, 1983 (1959).
9. L. Kaplan and K. E. Wilzbach, ibid., 77, 1297 (1955).
0. L. Melander, "Isotope Effects on Reaction Rates", Ronald Press Company, N. Y., 1960.
1. R. West, J. Am. Chem. Soc., 76, 6015 (1954).
2. L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, ibid., 79, 3295 (1957).
3. L. H. Sommer and O. F. Bennett, ibid.,1009 (1957).
4. L. H. Sommer and O. F. Bennett, ibid.,n81, 251 (1959).
5. L. H. Sommer and C. L. Frye, ibid., 81, 1013 (1959).
6. L. H. Sommer, and C. L. Frye, ibid., 82, 3796 (1960).
7. L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, R. Pepinsky, J. Am. Chem. Soc., 83, 2210 (1961).
8. L. H. Sommer, P. G. Campbell, and D. R. Weyenberg, 135th Meeting of the American Chemical Society, Boston, Mass., April 5-10, 1959, Abstracts of Papers, p. 23 M.
9. O. W. Steward and O. R. Pierce, J. Am. Chem. Soc., 83, 1917(1961).
0. L. H. Sommer and R. P. Pioch, ibid., 76, 1606 (1954) and references contained therein.

A. B. Thomas and E. G. Rochow, J. Inorg. Nucl. Chem., 4, 205(1957).

H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 72, 2178 (1950).

L. H. Sommer and G. A. Baughman, ibid., 83, 3347 (1961).

C. G. Swain, R. M. Esteve, and R. H. Jones, ibid., 71, 965(1949).

A. D. Allen, J. C. Charlton, C. Eaborn, and G. Modena, J. Chem. Soc., 1957, 3668.

A. D. Allen and G. Modena, ibid., 3671.

E. Ackerman, Acta Chem. Scand., 10, 298 (1956).

E. Ackerman, ibid., 11, 373 (1957).

ACTIVE NITROGEN

R. L. Middaugh October 17, 1961

I. INTRODUCTION

In 1900 Lewis reported the first investigation of the yellow afterglow produced by an electric discharge in a vacuum tube containing nitrogen (44). In 1911 Strutt (later Lord Rayleigh) published the first of a long series of papers on the reactions of this chemically active form of nitrogen (56). Since World War II there has been a revival of interest in active nitrogen, with the result that the mechanisms of the glow itself and of many of the reactions of active nitrogen with other compounds seem well established. Edwards, Jennings and Linnett, and Mitra have written reviews of active nitrogen (15,29,46).

II. PRODUCTION OF ACTIVE NITROGEN

The glow has been produced in both static and flow systems at pressures up to a few mm. of Hg by condensed and uncondensed electrode discharge, and by high-frequency electrodeless discharge (19,44,60). A condensed discharge gives a brighter glow than an uncondensed discharge (60). Nitrogen gas has also been activated by bombardment with electrons and by arc discharge at pressures of up to one atmosphere (36).

The presence of impurities has a very pronounced effect on the glow. It is enhanced when about 0.1% of the gas is an electronegative impurity such as oxygen; larger amounts quench the glow (44). The condition of the walls is important to the duration of the glow, as is the total pressure in the system. Metaphosphoric acid is often used as a poison on the walls. At pressures above five mm. of Hg, the lifetime of the glow is very short. The intensity of the glow is second order with respect to the active species, first order in molecular nitrogen, and proportional to $T^{-0.64}$ where T is the absolute temperature (4,52,65). Nitrogen-atom recombination is second order with respect to atomic nitrogen and first order with respect to molecular nitrogen; but at lower pressures, a pseudo-first-order recombination at the walls becomes important, and the atom decay follows the rate expression:

$$-\frac{d[N]}{dt} = k_1[N]^2[M] + k_w[N] \qquad (26,27,34,65).$$

III. PHYSICAL PROPERTIES OF ACTIVE NITROGEN

Constantinides traced the surprisingly high electrical conductivity of the glowing gas to electrons emitted by the electrodes used to measure the conductivity (9). Benson found the concentration of free electrons to be one in every 2.3×10^8 nitrogen molecules, a much lower concentration than that of the active species (3).

The spectrum of the afterglow consists mainly of the first positive system of nitrogen, but with anomalously high population of the tenth, eleventh and twelveth vibrational levels in the B state. There is also a lesser maximum at the sixth, seventh, and eighth levels (32). In addition, β- and γ- bands of NO appear as impurities.

The energy content of active nitrogen has been measured by several methods. A heat release of two electron-volts per mole was obtained by the addition of N_2O, which is known to relax vibrationally excited molecules (33). The failure of active nitrogen to react with H_2, HCl, N_2O, H_2O, CO_2, and CO, all of which have dissociation energies of over 60,000 calories per mole, was used to assign an energy of 45,000 calories per mole of the active species (67). In contrast, iodine vapor (ionization potential 9.4 volts) was ionized by active nitrogen, while hydrogen and mercury (ionization potential 10.4 volts) were not; and NO and CO were excited to energy levels of 6.44 and 8.2 to 9.0 volts, respectively (9,40). Kenty and Turner found a critical voltage of 10.8 volts required for bombarding electrons to activate nitrogen (36).

IV. SPECIES PRESENT IN ACTIVE NITROGEN

Charged species are not important to the glow. Ion traps and magnetic fields have no effect on the glow, and removal of practically all of the free electrons by the addition of a small amount of benzene vapor only enhances and prolongs the glow (3, 41).

Both ground-state atomic nitrogen and vibrationally excited ground-state molecular nitrogen have been proposed as active species in active nitrogen, and both have been shown to be present. Mass spectrometry shows an m/e 14 appearance potential at the ionization potential of $N(^4S)$, within experimental error (4,28). The presence of $N(^4S)$ is also shown by vacuum ultraviolet absorption spectroscopy and by micro-wave magnetic resonance (23,61). The heat released when H_2O is added is used as evidence of vibrationally excited N_2 in active nitrogen (33). Using the argon continuum as background, the absorption spectrum of active nitrogen shows ten percent of the nitrogen to be in the first excited vibrational level of the ground state, accounting for a third of the heat release observed with N_2O (13). The weakening of the CN emission of BrCN/active nitrogen flames by addition of NH_3 also points to vibrationally excited molecules as the active species, since NH_3 is known to deactivate vibrationally excited molecules, and it has been shown that destruction of NH_3 by active nitrogen leaves the concentration of atomic nitrogen unchanged (35,37).

Vacuum ultraviolet emission spectra of the nitrogen afterglow show bands of the nitrogen $a^1\Pi g - X^1\Sigma_g^+$ transition (61). Using an ozonizer to activate nitrogen at one atmosphere pressure, Noxon observed the Vegard-Kaplan bands of the forbidden $A^3\Sigma u^+ - X^1\Sigma_g^+$ transition (48). Dilution of nitrogen with inert gases before activation gives several new bands which cannot be seen in the afterglow of pure nitrogen (24,43,62).

Several methods have been used to determine the relative and absolute concentrations of the active species. The first of these was the increase in weight of phosphorus exposed to the gas (56). This was abandoned in favor of reactions with NO and hydrocarbons (57,58). Strutt estimated the concentration of the active species to be about 2.5 percent. Clyne and Thrush found one-fourth to one-half percent atomic nitrogen; another group reported one-tenth percent atomic nitrogen (6,57,61). The latter study also reported the presence of the metastable ^2D and ^2P states of atomic nitrogen in 1/500th the concentration of the ^4S state.

V. THE MECHANISM OF THE AFTERGLOW

When two $N(^4S)$ atoms come together the N_2 entity can be in one of four states: $^7\Sigma_u^+$, $^5\Sigma_g^+$, $^3\Sigma_u^+$, $^1\Sigma_g^+$, corresponding to the pairing of none, two, four, or six electrons. The triplet and singlet states are of comparatively low energy and are not involved in the glow. The septet state is of higher energy than the separate ground state atoms, and is unstable. The energy curve for the weakly bonded quintet state crosses the curves of some of the other molecular states in vibrationally excited levels. The radiationless, collision-induced transitions from the quintet state to other states results in the anomalous vibrational level populations of those states. Bayes and Kistiakowsky (2) have summarized the reactions that explain most of the features of the afterglow spectrum:

$$N(^4S) + N(^4S) + M \rightleftarrows N_2(^5\Sigma_g^+) + M$$

$$N_2(^5\Sigma_g^+) + M \rightarrow \begin{cases} N_2(B^3\Pi_g)_{v=12,11,10} + M \\ N_2(Y^3\Sigma_u^-)_{v=8,7,6} + M \\ N_2(^3\Delta_u) + M \\ N_2(a^1\Pi_g) + M \end{cases}$$

$$N_2(B^3\Pi_g)_{v=12,11,10} \rightarrow N_2(A^3\Sigma_u^+)_{v=8,7,6} + h\nu \quad \text{(group 1)}$$

$$N_2(Y^3\Sigma_u^-)_{v=8,7,6} \rightarrow N_2(B^3\Pi_g)_{v=4,3,2} + h\nu \quad \text{(group 2)}$$

$$N_2(B^3\Pi_g)_{v=4,3,2} \rightarrow N_2(A^3\Sigma_u^+)_{v=2,1,0} + h\nu \quad \text{(group 3)}$$

$$N_2(^3\Delta_{3u}) \rightarrow N_2(B^3\Pi_g)_{v=7,6,5} + h\nu$$

$$N_2(B^3\Pi_g)_{v=7,6,5} \rightarrow N_2(A^3\Sigma_u^+)_{v=4,3,2} + h\nu \quad \text{(group 4)}$$

$$N_2(a^1\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + h\nu$$

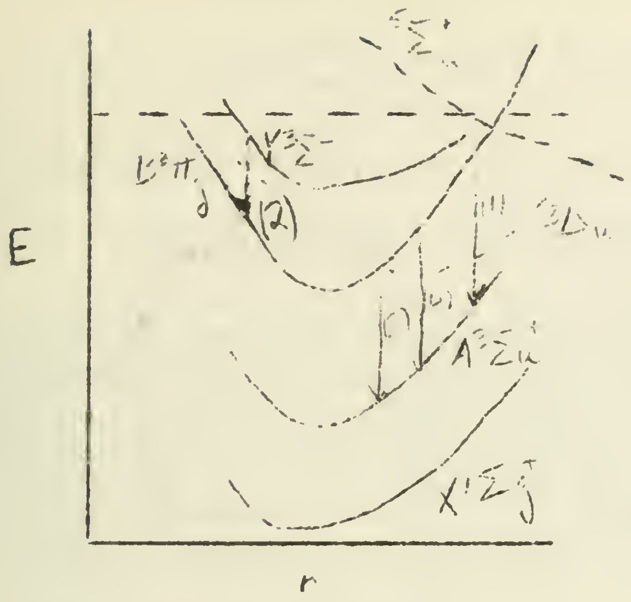
Certain methods have been used to [illegible]

4. The [illegible]

[illegible]

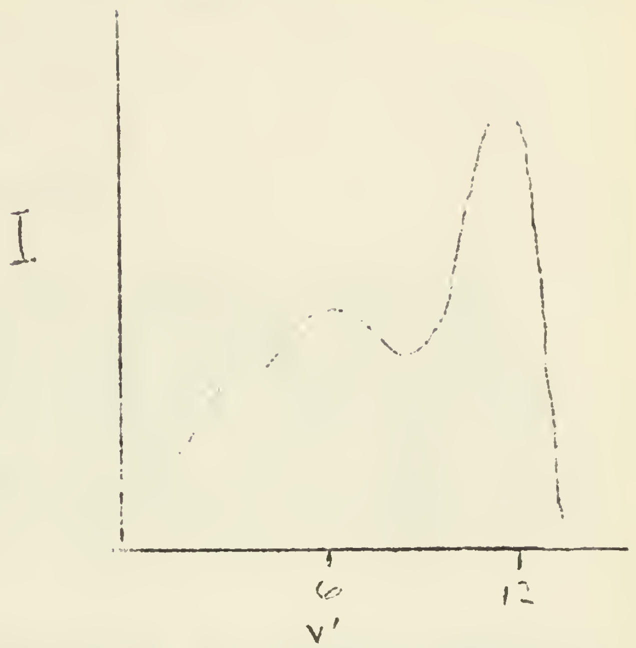
$$[illegible]$$

Figure 1



Energy level diagram for N_2

Figure 2



I = integrated intensity of radiation from the v' vibrational level of $N_2(B^3\Pi_g)$ to all other energy levels.

An increase in pressure lowers the v' maximum to 9, 10, and lowering the temperature increases it to a sharp peak at v'= 12 (42,55). Experiments using $^{15}N_2$ and $^{14}N_2$ showed the same vibrational distribution for higher v', but not for lower v' (38). This suggested the superposition of some other system on the first positive system.

VI. CHEMICAL REACTIONS OF ACTIVE NITROGEN

A. With Metals

Active nitrogen forms nitrides with metals, and excites their atomic spectra. Nitrides of Hg, Cd, Zn, Mg, Tl, Ca, a Bi-Pb-Sn alloy, Sn, and Pb, and spectra of Na, K, Mg, Hg, Tl, Ni, Cd, and Zn are reported (49,58,59,60). Active nitrogen forms a monolayer on a tungsten filament (36).

B. With Hydrogen

Hydrogen has no effect on the glow except to dilute it, and no chemical reaction takes place (37,40,56,57,67). Atomic hydrogen generated in a separate discharge reacts with active nitrogen to give ammonia and some hydrazine, the spectrum of the flame being the same as of the HN_3/ and N_2H_4/atomic hydrogen flames (19). The main features of the flame are, in addition to the first positive system of nitrogen, the second positive system of N_2 and emission due to $NH(^3\Pi)$. The following mechanism has been proposed:

$$\begin{tikzcd}
 & \mathrm{NH}(^3\Pi)_{\text{high } v} & \mathrm{NH}(^3\Pi)_{\text{high } v} + \mathrm{N_2}(B^3\Pi g) \arrow[dr] & \\
\mathrm{N}(^4S) + \mathrm{H}(^2S) \arrow[r] & \mathrm{NH}(^5\Sigma^-) \arrow[u] & \mathrm{NH}(^5\Sigma^-) + \mathrm{N_2}(B^3\Pi_g^-) \arrow[r] & \left[\mathrm{N_3H}\right] \text{ activated complex} \\
 & & \mathrm{NH}(^5\Sigma^-) + \mathrm{N_2}(^5\Sigma^+) \arrow[ur] &
\end{tikzcd}$$

$$[\mathrm{N_3H}] \rightarrow \mathrm{N_2}(C^3\Pi_u) + \mathrm{NH}(^3\Pi)_{\text{low } v}$$

$$\mathrm{N_2}(C^3\Pi_u) \rightarrow \text{2nd positive system}$$

C. With Inorganic Halogen Compounds

Halogen spectra are excited by reaction of the halogens or hydrogen halides with active nitrogen, weakly in the case of chlorine, more strongly with bromine and iodine. The main product of these reactions is X_2, with NH_4X and NH_2X in smaller amounts from the reaction with HX (14,45,60,67). The chlorides of boron and silicon give the spectra of the nitrides, but that of titanium does not (30,31). The salts CuCl, $SnCl_2$, $SnCl_4$, and HgI_2 give blue-green to violet flames with active nitrogen (60).

D. With Group Six

Oxygen reacts with active nitrogen only at elevated temperatures, giving NO + O (6,40,56,57,67). Ozone gives N_2O, with the following series of reactions proposed:

$$\mathrm{N + O_3 \rightarrow NO + O_2;} \quad \mathrm{NO + O_3 \rightarrow NO_2 + O_2;} \quad \mathrm{NO + O \rightarrow NO_2;} \quad \mathrm{NO_2 + N \rightarrow N_2O + O}$$

The reaction follows the rate expression:

$$\frac{d[\mathrm{N_2O}]}{dt} = (k[\mathrm{O_3}] + k'[\mathrm{O_2}])[\mathrm{N}] \qquad (5).$$

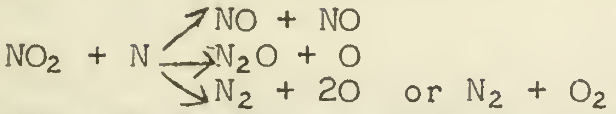
A mixture of nitrogen and oxygen diluted with argon and subjected to a discharge gives β-bands of NO (53). Mixed oxides of nitogen are formed by electric discharge through liquid air (16). Water dilutes, but does not react with, active nitrogen(67).

Both sulfur and H_2S give a blue flame that is not the same as the sulfur glow in a discharge tube (60). Hydrogen sulfide deposits an easily hydrolyzable brown polymer containing nitrogen and sulfur on the walls of the vessel (66). Selenium has no effect on the glow (56).

E. With Group Five

Nitrous Oxide does not react with active nitrogen, except to dissipate the vibrational energy of the nitrogen (33,67). Nitric oxide reacts with active nitrogen to give N_2 and O. At greater than stoichiometric flow rates, NO_2 is produced by reaction of NO and O (6,7,8,22,33,37,40,53,67). Since NO_2 can be used to titrate oxygen atoms according to the reaction $NO_2 + O \rightarrow NO + O_2$, the stoichiometry of the NO + N reaction can be checked. Titration of N atoms with NO, and O atoms produced in that titration with NO_2 gives titration ratios of 1.05 and

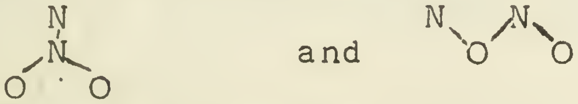
1.02 (8). Nitrogen dioxide reacts with active nitrogen by three paths:



$$NO_2 + N \rightarrow \begin{cases} NO + NO \\ N_2O + O \\ N_2 + 2O \text{ or } N_2 + O_2 \end{cases}$$

(8,21,37,63).

Two transition states have been proposed to account for the variety of products:



(8).

Both NH_3 and N_3H are decomposed to the elements by active nitrogen (18,35,37). By shortening the distance between the point of activation of the nitrogen and the introduction of NH_3 it was found that destruction of NH_3 is due not to atomic nitrogen but to a product of the atom recombination (35).

Phosphorus vapor reacts with active nitrogen to give red phosphorus and a phosphorus-nitrogen compound that was used as a measure of the concentration of the active species by Strutt (56,57).

F. With Carbon Compounds

Carbon monoxide and CO_2 do not react chemically with active nitrogen, but CS_2 gives a blue flame and deposits an explosive dark polymer thought to be CS (66,67).

The CN spectrum is obtained from flames of compounds of the type XCN, where X is a halogen, CN, or H, and from ethanol, ether, and alkyl halides (1,12,20,54,56,60). Products from chloromethanes vary according to the relative amounts of Cl and H available, from Cl_2 and CNCl for CCl_4 to HCl, HCN, and H_2 for CH_3Cl (54). Amines give HCN and NH_3 (10,51). The CN spectrum from CCl_4 and HCN flames shows an unusually high intensity of the v'=7 level. This has been attributed to a second reactive species, because of the shift in relative intensities of the v'=0 and v'=7 lines with change in pressures of CCl_4, HCN, and active nitrogen (1,12).

Carbon does not react with active nitrogen, but gives a high yield of HCN when the active nitrogen also contains atomic hydrogen (47,56,60). Hydrocarbons in general give HCN with varying amounts of $(CN)_2$, NH_3, H_2, and lower olefins (10,17, 25,39,45,50,58,64). With acetylenes, cyanoacetylenes were observed by mass spectrometry (25). The formation of NH_3 seems to depend on the relative number of methyl groups present in the molecule. Thus, polypropylene and polyisobutylene give appreciable amounts of NH_3, but linear polyethylene does not (64).

While studying the methyl silanes, Dewhurst and Cooper found the yield of NH_3 increased as the degree of substitution increased, leading to the conclusion that the silicon hydrogens do not go to form NH_3, but HCN only. Using CH_3[illegible], the main products were HCN and NH_2D, with only traces or less of DCN, NHD_2, NH_3, and ND_3. This indicates that NH_3 is formed [illegible] abstraction of two

hydrogens from carbon at the same time, and that HCN formation involves a hydrogen atom not originally bonded to the carbon atom. Some H_2 was also formed from the less substituted methyl silanes (10,11).

The initial step in most of the chemical reactions of active nitrogen is generally assumed to be the formation of a complex, N•M, where M is the compound which is reacting. This is followed by fragmentation to give products (54,64,66). It is the composition of these fragments that is the subject of discussion.

VII. CONCLUSION

The chemistry of active nitrogen involves free radicals as intermediates. Comparison with the chemistry of nitrogen-containing free radicals produced by other methods might provide valuable insight into this area of chemistry.

Bibliography

1. K. D. Bayes, Can. J. Chem. 39, 1074 (1961).
2. K. D. Bayes and G. B. Kistiakowsky, J. Chem. Phys. 32, 992 (1960).
3. J. M. Benson, J. Appl. Phys. 23, 757 (1952).
4. J. Berkowitz, W. A. Chupka and G. B. Kistiakowsky, J. Chem. Phys. 25, 457 (1956).
5. M. C. Chen and H. A. Taylor, ibid., 34, 1344 (1961).
6. M. A. A. Clyne and B. A. Thrush, Nature 189 , 56 (1961).
7. M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. A261, 259 (1961).
8. M. A. A. Clyne and B. A. Thrush, Trans. Faraday Soc. 57, 69 (1961).
9. P. A. Constantinides, Phys. Rev. 30, 95 (1927).
10. H. A. Dewhurst, J. Phys. Chem. 63, 1976 (1959).
11. H. A. Dewhurst and G. D. Cooper, J. Am. Chem. Soc. 82, 4220 (1960).
12. R. N. Dixon and R. W. Nicholls, Can. J. Phys. 36, 127 (1958).
13. K. Dressler, J. Chem. Phys. 30, 1621 (1959).
14. H. B. Dunford and B. E. Melanson, Can. J. Chem. 37, 641 (1959).
15. J. W. Edwards, "Chemical and Physical Studies of Trapped Radicals, Formation and Trapping of Free Radicals, A. M. Bass and H. P. Broida, Eds., Academic Press, New York 1960, p. 257.
16. H. Gaensslen, Anales Real Soc. Espan. Fis. y Quim. 56B, 927 (1960).
17. P. A. Gartaganis and C. A. Winkler, Can. J. Chem. 34, 1457(1956).
18. H. Guenebaut, Compt. rend. 249, 2778 (1959).
19. H. Guenebaut, G. Pannetier, and P. Goudmand, J. Chim. Phys. 58, 513 (1961).
20. C. Haggart and C. A. Winkler, Can. J. Chem. 38, 329 (1960).
21. P. Harteck and S. Dondes, J. Chem. Phys. 29, 234 (1958).
22. P. Harteck, R. Reeves and G. Mannella, ibid . 29,608 (1958).
23. M. A. Heald and R. Beringer, Phys. Rev. 96, 645 (1954).
24. L. Herman and R. Herman, Nature 191, 346 (1961).
25. J. T. Herron, J. L. Franklin, and P. Bradt, Can. J. Chem. 37, 579 (1959).
26. J. T. Herron, J. L. Franklin, P. Bradt, and V. H. Dibeler, J. Chem. Phys. 29, 230 (1958).

27. J. T. Herron, J. L. Franklin, P. Bradt, and V. H. Dibeler, ibid. **30**, 879 (1959).
28. D. S. Jackson and H. I. Schiff, *ibid*. **23**, 2333 (1955).
29. K. R. Jennings and J. W. Linnett, Quart. Rev. **12**, 116 (1958).
30. W. Jevons, Proc. Roy. Soc. **A89**, 187 (1913).
31. W. Jevons, *ibid*. **A91**, 120 (1915).
32. W. Jevons, *Report on Band Spectra of Diatomic Molecules*, Physical Soc. London, 1932, p. 206.
33. F. Kaufman and J. R. Kelso, J. Chem. Phys. **28**, 510 (1958).
34. R. Kelly and C. A. Winkler, Can. J. Chem. **37**, 62 (1959).
35. R. Kelly and C. A. Winkler, *ibid*. **38**, 2514 (1960).
36. C. Kenty and L. A. Turner, Phys. Rev. **32**, 799 (1928).
37. G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. **28**, 665 (1958).
38. G. B. Kistialowsky and P. Warneck, *ibid*., **27**, 1417 (1957).
39. N. V. Klassen, M. Onyszchuk, J. C. McCabe, and C. A. Winkler, Can. J. Chem. **36**, 1217 (1958).
40. H. P. Knauss, Phys. Rev. **32**, 417 (1928).
41. W. B. Kunkel, Bull. Am. Phys. Soc. [2] **2**, 87 (1957).
42. U. H. Kurzweg and H. P. Broida, J. Molec. Spectr. **3**, 388 (1959).
43. F. LeBlanc, Y. Tanaka, and A. Jursa, J. Chem. Phys. **28**, 979 (1958).
44. P. Lewis, Astrophys. J. **12**, 8 (1900).
45. E. R. V. Milton and H. B. Dunford, J. Chem. Phys. **34**, 51 (1961).
46. S. K. Mitra, *Active Nitrogen, a New Theory*, Indian Assoc. for Cult. of Sci., Calcutta, 1945.
47. S. Miyazaki and S. Takahashi, J. Chem. Soc. Jap., Ind. Chem. Sect. **64**, A25 (1961).
48. J. F. Noxon, Bull. Am. Phys. Soc. [2], **2**, 44 (1957).
49. J. Okubo and H. Hamada, Phil. Mag. [7] **5**, 372 (1928).
50. G. Pannetier, P. Goudmand, H. Guenebaut, and L. Marsigny, J. Chim. phys. **57**, 959(1960).
51. G. Pannetier, H. Guenebaut, and L. Marsigny, Compt. rend. **249**, 1670 (1959).
52. Lord Rayleigh, Proc. Roy. Soc. **A176**, 1 (1940).
53. R. R. Reeves, G. Mannella, and P. Harteck, J. Chem. Phys. **32**, 946 (1960).
54. S. E. Sobering and C. A. Winkler, Can. J. Chem. **36**, 1223 (1958).
55. C. R. Stanley, Proc. Phys. Soc. **67A**, 821 (1954).
56. R. J. Strutt, Proc. Roy. Soc. **A85**, 219 (1911).
57. R. J. Strutt, *ibid*. **A86**, 56 (1911).
58. R. J. Strutt, *ibid*. **A91**, 303 (1915).
59. R. J. Strutt, *ibid*. **A92**, 438 (1916).
60. R. J. Strutt and A. Fowler, *ibid*. **A86**, 105 (1912).
61. Y. Tanaka, A. Jursa, and F. LeBlanc, "Vacuum Ultraviolet Spectra of the Afterglows of Pure N_2 and a Mixture of N_2 and O_2, "*The Threshold of Space*, M. Zelikoff, Ed., Pergamon Press, New York, 1957, p. 89.
62. Y. Tanaka, T. Namioka, and A. S. Jursa, Can. J. Phys. **39**, 1138 (1961).
63. G. J. Verbeke and C. A. Winkler, J. Phys. Chem. **64**, 319 (1960).
64. J. L. Weininger, *ibid*. **65**, 941 (1961).
65. T. Wentink, Jr., J. O. Sullivan, and K. L. Wray, J. Chem. Phys. **29**, 231 (1958).
66. R. A. Westbury and C. A. Winkler, Can. J. Chem. **38**, 334 (1960).
67. E. J. B. Willey and E. K. Rideal, J. Chem. Soc. 1927, 669.
68. W. G. Zinman, J. Am. Chem. Soc. **82**, 1262 (1960).

SULFUR FLUORINE COMPOUNDS

G. R. Feistel

October 24, 1961

I. INTRODUCTION

Much work has been done on sulfur fluorine compounds over the past years. Several review articles have been written covering all phases of the work (1,2). This seminar will cover only the sulfur-fluorine, sulfur-fluorine-oxygen, and sulfur-fluorine-carbon systems. The use of sulfur tetrafluoride as a fluorinating agent will also be mentioned, and examples demonstrating its versatility will be cited. A short discussion of the general problems and techniques of fluorine chemistry is also presented.

II. PROBLEMS AND TECHNIQUES OF FLUORINE CHEMISTRY

Since elemental fluorine is a very reactive substance, it reacts with most organic and inorganic compounds to give mostly simple substances if the reaction is allowed to go to completion. If the skeleton of the starting material is to be maintained, the fluorinating conditions must be controlled rigorously. Three methods have been widely used. They are direct fluorination with high dilution, fluorination using metal fluorides, and electrochemical fluorination. The last is gaining in usage. They are discussed separately below.

A. Direct Fluorination

In this method, the substance to be fluorinated and the fluorine are brought together highly diluted by nitrogen or argon <u>via</u> separate tubes to a reactor chamber packed with a metal packing. Gold plated copper, copper, cobalt, and nickel have been used as packings. Usually the fluorine is in excess in order not to give mixed products. The reaction is controlled by an efficient cooling system.

This method requires a pure source of elemental fluorine, which is one of the bad features of the method. This method also suffers from local heating effects. Several different designs for reactors have been mentioned in the literature.

B. Fluorination with Metallic Fluorides

Fluorination(3) may be carried out by passing the substances to be fluorinated over a metal fluoride in which the metal is a good oxidizing agent. Cobaltic fluoride has been the most used; however, CeF_4, BiF_5, and UF_6 have also been used.

Two methods have been used: 1. the vapor phase method in which the compound is passed over the heated metal fluoride, and 2. the liquid phase method in which a perfluorinated hydrocarbon is used as a solvent and the substance is suspended in the solvent. Some examples (4) of its use are

$$CS_2 + 14CoF_3 \rightarrow CF_3SF_5 + 14CoF_2 + SF_6$$

$$CH_3SH + 12CoF_3 \rightarrow CF_3SF_5 + 12CoF_2 + 4HF$$

The main problem is temperature control. If the temperature is too low, the metal fluoride is deactivated by fluorocarbon resins forming

SULFUR FLUORINE COMPOUNDS

G. R. Pelabi   October 23, 1952

I. INTRODUCTION

Much work has been done on sulfur fluorine compounds over the past years. Several review articles have been written covering all phases of the area (1-6). This seminar will concentrate on sulfur-fluorine, sulfur-fluorine-oxygen, and sulfur-fluorine-carbon systems. The use of sulfur tetrafluoride as a fluorinating agent will also be mentioned, and examples demonstrating its versatility will be given. A short discussion of the general problems and techniques of fluorine chemistry is also presented.

II. PROBLEMS AND TECHNIQUES OF FLUORINE CHEMISTRY

Since elemental fluorine is a very reactive substance, it reacts with most organic and inorganic compounds to give not only simple substitution or addition products but also degradation. If the skeleton of the starting material is to be maintained, the fluorinating conditions must be controlled rigorously. Three methods have been widely used. They are direct fluorination with high dilution, fluorination using metal fluorides, and electrochemical fluorination. The last is gaining in usage. They are discussed separately below.

A. Direct Fluorination

In this method, the substance to be fluorinated and the fluorine are brought together slowly diluted by nitrogen or argon via separate tubes in a reactor packed with a metal packing. Gold plated copper, copper, nickel, and monel have been used as packings. Usually the fluorine is in excess in order not to give mixed products. The reaction is conducted in an efficient cooling system.

This method requires a large source of elemental fluorine, which is one of the disadvantages of the method. The method also suffers from local heating effects. Several different designs for reactors have been mentioned in the literature.

B. Fluorination with metallic fluorides

Fluorination may be carried out by passing the substance to be fluorinated over a metal fluoride which operates as a good oxidizing agent. Cobaltic fluoride has been the most used; however, CeF_4, AgF_2 and MnF_3 have also been used.

Two methods have been used: 1, the vapor phase method in which the compound is passed over the heated metal fluoride, and 2, the liquid phase method in which a perfluorinated hydrocarbon is used as a solvent and the substance is suspended in the solvent. Some examples (1) of the method are

$$CS_2 + 10CoF_3 \rightarrow CF_3SF_5 + 10CoF_2 + S$$

$$C_2H_5SH + 18CoF_3 \rightarrow CF_3SF_5 + 18CoF_2 + HF$$

The main problem is temperature control. If the temperature is too low, the metal fluoride is regenerated by fluorination using fluorine on the surface, and if too high, there is extensive bond cleavage.

C. Electrochemical Fluorination

Many substances when dissolved in anhydrous hydrogen fluoride(3) give conducting solutions, and by electrolysis of these solutions the substances can be fluorinated. Since the products as a rule do not conduct, the end of the reaction is noted by a drop in current, and the product is not fluorinated destructively. Usually the product is not soluble in anhydrous hydrogen fluoride and can be drained off, thus allowing more or less continuous fluorination. Substances which do not dissolve in anhydrous hydrogen fluoride can be fluorinated by using suspensions and adding a salt to serve as a conducting medium.

There are two serious drawbacks to the method. One is that when a conducting salt is used it is hard to tell when the reaction is completed and destructive fluorination may result. Another is that if the compound contains oxygen, or the solvent is wet or there is some atmospheric oxygen present, OF_2 is formed, which is very explosive.

This method affords good control of the rate of fluorination and promises to be the most useful of those mentioned.

III. BINARY SULFUR FLUORIDES

Several fluorides of sulfur are claimed to have been isolated. Among these are SF_6, S_2F_{10}, SF_4, SF_2, and S_2F_2. Also discussed under this heading is SF_5Cl.

A. Sulfur Hexafluoride and Sulfur Decafluoride

Sulfur hexafluoride and disulfur decafluoride are prepared by direct reaction of sulfur with fluorine. Supposedly the whole series of fluorides is formed in this reaction. These two, however, can be isolated by washing with NaOH solution, inasmuch as neither of them is attacked readily by base. They can be separated by low-temperature distillation.

Sulfur hexafluoride has an octahedral structure and a S-F bond length(5) of 1.58 A. It is very inert and reacts with alkali metals only at high temperatures. It exchanges fluorine only slowly or not at all with HF. This chemical inertness makes it a good substance for an electrical insulator. The bond energy for SF_6 is 71.7 kcal./mole (6) while that for SF_4 is 78-79 kcal./mole (1). Since SF_4 is more reactive than SF_6, this means that the stability of SF_6 can be attributed to a kinetic effect rather than a thermodynamic one. Calculations (7) indicate that bonding by a d^2sp^3 hybrid is a poor model because the overlap integral is too small. Provision must be made for the contraction of the d orbitals in the hybrid.

Disulfur decafluoride contains two SF_5 groups bonded through the sulfur. The sulfur atoms are in octahedral positions. The S-F distance is 1.56 A and the S-S distance(8) is 2.21 A. Disulfur decafluoride is said to have hindered rotation around the S-S bond with the free model and the interlocking, non-rotating model contributing about equally. This is probably a poor estimate of the contributions since it comes from electron diffraction data. Infra-red(9) and Raman data also agree with the structure although they give no information about hindered rotation.

B. Sulfur Tetrafluoride

Sulfur tetrafluoride is best made by the reaction of SCl_2 with NaF in acetonitrile according to the equation(10)

$$3SCl_2 + 4NaF \rightarrow SF_4 + S_2Cl_2 + 4NaCl$$

It can also be prepared(11) in a very pure form by allowing sulfur and boron to react with fluorine at $-75^\circ C$ to form BF_3SF_4, which can be purified and the SF_4 released by treating with AsF_5 or TeF_4.

Sulfur tetrafluoride is thought to have the trigonal bipyramidal structure(12,13,14) with the lone pair of electrons in the equatorial plane. Sulfur tetrafluoride has been studied by nmr and a mechanism for fluorine exchange has been proposed.

The chemistry of SF_4 will be discussed in a later section.

C. Sulfur Difluoride and Disulfur Difluoride

These compounds have been reported but have not been definitely characterized. Both have been reported as breakdown products of SF_6 and were identified by infrared spectra. However the paper gives no details on assignments or even the spectra (15).

D. Pentafluoro Sulfur Chloride

This compound has been obtained by the fluorination of S_2Cl_2(16). It is stable in acids but decomposes in base. It is stable up to 250°C in glass. SF_5Cl has C_{4v} symmetry with the S-F bond distance 1.576 A and the S-Cl distance of 2.031 A. (17)

Pentafluoro sulfur chloride reacts as if the chlorine carries a partial positive charge. Thus it reacts with benzene under Friedel-Crafts conditions to give chlorobenzene (1). It also liberates bromine and iodine from aqueous solutions of the potassium salts.

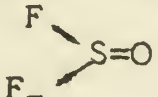
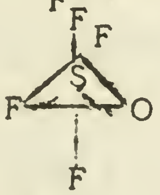
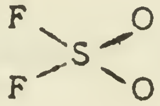
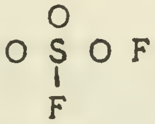
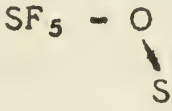
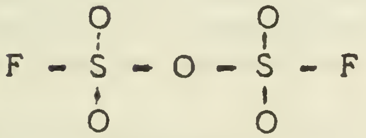
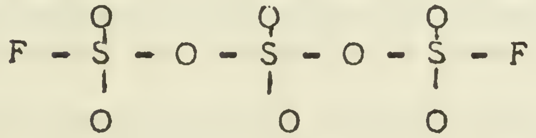
Pentafluoro sulfur chloride reacts with olefins in the following manner.

$$SF_5Cl + RCHCH_2 \rightarrow RCHClCH_2SF_5$$

It hydrolyzes to give sulfate, fluoride, and chloride ions. The mechanism of hydrolysis is thought to involve oxidation-reduction(1).

IV. SULFUR-FLUORINE-OXYGEN COMPOUNDS

Many compounds have been isolated containing only sulfur, fluorine, and oxygen. Below is a list with the proposed structures where known.

	Structure	Angles and Distances	Method
SOF_2		$r_{S-O} = 1.412A$ $r_{S-F}=1.585A$ $<FSF = 92^{\circ}49', <OSF=106^{\circ}49'$	microwave
SOF_4		Gives 1 nmr line at room temperature.	nmr
SOF_6	F_5SOF		nmr
SO_2F_2		$r_{S-F} = 1.56A, r_{S-O}=1.43A$ $<FSO = 105^{\circ}, <FSF = 100^{\circ}, <OSO= 130^{\circ}$	Electron diffraction
SO_3F_2	 $O\overset{O}{\underset{F}{S}}OF$		nmr and chemical
S_2OF_{10}	 n nonlinear SOS.		Raman
$S_2O_2F_{10}$	F_5SOOSF_5	$r_{S-F} = 1.56$ A, $r_{O-O} =1.47A$. $r_{S-O} = 1.66A$, $<SOOS$ dihed.= 107° $<SOO = 105^{\circ}$	Electron Diffraction
$S_2O_5F_2$	 $F-\overset{O}{\underset{O}{S}}-O-\overset{O}{\underset{O}{S}}-F$		nmr and chemical
$S_2O_5F_4$	doubtful		
$S_2O_6F_2$	 $F-\overset{O}{\underset{O}{S}}-O-O-\overset{O}{\underset{O}{S}}-F$		nmr and chemical
$S_3O_8F_2$	 $F-\overset{O}{\underset{O}{S}}-O-\overset{O}{\underset{O}{S}}-O-\overset{O}{\underset{O}{S}}-F$		chemical

Many of these compounds are stable in water and hydrolyze only slowly in aqueous base. Some of the reactions of the above compounds are discussed below.

A. SOF_4

When a cold, neutral, aqueous potassium iodide solution is run into a bulb containing SOF_4, iodine flakes are liberated (19). However after a few seconds, the iodine starts decreasing, and a colorless solution results. The net reaction appears to be a sum of the two reactions described by the equations

$$SOF_4 + H_2O \rightarrow SO_2F_2 + 2HF$$

$$SOF_4 + 2H_2O \rightarrow SO_3F^- + 3HF + H^+$$

Thionyl tetrafluoride reacts with base according to

$$SOF_4 + 4OH^- \rightarrow SO_3F^- + 2H_2O + 3F^-$$

B. $S_3O_8F_2$

This compound hydrolyzes slowly in aqueous base as follows

$$S_3O_8F_2 + 4OH^- \rightarrow 2SO_3F^- + SO_4^{--} + 2H_2O$$

From this reaction the structure given in the table above is suggested (20).

C. SO_2F_2

This compound is particularly stable, almost as stable as SF_6. Its rate of hydrolysis in water and base is very slow (21). However, it is rapidly hydrolyzed in concentrated HF.

V. CARBON-SULFUR-FLUORINE COMPOUNDS

Compounds of this type are usually derivatives of SF_6, however some derivatives of SF_4 and even SF_2 have been made.

Derivatives of SF_6 can be made in two ways. One is the already discussed method using SF_5Cl. The other and older method is the fluorination of mercaptans or thio-ethers, giving the mono- and di-sbustituted products, respectively.

Derivatives of SF_4 result from the above method where the product has not been completely fluorinated (4). The aromatic analogs of SF_4 can be prepared by treating the corresponding disulphide with silver difluoride in an inert solvent (22).

Derivatives of SF_2 can be made from the corresponding perfluoro alkyl sulphenyl chlorides by treating them with AgF or HgF_2. This does not work for aromatic compounds (23).

The disubstituted derivatives of SF_6 might be cis and trans isomers. The trans isomer is the one that is found in compounds such as $(R_f)_2SF_4$ whereas in a compound in which R is a ring containing the sulfur, the sulfur is substituted cis (24).

The derivatives of SF_6 are stable to hydrolysis, whereas those of SF_4 and SF_2 hydrolyze readily. No compound with more than two substituents has been described.

VI. SULFUR TETRAFLUORIDE AS A FLUORINATING AGENT

Smith has discovered a general reaction of sulfur tetrafluoride which enables one to fluorinate a carbonyl group or inorganic oxide or sulfide to the corresponding fluorocarbon or inorganic cloride. Several examples are given below.

$$CH_3COCH_3 + SF_4 \rightarrow CH_3CF_2CH_3 + SOF_2 \qquad (25)$$

$$CH_3CHO + SF_4 \rightarrow CH_3CHF_2 + SOF_2 \qquad (25)$$

$$CHCCO_2H + 2SF_4 \rightarrow CHCCF_3 + 2SOF_2 + HF \qquad (25)$$

$$C_6H_5\overset{O}{As}(OH)_2 + SF_4 \rightarrow C_6H_5AsF_4 + 3SOF_2 + 2HF \qquad (26)$$

$$I_2O_5 + 5SF_4 \rightarrow 5SOF_2 + 2IF_5 \qquad (27)$$

$$2NaF + GeO_2 + 2SF_4 \rightarrow Na_2GeF_6 + 2SOF_2 \qquad (28)$$

A mechanism has been proposed for the reaction of SF_4 with a carbonyl group. Another reaction of SF_4 is the one with BF_3 to give a compound with the formula BF_3SF_4. Possible structures have been discussed (29).

VII. CONCLUSION

There are many unresolved problems in structure, and the field of kinetics has hardly been touched in the field of sulfur-fluorine chemistry.

BIBLIOGRAPHY

1. H. L. Roberts, Quart. Rev., 15, 30 (1961).
2. G. H. Cady, Adv. Inorg. Radiochem., 2 , 105 (1960).
3. J. Burdon, J. C. Tatlow, and M. Stacey, Adv. in Fluorine Chem., 1, 129, 166 (1960).
4. G. A. Silvey and G. H. Cady, J. Am. Chem. Soc., 72, 3624 (1950).
5. L. O. Brockway and L. Pauling, Proc. Natl. Acad. Sci. (U.S.), 19, 68 (1933).
6. R. K. Curran, J. Chem. Phys., 34, 1069 (1961).
7. D. P. Craig and E. A. Magnusson, J. Chem. Soc., 4895 (1956).
8. R. B. Harvey and S. H. Bauer, J. Am. Chem. Soc., 75, 2840(1953).
9. R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc., 53, 1545, 1557 (1959).
10. C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, J. Am. Chem. Soc., 82, 539 (1960).
11. N. Bartlett and P. L. Robinson, Proc. Chem. Soc., 230, (1957).
12. F. A. Cotton, J. W. George, and J. S. Waugh, J. Chem. Phys., 28, 994 (1958).
13. E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc., 81, 1084 (1959).
14. R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc., 52, 1052 (1956).
15. D. Edelson, C. A. Bieling, and G. T. Kohmann, Ind. Eng. Chem., 45, 2094 (1953).
16. H. L. Roberts, J. Chem. Soc., 665 (1960).
17. R. Kewley, K. S. R. Murty, and T. M. Sugden, Trans. Faraday Soc., 56, 1732 (1960).

18. J. R. Case, J. Chem. Soc., 2066, 2070 (1961).
19. F. B. Dudley, G. H. Cady, and D. F. Eggers, J. Am. Chem. Soc., 78, 1553 (1956).
20. H. A. Lehmann and L. Z. Kolditz, Z. Anorg. u. allgem. chem., 272, 73 (1953).
21. K. Z. Wiechert, Z. anorg. u. allgem. Chem., 261, 310 (1950).
22. W. A. Shepard, J. Am. Chem. Soc., 82, 4751 (1960).
23. E. Kober, J. Am. Chem. Soc., 81, 4810 (1959).
24. N. Muller, P. C. Lauterbur, and G. F. Svatos, J. Am. Chem. Soc., 79, 1043 (1957).
25. W. R. Hasek, W. C. Smith, and V. A. Engelhardt, J. Am. Chem. Soc., 82, 543 (1960).
26. W. C. Smith, J. Am. Chem. Soc., 82, 6176 (1960).
27. A. I. Oppegard, W. C. Smith, E. L. Muetterties, and V.A. Engelhardt J. Am. Chem. Soc., 82, 3835 (1960).
28. R. D. W. Kemmitt, J. Chem. Soc., 2496 (1961).
29. F. A. Cotton and J. W. George, J. Inorg. Nuclear Chem., 7, 397 (1958).

MAGNETOCHEMISTRY - TECHNIQUES OF MEASUREMENT AND RECENT MAGNETIC STUDIES

R. J. Niedzielski October 31, 1961

I. INTRODUCTION

The magnetic properties of inorganic compounds have been studied for over 100 years. The applications of this technique are many and varied. Thus, a contemporary text lists the following as examples of the technical information which can be obtained in chemical analysis by magnetic methods: oxygen in air, carbon in steel, phase transformations, geological applications, single crystal studies, molecular structure, and magnetic titrations (1).

The study of coordination compounds makes up what is perhaps the most active single branch of magnetochemistry. The value of magnetic measurements in this area of inorganic chemistry has greatly increased within the last 25 years. This has come about chiefly because of the advance of valency theory during this time, enabling a better correlation of the effective magnetic moment of an atom to be made with its valency, bond type, and stereochemistry.

II. GENERAL CONSIDERATIONS

No attempt will be made to deal with the theoretical aspects of this subject. These may be found in any of the standard works(2-5). A summary of fundamentals will be given here.

The origin of magnetic susceptibility lies in the electrical nature of the atom. It is known that the movement of an electric charge produces a magnetic effect. An electron revolving in an orbit around a nucleus may thus be likened to an electric current in a loop of wire. The spin and orbital motions of this electron are responsible for the observed magnetic moments of substances.

Chemical substances may be classified on the basis of their behavior when placed in a magnetic field. The extent to which a material becomes magnetized is measured by its magnetic moment per unit volume, known as the intensity of magnetization, I. The total number of lines of force per unit area inside the material is given by

$$B = H + 4\pi I \quad ,$$

where B is the magnetic induction and H the strength of the magnetic field in a vacuum. The volume susceptibility of the material, K, is given by the ratio I/H. This is the term generally measured experimentally, but the gram susceptibility is usually of more interest

$$\chi = K/\rho \quad ,$$

where ρ is the density. For chemical compounds the molar susceptibility χ_M is more important. Values of χ_M vary from -3×10^{-6} for diamagnetic substances to as high as $+10{,}000 \times 10^{-6}$ for paramagnetic substances.

With the substance in the magnetic field, the intensity of magnetization experienced may be either slightly smaller, or slightly larger, than that produced in a vacuum by the same field. If the former arises, the substance is diamagnetic; paramagnetic substances exhibit the latter effect.

Diamagnetism is a property of all atoms, regardless of whether or not they possess an overall paramagnetism. The phenomenon arises from the tendency of all electrons in closed shells to orient their planes of rotation in such a manner so as to experience a minimal interaction with the applied field. In diamagnetic substances the flux density is less than that of the surrounding magnetic field, and the susceptibility is independent of temperature. In practice the calculation of atomic and molecular diamagnetic susceptibilities is very difficult, and agreement with experimentally observed values is only approximate. Pascal's approach is usually followed in evaluating this contribution (6). This involves the use of "constitutive corrections" for the deviations observed.

Normal paramagnetism is found in those substances the atoms or molecules of which behave as though they have a permanent magnetic moment. This behavior is associated with the presence of unpaired electrons, or an incomplete electronic level. Application of a magnetic field leads to orientation of this moment. When paramagnetism is present, its effect is generally much greater than the diamagnetism present, and consequently it overshadows the latter. Paramagnetism is inversely proportional to the absolute temperature.

It can be shown that ideally,

$$\chi_M = N^2 \mu^2 / 3RT,$$

where N is Avogadro's Number, μ the magnetic moment, R the universal constant, and T the absolute temperature. A precise expression will also include a term for the relatively small contribution of the diamagnetic portion of the susceptibility. The value of μ thus obtained is known as the "effective magnetic moment"

$$\mu_{eff} = 2.84 \sqrt{\chi'_M (T)}$$

A convenient unit of magnetic moment is the Bohr magneton, which is given by the expression

$$\beta = eh / 4\pi mc,$$

where h is Planck's constant, e the electronic charge, c the velocity of light, and m the electron mass.

The effective magnetic moment of many ions of the transition elements expressed in Bohr magnetons is readily given by the expression

$$\mu_\beta = \sqrt{n (n + 2)} ,$$

where n is the number of unpaired electrons.

Provided that the compound being investigated is magnetically dilute, and is governed by the above simple expressions, the number of unpaired electrons may be deduced from the magnetic moment. It may then be possible to infer the valency, bond type, and/or the stereochemistry of the metal atom.

The above presentation has been a rather generalized one. For more detailed coverage any of the excellent sources available may be consulted (6-8).

III. TECHNIQUES OF MEASUREMENT

A. The Gouy Method

When reasonable amounts of a substance are available, the Gouy method is the most convenient for measuring magnetic susceptibilities. A cylindrical column of material of cross-sectional area A and length l is suspended from a sensitive balance between the poles of a magnet so that one end of the material is subjected to the strong magnetic field. The other end of the specimen is in a region of negligible field strength. The difference in the pull on the balance, usually expressed in milligrams, is then observed with the magnet on and then off. The following expression is used:

$$\chi_g = (Kv + 2gv\delta w/AH_1^2) / W$$

The general practice is to calibrate the tube used with a material of known susceptibility. Then

$$\chi_g = (a + b\,\delta w)/W$$

where a and b are constants for any particular tube and field strength, respectively. Substances commonly used for calibration include H_2O, $CuSO_4.5H_2O$, or $NiCl_2$. Recently, use of $[Nien_3]S_2O_3$ (9) or $Hg[Co(CNS)_4]$ (10) as calibrants has been advocated.

The accuracy of measurements on powdered samples by the Gouy method is limited by the uniformity and reproducibility of packing.

A typical apparatus of the Gouy type has been described in the literature(11). Recently, Figgis and Nyholm constructed an instrument capable of determining gram-susceptibilities in the range $1 - 500 \times 10^{-6}$ to within an accuracy of about 0.5% in favorable circumstances (12). Devised chiefly for measurement of the temperature variation of magnetic susceptibilities, the apparatus can be used in the range $80 - 500^{\circ}$K., with the mean temperature of the specimen controllable to within 0.1°.

B. The Quincke Method

This method is similar in principle to the Gouy method and is well adapted to measurements on liquids (6). The force on the liquid sample is measured in terms of the hydrostatic pressure developed when the liquid is placed in a capillary tube so that the meniscus stands in a strong magnetic field. For a diamagnetic substance the change in height of the meniscus may be several millimeters. An adaptation of this technique has been described for gases(13). The method used consisted of balancing the gas magnetically against an aqueous solution of $NiCl_2$.

Provided that the compound being investigated is magnetically dilute, and is governed by the above simple assumptions, the number of unpaired electrons may be deduced from the magnetic moment. It may then be possible to infer the valence, bond type, and/or the stereochemistry of the metal atom.

The above presentation has been somewhat generalized and for more detailed coverage any of the excellent reviews available may be consulted (4-8).

III. TECHNIQUES OF MEASUREMENT

A. The Gouy Method

When appreciable amounts of a substance are available, the Gouy method is the most convenient for measuring magnetic susceptibilities. A cylindrical column of material of cross-sectional area A and length l is suspended from a sensitive balance between the poles of a magnet so that one end of the material is subjected to the strong magnetic field. The other end of the specimen is in a region of negligible field strength. The difference in the pull on the specimen, usually expressed in milligrams, is then observed with the magnet on and then off. The following expression is valid:

$$\chi = (K) \times \Delta w / [illegible]^2 / W$$

The general practice is to calibrate the tube used with a material of known susceptibility. Then

$$\chi = (a + b\Delta w)/W$$

where a and b are constants for any particular tube and field strength, respectively. Substances commonly used for calibrating include H_2O, $CuSO_4 \cdot 5H_2O$, or $NiCl_2$. Recently, use of $[Ni(en)_3]S_2O_3$(9) or $Hg[Co(CNS)_4]$ (10) as calibrant has been advocated.

The accuracy of measurements on powdered samples by the Gouy method is limited by the uniformity and reproducibility of packing.

A typical apparatus of the Gouy type has been described in the literature(11). Recently, Figgis and Nyholm constructed an instrument capable of determining gram-susceptibilities in the range 1 - 300 × 10^{-6} to within an accuracy of about 0.1% in favorable circumstances (12). Designed chiefly for measurement of the temperature variation of magnetic susceptibilities, the apparatus can be used in the range 80 - 300°K., with the exact temperature of the specimen controllable to within 0.1°.

B. The Quincke Method

This method is similar in principle to the Gouy method and is well adapted to measurements on liquids (8). The force on the liquid sample is measured in terms of the hydrostatic pressure developed when the liquid is placed in a capillary tube so that the meniscus stands in a strong magnetic field. For a diamagnetic substance the change in height of the meniscus may be several millimeters. An adaptation of this technique has been described for gases(13). This method also consisted of balancing the gas magnetically against an aqueous solution of $NiCl_2$.

C. The Faraday Method

If a substance is placed in a region where the strength of the field changes with displacement along an axis, the substance will be subjected to a force. The sample is moved along the axis until a maximum in the force is experienced. This force is proportional to the field strength and the field gradient. The Faraday method is the method of choice when only a small amount of material is available (0.1 to 10 mg). Because of this, the technique has proved to be useful in the measurement of magnetic properties of the actinide elements(14).

D. The Sucksmith Method

The Sucksmith method is a vertical force method. Rather than using a balance, a ring of phosphor bronze, fixed at its upper side, is used to suspend the sample(6). Movement of a lamp filament image coincident with the ring movement is observed.

E. Paramagnetic Resonance Methods

The shifts of proton resonance lines of inert reference molecules in solution caused by paramagnetic substances are used for the determination of paramagnetic susceptibilities. Values obtained by this technique have been found to be in excellent agreement with literature values of susceptibilities (15). The method can also be used to advantage when very small amounts of substance are available; less than 0.03 milliliter of solution can be measured. An investigation was also made of the anomalous results obtained with diamagnetic species (16).

A similar technique employing two concentric cylindrical glass tubes has been introduced (17). Recent application of the method has yielded mixed results (18).

IV. RECENT MAGNETIC STUDIES

A. Hydrolysis of Fe(III)

The hydrolysis of the iron(III) ion has been studied by a combination of spectrophotometric and magnetic methods (19,20). The study originated during attempts to obtain structural information on hydrous oxides and hydroxides of the transition metals.

Hydrous ferric oxide, which is gel-like in character, shows many unusual properties. One of these is a subnormal magnetic moment. Various attempts to explain these results, as well as the structure, showed a wide area of disagreement among early workers(20). Most of these studies were undertaken on the solid and the colloidal system. In the present study, this approach was abandoned, and instead the nature of the ionic species formed during hydrolysis of iron(III), up to the gel formation, was studied.

The initial work (20) showed the presence of a diamagnetic species in substantial amounts in partially hydrolyzed iron(III) solutions. This result was in good agreement with Hedstrom's study based on electrochemical techniques (21). This species was formulated as a binuclear complex, with exchange interactions between adjacent iron atoms destroying the paramagnetism.

Recently this study was repeated on aged solutions of iron(III) perchlorate of varying pH (22). Again good agreement was reached for equilibrium data between the spectrophotometric and magnetic methods. A linear structure for the polymer formed in these solutions was proposed.

B. The δ Bond of Copper(II) Acetate

The magnetic susceptibility of copper(II) acetate 1-hydrate at room temperature had long been known to be anomalously low. The results of the paramagnetic resonance absorption study of this compound led to the postulate that strong interactions took place between neighboring copper atoms (23). A basis for this approach was the earlier X-ray structure study of the crystal (24), which showed the compound to be a binuclear molecule. The outstanding feature of the structure was the close distance of approach of the copper atoms.

An extensive magnetic study of the above compound was undertaken by Figgis and Martin (25). The result of this study indicated the existence of very weak covalent copper-copper bonds. It was suggested that a δ bond was fomed betwean the copper atoms by the lateral overlap of the $3\ d_{x^2-y^2}$ orbitals. A critical evaluation of the paramagnetic resonance spectrum of the above compound confirmed the presence of a δ bond, one of the few such bonds postulated (26). Ross and Yates also calculated the singlet-triplet separation for δ and σ bonds (27).

The study was later extended to other copper (II) n-alkanoates. Both solid (28) and solution (29) studied in dioxane and benzene established binuclear structures and δ bonding in the series of compounds copper(II) acetate to copper(II) behenate. Copper(II) formate alone persisted in the mononuclear form (30). However, by use of heterocyclic amines and dioxane as coordinating ligands, the copper(II) formate was "conditioned" into adopting the binuclear copper(II) acetate structure (31). The crystal structure of anhydrous copper(II) formate has recently been determined (32). The result verifies the earlier magnetic work.

Independent studies of the polarized absorption spectra of the copper(II) n-alkanoates lend further support to the above work (33,34).

The temperature dependence of susceptibility of a series of copper(II) complexes was studied by Figgis and Harris (35). The results largely refuted the earlier assignment of tetrahedral configuration to a number of copper(II) complexes (36).

C. Tetrahedral Ni(II) Complexes

A recent report presented a detailed analysis of the evidence for the existence of tetrahedral complexes of Ni(II) (37). Venanzi earlier had detailed the factors determining the formation of tetrahedral nickel(II) complexes (38,39). Since that time a number of publications have appeared, in which the presence of nickel(II) in tetrahedral coordination is reported (40-44). Generally the ligands used are of the triaryl-phosphine or -phosphine oxide type, thus perhaps "forcing" the tetrahedral configuration of nickel(II). Magnetic data are used extensively in these studies.

V. CONCLUSION

This presentation has necessarily been brief and somewhat limited in its scope. The work cited is merely illustrative of the large volume of work being done. Thus no mention was made of the study being conducted of the $\underline{d}^3$ and $\underline{d}^4$ configurations of the second and third transition series(45,46). Some interesting work is also under way on polynuclear compounds, the long-neglected area between the magnetically dilute compounds and the ferromagnetic compounds, upon which most of the work so far has been concentrated(47 In connection with the work mentioned above on nickel(II) complexes may be cited the magnetic investigations of spin-free cobalt(II) complexes (48). Some unusual magnetic properties of cobalt(II) complexes have only recently been reported (49).

The question of consideration of the orbital contribution to the overall magnetic moment may also arise. This contribution arises from orbital degeneracy in the $\underline{d}_{xz}$ and d_{yz} levels (14). Thus the ligand field may not completely "quench" the total orbital angular momentum of an ion. In ideal cases, one may infer something about the stereochemistry of an atom from the amount of orbital contribution, that is, the deviation of the observed magnetic moment from the spin-only value.

It is hoped that this report will have left a better feeling for the techniques involved in magnetic studies, and also an appreciation for the work that has been done utilizing this method.

BIBLIOGRAPHY

1. A. R. Kaufmann, in Physical Methods in Chemical Analysis, Ed. by W. G. Berl, Volume II, Academic Press Inc. Publishers, New York, (1951), p. 229.
2. S. S. Bhatnagar and K. N. Mathur, Physical Principles and Applications of Magnetochemistry, Macmillan and Co., Ltd., London (1935).
3. J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, London (1948).
4. E. C. Stoner, Magnetism and Atomic Structure, Methuen and Co., Ltd., London (1926).
5. L. F. Bates, Modern Magnetism, Cambridge University Press, London (1951).
6. P. W. Selwood, Magnetochemistry, 2nd Edition, Interscience Publishers, Inc., New York (1956).
7. R. S. Nyholm, J. Inorg. Nucl. Chem., 8, 401 (1958).
8. R. S. Nyholm, Quart, Revs., 7, 377 (1953).
9. N. F. Curtis, J. Chem. Soc., 3147 (1961).
10. B. N. Figgis and R. S. Nyholm, J. Chem. Soc., 4190 (1958).
11. F. G. Baddar, O. M. M. Hilal, and S. Sugden, J. Chem. Soc., 132 (1949).
12. B. N. Figgis and R. S. Nyholm, J. Chem. Soc., 331 (1959).
13. A. P. Wills and L. G. Hector, Phys. Rev., 23, 209 (1924).
14. B. N. Figgis and J. Lewis, in Modern Coordination Chemistry, Ed. by J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., New York, (1960), p. 400.
15. D. F. Evans, J. Chem. Soc., 2003 (1959).

VI CONCLUSION

[illegible]

[illegible]

[illegible]

BIBLIOGRAPHY

1. [illegible]
2. [illegible]
3. [illegible]
4. [illegible]
5. [illegible]
6. [illegible]
7. [illegible]
8. [illegible]
9. [illegible]
10. [illegible]
11. [illegible]
12. [illegible]
13. [illegible]
14. [illegible]
15. [illegible]

16. D. F. Evans, Proc. Chem. Soc., 115 (1958).
17. C. A. Reilley, H. M. McConnell, and R. G. Meisenheimer, Phys. Rev., 98, 264 (A) (1955).
18. S. F. Eilers, B. S. Thesis, University of Illinois, (1961).
19. L. N. Mulay and P. W. Selwood, J. Am. Chem. Soc., 76, 6207 (1954).
20. L. N. Mulay and P. W. Selwood, J. Am. Chem. Soc., 77, 2693(1955).
21. B. O. A. Hedstrom, Ark. Kemi, 6, 1 (1953).
22. L. N. Mulay and M. C. Naylor, in Advances in the Chemistry of the Coordination Compounds, Ed. by S. Kirschner, The Macmillan Co., New York, (1961), p. 520; See also: Chem. and Eng. News, 39, Sept, 1961, p. 42.
23. B. Bleaney and K. D. Bowers, Proc. Roy. Soc., 214A, 451 (1956).
24. J. N. van Niekirk and F. R. L. Schoening, Acta Cryst., 6, 227(1953).
25. B. N. Figgis and R. L. Martin, J. Chem. Soc., 3837 (1956).
26. I. G. Ross, Trans. Faraday Soc., 55, 1057 (1959).
27. I. G. Ross and J. Yates, Trans. Faraday Soc., 55, 1064 (1959).
28. R. L. Martin and H. Waterman, J. Chem. Soc., 2545 (1957).
29. R. L. Martin and A. Whitley, J. Chem. Soc., 1394 (1958).
30. R. L. Martin and H. Waterman, J. Chem. Soc., 1359 (1959).
31. R. L. Martin and H. Waterman, J. Chem. Soc., 2960 (1959).
32. G. A. Barclay and C. H. L. Kennard, J. Chem. Soc., 3289 (1961).
33. R. Tsuchida and S. Yamada, Nature, 176, 1171 (1955).
34. R. Tsuchida, S. Yamada, and H. Nakamura, Nature, 178, 1192 (1956).
35. B. N. Figgis and C. M. Harris, J. Chem. Soc., 855 (1959).
36. P. Ray and D. N. Sen, J. Indian Chem. Soc., 25, 473 (1948).
37. D. W. Meek, Inorganic Seminars, University of Illinois, 1960-61,p.23
38. L. M. Venanzi, J. Chem. Soc., 719 (1958).
39. L. M. Venanzi, J. Inorg. Nucl. Chem., 8, 137 (1958).
40. F. A. Cotton and D.M.L. Goodgame, J. Am. Chem. Soc., 82, 5771(1960).
41. D. M. L. Goodgame and F. A. Cotton, J. Am. Chem. Soc., 82, 5774 (1960).
42. F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, J. Am. Chem. Soc., 83, 344 (1961)
43. C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, J. Chem. Soc., 2705 (1961).
44. N. S. Gill and R. S. Nyholm, J. Chem. Soc., 3997 (1959).
45. B. N. Figgis, J. Lewis, and F. E. Mabbs, J. Chem. Soc., 3138(1961).
46. A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, J. Chem. Soc., 3132 (1961).
47. A. Earnshaw and J. Lewis, J. Chem. Soc., 396 (1961).
48. F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, J. Am. Chem. Soc., 83, 1780 (1961).
49. R. C. Stoufer, D. H. Busch, and W. B. Hadley, J. Am. Chem. Soc., 83, 3732 (1961).

NEW SELECTIVE REDUCING AGENTS
Factors Affecting the Selectivity of Hydridic Reducing Agents

Violet I. Imhof November 7, 1961

I. INTRODUCTION

Reductions involving the complex metal hydrides may conveniently be discussed in terms of Lewis acid base theory. Although this is not an entirely satisfactory scheme, it does lend some order to the mass of information accumulating on the reactions of these compounds.

Lithium aluminum hydride and sodium borohydride, the two best known complex hydrides, differ greatly in their reducing abilities. Sodium borohydride is a fairly mild reducing agent, which reduces only aldehydes, ketones, and acid chlorides of the common organic functional groups and can even be used as a reagent in aqueous solution. Lithium aluminum hydride, on the other hand, is quite powerful and reduces nearly all of the common polar organic functional groups. The specific reactions of these two compounds have been well reviewed (1,2) and will be discussed only in comparison with the reactions of the reducing agents described below.

The new selective reducing agents have been studied in an attempt to find some means of utilizing the middle ground of reducing strength between the very powerful $LiAlH_4$ and the mild $NaBH_4$. Clearly this may be accomplished either by increasing the reducing strength of $NaBH_4$ or reducing that of $LiAlH_4$. At least four approaches are possible. Reducing properties might be expected to be affected by a change in the complex anion, a change in the cation, a change in the Lewis acid-base character of the reagent, or a change in the solvent.

II. SUBSTITUTION IN THE COMPLEX ANIONS

The reduction of a simple carbonyl compound with $NaBH_4$ involves four successive stages

$$R_2C=O + BH_4^- \rightarrow H_3B[OCHR_2]^-$$

$$R_2C=O + H_3B[OCHR_2]^- \rightarrow H_2B[OCHR_2]_2^-$$

$$R_2C=O + H_2B[OCHR_2]_2^{=} \rightarrow HB[OCHR_2]_3^-$$

$$R_2C=O + HB[OCHR_2]_3^- \rightarrow B[OCHR_2]_4^-$$

This scheme is supported by the kinetic data obtained by Garrett and Lyttle (3) for the C-20 reduction of 3α-hydroxy-11α-acetoxypregnan-20-one. Their overall rate expression is consistent with this four-step mechanism, if the first step is the rate-determining step and the rest considerably faster. Later H.C. Brown's group found that reductions of representative ketones followed simple second-order kinetics, first order in borohydride and in ketone concentration. The preparation of the intermediate,

$NaB[(CH_3)_2CHO]_3H$, further confirmed this poslutate. Also the reaction of $NaBH_4$ with acetone in isopropyl alcohol has a measurable rate, where $k_2=0.078$ l./mol.min., and in diglyme has a negligible rate at room temperature. However, $NaHB[OCH(CH_2]_3$ reacts with acetone at a rate too fast to measure in either solvent (5).

The triisopropoxy derivative is a much stronger reducing agent than its parent, $NaBH_4$, as evidenced by its reduction of alcohols and esters. The tri-methoxy, (6,7) -ethoxy, and *t*-butoxy(5) derivatives are also known. They are prepared by the action of sodium hydride on the alkyl borates. Unfortunately, the tri-methoxy and -ethoxy compounds disproportionate into $NaBH_4$ and sodium tetraalkoxy-borohydride in solvents. This decreases their usefulness in the slower reactions (8). However, studies indicate that $NaBH(OCH_3)_3$ is also a stronger reducing agent than $NaBH_4$. (9)

The effect of the alkoxy groups as substituents may be rationalize in terms of the strengths of the related Lewis acids. Alkyl borates are very weak Lewis acids, presumably because resonance stabilization reduces the tendency of the boron to coordinate. Thus the transfer of hydride particle from the parent boro-hydride ion requires its separation from the strong Lewis acid, borane, whereas transfers from the trialkoxyborohydride ion requires its separation from the much weaker Lewis acid, the alkyl borate (5).

The compound $LiBH_3CN$ has also been reported (10). It is a weaker reducing agent than $NaBH_4$ and reduces only aldehydes and α-hydroxyketones (11).

Although alkali-metal hydrides react readily with alkyl borates to give the trialkoxyborohydrides, the analogous reaction with aluminum alkoxides is rather slow. However, Hesse and Schrödel (12) did succeed in preparing $NaAlH[OC_2H_5]_3$ by this method. Its reducing properties are given in Chart I. The similar lithium analog has also been prepared (13) *in situ* through the reaction of $LiAlH_4$ with either, ethanol, or ethyl acetate. The diethoxy compound, $LiAlH_2(OC_2H_5)_2$ (14), has proven useful in the reduction of acyl dimethylamides to aldehydes.

Lithium aluminum hydride in ether reacts with four moles of methyl, ethyl, and isopropyl alcohols but with only three moles of *t*-butyl or *t*-amyl alcohol. With these tertiary alcohols, the fourth mole reacts only after prolonged heating at high temperatures (15,16). Both $LiAlH[OC(CH_3)_3]_3$ and $LiAlH[OC(CH_3)_2CH_2CH_3]_3$ are prepared in this way. Since $LiAlH[OC(CH_3)_3]_3$ is insoluble in ether, it precipitates when the third equivalent of *t*-butyl alcohol is added to $LiAlH_4$ in this solvent. Although it is readily soluble in both diglyme and tetrahydrofuran, the reaction stops at three equivalents in these solvents too. Hence its formation cannot be attributed to its low solubility in ether. Since the solution of $LiAlH_4$ in ether stays clear on the addition of one and two equivalent of *t*-butyl alcohol, it is likely that $LiAlH_2[OC(CH_3)_3]_2$, and possibly even $LiAlH_3[OC(CH_3)_3]$, exist as distinct species. The product obtained on the addition of the third equivalent of *t*-butyl alcohol may be either pure $LiAlH[OC(CH_3)_3]_3$ or a mixture of tetra- and mono- or di-*t*-butoxy derivatives. However, $LiAl[OC(CH_3)_3]_4$ is

insoluble in all the common solvents, whereas the reaction product is quite soluble in diglyme and tetrahydrofuran. This rules out the presence of $LiAl[OC(CH_3)_3]_4$ except in trace amounts.

The alkoxy derivatives of lithium aluminum hydride are weaker reducing agents than their parent (17,18,19). Here then, the effect of the alkoxy group is just the reverse of that found for the borohydrides. Unfortunately little is known about the relative Lewis-acid strengths of aluminum hydride and the aluminum alkoxides. Theory will at least allow a rationalization of the observed results. Borate esters are weak acids, presumably because of resonance effects which satisfy the electron deficiency of the boron and overshadow the electron-withdrawing induction effects of the alkoxides, which would tend to increase acid strength. It would be expected that these resonance effects would not be as important for aluminum. Hence, the difference in the effect of the alkoxy substituents is a result of the different capacities of boron and aluminum to participate in resonance interactions involving double-bonded structures with the oxygen atom of the substituent (16).

III. CHANGES IN THE CATION

Metal borohydrides have been prepared with most of the common alkali- and alkaline earth-metals. Lithium borohydride is considerably stronger than $NaBH_4$ (20,21). In isopropyl alcohol the rate of acetone reduction is several times greater with $LiBH_4$ than with $NaBH_4$, although there is no measurable difference in aqueous solution. This suggests that the enhancing power of the lithium ion is greatest for solvents of low dielectric constant(22). The reducing power of KBH_4 is quite similar to that of $NaBH_4$(30).

The borohydrides of all the Group II metals except radium have been prepared (23,24,25,27). These borohydrides are stronger reducing agents than those of the alkali metals. Aluminum borohydride is also known (23,26). Kollonitsch and coworkers report that the reducing power of the borohydrides is least for the alkali metals, intermediate for the alkaline earths, and greatest for $Al(BH_4)_4$. They note that this parallels the increase in the covalent character of the compounds (26).

Whereas most of the alkali- and alkaline earth-borohydrides can be prepared at least <u>in situ</u> by the addition of the appropriate halide to a $NaBH_4$ solution, the situation when aluminum chloride is used is somewhat different. Diglyme solutions of aluminum chloride and $NaBH_4$ in a 1:3 molar ratio were clear with no evidence for the formation of the insoluble sodium chloride. None-the-less, they are potent reducing agents (29), the reducing activity of which almost approached that of $LiAlH_4$. They are unsuited for reducing unsaturated compounds, however, since they react with olefinic double bonds to give organoboranes (30). Since no sodium chloride precipitate is formed, the reaction is not likely the simple formation of $Al(BH_4)_3$. It is possible though that the reaction produces small amounts of $Al(BH_4)_3$, which are consumed by the organic component as fast as they are formed (29).

insoluble in all the common solvents, whereas the reaction product is quite soluble in diglyme and tetrahydrofuran. This rules out the presence of $LiAl[OC(CH_3)_3]_4$ except in trace amounts.

The alkoxy derivatives of lithium aluminum hydride are weaker reducing agents than their parent (17,18,19). Here then, the effect of the alkoxy group is just the reverse of that found for the borohydrides. Unfortunately little is known about the relative Lewis-acid strengths of aluminum hydride and the aluminum alkoxides. Theory will at least allow a rationalization of the observed results. Borate esters are weak acids, presumably because of resonance effects which satisfy the electron deficiency of the boron and overshadow the electron-withdrawing inductive effects of the alkoxides which would tend to increase acid strength. It would be expected that these resonance effects would not be as important for aluminum. Hence, the difference in the effect of the alkoxy substituents is a result of the different capacities of boron and aluminum to participate in resonance interactions involving double-bonded structures with the oxygen atom of the substituent (11).

III. CHANGES IN THE CATION

Metal borohydrides have been prepared with most of the common alkali- and alkaline earth-metals. Lithium borohydride is considerably stronger than $NaBH_4$ (20,21). In isopropyl alcohol the rate of acetone reduction is several times greater with $LiBH_4$ than with $NaBH_4$, although there is no appreciable difference in aqueous solutions. This suggests that the enhancing power of the lithium ion is greatest for solvents of low dielectric constant (13). The reducing power of KBH_4 is quite similar to that of $NaBH_4$ (22).

The borohydrides of all the Group II metals except radium have been prepared (23,24,25,26). These borohydrides are stronger reducing agents than those of the alkali metals. Aluminum borohydride is also known (23,24). Kollonitsch and coworkers report that the reducing power of the borohydrides is least for the alkali metals, intermediate for the alkaline earths, and greatest for $Al(BH_4)_3$. They note that this parallels the increase in the covalent character of the compounds (26).

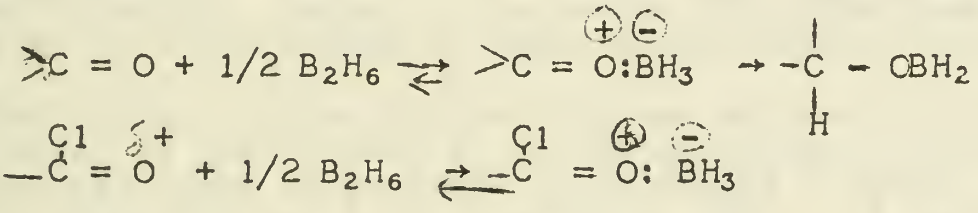
Whereas most of the alkali- and alkaline earth-borohydrides can be prepared at least *in situ* by the addition of the appropriate halide to a $NaBH_4$ solution, the situation when aluminum chloride is used is somewhat different. Adding solutions of aluminum chloride and $NaBH_4$ in a 1:3 molar ratio gave clear with no evidence for the formation of the insoluble sodium chloride. Nevertheless, they are better reducing agents (27), the reducing activity in fact almost approaching that of $LiAlH_4$. They are unsuited for reducing unsaturated compounds, however, since they react with olefinic double bonds to give organoboranes (28). Since no sodium chloride precipitate is formed, the reaction is not likely the simple formation of $Al(BH_4)_3$. It is possible though that the reaction produces small amounts of $Al(BH_4)_3$, which are destroyed by the organic compound as fast as they are formed (27).

Several aluminum hydrides with cations other than lithium have been prepared (1,31,32,33). Their reducing properties are quite similar to those of $LiAlH_4$. Thus as yet no conclusion is possible on the effect of a change in cation on the strengths the aluminum hydrides.

IV. USE OF ACIDIC REAGENTS

The reducing agents discussed to this point have been Lewis bases, functioning by attack on an electron-deficient center in the compound to be reduced. Since reducible groups would be expected to show quite different reactivities toward an electrophilic reagent, the properties of diborane, a strong Lewis acid, as a reducing agent were studied by H. C. Brown and his group.

Diborane is conveniently prepared by addition of a diglyme solution of $NaBH_4$ to boron trifluoride-etherate in the same solvent. Alternatively, when the group to be reduced is unaffected by $NaBH_4$, the diborane may be generated <u>in situ</u> by adding the BF_3 etherate in diglyme to a diglyme solution of $NaBH_4$ and the compound (50). The reaction of diborane with most of the common organic groups was studied by Brown and Sabba Rao (44), It is interesting that although aldehydes and ketones are reduced, chloral and acetyl chloride are inert to diborane. It has been noted that those aldehydes and ketones which react readily with B_2H_6 also form stable addition compounds with BF_3 (43). Chloral and acetyl chloride add BF_3 only with difficulty. Thus the first stage of the reaction might reasonably be an acid-base interaction, with boron coordinated to oxygen, followed by a hydride transfer. The inductive effect of the chlorine in chloral and acetyl chloride would decrease the basic character of the carbonyl oxygen and hence hinder the reaction.

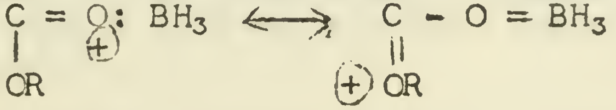


$$>C=O + 1/2\,B_2H_6 \rightleftarrows\ >C=\overset{\oplus}{O}:\overset{\ominus}{B}H_3 \rightarrow -\underset{H}{\overset{|}{C}}-OBH_2$$

$$-\overset{Cl}{C}=\overset{\delta+}{O} + 1/2\,B_2H_6 \rightleftarrows -\overset{Cl}{C}=\overset{\oplus}{O}:\overset{\ominus}{B}H_3$$

This same type of argument can be extended to cover the rapid reduction of nitrites with B_2H_6(44). The nitrogen atom adds to BF_3 to give moderately stable addition compounds and is thus fairly basic. Presumably then the initial step of the reaction is an attack in this basic center.

There are two factors which account for the slow reaction noted with esters. First, the addition of the BH_3 particle to the carbonyl oxygen atom must compete with its addition to the alkoxy oxygen. Second, the transfer of a hydride ion from boron to carbon is hindered by the stabilization of the carbonyl group through resonance interactions with the alkoxy group,



$$\underset{OR}{\overset{|}{\underset{|}{C}}}=\underset{\oplus}{O}:\overset{\ominus}{B}H_3 \longleftrightarrow \underset{\oplus OR}{\overset{|}{\underset{\|}{C}}}-O=\overset{\ominus}{B}H_3$$

Several aluminum hydrides with cations other than lithium have been prepared (1,3,7,25,31). Their reducing properties are quite similar to those of $LiAlH_4$. Thus [illegible] is possible in the effect of a change in cation on the strength of the aluminum hydrides.

IV. Use of Acidic Reagents

The reducing agents discussed to this point have been Lewis bases, functioning by attack on an electron-deficient center in the compound to be reduced. Since reducible groups would be expected to show quite different reactivities toward an electrophilic reagent, the properties of diborane, a strong Lewis acid, as a reducing agent were studied by H. C. Brown and his group.

Diborane is conveniently prepared by addition of a diglyme solution of $NaBH_4$ to boron trifluoride-etherate in the same solvent. Alternatively, when the group to be reduced is unaffected by $NaBH_4$, the diborane may be generated in situ, by adding the BF_3 etherate in diglyme to a diglyme solution of $NaBH_4$ and the compound (59). The reaction of diborane with most of the common organic groups was studied by Brown and Subba Rao (60). It is interesting that although aldehydes and ketones are reduced, chloral and acetyl chloride are inert to diborane. It has been noted that those aldehydes and ketones which react readily with B_2H_6 also form stable addition compounds with BF_3 (61). Chloral and acetyl chloride add BF_3 only with difficulty. Thus the first stage of the reaction might reasonably be an acid-base interaction, with boron coordinated to oxygen, followed by a hydride transfer. The inductive effect of the chlorine in chloral and acetyl chloride would decrease the basic character of the carbonyl oxygen and hence hinder the reaction.

$$RC=O + 1/2\,B_2H_6 \rightleftharpoons R-\overset{+}{C}=O-\overset{-}{B}H_3 \longrightarrow -C-OBH_2$$

$$Cl_3C-C=O + 1/2\,B_2H_6$$ [illegible]

This same type of argument can be extended to cover the rapid reduction of nitriles with B_2H_6 (60). The nitrogen also adds to BF_3 to give moderately stable addition compounds and is thus fairly basic. Presumably then the initial step of the reaction is an attack on this basic center.

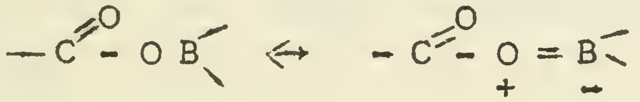
There are two factors which account for the slow reaction noted with esters. First, the addition of the BH_3 particle to the carbonyl oxygen does not compete with its addition to the ether oxygen. Second, the transfer of a hydride ion from boron to carbon is hindered by the stabilization of the carbonyl group through resonance interaction with the alkoxy group.

$$-C=O + BH_3 \rightleftharpoons -C=O-BH_3$$

[illegible]

Finally, there is the rapid reaction of carboxylic acids to consider. Here the first step is the formation of a triacylborane, $(RCO_2)_3B$, which is readily reduced by diborane or $NaBH_4$. In these triacylboranes, the electron pairs of the acyl oxygen atoms will be affected by the electron deficiency of the boron. Thus instead of the usual resonance with the carbonyl group, the resonance will involve the acyl oxygen and the boron atoms. Hence the carbonyl group here should more closely resemble those in aldehydes and ketones than those in esters,

$$3\ RCO_2H + 1/2\ B_2H_6 \rightarrow (RCO_2)_3B + 3H_2$$



Competition studies showed that reactivity toward diborane decreased in the order: carboxylic acids > olefins > ketones > nitriles > epoxides > esters > acid chlorides (45). The order with alkali-metal borohydrides is: acid chlorides > ketones > epoxides > esters > nitriles > carboxylic acids.

Diborane reacts with most olefins to give trialkyl boranes. However with some bulky olefins, the disubstituted borane may be formed (46). Thus:

$$B_2H_6 + (CH_3)_2C = CHCH_3 \rightarrow 2[(CH_3)_2CHCHCH_3]_2\ BH$$

This compound, bis-3-methyl-2-butylborane, is also a selective reducing agent. In constrast to BH_3, it does not react with carboxylic acids. Hence, it is useful for reductions and hydroborations in the presence of unprotected carboxyl groups (47).

The acidic hydride in the aluminum system which has proven most useful is that formed in 3:1 $AlCl_3$:$LiAlH_4$ solutions. Here, the reducing agent is presumed to be AlH_2Cl (39,40). This reagent converts aryl ketones to aryl methanes (48). It reduces acetals and ketals (35) to ethers and cyclochemiacetals to hydroxy ethers(36); this is not accomplished by $LiAlH_4$ alone. The yield of bromohydrin in the reduction of 3-bromoacids and esters is markedly improved by this reagent since it retards attack on the bromine (37). The use of this reagent is covered in an excellent review by Rerick(42).

V. EFFECT OF SOLVENT

Lithium aluminum hydride is so powerful a reducing agent that possible solvents are limited to hydrocarbons, ethers, and tertiary amines. It is insoluble in hydrocarbons and readily soluble in ethers. In the ethers commonly used; diglyme, tetrahydrofuran, and ethyl ether, there is no significant change in the reducing ability of the hydride with a solvent change. Pyridine has also been used as a solvent (49).

Sodium borohydride may be used in a wider range of solvents. For preparative work, it is often used in water or methanol although it does slowly react with them. For quantitative work, isopropyl alcohol is suitable since it inert to the hydride (28). Second-order

Finally, there is the rapid reduction of carboxylic acids to consider. Here the first step is the formation of a triacyloxyborane, $(RCO_2)_3B$, which is readily reduced by diborane or $NaBH_4$. In these triacyloxyboranes, the electron pairs of the acyl oxygen atoms will be attracted by the electron deficiency of the boron. Thus instead of the usual resonance with the carbonyl group, the resonance will involve the acyl oxygen and the boron atoms. Hence the carbonyl group here should more closely resemble those in aldehydes and ketones than those in esters.

$$3\,RCO_2H + 1/2\,B_2H_6 \rightarrow (RCO_2)_3B + 3H_2$$

$$-\overset{O}{\overset{\|}{C}}-O-\overline{B} \longleftrightarrow -\overset{O}{\overset{\|}{C}}-\underset{+}{O}=\overline{B}$$

Competition studies showed that reactivity toward diborane decreased in the order: carboxylic acids, olefins, ketones, nitriles, epoxides, esters, acid chlorides (45). The order with sodium borohydride is: acid chlorides, ketones, epoxides, esters, nitriles, carboxylic acids.

Diborane reacts with most olefins to give trialkyl boranes, however with some bulky olefins, the disubstituted borane may be formed (56). Thus:

$$B_2H_6 + (CH_3)_2C=CHCH_3 \rightarrow 2[(CH_3)_2CHCH(CH_3)]_2BH$$

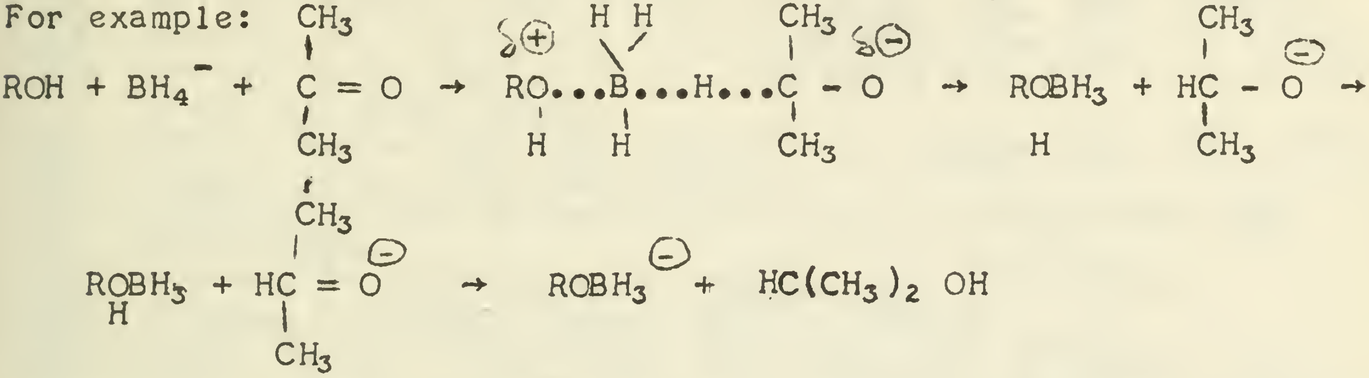
This compound, bis-3-methyl-2-butylborane, is also a selective reducing agent. In contrast to B_2H_6, it does not react with carboxylic acids. Hence, it is useful for reductions and hydroborations in the presence of unprotected carboxyl groups (57).

The acidic hydride in the aluminum hydride system which has proven most useful is that formed in 1:1 AlH_3:$AlCl_3$ solutions. Here, the reducing agent is presumed to be AlH_2Cl (39,60). This reagent converts aryl epoxides to aryl carbinols (60). It reduces ketals and acetals (35) to ethers and cyclohexanone ketals to hydroxy ethers(36); this is not accomplished by $LiAlH_4$ alone. The yield of bromohydrin in the reduction of bromoketones and esters is markedly improved by this reagent since it reduces attack on the bromine (37). The use of this reagent is covered in an excellent review by Eliel(61).

V. EFFECT OF SOLVENT

Lithium aluminum hydride is so powerful a reducing agent that possible solvents are limited to hydrocarbons, ethers, and tertiary amines. It is insoluble in hydrocarbons and readily soluble in ethers. In the ethers commonly used; diglyme, tetrahydrofuran, and ethyl ether, there is no significant change in the reducing ability of the hydride with a solvent change. Pyridine has also been used as a solvent (19).

Sodium borohydride may be used in a wider range of solvents. For preparative work, it is often used in water or methanol although it does slowly react with them. For quantitative work, isopropyl alcohol is suitable since it is inert to the hydride (20). Secondary-rate constants were measured for the reduction of several simple ketones in this solvent at 0°C. In diglyme and triglyme, in which the reagent is also soluble, the rates became much slower. This indicates that the solvent is involved in the hydride transfer. For example:



$$ROH + BH_4^- + (CH_3)_2C{=}O \rightarrow \overset{\delta+}{RO}\cdots BH_2H\cdots H\cdots \overset{\delta-}{C(CH_3)_2{-}O} \rightarrow ROBH_3H + (CH_3)_2HC{-}O^- \rightarrow$$

$$ROBH_3H + (CH_3)_2HC{=}O^- \rightarrow ROBH_3^- + HC(CH_3)_2OH$$

In terms of this hypolthesis the slow reaction in diglyme would be due to the poor donor properties of the ether oxygen atom compared to those in alcohols.

VI. CONCLUSION

Much progress has been made in the field of selective reductions. This has greatly simplified many synthetic problems. It is possible that continued research in this field can allow a clearer understanding of the influence of structure on reducing character.

BIBLIOGRAPHY

1. Gaylord, N. G., "Reductions with Complex Hydrides," Interscience, New York, 1956.
2. Brown, W.G., "Reductions with Lithium Aluminum Hydride", in "Organic Reactions", Vol. VI, 469 (1951).
3. Garrett, E. R., and Lyttle, D. A., J. Am. Chem. Soc., 75, 6051 (1953).
4. Brown, H. C. Wheeler, O. H., and Ichikawa, K., Tetrahedron, 1, 214 (1957).
5. Brown, H. C., Mead, E. P., and Shoaf, C. J., J. Am. Chem. Soc., 78, 3616 (1956).
6. Brown, H. C., Schlesinger, H. I., Sheft, I., and Ritter, D.M., Ibid., 75, 192 (1953).
7. Brown, H. C., and Mead, E. J., Ibid., 75, 6263 (1953).
8. Brown, H. C. Mead, E. J. and Tierney, P. A., Ibid., 79, 5400(1957).
9. Brown, H. C. and Mead, E. J. Ibid., 75, 6263 (1953).
10. Wittig, E., Ann., 573, 209 (1951).
11. Drefahl, G., and Keil, E., J. Prakt. Chem., 6, 80 (1958).
12. Hesse, G., and Schrödel,R., Ann., 607, 24 (1957).
13. Brown, H. C., Shoaf, J., and Garg, C. P., Tetrahedron Letters, 3, 9 (1959).
14. Brown, H. C., and Tsukamoto, A., J. Am. Chem. Soc., 81, 502(1959).
15. Brown, H. C., and McFarlin, R. F., Ibid., 78, 252 (1956).
16. Idem., Ibid., 80, 5372 (1958).
17. Brown, H. C., and Subba Rao, B. C., Ibid., 80, 5377 (1958).
18. Wheeler, O. H., and Mateos, J. L., Can. J. Chem., 36, 1431 (1958).
19. Idem., Chem. and Ind., 395 (1957).
20. Paul, R., and Joseph, N., Bull. soc. chim. France, 758(1953).
21. Nystrom, R. F., Chaikin, S. W., and Brown, W. G., J. Am. Chem. Soc., 71, 3245 (1949).
22. Brown, H. C., J. Chem. Ed., 38, 173 (1961).

23. Schlesinger, H. I., Brown, H. C., and Hyde, E. K., J. Am. Chem. Soc., 75, 212 (1953).
24. Kollonitsch, J., and Fuchs, O., Nature, 173, 125 (1954).
25. Kollonitsch, J., Fuchs, O., and Gabor, V., Ibid., 175, 346(1955).
26. Kollonitsch, J., and Fuchs, O., Ibid,, 176, 1081 (1955).
27. Wiberg, E., and Bauer, R., Z. Naturforsch., 5b, 397 (1950).
28. Brown, H. C., Mead, E. J., and Subba Rao, B. C., J. Am. Chem. Soc., 77, 6209 (1955).
29. Brown, H. C., and Subba, Rao, B. C., Ibid., 78, 2582 (1956).
30. Idem., Ibid., 81, 6423 (1959).
31. Schwab, W., and Wintersberger, K., Z. Naturforsch., 8b, 690 (1952).
32. Wiberg, E., and Bauer, R., Ibid., 5b, 397 (1950).
33. Wiberg, E., Angew. Chem., 65, 16 (1953).
34. Olah., G. A., J. Am. Chem. Soc., 81, 3165 (1959).
35. Eliel, E. L., and Badding, V. G., Ibid., 81, 6087 (1959).
36. Eliel, E. L., and Rerick, M., J. Org. Chem., 23, 1088 (1958).
37. Nystrom, R. F., J. Am. Chem. Soc., 81,610 (1959).
38. Idem., Ibid., 77, 2544 (1955).
39. Finholt, A. E., Bond, A. C. Jr., and Schlesinger, H. I., Ibid, 71, 1199 (1947).
40. Wiberg, E., and Schmidt, M., Z. Naturforsch., 6b, 4601 (1951).
41. Eliel, E. L. and Rerick, M., J. Am. Chem. Soc., 82, 1367 (1960).
42. Rerick, M., "The Mixed Hydrides", Metal Hydrides, Beverly, Mass., 1960.
43. Brown, H. C., Schlesinger, H. I., and Burg, A. B., J. Am. Chem. Soc., 61, 673 (1939).
44. Brown, H. C., and Subba Rao, B. C., Ibid., 82, 681 (1960).
45. Brown, H. C., and Korytnyk, W., Ibid., 82, 3866 (1960).
46. Brown, H. C., and Zweifel, G., Ibid., 82, 3222 (1960).
47. Brown, H. C., and Bigley, D. B., Ibid., 83, 486 (1961).
48. Nystrom, R. F., and Berger, R. A., Ibid., 80, 2896 (1958).
49. Lansbury, P. T., Ibid., 83 429 (1961).
50. Brown, H. C., and Subba Rao, B. C., J. Org. Chem., 22, 1135(1957).

CHART I
Reducing Properties of Various Hydrides

Reactant	Reaction Product	LAH	NBH	LBH	KBH	NBH. $AlCl_3$	LAH. $AlCl_3$	NBH salt	KBH LiCl	LBH LiH	LAH LiH	NaBH $(OMe)_3$	B_2H_6	NaAlH $(OEt)_3$	LiAlH $(O\underline{t}Bu)_3$
RCHO	RCH_2OH	+	+	+	+	+	+					+	+	+	+
RCOR	RCHOHR	+	+	+	+	+	+					+	+	+	+
RCOCl	RCH_2OH	+	+	+	+	+	+	+				+	−	+	−
RCOCl	RCHO														+
RCOOH	RCH_2OH	+	−	+	−	+						+	+		
RCOONa	RCH_2OH	+	−	−	−	−						−			
RCN	RCHORCH	+	−	−	−									+	
RCOOR	RCH_2OH	+	−	+	−	+	+	+	+			+	−	+	−
RCN	RCH_2NH_2	+	−	−	−	+	±			−		+	+	−	−
$RCONR_2$	RCH_2NR_2	+	−	−	−	+	+		+	−					
$RCONR_2$	RCHO	±													
RCOR	RCH_2R	+					+								
$ArNO_2$	$ArNH_2$	−	−	±	−		−			−	+	−	−		−
RNO_2	RNH_2	+	−		−					−			−		
$>C=C<$	$[CH-CH]_3B$	−	−	−	−	+						−	+		−
RX	RH	±	±	−	−	+	−			+		−		±	−
$RRC(OR)_2$	RRCHOR	−	−	−	−		+			−					
RCHOHR	RCH_2R	−	−	−	−		+								
RCHO	RCH_3	−	−	−	−		+								
RCOOH	RCH_3	−	−	−	−		+								
$\overset{O}{>C-C<}$	$CH-COH$	+	−			+	+							+	
$ROSO_2Ar$	RH	+				+				+					
$>C=C<$	$CH-CH$	±	−	−	−		−								

Key:
LAH - $LiAlH_4$
NBH - $NaBH_4$
LBH - $LiBH_4$
KBH - KBH_4

± - Reaction depends on nature of

CHEMISTRY OF GERMANIUM(IV)

R. M. Klein November 22, 1961

I. INTRODUCTION

The classical descriptive chemistry of germanium(IV) is well covered in two reviews by Johnson, one dealing with inorganic compounds of germanium (1) and the other with organic compounds (2). This seminar will concentrate mainly on more recent work relating to the types of species of tetravalent germanium which may be present in solution in various media. Some mention will also be made of the more interesting preparative work which has been done recently.

II. INORGANIC COMPOUNDS

A. Types of Compounds

Germanium tetrachloride can be prepared by direct reaction of the elements or reaction of hydrochloric acid with germanium dioxide. A convenient method of preparing germanium tetrafluoride is by heating barium fluorogermanate in a quartz container. Germanium forms no ammine complexes, and addition of gaseous ammonia to germanium tetrachloride gives a product analyzing to $GeCl_4 \cdot 6NH_3$. This is actually the imide, $Ge(NH)_2$, mixed with ammonium chloride(1). All the tetrahalides have been prepared, as well as trihalogermanes, and mixed halides such as those formed as indicated by the equation (3),

$$GeCl_4 + SbF_3 \rightarrow GeCl_3F + GeCl_2F_2 + GeClF_3.$$

These products all disproportionate immediately into the corresponding pure tetra halides.

Recently, mono- and di-fluorogermanes have been prepared for the first time by slowly passing monobromogermane, at 25° and in a vacuum, through a column packed loosely with a mixture of silver(I) fluoride and glasshelices(4). The monofluorogermane, H_3GeF, does not hydrolyze readily with water to give GeH_3OH or $(GeH_3)_2O$, but it reacts with liquid ammonia at -78° to give the diadduct, which yields $[GeH_3NH_3]^+F^-$ at room temperature.

Germanium(IV) also forms heteropoly acids with molybdate and tungstate. The 12-tungstate, $[GeO_4 \cdot 12WO_3]^{4-}$, goes to an 11-tungstate at pH 3.2-4.2, and decomposes into germanates and tungstates at pH 7.3. The less stable molybdates show similar behavior but decomposition into germanate and molybdate is complete at pH 5.4(5).

The chemistry of the germanates will be discussed in a later section. A complete listing of inorganic germanium compounds is given in the review article by Johnson(1).

B. Studies of Inorganic Reactions

A comparison of the hydrolysis rates of chlorotriphenyl germane and chlorotriphenyl silane and some of their derivatives in acetone and acetone-ether has been carried out using rapid-reaction techniques (6). The hydrolysis of the silicon compound was found to be complete with a rate constant $k_{Si} = 4.0\ sec^{-1}$, whereas that of the germanium compound is only 10% complete, $k_{Ge} = 0.02\ sec^{-1}$. Also, adding a p-methyl group to the phenyl ring decreases the hydrolysis rate, and for Ø_3GeCl, $k_{\text{Ø}H}/k_{\text{Ø}CH_3} = 1.45$. The hydrolysis is also less rapid in acetone than in the less polar acetone-ether by a factor of 2.7 at 25°.

These results are interpreted in terms of a stronger $p\pi - d\pi$ interaction between silicon and oxygen than between germanium and oxygen.

No evidence could be cited from these studies either to justify or exclude definitely a five-covalent intermediate in the mechanism for this reaction.

Germanes can also exchange a hydrogen atom for a halogen or pseudo-halogen atom or group. Hence, when excess $(C_4H_9)GeH_3$ or $(C_4H_9)_2GeH_2$ is allowed to react with HgX_2(X=Cl,Br,I,SCN, or CN), a monosubstituted compound, $(C_4H_9)GeH_2X$ or $(C_4H_9)_2GeHX$, is formed(7,8

The hydrogen-halogen exchange rate between alkyl germanes and alkyl chlorides has been studied (9). For the reaction represented by the equation

$$R_3GeH + R'X \rightarrow R_3GeX + R'H$$

the yield was quantitative for X=Br and I, but only 80% when X=Cl. This is in marked contrast to the corresponding reactions with silanes, where there is no reaction with alkyl halides even in the presence of an aluminum trichloride catalyst. The reaction with the germanes also proceeded faster (i.e., indicative of a weaker Ge-H bond) in the series $R_3GeH < R_2GeH_2 < RGeH_3$.

III. ORGANIC COMPOUNDS CONTAINING GERMANIUM(IV).

A rather complete listing of compounds of this class is given in Johnson's review article (2). Alkyl and aryl germanes and halogermanes are synthesized by the commonly known procedures, the actual final product of the catalyzed reaction being determined by the temperature of the reaction, the catalyst, the manner in which the catalyst is associated with the germanium, and possibly the time of contact.

Recently, the first perfluoroalkyl derivative of germanium to be synthezied has been reported (10), wherein

$$GeI_2 + F_3CI \xrightarrow[100\text{-}105^{\circ},\ 10\ days]{sealed\ tube} CF_3GeI_3.$$

The fact that this type of compound cannot be synthesized from digermane indicates the strength of the Ge-Ge bond in that compound.

e. Stability of Inorganic [illegible]

A comparison of the hydrolytic rates of [illegible] germane and [illegible] and some of their derivatives in acetone and [illegible] has been [illegible] compounds (6). The hydrolysis of the silicon compound was found to be complete within [illegible] whereas that of the germanium compound is only [illegible] complete. [illegible] the hydrolysis [illegible] rate [illegible] in [illegible] the [illegible] by a factor of [illegible].

These results are interpreted in terms of stronger [illegible] interaction between silicon and oxygen than between germanium and oxygen.

No evidence could be cited from these studies either to justify or refute definitely a [illegible]-covalent intermediate in the mechanism for this reaction.

[illegible] exchange, [illegible] group. [illegible] is allowed to react with [illegible] a [illegible] compound, [illegible]

The hydrogen [illegible] rate [illegible] germanes and [illegible] has been studied [illegible] by the equation

[illegible]

the [illegible] This is in [illegible] contrast to the corresponding [illegible] there is no [illegible] presence of [illegible]. The [illegible] germanium [illegible]

iii. [illegible] Compounds of Germanium [illegible]

A rather [illegible] listing of compounds of this class is given in Johnson's review article (11) [illegible] halogermanes [illegible] by the [illegible] of the [illegible] which the [illegible] association with the [illegible] the type of compound.

Recently, the first perfluoroalkyl derivative of germanium to be synthesized has been reported (111) through

$$GeI_4 + CF_3I \xrightarrow{\text{sealed tube}} [illegible]$$
100-180°, 10 days

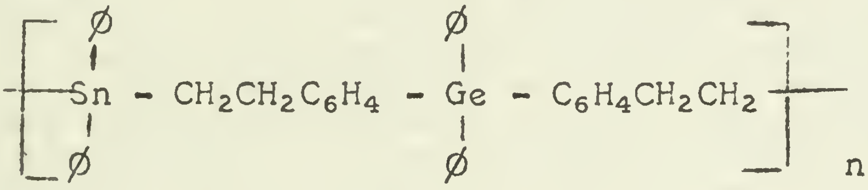
The fact that this type of compound [illegible] indicates the strength of the [illegible] bond in these compounds.

Organic compounds containing both silicon and germanium can be prepared by either of the following reaction types (11);

$$(CH_3)_3GeCl + LiOSi(CH_3)_3 \rightarrow LiCl + (CH_3)_3GeOSi(CH_3)_3$$

$$(CH_3)_2GeCl_2 + 2CH_3\ OSi(CH_3)_3 \rightarrow 2CH_3Cl + [(CH_3)_3SiO]_2Ge(CH_3)_2.$$

Some interesting polymers containing germanium have been described in the recent literature. Addition of $\emptyset_2SnH_2$ to $\emptyset_2Ge(C_6H_4CH=CH_2)_2$ gives the glass-like polymer



$$\left[-\overset{\emptyset}{\underset{\emptyset}{Sn}} - CH_2CH_2C_6H_4 - \overset{\emptyset}{\underset{\emptyset}{Ge}} - C_6H_4CH_2CH_2-\right]_n ,$$

where n equals approximately 45 (12).

Another germanium-containing vinyl polymer forms from the radical polymerization of $CH_2=C(CH_3)COOGe(Et)_3$. This monomer forms when triethylchloro germane and methyl-methacrylate are caused to react in ethanol (13).

IV. COORDINATION COMPOUNDS OF GERMANIUM(IV)

Germanium is well-known to have a tetrahedral distribution of the bonds in its four-covalent complexes. A coordination number of six is known for solid anionic species such as $[GeF_6]^=$ and $[GeCl_6]^=$. Numerous adducts of germanium tetrahalides with various donor molecules have been studied, but most of these are too easily hydrolyzed to have been fully characterized.

The solid 1:2 adduct formed between germanium tetrachloride and pyridine has been studied by both x-ray and infra-red methods(14). The x-ray data show that the trans-octahedral complex is formed, whereas the infra-red data support this conclusion somewhat and also indicate little, if any, electronic interaction between the acceptor and donor atoms.

The compound $(CH_3)_3GeOCH_3$ forms a stable, solid 1:1 adduct with boron trifluoride, the strength of the oxygen as a donor here indicating very weak or no $p\pi$-$d\pi$ bonding between oxygen and germanium(15).

The analogous digermanium ether, $[(CH_3)_3Ge]_2O$, forms $(CH_3)_3GeF$ and B_2O_3 at 25°, and apparently any BF_3 adduct formed here dissociates at about -80°. A four-centered mechanism is proposed to explain the formation of these products (15).

Useful phthalocyanine (ptal.) complexes of germanium(IV) have been prepared and various functional groups included in the complex (16). Some of the more interesting products which may be obtained are listed below.

1) $GeCl_4 + ptal \xrightarrow[reflux]{quinoline} GeCl_2ptal$
2) $GeCl_2ptal + H_2O \rightarrow Ge(OH)_2\ ptal.$
3) $Ge(OH)_2\ ptal + \emptyset Oh \rightarrow Ge(O\emptyset)_2\ ptal.$

V. DETERMINATION OF GERMANIUM(IV) SPECIES PRESENT IN VARIOUS AQUEOUS MEDIA

A. Studies of Germanate Solutions

Prior to the studies by Everest and co-workers (starting in 1954), the best evidence fot the types of germanates present in aqueous solutions of varying pH was presented by Carpeni (17). His pH titrations of germanium dioxide solutions of varying concentrations with alkali showed an "isohydric point", or a point where the curves for all the different concentrations come together, at pH 8.85. This indicates the presence of two and only two species at this point, and his data show these to be the monogermanate, $GeO_3^{=}$, and the pentagermanate, $Ge_5O_{11}^{=}$, anions. Although Carpeni believed that pentagermanic acid was the principal species present in pure germanium dioxide solutions (18), souchay (19) postulated that monogermanic acid was initially present, polymerizing to pentagermanate as the pH rose, and finally depolymerizing back to monogermanate at very high pH.

Since germanium dioxide is soluble in both acid and base, Everest decided to use anion exchange as a method of determining the nature of the ions present in solution at various pH values in the presence and absence of other anions (20). In this way he was able to determine the quantities of the various species adsorbed and, knowing the capacities (in equivalents) of the resin samples used, he calculated the ionic form in which the germanium is adsorbed at various pH values.

The value necessary to define the germanate species present was designated R, where

R= number of germanium atoms in one equivalent of germanate ion adsorbed.

This could be calculated in three different ways, depending on the medium used;

a) Generally, $$R=\frac{(\text{moles of Ge adsorbed per equivalent of resin})}{(\text{1-equivalents of other species adsorbed per equivalent of resin})}$$

b) When the chloride form of the resin is used but no other chloride ion is added,
$$R= (\text{moles of Ge adsorbed})/(\text{equivalents of } Cl^- \text{ in solution at equilibrium}).$$

c) If all the germanate is washed off the resin and an equivalent amount of OH^- or $CO_3^=$ allowed to adsorb and then this is washed off by passing an excess of 0.5N NaCl through the column, the alkali liberated is determined and
$$R=(\text{moles of Ge adsorbed})/(\text{equivalents of alkali}).$$

The results of this study are included in Table 1. They indicate only the adsorption of $HGeO_3^-$(R=1) and Ge_5O_{11}=(R=2.5), the latter forming at intermediate pH (about 6.9-9.4) with the former forming at low pH values and again at higher ones (>9.4) due to depolymerization of pentagermanate in strongly alkaline solutions.

If any of the intermediate polyanions [e.g., Ge_4O_9= (R=2), $HGe_2O_5^-$ (R=2), or $Ge_2O_5^=$ (R=1)] are formed they are adsorbed in a narrow pH range, if at all, and were not detected. Such compounds as $M_2Ge_4O_9$ and $M_2Ge_2O_7$ have been isolated as solid salts in Na_2O-GeO_2 and K_2O-GeO_2 systems (21), but no evidence exists for these species in solution.

B. [illegible]

1. Studies of Permanganate Reduction.

[illegible]

Since permanganate [illegible] at various pH values.

The [illegible]

[illegible]

This should be [illegible]

a) [illegible]

b) [illegible]

c) [illegible]

[illegible]

The [illegible]

If [illegible]

Further studies of this nature (22) showed that, as the chloride ion concentration was increased, R also increased, indicating that the pentagermanate ion is more strongly adsorbed than the monogermanate ion, probably as a result of the lesser acidity of the acid H_2GeO_3(pK_1=9.1) as compared with the acid $H_2Ge_5O_{11}$(pK_1=6.2).

Studies of the germanates in more concentrated solutions, inspired by other reports of possible heptagermanate species, $HGe_7O_{26}^{\equiv}$ (24) showed that R increased to the value of 3.5 which would be expected for this ion (23). Although this could indicate also that the solutions at lower concentration contained a mixture of mono- and heptagermanates and no pentagermanate, it seems more likely that the equilibrium

$$\text{mono} \rightleftarrows \text{penta} \rightleftarrows \text{hepta}$$

is actually established. This is displaced to the right by increasing the germanium concentration and to the left by increasing the pH above 9.

The possibility of even more highly condensed species has been mentioned in the case of concentrated germanium solutions containing glycerol at pH 8. Here the R value approaches 5.8 and could be due to the species $H_2Ge_{11}O_{24}^{=}$ (R=5.5) or $H_2Ge_{12}O_{26}^{=}$ (R=6)(26).

B. Studies in the Presence of Other Anions

Extending the studies of germanium anions by ion-exchange, Everest has used similar techniques to determine the nature of the species resulting with other anions present. The results of these studies appear in Table 2. It is noticed that in the presence of sulfate or phosphate ion, the complexes $[GeO_2(SO_4)]^{=}$ and $[HGeO_2(PO_4)]^{=}$ are formed in the same pH range, 7-9, as the condensation of monogermanic acid to give pentagermanic acid. Hence the same type of condensation seems to take place with other oxyacids, through apparently not to the same degree as the formation of $Ge_5O_{11}^{=}$.

Oxalate, however, forms no complex with Ge above pH=7. Below this value a 3:1 complex seems to be formed when excess oxalate is present, and this can add a proton at very low pH to give $[HGe(ox)_3]^{-}$. The germanium-oxalate complex seems to decompose between pH 4.4 and 6.8.

Studies with some polyhydric alcohols indicate very weak, doubly charged 1:1 and 2:1 complexes with ethylene glycol at pH>11(26) and complexes varying in ratio from 1:1 to 3:1 with increasing pH for glycerol (26,27). For mannitol, these simple complexes are formed but, as the pH is lowered, a polymeric species seems to result which, at very low pH values, has the composition $[Ge_n(mann)_{n+1}]^{=}$ (26,27).

The strength of the bonds formed in the complexes decreases in the order mannitol > glycerol > ethylene glycol. The 2:1 and 3:1 complexes are postulated to be derivatives of the octahedral $[Ge(OH)_6]^{=}$ species, with elimination of water between the hydroxy groups on the germanium and two of the hydroxy groups on each ligand.

[illegible]

[illegible]

[illegible]

[illegible] This is concerned with the right [illegible]

[illegible]

[illegible]

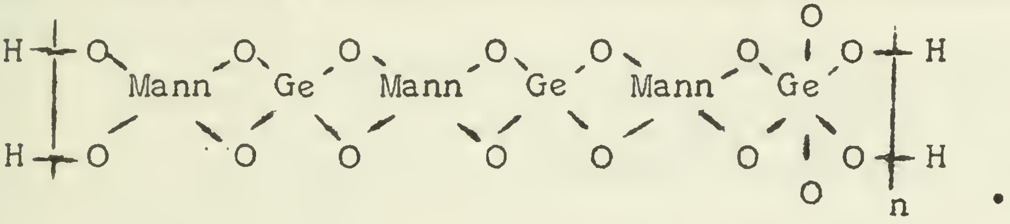
[illegible]

[illegible]

[illegible]

[illegible]

The 1:1 mannitol complex is most probably a tetrahedron where mannitol is tridentate with one free hydroxy group left to ionize. The polymeric structure is probably linear, with alternating mannitol and germanate units, being mostly tetrahedral with some octahedral sites necessary to explain the charge on the compound;



Similar ion-exchange studies have been made using hydroxy-acids such as tartaric, lactic, and mucic(28). Furthermore, by means of conductance, pH, and optical rotation methods, lactic, tartaric, mandelic, and maleic acid systems with germanium dioxide have been studied (29).

Tartrate acts as a quadridentate ligand in the very stable 1:1 complex formed with germanium, the other two positions in the coordination octahedron being filled by water with ionizable hydrogen atoms. The 3:2 complex most likely consists of two octahedra joined by a bridging tartrate group.

The structures of the various lactate and mucate complexes can also be well defined in terms of the $[Ge(OH)_6]^{=}$ octahedron or GeO_4 tetrahedron (28).

Vartapetian (29), in plotting pH or optical rotation *vs.* the ratio of Ge/d-tartaric acid, found sharp breaks in each curve at the ratio 1:1. This indicates the formation of a complex of this composition. The pH of the germanium solution decreases on addition of various hydroxy-acids, and the optical rotation of the active acids is reinforced on complexing. Using these methods, Vartapetian was able to calculate stability constants for the various complexes. As expected, tartaric acid proved to form the strongest complex, probably as a result of the presence of two chelating positions on the same carbon skeleton.

A listing of the combining ratios of germanium and 24 hydroxy-acids has been given by Clark (30).

Finally, the solutions of germanium tetrachloride in hydrochloric acid were studied by the ion-exchange method (31) and by solvent extraction into carbon tetra chloride (32). In this case, the solution must be acidic enough ($>$6 *M* HCl) to prevent hydrolysis to germanium dioxide. Everest found evidence of partially hydrolyzed species, $[Ge(OH)_xCl_{5-x}]^-$ or $[Ge(OH)_xCl_{6-x}]^{=}$ (x=3-4) between 6-9*M* HCl, and postulated that, below this acid concentration, GeO_2 (or H_2GeO_3) is the species present, whereas at hydrochloric acid concentrations greater than 9 *M*, germanium tetrachloride forms a separate phase. Hence, no evidence for the existence of the complex species $GeCl_5^-$ or $GeCl_6^{=}$ was found. The fact that cesium and rubidium chloro germanates can be precipitated from 7*M* HCl indicates that the $GeCl_6^{=}$ anion is present, but at too low a concentration to be adsorbed.

[illegible]

Similar fluorescence [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

The distribution ratio

$$D = ([\mathrm{GeCl_4}]_{org} / \sum[\mathrm{Ge}]_{aq})$$

was studied as a function of four varying concentrations, and it was found (32),

a) D was independent of the germanium concentration, indicating that germanium tetrachloride was also present in the aqueous phase.

b) D increased with increasing chloride ion concentration.

e) D increased at a decreasing rate with increasing hydrogen ion concentration.

d) D increased slowly with increasing HCl concentration up to 5*M* HCl, then increased rapidly to its maximum at 14*M* HCl.

The slopes of the curves obtained by plotting log D *vs*. chloride or hydrogen ion concentration provided a method for calculating *i*, and *j* in the formula for the species $\mathrm{GeCl}_i(\mathrm{OH})_j(\mathrm{H_2O})_k$, which is believed present in the aqueous layer. The value for *i* was 4.0 in 1.5 *M* chloride solution, showing the stability of the chloro-complex. At higher acid concentration (12.0*M* HCl), *i*=4.2 and *j*=0.7, indicating a negatively charged species with a coordination number of six. However, the constancy of D at higher acid concentrations again indicates that the formation of $\mathrm{GeCl_6}^{=}$ does not take place in solution. This evidence is also supported by Waddington and Klanberg (33), who found no $\mathrm{GeCl_6}^{=}$ species even in liquid anhydrous hydrochloric acid.

VI. CONCLUSION

Various types of compounds formed by tetravalent germanium have been described. Present investigations are chiefly concerned with attempts to determine the natures of the various species present in different aqueous media. The ion-exchange studies leave something to be desired, for the method is open to question and the results may be interpreted ambiguously.

It may be inferred from a majority of the data that mono- and penta-germanate ions predominate in such solutions, though other condensed species must also exist. Germanium forms a number of complexes of varied formulae with acids and bases, depending on the relative concentrations of the species and the pH of the solution. The nature and structure of these complex ions provides an interesting area for further study.

TABLE 1

Germanate Species Present in Various Aqueous Media

Medium	pH	R	Species Adsorbed	Ref.
1.8mmolesGe, 1.8 mmoles Cl^-	9.4-6.9	2.5	$Ge_5O_{11}^{=}$	20
" " " " " "	9.4-10.42	2.53-1.77	$Ge_5O_{11}^{=}$, $HGeO_3^-$	20
" " " " " "	11.28-12.84	0.57-0.30	$GeO_3^{=}$	20
1.8mmolesGe, 0-0.3mmoles Cl^-	8.68-4.24	2.46-0.58	$Ge_5O_{11}^{=}$, $HGeO_3^-$, $GeO_3^{=}$	20
0.8-2.8g GeO_2/100 ml	9.0	3.5	$H_2Ge_7O_{16}^{=}$	23
Ge, glycerol	<8	5.8	$H_2Ge_{11}O_{24}^{=}$ or $H_2Ge_{12}O_{26}^{=}$	26

TABLE 2

Germanium Species Present With Other Anions

Medium	pH	Species Adsorbed	Ref.
Ge, $SO_4^{=}$	7-9	$[GeO_2(SO_4)]^{=}$	22
Ge, $PO_4^{\equiv}$	7-9	$[HGeO_2(PO_4)]^{=}$	22
Ge, oxalate	>7	$Ge_5O_{11}^{=}$	25
Oxalate/Ge=4.82	4.4-6.8	$[Ge(ox)_3]^{=}$	25
"	3-4.5	$[Ge(OH)_2(ox)_2]^{=}$ or $[GeO(ox)_2]^{=}$	25
ethylene glycol, Ge	>11	$[GeO_2(C_2H_4(OH)_2)]^{=}$ and $[GeO(C_2H_4(OH_2)_2]^{=}$	26
glycerol, Ge	>9	$[GeO_2(glyc)]^{=}$, $Ge_5O_{11}^{=}$	27, 26
" "	12	$[Ge(glyc)_3]^{-}$	26
" "	10-11	$[GeO(glyc)_2]^{=}$	26
Ge, mannitol	<8	$[GeO_2(mann)]^{=}$	27
" "	>10.6	$[GeO(mann)_2]^{=}$	27
Mannitol-Ge	>12	$[Ge(mann)_3]^{=}$	26
mannitol-Ge	6	$[Ge_4(mann)_3]^{=}$	26
tartrate/Ge=5:1	>11	$[1:1\ complex]^{=}$	28
tartrate/Ge=100:1	>11	$[3:2\ complex]^{=}$	28
HCl, Ge	6-9M HCl	$[Ge(OH)_xCl_{5-x}]^-$ or $[Ge(OH)_xCl_{6-x}]^{=}$ (x=3 to 4)	31
HCl, Ge	12M HCl	$[GeCl_{4.2}(OH)_{.7}(H_2O)]^-$	32

REFERENCES

1. O. H. Johnson, Chem. Revs., 51, 431 (1952).
2. O. H. Johnson, ibid., 48, 259 (1950).
3. H. S. Booth and W. C. Morris, J. Am. Chem. Soc., 58, 90(1936).
4. T. N. Srivastaa and M. Onyszchuk, Proc. Chem. Soc., 1961,105.
5. P. Souchay and A. Tchakirian, Ann. Chim. [12] 1, 232, 249 (1946).
6. J. R. Chipperfield and R. H. Prince, Proc. Chem. Soc., 1960,385.
7. H. H. Anderson, J. Am. Chem. Soc., 83, 547 (1961).
8. H. H. Anderson, ibid., 82, 3016 (1960).
9. M. Lesbre and J. Satgé, Compt. rend., 252, 1976(1961).
10. H. C. Clark and C. J. Willis, Proc. Chem. Soc., 1960, 282.
11. H. Schmidbaur and M. Schmidt, Ber., 94, 1138 (1961).
12. J. G. Noltes and G. J. M. Van der Kerk, Rec. trav. chim., 80, 623 (1961).
13. H. S. Kolesnikov, S. L. Davydova, and N. V. Klimentova, J. Polymer Sci., 52, 55 (1961).
14. R. Hulme, G. J. Leigh, and I. R. Beattie, J. Chem. Soc., 1960,366.
15. J. E. Griffiths and M. Onyszchuk, Can. J. Chem., 39, 339 (1961).
16. R. D. Joyner and M. E. Kenney, J. Am. Chem. Soc., 82, 5790(1960).
17. G. Carpeni, Bull. Soc. Chim. France, 1948, 629.
18. G. Carpeni, ibid., 1952, 1010.
19. P. Souchay, ibid., 1951, 938, 1953, 390, 395.
20. D. A. Everest and J. E. Salmon, J. Chem. Soc., 1954,2438.
21. R. Schwarz and F. Heinrich, Z. anorg. allgem. Chem., 205,43,(1932)
22. D. A. Everest and J. E. Salmon, J. Chem. Soc., 1955, 1444.
23. D. A. Everest and J. C. Harrison, ibid., 1959, 2178.
24. E. R. Shaw, J. F. Corwin, and J. W. Edwards, J. Am. Chem. Soc., 80, 1536 (1958).
25. D. A. Everest, J. Chem. Soc., 1955, 4415.
26. D. A. Everest and J. C. Harrison, ibid., 1960, 745.
27. D. A. Everest and J. C. Harrison, ibid., 1957, 4319.
28. D. A. Everest and J. C. Harrison, ibid., 1960, 3752.
29. O. Vartapetian, Ann. chim. (France), 2, 914 (1957).
30. E. R. Clark, Nature, 180, 904 (1957); 183, 536 (1959).
31. D. A. Everest and J. C. Harrison, J. Chem. Soc., 1957, 1820.
32. R. L. Benoit and P. Clerc, J. Phys. Chem., 65, 676 (1961).
33. T. C. Waddington and F. Klanberg, Naturwissenschaften 46, 578 (1959).

PROPERTIES OF METALLOPORPHYRINS

Willard B. Howe November 14, 1961

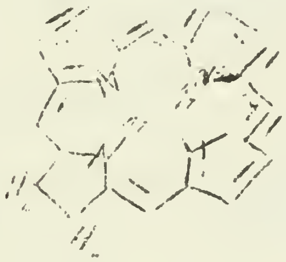
I. INTRODUCTION

Although many biologically important porphyrins had been isolated by 1900, very little quantitative data regarding their physical and chemical properties was accumulated until the nineteen thirties when Stern (1) began to publish information on porphyrin and metalloporphyrin visible absorption spectra.

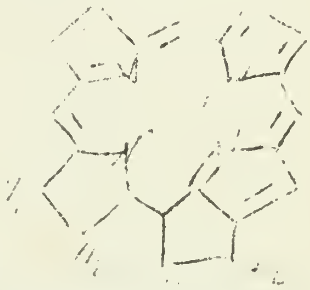
In this author's view, there were two major causes for this lack of information. Until the nineteen thirties, few pure samples of natural or synthetic porphyrins or their metal derivitives had been obtained. Secondly, the literature abounded in trivial names for these compounds. This latter problem was not resolved until H. Fischer and R. Willstatter and their coworkers established the structures of many of these compounds by synthesis (2,3).

In order that the structures of the compounds be understood, porphyrins need to be classified. Three general classes are included below:

porphin



chlorin



phorbin

During this report, the systematic name will be given the first time a porphin is mentioned. Thereafter the shorter, trivial name will be used.

II. PORPHYRIN ACIDITY

Porphyrins possess four pyrrole nitrogen atoms, only two of which are protonated. Hence it would seem logical that, under appropriate conditions, mono- and di-cations could be formed. This has been accomplished in nonaqueous solvents such as acetic and formic acids and has been measured spectrophotometrically.(4).

In cimplex formation with a divalent metal, the following occurs:

$$M^{2+} + PH_2 \longrightarrow MP + 2H^{+}$$

where PH_2 represents the molecule of any porphyrin. It is clear from this reaction that any measure of a MP stability constant must account for the first and second ionization constants of the porphyrin which forms the complex. If these constants are evaluated according to the

equations below:

$$H^+ + P^{2-} \longrightarrow PH^- \qquad (1)$$

$$K_1 = \frac{[PH^-]}{[P^{2-}][H^+]} \qquad (1a)$$

$$H^+ + PH^- \longrightarrow PH_2 \qquad (2)$$

$$K_2 = \frac{[PH_2]}{[PH^-][H^+]} \qquad (2a)$$

$$K_f \text{ apparant} = \frac{[MP][H^+]^2}{[M^{2+}][PH_2]} \qquad (3)$$

then, by substitution of (1a) and(2a) into (3) ,

$$K_f \text{ apparant} = \frac{[MP]}{[M^{2+}][P^{2-}]/K_1 \cdot K_2} \qquad (4).$$

Since:

$$K_f = \frac{[MP]}{[M^{2+}][P^{2-}]} \qquad (5)$$

then, by substitution of (5) into (4)

$$K_f \text{ apparant} = \frac{K_f}{K_1\ K_2}$$

In only one case (5), has there been even an approximate evaluation of K_1 and K_2. Solutions of 1,3,5,7-tetramethyl-2,4,6,8-tetraethylporphin (etioporphin I) in methanol and benzene were titrated using sodium triphenylmethide as a base. By assuming the pK_a of methanol to be 16, the value of the sum, pK_1 pK_2, was estimated to be about 32.

III. METALLOPORPHYRIN STABILITY STUDIES

The low solubilities of metalloporphyrins, particularly in water, have prevented the estimation of all but one stability constant. By employing a detergent to "dissolve" the parent porphyrin, 1,3,5,8-tetramethyl-2,4-diethylporphin-6,7-dipropionic acid, a stability constant of the order of magnitude of 10^{29} was estimated for the corresponding zinc derivitive (4). However, this involved the evaluation of the distribution constant:

$$PH_2 \text{ aq.} \rightleftarrows PH_2 \text{ detergent}$$

which is an important source of experimental error.

Other stability studies are essentially qualitative and may be grouped into [illegible] classes.

1. Exchange reactions have been run using tetraphenyl porphin and iron (III), cobalt (II), copper (II), zinc (II), magnesium (II), and sodium (I). These were conducted in pyridine in order to dissolve an appreciable quantity of the metal complex. In similar fashion an exchange reaction was attempted between chlorophyll a and magnesium (II) (6). In only the case of sodium ion was the exchange rate rapid. The other compounds showed negligible rates of exchange even after several days (7).

2. Replacement reactions of the type,

$$MP + M_1 \longrightarrow M_1P + M ,$$

constitute a second means for gaining a measure of metal-ligand relative stabilities. The investigation of such reactions as these:

$$Na_2\phi_4P + 2Li^+ \xrightarrow{\text{pyridine}} Li_2\phi_4P + 2Na^+$$

$$Cu^{2+} + Zn\phi_4P \xrightarrow{\text{pyridine}} Cu\phi_4P + Zn^{2+},$$

led Barnes and Dorough (8) to the following conclusions: small divalent ions such as copper (II) and zinc (II) replaced large divalent ions such as mercury (II) and lead (II), that divalent ions replaced monovalent ions, and that small monovalent ions replacedlarge monovalent ions. Furthermore, the large divalent cations, mercury (II) and lead (II), as well as monovalent cations, underwent rapid replacement.

Since all reactions either went to completion or failed measurably to proceed, no equilibrium constants could be determined. However, the qualitative order of decreasing stabilities was copper (II) zinc (II) mercury (II) lead (II) lithium (I) sodium (I) potassium (I). The relatively rapid replacement rates for mercury (II) and lead (II) ions were rationalized on the basis of their large size, which could prevent their assumption of a position within the plane of the porphyrin ring. This effect might well be accentuated by steric hindrance between the metal ions and the ortho hydrogen atoms of the phenyl groups.

In contrast to the study above, Caughey and Corwin (8) failed to replace zinc in zinc 1,3,5,8-tetramethyl-2,4,6,7-tetraethylporphin (etioporphyrin II) by nickel (II), copper (II), or tin (II) cations.

Thus, there is established the fact that the organic residue affects the reaction. This author attributes the inhibition of zinc replacement to a rate phenomenon.

3. A second type of replacement reaction was briefly investigated by Melville and Corwin (9). They were studying competitive reaction rates between cations and the two porphyrins, etioporphyrin II and etiochlorin II. From a solution 10^{-4} molar in each porphyrin and in copper acetate, only copper etioporphyrin formed. When magnesium ion replaced copper ion, magnesium etiochlorin is formed at first. This was followed by a slow but quantitative conversion of all of the magnesium ion to the etioporphyrin chelate. The authors venturedto conclude that porphyrin complexes are more stable than chlorin complexes,

and that the energy of activation for decomposition of a copper (II) complex is considerably greater than that for a magnesium (II) complex. Considering the data available, these are very tenuous generalizations.

4. Formation and dissociation reactions provide a fourth method to evaluate stabilities of complexes. The only available data is qualitative and may best be summarized in Table I (4).

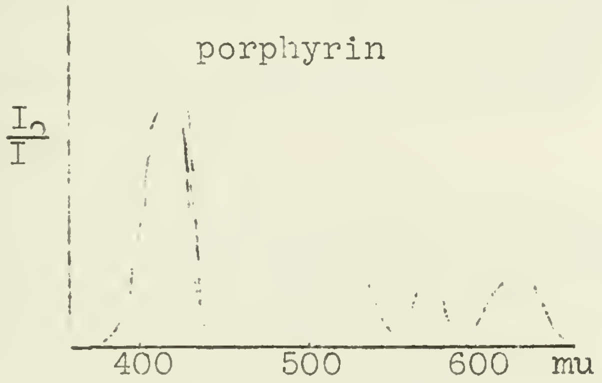
Table I

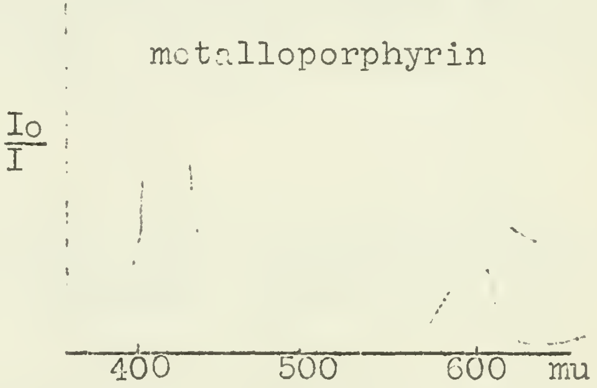
Acid	Cation	Porphyrin
H_2SO_4 conc.	Cu (II), Mn (II), Co (II), Ni (II), Fe (III), Co (III)	hematoporphyrin IX *
H2SO4 conc.	Cu (II), Ag (II), Co (II), Ni(II)	protoporphyrin IX dimethyl ester
H2SO4 conc.	Cu (II), Co(II), Ni (II), Fe (III)	etioporphyrin II
HCl dil.	Zn (II), Cd (II), Pb (II)	protoporphyrin IX dimethyl ester
water	Ag (I), K (I), Na (II), Li (I), Pb (II), Hg (II)	Tetraphenylporphin

* 1,3,5,8-tetramethyl-2,4-bis(-hydroxyethyl)porphin-6,7-dipropionic acid

In each series, the rate of dissociation decreases from left to right.

5. The visible and near ultraviolet absorption spectra of porphyrin complexes have been used to evaluate relative stabilities. Spectra, typical of porphyrins and porphyrin complexes are shown below:





It has been suggested(11) that the four low intensity bands are associated with two degenerate → transitions which are split by tautomerism of the two protons which are bonded to the nitrogen atoms. Credence is lent to this hypothesis by the fact that protoporphyrin IX dihydrochloride has the same type of spectrum as those of metalloporphyrins.(11). The intense absorption band near 400 mu is attributed to another → transition which is little affected by tautomerism or coordination of the pyrrole nitrogen atoms.

It has been noted (8,10,11) that there is a hypsochromic shift of the and metalloporphyrin absorption bands which closely corresponds to the increase in "stability" of many metal porphyrins (Table II).

Table II
Beta Band max. (10)

Porphyrin	Zn (II)	Cu (II)	Co (II)	Ni (II)	Pd (II)	Pt (II)
mesoporphyrin IX	570	561	552	550		
protoporphyrin IX	586	578	573	567		
tetramethylhemataporphyrin		565	560	557		
tetraphenylporphin	572	560		550	524	510
etioporphyrin II	574	563	560	554		
phthallocyanine	649	648	642	641		

Two effects should account for the increase in frequency. An increase in electron affinity of the complexing metal would be expected to cause localization of the nonbonding electrons in pi orbitals of the nitrogen atoms. This, in turn, might be expected to increase the frequency of any transition involving them. The ability of the cation to donate electrons by d bonding would also affect any transition in the ligand which is closely associated with the nitrogen atoms.

From an analysis of all available spectral data, Phillips (4) has proposed this series of relative porphyrin stabilities: Pt (II) $>$ Pd (II) , Ni (II) $>$ Co (II) $>$ Ag (II) $>$ Cu (II) $>$ Zn (II) $>$ Mg (II) $>$ Li$_2$ $>$ Na$_2$ $>$ K$_2$ $>$ Ag$_2$(II).

The inversion of nickel (II) and copper (II) from the normal order (12,13), is readily reconsiled by a molecular orbital approach. Under the influence of the porphyrin copper (II) must enter into dsp^2 hybrid bonding rather than the slightly distorted tetrahedral bonding associated with weak-field ligands.

IV. IRON COMPLEXES

It is noteworthy that, in thesections above, no data are included for relative stabilities of iron (II) complexes. This lack is caused by a defficiency of data on iron (II) porphyrins comparable to that data mentioned for the other cations.

Ferrous and ferric complexes are especially insoluble in water. Hence, most investigations, involving these ions in water, have been accomplished by using porphyrins, containing propionic acid residues, which are neutralized so as to dissolve the complexes. This requires a basic medium in which ferrous and ferric porphyrins tend to dimerize.

If heme or hemoglobin is treated with any of a series of nitrogenous bases, or hydroxide ion, diamagnetic complexes result (4,16), and each of these isa member of a class of compounds referred to as hemochromes or hemochromogens.

During this process the alpha- and beta-spectral bands are shifted to lower wavelengths. For instance, iron (II) mesoporphyrin IX with two ligands on the Z axis undergoes these shifts: alpha (605 560 mu), beta (548 520 mu) (10). These hemochromogen bands are quite insensitive to changes in frequency or extinction coefficient with variance

Of Z-axis ligands (10). These absorption bands have provided consequentially an excellent method to analyse total hemochromogen in a sample (15).

Several equilibria have been extensively studied, particularly those involving pyridine-cyanide ion and iron protoporphyrin IX complexes.

If P is (protoporphyrin IX $)^{2-}$ then various reactions may be expressed as:

$$[Fe(II)(H_2)P]_2^0 + 4\,py \rightarrow 2[Fe(II)py_2P]^0 \quad \log K_{f1} = 10.94 \quad (4)$$

$$[Fe(III)(H_2O)_2P]_2^{2} + 4py \rightarrow 2[Fe(III)py_2P]^{1} \quad \log K_{f2} = -0.12 \quad (17)$$

$$[Fe(II)(H_2O)_2P]_2^{0} + 4CN^- \rightarrow 2[Fe(II)(CN)_2P]^{2-} \quad \log K_{f3} = 9.9 \quad (4)$$

$$[Fe(III)(H_2O)_2P]_2^{2} + 4CN^- \rightarrow 2[Fe(III)(CN)_2P]^- \quad \log K_{f4} = 12.2$$

That the magnitude of K_{f1} is larger than K_{f2} may be qualitatively rationalized on the basis of the change in formal charge of the iron atoms. Iron (II) ions, from electrostatic considerations, would be expected to undergo less d double bonding to the pyridine rings than would the less positively charged iron (II). On the other hand, from strictly electrostatic considerations, the attraction of Iron (III) for cyanide ion would be expected to increase the value of K_{f4} above that for K_{f3}, even if iron (II) would double bond to cyanide ion more than would iron (III).

$$[Fe(II)(H_2O)_2P]_2^{0} + 2py + 2CN^- \rightarrow 2[Fe(II)pyCnP]^- \quad \text{Log } K_{f5} \; 16.9 \; (4)$$

$$[Fe(III)(H_2O)P]_2^{2+} + 2py + 2CN^- \rightarrow 2[Fe(III)pyCNP] \quad \text{Log } K_{f6} \; 12.56 \; (4)$$

From the K_f values reported it is seen that the mixed complexes of both iron (II) and iron (III) possess greater stability constants than the pure cyanide complexes. This again may be rationalized on the basis of electrostatics. In both cases, the negative charges associated with dicyanide complexes would tend to reduce their stabilities in comparison to the mixed complex.

V. OTHER HEMOCHROMOGENS

Manganese (II) and (III)(18) porphyrins behave similarly to iron (II) and (III) analogues. Both yeild complexes with nitrogenous bases such as pyridine, picolines and cyanide which may be either of the pure or the mixed class.

However, for zinc (II), mercury (II), nickel (II), copper (II), and cadmium (II) derivitives, only one pyridine molecule complexes with the metalloporphyrin. See Table III.

Table III

Porphyrin	Cation	Log K
Tetraphenylporphin	Zn(II)	3.57
	Cd(II)	3.13
	Hg(II)	1.08
	Cu(II)	-1.3
Tetraphenylchlorin	Ni(II)	-1.3
	Zn(II)	3.73

It can be seen from the above data that the stabilities of the IIB series of complexes decreases as the ionic radius of the metal increases. This is to be expected if bonding is primarily electrostatic. However, for copper (II) and nickel (II) compounds, where there is a marked tendency toward tetracoordination, the equilibrium constant becomes quite small.

V. CONCLUSIONS

At present there is still a profusion of uncoordinated literature, much of which is contradictory, concerning metalloporphyrins.

Comparison of properties of dissolved metalloporphyrins is severely hindered due to their low solubilities in most solvents.

In the case of iron (II) and iron (III) complexes the electronic state of the metal ion is very easily modified by the addition of a basic ligand on the Z axis.

Bibliography

1. Stern, A. and Wenderlein, H., Z. phys. Chem., A170, 339 (1934)
2. Fischer, H. and Orth, H., Die Chemie des Pyrrols Bd. II Pyrrol Farbstoff Erste Halfte, Leipzig Akad. Verlages, 1937; Zweite Halfte Fischer, H. and Stern, A., Leipzig Akad Verlages, 1940
3. Lemberg, R. and Legge, J.W., Hematin Compounds and Bile Pigments, Interscience Publishers, Inc., New York, 1948
4. Phillips, J.N., Revs. of Pure and Applied Chem., 10, 35, (1960)
5. McEwan, W.K., J. Am. Chem. Soc., 58, 1124, (1936)
6. Stranks, D.R. and Wilkins, R.J., Chem. Revs., 57, 789(1957)
7. Barnes, J.W., and Dorough, G.D., J. Am. Chem. Soc., 72, 4045 (1950)
8. Caughey, W.S. and Corwin, A.H., J. Am. Chem. Soc., 77, 1509 (1955)
9. Corwin, A.H. and Melville, M.H., J. Am. Chem. Soc., 77, 2755(1955)
10. Williams, R.J.P., Chem. Revs., 56, 299, (1956)
11. Thomas, D.W., Martell, A.E., Archives of Biochem. and Biophysics 76, 286, (1958)
12. Mellor, D.P. and Melory, L., Nature, 159, 370 (1947)
13. ibid., 161, 436 (1948)
14. Lemberg, R. and Falk, J.E., Biochem. J., 49, 674 (1951)
15. Hogness, T.R., Zscheile, F.P., Sidwell, A.E. and Barron, E.S.G., J Biol. Chem., 118, 1 (1937)
16. Havemann, R., Z. phys. Chem. (Leipzig) 209, 135 (1958)
17. Shack, J. and Clark, W.M., J. Biol Chem., 171., 143 (1947)
18. McConnel, A. and Wang, J.H., J. Am. Chem. Soc., 80, 6526, (1958)
19. Miller, J.R., Dorough, G.D., J. Am. Chem. Soc., 74, 3977 (1952)

RECENT DEVELOPMENTS IN THE CHEMISTRY OF THE ZEOLITES

L. V. Interrante December 5, 1961

I. Introduction

The zeolites have been known for many years as a mineral class (1), but only within the last two decades has a real understanding of their properties and chemistry been attained. In 1938 (2), Barrer began a series of investigations that resulted in (a) the determination of the properties and structure of most of the natural zeolites, (b) a general method of synthesis of these and new zeolitic structures, and (c) the recognition of the potential applications of these materials.

Recently the zeolites "type A" (3) and "type X" (27,4) were synthesized by Breck and Milton and shortly thereafter became commercially available. The unique sorptive properties of these materials as well as their availability has largely been responsible for the recent revival of interest in this field.

II. Structure

The zeolites are characterized by porous anionic frameworks capable of reversibly occluding "guest" molecules when activated. These frameworks usually consist of aluminum and silicon atoms tetrahedrally coordinated to oxygen atoms and linked together <u>via</u> oxygen bridges. Three general classes of zeolites are distinguished, the Fibrous, Laminar, and Network types, differing in the relative bond strengths along the three axes of the crystal (5). This seminar will be concerned chiefly with the Network type in which the bond strengths are equivalent along all three axes.

The composition of the zeolites may be represented by the general formula, $M_{2/n}O.Al_2O_3.YSiO_2.XH_2O$, where M is a cation of charge n, required for overall electrical neutrality due to the AlO_4 units present in the framework. The water molecules are loosely bound in the zeolite lattice and may be removed, often without significant change in the crystal structure by outgassing at temperatures of the order of 300°C (6).

Structural determinations of the anionic frameworks of a number of zeolites have been accomplished using powder and single crystal x-ray data as well as molecular sieve properties (7,8,9). These structures are characterized by large cavities separated by "windows" of oxygen rings, forming intracrystalline channels or pores of fixed dimension. The cations associated with these lattices are loosely bound and occupy positions of lowest energy in free space between AlO_4 tetrahedra (10,11).

For most zeolites the replacement $M_{1/n}Al \rightleftarrows Si$ is possible with retention of the same structure, illustrating the equivalence of aluminum and silicon in the framework. The most notable exception to this was the zeolite type A which was previously synthesized in only one form, having the constant composition $M_{2/n}O \cdot Al_2O_3 \cdot 2SiO_2$ and shown to involve an alternating arrangement of aluminum and silicon atoms (3,12,13). However, Kerr has recently shown that more siliceous zeolites with this structure can be prepared (14).

III. Synthesis

The zeolites are synthesized by hydrothermal methods in which the components are heated in the presence of an aqueous phase at temperatures ranging from 60 to 450°C. Periods of anywhere between 15 minutes and several weeks are required to effect crystallization (15). Probably the most useful approach involves the preparation of a hydrous gel by reaction of appropriate sources of $M_{2/n}O$, Al_2O_3, and SiO_2 (15). Variation of the cation M and the use of mixed cation sources has been employed by Barrer to obtain a variety of different crystalline phases (16,17,18). In this method water acts as a filler around which the zeolite lattice is thought to grow (19).

Certain inorganic salts have also been used successfully as fillers or "mineralizing agents"(15,20). In this case removal of the filler necessitates hydrothermal extraction with distilled water. Finally, natural or synthetic zeolites may be recrystallized into new zeolite structures by hydrothermal treatment with aqueous alkali, with or without added inorganic salts (20,21).

The mechanisms of growth have not been explored for the zeolites in any extensive way. However, Kerr (22) has shown that the crystallization of zeolite type A from amorphous gels is preceded by an induction period during which time nucleation occurs. Furthermore, Barrer has proposed that a close correlation exists between the formation of framework minerals and the alkalinity of the crystallization solution (15). Finally, the "simplexity principle", originated by Goldsmith (23), and "Lowenstein s Rule"(24) are mentioned as factors influencing the arrangement of AlO_4 and SiO_4 tetrahedra in the zeolite framework.

IV. Sorption

The adsorption of guest molecules by a zeolite lattice has recently been placed on a thermodynamic basis by Barrer, who showed that a decrease in chemical potential accompanies this process and results in a lower energy situation for the filled structure (19,25,26).

The most important factor governing zeolitic sorption is the relationship between the pore structure of the zeolite and the "critical diameter" of the sorbate molecules, defined as "the diameter of the smallest cylinder which will accommodate a model of the molecule, constructed using the best available van der Waals radii, bond angles, and bond lengths"(27). Thus, due to the rigid nature of the zeolitic framework, the tendency to assume a filled structure, and the large capacity for sorbate molecules, quantitative separations may be carried out solely on the basis of molecular shape (3,6,14,28,29,30).

The molecular sieve properties of the zeolites provide a useful classification of these materials on the basis of their pore size (Table 1). The most open zeolite structure is that of faujasite or its synthetic analog, type X. This zeolite is capable of occluding cyclic as well as branchedchain molecules and has been shown to occlude benzene reversibly at temperatures as high as 427°C. (31).

Barrer has studied the effect of cation radius and density upon the sorption capacity of various zeolites (32,33). Substitution of increasingly larger cations in a zeolite in general leads to a decrease in the sorption capacity and, due to partial blocking of the pores in some cases, alters the molecular sieve properties.

An increase in cation density also lowers the sorption capacity and often markedly changes the molecular sieve properties of the zeolite. Cation density may be varied either by the use of structurally equivalent forms of variable composition, leading to the replacement $M_{1/\underline{n}}Al \rightleftarrows Si$, or by the cation exchange $2Na \rightleftarrows Ca$.

In the case of the type A structure, these two methods apparently yield equivalent results. The conversion, type 4A ⇄ Type 5A, is accomplished by the cation exchange $2Na \rightleftarrows Ca$. The effect of this exchange is to enable the occlusion of straight-chain hydrocarbons (3). The same result is achieved in Na ZK-4 where the increased $Al_2O_3:SiO_2$ ratio also results in a lower cation density and larger effective pore diameter(14).

Other factors shown to influence sorptive properties are the presence of a preadsorbed phase in the zeolite (3,34) and the polarity, polarizibility, quadripole moment, and vapor pressure of the sorbate molecules (3,6,35).

Besides the occlusion of volatile sorbates, it has also been demonstrated that certain inorganic salts may be reversibly occluded from aqueous solution or from melts of the salt (36).

V. Ion Exchange

The mobility of the zeolite cations is demonstrated by a recent study of the electrical conductivity of anhydrous zeolites, in which an "usually high conductivity for ionic crystals" was observed (37). Thus, in aqueous solution zeolite cations can be readily exchanged for others if certain size and charge requirements are satisfied.

Exchange equilibria have been studied for zeolite type A by Barrer, who found that the exchanges generally obey the ideal mass action equation for a single homogeneous group of exchange sites(38).

The "ion-sieve" behavior of the zeolites has been the subject of a number of investigations, and its analogy to molecular sieve action has been demonstrated (13). In this manner the limits of exchange and, therefore, the effective pore diameters of a number of zeolites have been determined (Table 2). Moreover, the extent of exchange has been shown to be quite dependent upon the radius of the exchanging cation. In a study of the exchange

Table 1 - Zeolite Classification Based Upon Molecular Sieve Properties

Molecular Size Increasing

Molecules	Size limit	Type
He, Ne, Ar, O_2, N_2, H_2O	Size limit for Ca- and Ba-mordenite and levynite about here (~3.8Å)	Type 5
Kr, Xe CH_4 C_2H_6 CH_3OH CH_3CN	Size limit for Na-mordenite and type 4A (Na form) about here (~4.0Å)	Type 4
C_3H_8 C_2H_5Cl C_2H_5Br C_2H_5OH $\underline{n}$-C_4H_{10} $\underline{n}$-C_7H_{16} $\underline{n}$-$C_{14}H_{30}$ CHF_2Cl $(CH_3)_2NH$ B_2H_6 CF_4 C_2F_6 CF_2Cl_2 CF_3Cl $CHFCl_2$	Size limit for Ca-chabazite, type 5A (Ca form) Barrer's Ba-zeolite, and gmelinite about here (~4.9Å.)	Type 3
SF_6 $CHCl_3$ $CHBr_3$ CHI_3 $(CH_3)_2CHOH$ $\underline{n}$-C_3F_8 iso-C_4H_{10} iso-C_5H_{12} B_5H_9 $(CH_3)_3N$ $(C_2H_6)_3N$ $C(CH_3)_4$ $C(CH_3)_3Cl$ $C(CH_3)_3Br$ $C_2F_2Cl_4$ C_6H_6 $C_6H_5CH_3$ $B_{10}H_{14}$ Napth. Quin. $C_6F_{11}CF_3$	Size limit for type 10x (Ca form) about here (~8Å.)	Type 2
1,3,5tri-ethyl benzene 1,2,3,4,5,6,7,8,13,14,15,16-decahydro-chrysene	Size limit for type 13 x (Na form) about here (~10Å.)	Type 1
$(\underline{n}$-$C_4F_9)_3$		

Table 2 Ion-Sieve Properties

EXCHANGER	EXCHANGE	NO EXCHANGE
ultramarine	K^+(1.33A.)	Cs^+(1.69A.)
analcite	Rb^+(1.48A.)	Cs^+(1.69A.)
chabazite	Cs^+(1.69A.)	$(CH_3)_4N^+$(2.4A.)
Type 4A	$(CH_3)_3NH^+$(2.25A.)	$(CH_3)_4N^+$(2.4A)
Faujasite	$(CH_3)_4N^+$(2.4A.)	$(C_2H_6)_4N^+$(~4A.)

of organic cations for sodium in faujasite, the extent of exchange was found to decrease from almost complete exchange to no exchange in the order, $NH_4^+ > NH_3Me^+ > NH_3Et^+ > NH_2Me_2^+ > NHMe_3^+ > NMe_4^+ > NEt_4^+ >$ (13).

VI. The Properties of Intracrystalline Water in Zeolites

The behavior of water sorbed in zeolites has been the object of considerable attention. Barrer, in a study of the sorption capacity of various group I and group II cation - exchanged chabazites for water, observed a relationship between the amount of H_2O sorbed and the primary hydration number of the cations in aqueous solution (32). (Table 3)

Table 3 Amount of H_2O Sorbed as a Function of the Cation

	Ca^{+2}	Li^+	Na^+	K^+	Rb^+	Cs^+
H_2O Molecules per Cation in natural chabazite	6.5	3.1	3.0	2.5	2.3	2.0
Primary Hydration Numbers	6-8	6	5	3	2	-

However, for large amounts of water sorbed, no clear correlation exists between the heat of sorption and the cation present (39,40). In this case the anionic oxygen atoms appear to determine the energy of sorption, with cations exerting only moderating influences.

The diffusion of water into zeolites has been studied by Pemsler (41) and Barrer (42.43), who determined the diffusion coefficients for a variety of zeolites using heavy water as a tracer. The relative magnitudes of the coefficients obtained were in agreement with the pore structures previously suggested for the zeolites.

VII. Stability

The effect of an intracrystalline filler upon the thermodynamic stability of the zeolites has already been mentioned. This effect is used to explain the increased thermal stability of the zeolites with increasing cation radius, in which the larger cationic volume is thought to lower the energy of the dehydrated lattice (44). Apparently contrary to this is the observed decreased in thermal stability with decrease in the Al_2O_3:SiO_2 ratio (45). In this case the effect of the larger cationic volume is offset by the greater instability of the more high charged anionic framework.

The products of the thermal decomposition of the zeolites have been studied in the case of the chabazites by Barrer (45) and for various calcium zeolites by Koizumi (46). These range from amorphous and glassy phases to quartz, felspars, and modified zeolite structure.

The zeolite framework is quite unstable to acids, resulting in rupture of the lattice bonds and complete lattice breakdown(47). This effect has been used to explain the decreased stability of the ammonium forms of a number of zeolites (3,13,33). In these cases, loss of ammonia occurs, apparently resulting in recombination of the protons with the zeolite oxygen atoms and subsequent rupture of the lattice bonds. Barrer has found that this effect is most pronounced with the more aluminous zeolites, in which the increased number of cations per unit cell leads to a greater number of lattice-bond ruptures and therefore greater probability of structural decomposition (33).

VIII. Germanium and Gallium Analogs.

The preparation of zeolite structures in which other atoms replace aluminum and silicon, apparently has been limited to those structures in which the higher congeners of these elements, gallium and germanium, are present. Barrer has reported the crystallization of a gallosilicate of the thomsonite structure (a fibrous zeolite), aluminogermanates of the faujasite, type A and harmotone structures and gallogermanates of the thomsonite, faujasite and type A structures from the corresponding sodium gels (18). These zeolites are apparently completely analogous to their aluminosilicate counterparts, differing only in the increased unit-cell dimensions by virtue of the larger ionic radii of gallium and germanium.

IX. Conclusions

The zeolites have received a great deal of attention in recent years resulting in a far better understanding of their chemistry and properties. The demonstrated usefulness of these materials in a variety of operations assures the continued interest in this field.

Bibliography

1. Dana, E.S., Systems of Mineralogy , 6th Ed., John Wiley and Sons, New York (1892). Pp. 570-610.
2. Barrer, R. M., Proc. Roy. Soc., (London), A167, 392 (1938).
3. Breck, D. W., W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, J. Am. Chem. Soc., 78, 5963 (1956).
4. Milton, R. M., U. S. 2,882,244; Apr. 14, 1959, C.A., 53, 13454 (1959).
5. Barrer, R. M., Quart. Revs., 3, 293 (1949).
6. Barrer, R. M., Brit. Chem. Eng., 4, 267 (1959).
7. Barrer, R. M., and I. S. Kerr, Trans. Faraday Soc., 55, 1915 (1959).
8. Barrer, R. M., F. W. Bultitude, and I. S. Kerr, J. Chem. Soc., 1959, 1521.
9. Barrer, R. M., F. W. Bultitude, and J. W. Sutherland, Trans. Faraday Soc., 53, 1111 (1957).

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

Bibliography

1. [illegible]
2. [illegible]
3. [illegible]
4. [illegible]
5. [illegible]
6. [illegible]
7. [illegible]
8. [illegible]
9. [illegible]

10. Lewis, P. H., J. Phys. Chem., 63, 527 (1959).
11. Howell, P. A., Acta. Cryst., 13, 737 (1960).
12. Reed, T. B., and D. W. Breck, J. Am. Chem. Soc., 78, 5972 (1956).
13. Barrer, R. M., and W. M. Meier, Trans. Faraday Soc., 54, 1074 (1958).
14. Kerr, G. T., Private communication; to be published J. Am. Chem. Soc., Dec. 1961.
15. Barrer, R. M., Trans. Brit. Ceram. Soc., 56, 155 (1957).
16. Barrer, R. M., and P. J. Denny, J. Chem. Soc., 1961, 971.
17. Idem. Ibid., 1961, 983.
18. Barrer, R. M., J. W. Baynham, F. W. Bultitude, and W. M. Meier, J. Chem. Soc., 1959, 195.
19. Barrer, R. M., J. Phys. Chem. Solids, 16, 84 (1960).
20. Barrer, R. M., J. Chem. Soc., 1948, 127.
21. Kiriyama, R. K. Yamada, M. Koizumi and R. Kitagaki, Kobutsugaku zasshi 2, 347 (1956); C. A. 51, 4887 (1957).
22. Kerr, G. T., Private communication.
23. Goldsmith, J. R., J. Geol., 61, 439 (1953).
24. Loewenstein, W., Amer. Mineralogist, 39, 92 (1954).
25. Barrer, R. M., and G. C. Bratt, J. Phys. Chem. Solids,12, 130 (1959).
26. Barrer, R. M., and L. V. C. Rees, Trans. Faraday Soc., 55, 992 (1959).
27. Breck, D. W., W. G. Eversole, R. M. Milton, J. Am. Chem. Soc., 78, 2338 (1956).
28. Lowenberg, P., J. Appl. Chem., 9, 417 (1959).
29. Andrew, John, Jr., Ph.D. Thesis, Univ. of Delaware, 1957, Dissertation Abs. 18, 830 (1958).
30. Barrer, R. M., and D. W. Riley, J. Chem. Soc., 1948, 133.
31. Eberly, P. E., Jr., J. Phys. Chem., 65, 68, (1961).
32. Barrer, R. M., and D. A. Langley, J. Chem. Soc., 1958, 3817.
33. Barrer, R. M., and J. W. Baynham., J. Chem. Soc., 1956 , 2892.
34. Cannon, P., and C. Rutkowski, J. Phys. Chem., 63, 1292(1959)
35. Barrer, R. M., and W. I. Stuart., Proc. Roy. Soc. (London), A249, 464 (.959).
36. Barrer, R. M., and W. M. Meier, J. Chem. Soc., 1958, 299.
37. Freeman, D. C., Jr., and D. N. Stamires, J. Chem. Phys., 35, 799 (1961).
38. Barrer, R. M., and W. M. Meier, Trans. Faraday Soc., 55, 130 (1959).
39. Barrer, R. M., and G. C. Bratt, J. Phys. Chem. Solids, 12, 146 (1959).
40. Barrer, R. M., and G. C. Bratt., J. Phys. Chem. Solids, 12, 154 (1959).
41. Pemsler, P., Ph.D. Thesis, N. Y. Univ., 1954; Dissertation Abs. 18, 2005 (1958).
42. Barrer, R. M., and B. E. F. Fender, J. Phys. Chem. Solids, 21, 1 (1961).
43. Idem., Ibid., 21 , 12 (1961).
44. Barrer, R. M., and D. A. Langley, J. Chem. Soc., 1958, 3804.
45. Idem., Ibid., 1958, 3811.
46. Koizumi, M., and R. Roy, J. Geol., 68, 41 (1960).
47. Murata, K. J., Amer. Mineralogist, 28, 545 (1943).

10. Lewis, P. A., J. Chem. Phys. 26, 127 (1957).
11. Powell, R. E., [illegible]
12. [illegible]
    [illegible] (1956).
13. [illegible]
    [illegible]
14. [illegible] communication [illegible]
    [illegible] 1955.
15. [illegible]
16. [illegible]
17. [illegible] 1951, [illegible]
18. [illegible]
    [illegible] 1950, [illegible]
19. [illegible] (1950).
20. [illegible] 1948, [illegible]
21. [illegible]
    [illegible]
22. [illegible]
23. [illegible]
24. [illegible]
25. [illegible]
    [illegible]
26. [illegible]
    [illegible]
27. [illegible]
    [illegible]
28. [illegible]
29. [illegible]
    [illegible]
30. [illegible]
31. [illegible]
32. [illegible]
    [illegible]
33. [illegible]
    [illegible]
34. [illegible]
35. [illegible]
    [illegible]
36. [illegible]
37. [illegible]
    [illegible]
38. [illegible]
    [illegible]
39. [illegible]
    [illegible]
40. [illegible]
    [illegible]
41. [illegible]
    [illegible]
42. [illegible]
    [illegible]
43. [illegible]
44. [illegible]
    [illegible]
45. [illegible]
46. [illegible]
47. [illegible]

DIFFERENTIAL THERMAL ANALYSIS

R. A. Palmer December 5, 1961

I. INTRODUCTION

Although differential thermal analysis (DTA) has been used primarily in the earth sciences, considerable recent interest has been shown in its applications in chemistry, both qualitative and quantitative. This seminar will attempt to assess the value of DTA in inorganic chemistry particularly, as compared to the earth sciences, where the character of natural products is apparently a very strict limitation on the method. After a brief analysis of the theory and technique of DTA, a partial summary of quantitative and qualitative applications, realized and postulated, will be illustrated with reference to the recent literature.

II. ESSENTIAL NATURE OF DTA

Extensive reviews of DTA have appeared in the recent literature (1-6). The treatment here is necessarily in general terms, but seeks to bring out the significant aspects of the method necessary for orientation in the subsequent sections.

DTA is essentially a calorimetric method in that it is $\Delta \underline{H}$ that is detected and/or measured. It differs from other calorimetric methods in that it is a non-equilibrium method and is extremely dimensionally sensitive (i.e. sensitive to equipment geometry). Although its detection limits are potentially lower than other calorimetric methods in some cases, failure to recognize equipment limitations has led many investigators to make extravagant claims as to its qualitative and quantitative accuracy.

The basic technique is deceptively simple; voltage generated in a differential thermocouple as a result of one of its junctions being surrounded by a thermally active substance and the other by a thermally inert reference, is plotted (generally) as a function of linearly increasing temperature. Thus, the measured quantity is the difference in temperature of the sample and reference caused by the transformation taking place in the former and not in the latter. The resulting curve consists of "peaks"corresponding to each transformation (phase change or reaction), with endothermic peaks generally plotted below the base line and exothermic peaks above.

The apparatus employed has in the past varied widely in all respects, making correlation of data virtually impossible. However, recent developments in equipment design based on sound theoretical principles should greatly improve correspondence of data taken by different investigators and increase the value of quantitative applications of DTA (7-14). The essential elements in DTA apparatus are:

1. The sample holder, with identical cavities for sample and reference,
2. The differential thermocouple, with its two junctions centered in the cavities,
3. The reference thermocouple , which may be either in the reference material or the sample,
4. The furnace, symetrically constructed so as to heat both cavities at an identical linear rate, and
5. The controlling, amplifying, and recording system.

Refinements to this apparently simple system, which are essential to reproducible results, include:

1. precise control of heating rate,
2. pressure control, and
3. flow of a gas phase through the sample (where gaseous or liquid reaction products or secondary reactions are involved).

III. THE QUANTITATIVE PROBLEM

Several attempts at mathematical analysis of the DTA problem have appeared, beginning with that of Spiel in 1945. These are best summarized by Sewell and Honeyborne(2). Suffice it to say here that the thermodynamic significance of the peak area (A) can be shown to be theoretically valid (i.e. $\Delta \underline{H} = \underline{K}\,\underline{A}$) . However, solution of the equations involves numerous assumptions of conditions which can only be approached more or less closely in actual practice. The assumptions regarding sample thermal conductivi seem to be the least like ever to be realized — even when all other variables have been eliminated by proper equipment design and technique, this uncertainty remains. This is probably the root of the general despair with regard to quantitative DTA; however, though it limits the quantitative analysis value of DTA to a few individually evaluated systems (excluding virtually all natural products), other uses of the quantitive relationship are still valid.

The essential requirements for reproducible, thermodynamically significant and, thus, quantitive, data from DTA are then:

1. Rigid specifications on equipment symmetry and dimensional stability,
2. Linear heating rate,
3. Strictly reproducible technique, including control of sample form and diffusion of reaction products.*

The practical method of relating A to $\Delta \underline{H}$ is to use the internal standard technique of Barshad (16).

*It is significant to note that the theoretical proportionality of A to $\Delta \underline{H}$ is independent of heating rate (provided it is linear), reaction rate, and specific heat of the sample. In practice , heating rate is significant beyond certain limits. When it is too low, peaks are too shallow to evaluate, and when too high, near peaks may merge.

IV. SPECIFIC QUANTITATIVE AND SEMI-QUANTITATIVE USES OF THE INTEGRAL OF THE DTA PEAK

1. Analysis. - Each system must be evaluated, but for the most part, as discussed above, inherent problems as to sample conductivity prevent any general application of DTA (18).

2. ΔH_T. - Measurement of the heats of transition of phase changes is perhaps the most uncomplicated application of DTA. This is particularly true with crystal inversions and glass transitions, where no liquid or gas phases are involved. Heat of fusion determination is more complicated as a result of the greater difference in conductivity of the liquid and solid phases(15,17, 19,20).

3. ΔH_D. - Accurate measurement of heats of decomposition is probably beyond the scope of DTA except in simple systems. Even assuming that the decomposition is not complicated by attendant fusion or secondary reactions, one still must contend with lattice energy, and the thermodynamically desirable gas-phase dissociation energy is still not obtained.

4. ΔH_R. - Although not too much recent work has been reported in the area of heats of reaction, the advent of improved equipment would seem to open up new possibilities. Reactions in both liquid and solid phases are theoretically amenable to study, and (with proper equipment), introduction of a gas-phase reactant at constant temperature adds a new dimension to the method.

5. x and E_A^{*}. - Use of DTA for measurement of reaction order was first proposed by Borchardt and Daniels (21) for reactions in solutions and later elaborated on by Freedmann and Carroll (22). The extension of the method to heterogeneous reactions was made by Blumberg (26). The method has also been applied to decomposition of solids. The results of these investigators seem to demonstrate the accuracy of the method and the validity of their assumptions. Actually this is only an extension of the original relationship of $\Delta H = K A$ ∵ Obtaining x, E_A^{*}, frequency factor, and ΔH may be done in less than one day compared to perhaps a week by isothermal methods (21). A student experiment is described by Wendlandt (49).

6. Determination of Thermal Stability Ranges. - This can be only a preliminary determination since very slow decompositions may not be detected by DTA until long after they have begun. Confirmation by thermogravimetric analysis is essential. (27A).

7. Other recent papers report the use of isothermal DTA in the determination of the surface area of gas absorbants (28) and of regular DTA in evaluation of degree of crystallinity in high polymers (29,30,31).

V. QUALITATIVE VALUE OF DTA

Although the requirements for quantitative DTA are formidable and require both close sample form control and fairly elaborate and expensive equipment, there are many qualitative uses of DTA which should not be overlooked. For these uses equipment requirements are much less rigid; however, the temptation to push conclusions too far must always be resisted when using simpler equipment.

The more common and promising qualitative applications include:

1. *Analysis.* - Although not quantitative, DTA analysis for impurities or for the *presence* of constituents is both rapid and sensitive. Where accuracy is not too important, relative amounts of constituents in mixtures may be roughly evaluated.

2. *Detection of reactions or transitions.* - This is perhaps the single most valuable use of DTA. A quick run in even the simplest equipment often gives very useful data. This is particularly true in 0-order phase changes.

3. *Postulation of decomposition routes and reaction mechanisms.* - Here the value of data depends extensively on the equipment used and the sample form. Often formation of gaseous or liquid phases and/or secondary reactions involving the products hopelessly complicate the curve. However, in simpler systems and with proper equipment, DTA can yield valuable hints as to sequence of reactions and intermediates.

Some recent papers by Wendlandt, Bear, and Hill illustrate the complexities of sorting out various reactions (33-36).

5. *Estimation of catalytic effects* (35,35A)
6. *Estimation of radiation damage* (37)
7. *The course of synthesis reactions* (38)
8. *Properties of melts* (39)

VI. CORRELATION OF DTA WITH OTHER METHODS

Often DTA offers a rapid method of surveying the thermal behavior of a system and points the way to other investigations. In this respect it is frequently used in conjunction with thermogravimetric analysis (TGA) and X-ray crystallography. Slow decompositions missed by DTA are readily detected by TGA; and, like wise, 0-order phase changes, undetectable by TGA, are caught by DTA. X-ray crystallography is often used to analyze intermediates detected first by DTA. Several recent papers show very well how modern techniques of DTA complement TGA, X-ray, and other methods (40-42).

VII. SUMMARY AND CONCLUSIONS

Though quantitative analysis using DTA appears generally unfeasible, other quantitative uses of DTA are more promising. Determination of $\Delta \underline{H}_T$, $\Delta \underline{H}_R$, $\underline{E}_A^*$, and x, may be made more rapidly than and with accuracy comparable to conventional methods (18). However, essential to any quantitative use of DTA is reliable, fairly expensive equipment, careful and reproducible technique, and control

of sample form. Qualitatively, DTA offers the chemist a rapid, inexpensive method. In conjunction with other methods, the preliminary data from the thermograph of a system often facilitates further investi gations. The limitations of equipment in which numerous variables are not well controlled must be considered in extending conclusions from data.

SELECTED ANNOTATED BIBLIOGRAPHY

Reviews

1. R. R. West, "Differential Thermal Analysis" in The Deffect Solid State, Interscience, New York (1957). (160 References).
2. R. C. Mackenzie, "The Differential Thermal Analysis of Clays" Mineralogical Society (Clay Minerals Group), London (1957) - General survey by Mackinzie and excellent quantitative treatment by E. C. Sowell and D. B. Honeyborne with extensive bibliography.
3. W. J. Smothers and Yao Chiang, "Differential Thermal Analysis: Theory and Practice," Chemical Publishing Co., New York (1958) - The best general overall survey of the method and its applications a good place to start; 1600 references.
4. H. J. Borchardt, "An Introduction to DTA", J. Chem. Ed. 33, 103 (1956). - a very brief outline of the method, but good; 27 references.
5. P.F.S. Cartwright and D. W. Wilson, Annual Reports on the Progress of Chemistry, Vol. LVII, p. 461, The Chemical Society, London (1961) - survey for 1960; a short review with 13 references.
6. C. B. Murphy, "Differential Thermal Analysis", Anal. Chem., 32, 168R (1960), biennial review of pure chemistry covering period 1945 to 1959 (for DTA) with 81 references.

Apparatus

7. R. L. Stone, "DTA by the Dynamic Gas Technique", Anal. Chem., 32, 1582 (1960) - commercially available integrated equipment allowing for variation of pressure, gas phase, and temperature under quantitative conditions.
8. C.B. Murphy, J. A. Hill, and G. P. Schacher, "DTA and Simultaneous Gas Analysis" Anal. Chem., 32, 1374 (1960) - describes equipment similar to Stone's, but also allowing for collection of reaction gases.
9. A. Reisman, "Isobaric Dissociation of Alkali Metal Carbonate-hydrates Using Simultaneous DTA and TGA", Anal. Chem., 32, 1566 (1960) -
10. M. C. Mazières, "Dispositif de Microanalyse Thermique Differentell Compt. rend., 248, 2990 (1957) - describes apparatus for microanalysis of samples <50 μg using the thermocouple junctions as crucibles.
11. W. Lodding and L. Hammell, "High Temperature Pressure-Vacuum Furnace", Rev. Sci. Inst., 30, 885 (1959) - describes furnace design allowing temperatures up to 1900°C. and pressures of 650 psi, as well as vacuum operation.
12. R. L. Bohon, "DTA of Explosives and Propellents under Controlled Atmosphere," Anal. Chem., 33, 1451 (1961).
13. M. M. Markowitz, D.A. Boryta, and R.F. Harris, "The DTA of Perchlorates (III). The System $LiClO_4$-$LiNO_3$", J. Phys. Chem., 62, 827 (1958) - apparatus described for use with melts.
14. W. W. Wendlandt, "An Inexpensive Thermal Analysis Apparatus" J. Chem. Ed., 37, 94 (1960) - describes a practical simple apparatus suitable for qualitative work only.

Quantitative Techniques

15. I. G. Sabatier, "Measurement of Heats of Transformation by DTA". Compt. rend., 235, 574 (1952) - the internal standard method.
16. I. Barshad, "Temperature and Heat of Reaction Calibration of DTA Apparatus", Am. Minerologist, 37, 667 (1952).
17. I. C. Sabatier, "Measurement of Heats of Transformation by DTA" Bull. soc. franç. mineral, 77, 953 (1954). Use of the internal standard method illustrated.

Quantitative Applications

18. F. H. Stross and S. T. Abrams, "DTA of the System Na Stearate-Cetane", J. Am. Chem. Soc., 73, 2853 (1951) - accuracy of phase transition, ΔH claimed ± 1%.
19. S. Shiba , "DTA of Al Soaps", Bull. Chem. Soc. Japan, 34, 804, 809 (1961).
20. H. Suga, H. Chihara, S. Seki, K. Nakatsuka, and T. Shinoda, "Crystallographic Studies and Detection of Phase Transitions", Nippon Kagaku Zassni, 82, 24, 29 (1961).
21. H. J. Borchardt and F. Daniels, "The Application of DTA to the Study of Reaction Kinetics", J. Am. Chem. Soc., 79, 41 (1957) - Measuring ΔT, $\frac{\Delta T}{dt}$, and A for reactions in solution and determining $x + E_A$
22. E. S. Freemann and B. Caroll, "Application of Thermoanalytical Techniques to Reaction Kinetics", J. Phys. Chem., 62, 394 (1958). an expansion of the Borchardt-Daniels treatment.
23. H. J. Borchardt, "On the Rôle of the Gaseous Phase in Solid State Reactions", J.Am.Chem.Soc. 81, 1529(1959) - Indicates gaseous phas not involved in reactions between some sulfates and carbonates.
24. H. J. Borchardt, "Initial Reaction Rates" , J. Inorg. and Nuclear Chem. 12, 252 (1959) - excellently presented concise report.
25. V. M. Palmanabhan, S. C. Saraiya, and A. K. Sundaram, "Thermal Decomposition of some Oxalates", J. Inorg. and Nuclear Chem., 12, 356 (1959) - calculation of x and E_A*.
26. A. A. Blumberg, "DTA and Heterogeneous Kinetics", J. Phys. Chem., 63, 1129 (1959) - reaction of SiO_2 with aqueous HF.
27. G. Wada, "A Rapid Evaluation of E_A* using DTA", Nippon. Kagaku Zasshi, 81, 1656, (1960) - using method of Borchardt and Daniels.
27A. W. W. Wendlandt, "Thermal Properties of Quinolinium Phosphomolybdate", Anal. Chem., 32, 1011, (1960) - determination of drying temperature.
28. H. P. Schreiber and M. H. Waldman, "A Rapid Determination of Some Surface Areas of Solids", Can. J. Chem., 37, 1782 (1959) - accuracy of ± 10-15% claimed.
29. B. Ke , "Characterization of Polyolefins by DTA", J. Polymer Sci. 42, 15 (1960).
30. B. Ke, "DTA of High (Organic) Polymers ", J. Polymer Sci., 50, 79 (1961) - effect of dilutants on m.p.
31. B. Ke, "DTA of High Organic) Polymers" J. Polymer Sci., 50, 87(1961) - glass transitions and degree of crystalinity.

Qualitative Applications

32. V. Pechkovskii, "The Thermal Decomposition of $ZnSO_3$" Zhur. Priklad. Khim., 33, 1724 (1960).
33. J. A. Hill, "Observations on the Thermal Decomposition of Cupric Acetate Monohydrate", Anal. Chim. Acta. 24, 496, (1961)- use of Stone-type apparatus with provision for collection of gase
34. W. W. Wendlandt, T. D. George and G. R. Horton, "The Thermal Decomposition of Th(IV), U(IV), and Rare Earth Metal(III) Oxalate Hydrates", J. Inorg. and Nuclear Chem., 17, 273 (1961) - used with TGA.
35. J. L. Bear and W. W. Wendlandt, "The Thermal Decomposition of Tris(ethylenediamine) and Tris(propylenediamine) Chromium(III) Chloride and Thiocyanate Complexes". J. Inorg. and Nuclear Chem., 17, 286 (1961) - indicates complexity of assignment of peaks in complex reaction.

35A. S. K. Bhatthergya ",DTA of Solid State Catalyst Systems", Z. physik. Chem. (Leipzig), 214, 191(1960).

36. M. M. Markowitz, D. A. Boryta and R. F. Harris ,"DTA of Perchlorates(V). System $LiClO_4$-$KClO_4$",J. Phys. Chem., 65, 261 (1961).
37. C. B. Murphy and J. A. Hill, "Detection of Irradiation Effects by DTA", Nucleonics, 18, No. 2, 78 (1960) - use in evaluating reactor coolants and parts.
38. E. M. Bollin, J. A. Dunne, and P. F. Kerr, "DTA of Pyrosynthesis", Science , 131, 661 (1960) - Study of synthesis of sulfides.
39. H. J. Sreifert, "DTA of Eutectic Melts", Z. anorg. u. allgem. Chem., 307, 137 (1960).

Correlation of DTA With Other Methods

40. I. V. Koneeva and A. V. Novoselova, Zhur. Neorg. Khim., 4, 2220 (1959) - Thermal Decomposition of Selenates and Selenites by DTA, TGA, and X-ray.
41. R. M. Dell and S. W. Weller, Trans. Faraday Soc., 55, pt. 12, 2202 (1959) - a very extensive study using several methods.
42. M. M. Markowitz and D. A. Boryta , "A Convenient System of DTA and TGA", Anal. Chem., 32, 15 (1960) - DTA and TGA not simultaneous and DTA probably not very quantitative .
43. W. Lodding and L. Hammell, "DTA of Hydroxides in a Reducing Atmosphere" Anal. Chem., 32, 657 (1960) - method of separating peaks by control of atmosphere.
44. R. Notz, "Correlation of DTA and TGA" J. Am. Ceram. Soc., 43, 53 (1960).
45. P. Bussiere, "A Study of Solid Phases by Simultaneous DTA and TGA J. chim. phys., 58, 668 (1961).
46. P. D. Garn, "Thermal Analysis-a Critique", Anal. Chem., 33, 1247 (1961) - a consideration of correlation between DTA and TGA.
47. P. D. Garn and J. E. Kessler, "Effluence Analysis As an Aid to Thermal Analysis", Anal. Chem., 33, 952 (1961) - using gas chromatographic techniques to measure conductivity or density of effluent gases from DTA.
48. B. Claudel, M. Perria, and Y. Trambouze, "Influence of the Products of Decomposition on DTA", Compt. rend., 252, 107(1961)- radical difference in curve demonstrated by control of atmospher
49. W. W. Wendlandt, "Reaction Kinetics by DTA, a physical chemistr experiment", J. Chem. Ed. 38, 571 (1961).

OCTA-μ_3-CHLORO-HEXAMOLYBDENUM(II) ION COMPLEXES

R. Oehmke December 12, 1961

I. INTRODUCTION

The earliest reference to molybdenum dichloride is a description of its preparation by Blomstrand (1) in 1859. He prepared it first by the thermal decomposition of molybdenum(III) chloride according to the equation

$$6MoCl_3 \xrightarrow[\Delta]{CO_2 \text{ atmos.}} Mo_3Cl_6 + 3MoCl_4$$

He later found that the compound is formed as a byproduct in the preparation of molybdenum(V) chloride from the dioxide, carbon, and chlorine gas:

$$2MoO_2 + 2C + 5Cl_2 \xrightarrow[\Delta]{} 2MoCl_5 + 2CO_2.$$

In 1898, Muthman and Nagel (2) obtained the dichloride by the reduction of the pentachloride with hydrogen gas at 700-800°C. Later, Lindner and Coworkers (3-4) prepared it by passing vapors of phosgene, carbon tetrachloride, chloroform, or methylene dichloride mixed with nitrogen gas over glowing molybdenum powder. For example, with phosgene the reaction is

$$3Mo + 3\ COCl_2 \rightarrow Mo_3Cl_6 + 3CO$$

Attempts to prepare the compound, Mo_6Cl_{12}, by the direct combination of molybdenum and chlorine gave only the pentachloride even at temperatures as high as 1200°C.

II. DERIVATIVES

Blomstrand (1) obtained several derivatives. Among these were the bromo, iodo, and hydroxo derivatives of the type $[Mo_6\ Cl_8]X_4 \cdot 8H_2O$, and salts of the type $K_4[(Mo_6Cl_8)Cl_6]$. The bromo and iodo derivatives were obtained by dissolving the chloride, Mo_6Cl_{12}, in the appropriate hydrohalogen acid, collecting the crystals formed, and heating them gently to obtain the hydrated salts.

The hydroxide derivative was obtained by allowing an alkaline solution of the chloride to stand in air. If an ammoniacal solution was used, a crystalline, rather than amorphous, form of the compound was obtained.

By driving off water, Blomstrand (1) obtained three sharply defined compounds: a dark yellow-gold $[Mo_6Cl_8](OH)_4 \cdot 6H_2O$ at 35°C., a gold-brown $[Mo_6Cl_8](OH)_4 \cdot 4H_2O$ at 67-100°C., and a black brown $[Mo_6Cl_8](OH)_4 \cdot 2H_2O$ at 200-300°C. Above 300°C., decomposition occurs.

By adding a concentrated solution of the chloride, Mo_6Cl_{12}, to a saturated ammonium chloride solution, Lindner and Coworkers(4) obtained a yellow, crystalline compound, the analysis of which corresponded to $[Mo_6\ Cl_8](OH)_4 \cdot 16H_2O$. They also obtained a compound, $[Mo_6Cl_8]Cl_4 \cdot 2NH_3 \cdot 2EtOH$, which had the form of voluminous dark yellow needles, stable to 100°C., and a similar salt with one less molecule of ethanol. An acid, $H_2[Mo_6Cl_8]Cl_6 \cdot 2H_2O$, and the corresponding pyridinium salt were prepared and their "tri-nuclear structure" demonstrated by cryoscopic measurements in nitrobenzene.

In the same article, Lindner mentioned the preparation of the nitrates, $[Mo_6Cl_8](NO_3)_4$ and $[Mo_6Cl_8](NO_3)_4 \cdot 2EtOH$, from the chloride and alcoholic silver nitrate.

Sheldon (5), in more recent work, obtained two amine complexes, having the formulae $[(Mo_6Cl_8)Cl_4 \cdot 2C_5H_5N]$ and $[(Mo_6Cl_8)Cl_4 \cdot 2Et_3N]$, by mixing alcoholic solutions of the halide and the appropriate amine and adding petroleum ether to effect precipitation. The chloride is quite soluble in strong donor solvents, sparingly soluble in weak donors, and insoluble in water.

Sheldon (6) prepared addition compounds of triphenyl phosphine and arsine oxides. Two non-electrolytes having the formulae $[Mo_6\ Cl_8]Cl_4 \cdot 2(Ph_3PO)$ and $[Mo_6Cl_8]Cl_4 \cdot 2(Ph_3AsO)$, were obtained, as well as the four electrolytes summarized in Table I.

Table I COMPLEX ELECTROLYTES

Proposed Structure	Λ*	M	Formula Weight M
$[Ph_3PO)_2H]_2[(Mo_6Cl_8)Cl_6]$	52	840	2.6
$[(Ph_3PO)_2H]_2[(Mo_6Cl_8)Cl_6] \cdot 2Ph_3PO$	49	650	4.2
$[(Ph_3AsO)H]_2[(Mo_6Cl_8)Cl_6]$	43	810	2.9
$[Ph_3AsOH]_2[(Mo_6Cl_8)Cl_6]$	43	590	2.9

*Conductance ∼50 micromhos for three ions in nitrobenzene (20)

The data in Table I, as well as I.R. spectra, were presented to support the structures shown. One should note that the cation in two of the above electrolytes is represented as two molecules of donor sharing a proton by some type of hydrogen bonding.

Table II. I. R. SPECTRA

Group	$P \rightarrow O$	$As \rightarrow O$
Coordinated oxide	1061 cm^{-1}	852 cm^{-1}
Free oxide	1185 cm^{-1}	879 cm^{-1}

III. ACIDS

Sheldon used the chloro acid $[H_3O]_2[(Mo_6Cl_8)Cl_6].6H_2O$, in the preparation of the electrolytes just discussed. The chloroacid was first reported by Blomstrand (1) in 1859, and the bromo and iodo acids of the type $[H_3O]_2[(Mo_6Cl_8)X_6].6H_2O$ by Rosenheim and Kohn (7) in 1910. By heating in vacuo, these acids can be reconverted to the anhydrous salts used in their preparation. The acids are soluble in alcohol and nitrobenzene, and undergo hydrolysis in water to form insoluble hydrated species. Further information can be found in Gmelin (21).

IV. SALTS OF THE ACIDS

A number of salts have been derived from the acids. These contain, for the most part, "ammonium" type cations. Blomstrand(1) reported salts of the type $K_4[Mo_6Cl_8)Cl_8].2H_2O$. Lindner, et.al.(4), reported the species $(C_5H_5NH)_2[(Mo_6Cl_8)Cl_6].2H_2O$ and $K_2[Mo_6Cl_8)Cl_6].6H_2O$. They used the pyridinium salt in an attempt to determine the molecular weight. By cryoscopic methods using nitrobenzene, values of 678, 700, 773 were obtained.

Rosenheim and Kohn (7) obtained a yellow crystalline salt, having a molecular formula corresponding to the compound $(NH_4)_2[(Mo_6Cl_8)Cl_6].6NH_3$, by treating a solution of molybdenum(II) chloride in hydrochloric acid with gaseous ammonia. They also report the salt $(NH_4)_2[(Mo_6 Cl_8)Cl_6].2NH_3$ and the corresponding pyridinium derivative.

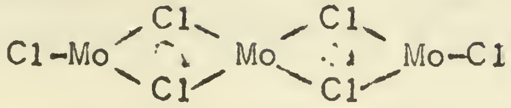
In addition to the phosphine and arsine oxide salts previously mentioned, Sheldon (8) obtained salts of the triethyl ammonium and triphenyl phosphonium cations. He also claimed that the compound, $K_2[(Mo_6Cl_8)(NCS)_6].6H_2O$ can be prepared by adding the dichloride to a concentrated solution of potassium thiocyanate. On the basis of titrimetric evidence, he also claims the existence of the ion $[(Mo_6Cl_8)(OH)_6]^{2}$.

Lindner (9), in 1927, reported four pyridinium salts, but from the formulae given, one might conclude that these were mixed salts of some type. Letting $M=(Mo_6Cl_8)$, these salts are written as $(C_5H_5NH)_3[MCl_7]$, $(C_5H_5NH)_3[MCl_7].2C_5H_5N$, $(C_5H_5NH)_3[MCl_7].C_5H_5N$, and $(C_5H_5NH)_5[MCl_9]$. These formulae are completely at odds with the octahedral type of coordination postulated for the $[Mo_6Cl_8]^{+4}$ ion.

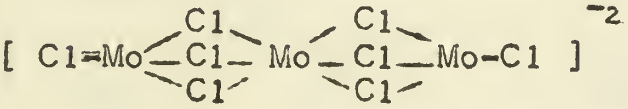
V. STRUCTURE

Early attempts to define the structure of the molybdenum chloride with the empirical formula $MoCl_2$ were based on cryoscopic and ebullioscopic measurements combined with an interpretation of chemical properties. Such methods led Blomstrand (1), Muthman and Nagel (2), Lindner (4), Rosenheim and Kohn(7), Koppel(10), and Liechte and Kempe (11) to propose a trinuclear structure. Thus

Lindner(12) in an effort to correlate all the data up to that time proposed the structure



for the compound in which they assumed to be Mo_3Cl_6 and the structure



for the $[Mo_3Cl_8]^{-2}$ ion found in the acids. These ions are now believed to have molecular compositions corresponding to $[Mo_6Cl_8]Cl_4$ Are $[(Mo_6Cl_8)Cl_6]^{-4}$, respectively.

In 1945, Brosset (13), after making attempts at ebulliscopic determinations, recalled from some earlier work that trivalent tungsten forms intermetallic bonds. He therefore made an x-ray study of the compound $[Mo_6Cl_8](OH)_4].16H_2O$. Using Lane, rotation, and Weissenberg methods, he made a Patterson projection analysis and found that the Mo-Mo distances were only about 2.6A. and that the structure corresponded to the D_{3d}^{5}-$R\bar{3}M$ space group. This is consistent with a structure represented by an octahedron with Mo atoms at its apices contained in a cube with chloride ions at its apices, such that one Mo atom appears in the center of each face of the cube. The short Mo-Mo distance (2.63Å.) as compared with the usual 2.73 Å. indicates some intermetallic bonding.

In a similar manner, Brosset (14)(17) studied the compound $[Mo_6Cl_8]Cl_4.8H_2O$ and using a method devised by Finbak(22) determined the structure of the chloro acid, $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ in ethanol. The results confirmed the conclusions of his first investigation.

In 1947, Brosset (16), on the basis of these data proposed two types of heteronuclear structures: (1) the polynuclear, such as that of palladium chloride, and (2) the staphylo-nuclear (from the Greek *staphylo*, meaning a grape cluster). The essential difference between these two types is that in polynuclear compounds each central atom functions as a nucleus, whereas in the staphylo type a whole group of similar atoms acts as a single nucleus.

At the same time, Pauling (15) predicted an $[Mo_6Cl_8]^{+4}$ nucleus because he had difficulty in finding a reasonable electronic structure for the $[Mo_3Cl_4]^{+2}$ ion.

In 1950, Vaughan, Sturdwant, and Pauling (18) studied the chloro acid and its ammonium salt in solution by x-ray techniques. They used $\underline{\sigma}(\underline{r})$ function plots, which are similar to electron diffraction curves, and came to the same conclusions as those drawn by Brosset.

Sheldon(5) has several comments on the structure of the ion, whcih he named octa- $_3$-chloro-hexamolybdenum(II) ion. He postulates that each molybdenum atom is surrounded by a tetragonal pyramid of chlorine ions, which are bonded by $\underline{d}_{x^2-y^2}\underline{s}\ \underline{p}^3$ hybrid orbitals.

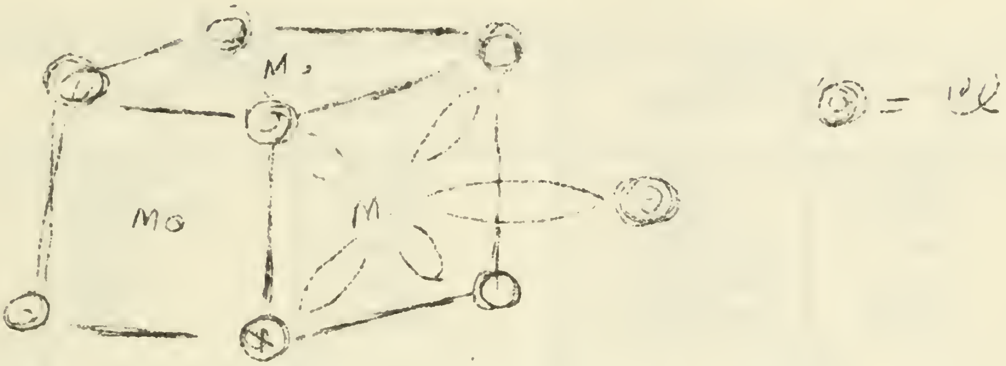


Figure 2 - $\underline{d}_{x^2-y^2}\underline{s}\ \underline{p}^3$ Bonding

of the remaining 4$\underline{d}$ orbitals, the $\underline{d}_{xz}$ and $\underline{d}_{yz}$ possess lobes directed along the Mo-Mo axes. It is thus possible for each molybdenum atom to use one of these orbitals to form a molecular orbitals, which give rise to a square planer structure of molybdenum atoms.

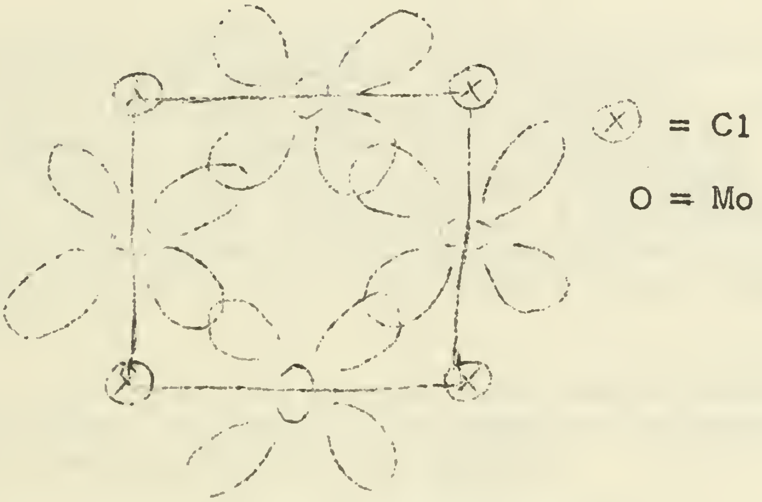


Figure 3 $\underline{d}_{xz}$,$\underline{d}_{yz}$ M.O.

A consideration of the symmetry of the octahedron shows that three such planes are possible. Sheldon further postulates, therefore, that each molybdenum atom contributes two $\underline{d}$ electrons to such intermetallic bonding. This leaves 2 $\underline{d}$ electrons and the $\underline{d}_{xy}$ and $\underline{d}_{z^2}$ orbitals. He proposes that the two electrons occupy the two orbitals singly and contribute further to Mo-Mo bonding and diamagnetism by pairing spins with the corresponding electrons on the adjacent atoms.

Essentially, then, the Mo(II) ion is actually in the Mo(VI) state, and uses all nine electrons for bonding. The Mo(II) ion thus becomes a d^0 case, which explains the paramagnetism and lack of d-d transition spectra. Sheldon has obtained the spectral data shown in Table III.

Table III. U.V. Bands of the $[Mo_6Cl_8]^{-2}$ Ion

Solvent	Band I		Band II	
	λ(mμ)	$\epsilon \times 10^{-3}$	λ(mμ)	$\epsilon \times 10^{3}$
5N H Cl	307.5	2.93	345	2.68
5N HBr	305(sh)	3.8	352.5	3.4
0.01N NaOH	300	3.8	~330(sh)	-
2N $HClO_4$	298	3.2	~330(sh)	2.4
2N H_2SO_4	298	3.05	~330(sh)	2.4

At less than 300 mμ, strong absorption takes place, and beyond 400 mμ no bands were found. These bands, with extinction coefficients of the order of 3×10^{-3} are not in keeping with the intensities of ligand field transitions. There remains the possibility that these bands may be superimposed on very wide d-d transition bonds.

In recent, but as yet unpublished work, Nyholm and coworkers have prepared true Mo(II) ion complexes of the types $[Mo^{II}(diarsine)(CO)_3I_2]$ and $[Mo^{II}(diarsine)_2(CO)_2I]I$. These compounds exhibit ligand field spectra, are diamagnetic, and contain carbon monoxide-type bonds. Sheldon (5) finds that even at 40 atmospheres and 110°C. the salt, $[Mo_6Cl_8]Cl_4$ is unaffected by carbon monoxide. If the Mo(II) ions were spin-paired to account for the diamagnetism in the $[Mo_6Cl_8]^{+4}$ ion, they should react with carbon monoxide-type ligands.

The data from a series of cryoscopic and conductance measurements (8) are given in Table IV as further evidence for the existence of the complex nucleus of $MoCl_2$.

Table IV Cryoscopic and Conductance Data

Compound	Conductance (Ω)		M apparent
$(H_3O)_2[(Mo_6Cl_8)Cl_6].6H_2O$	49	51	420
$(H_3O)_2[(Mo_6Cl_8)Cl_6].6H_2O$	56	53	575
$(H_3O)_2[(Mo_6Cl_8)Cl_6].6H_2O$	59	59	600
$[Mo_6Cl_8]Br_4$	9	$-^{b}$	$\gg 10^3$
$[Mo_6Cl_8]I_4$	23^{c}	23^{c}	$\sim 10^3$

b. $[Mo_6Cl_8]Cl_4$ was found to be insoluble in nitrobenzene.

c. Measured after standing

In a further study, Sheldon (19), using isotopic chloride exchange and bromide substitution in aqueous and moist ethanolic solutions of the acid, concluded that (1) the bonding in the octa-μ_3-chlorohexamolybdenum(II) ion is covalent; (2) only the six peripheial chloride groups exchange, and (3) the rate of substitution is independent of halide ion concentration and that both processes have similar rate constants. He states, therefore, that the rate determining step is one of aquation.

This then represents the type of data available on the Octa-μ_3-chloro-hexamolybdenum(II) complexes at this time. It seems to this author that some interesting stereochemical investigations should be possible.

BIBLIOGRAPHY

1. C. W. Blomstrand, J. prakt. chem., 77, 97 (1859).
2. N. Muthman and W. Nagel, Ber., 31, 2009 (1898).
3. K. Lindner, E. Haller, and H. Helwig, Ber., 55b, 1460 (1922).
4. K. Lindner, E. Haller, and H. Helwig, Z. anorg. allgem. Chem., 130, 210 (1923).
5. J. C. Sheldon, Nature, 184, 1210 (1959).
6. J. C. Sheldon, J. Chem. Soc., 750-2 (1961).
7. A. Rosenheim and F. Kohn, Z. anorg. Chem., 666, 2 (1910).
8. J. C. Sheldon, J. Chem. Soc., 1009 (1960).
9. K. Lindner, Z. anorg. allgem. Chem., 162, 203 (1927).
10. I. Koppel, Z. anorg. Chem., 77, 289 (1912).
11. L. P. Liechte and B. Kempe, Lieb, Ann., 169 354 (1873).
12. K. Lindner, Z. anorg.allgem. Chem., 162, 203 (1927).
13. C. Brosset, Ark. Kemi, Mineral., Geologi, 20A, No. 7, 1-10(1945).
14. C. Brosset, Ark. Kemi. Mineral., Geologi , 22A, No. 1, 1-10(1946).
15. L. Pauling, Chem. Eng. News, 25, 2970 (1947).
16. C. Brosset, Ark. Kemi. Mineral., Geologi, 25A, No. 19, 1(1947).
17. C. Brosset, Ark. Kemi., 1, 353 (1949).
18. P. A. Vaughan, J. H. Sturdwant, and L. Pauling, J. Am. Chem. Soc., 72, 5477 (1950).
19. J. C. Sheldon, J. Chem. Soc., 3106 (1960).
20. C. M. Harris and R. S. Nyholm, J. Chem. Soc., 4375 (1956).
21. Gmelin's Handbuch Der Anorganishen Chemie, Achte Auflage,
22. Chr. Finbak, Avhandl. Norske Videnskaps-Akad. Oslo. I. Mat.-Naturv. Klasse., No. 3, 3-16 (1943). (C.A. 39: 4283^4.)

[illegible]

[illegible]

BIBLIOGRAPHY

[illegible]

CHEMISTRY OF THE ATMOSPHERE

Agnes S. Chia December 12, 1961

I. INTRODUCTION

Atmospheric chemistry is the science dealing with studies of the composition of the atmosphere, of how the interplay between the atmosphere, the surface of the earth, biological activities, and the ever moving atmosphere itself constantly changes the composition as well as the geographical distribution of the various compounds in the atmosphere. It is atmospheric pollution in a very broad sense (1) and it is related to several branches of science. In this seminar, it is not intended to include everything. The geochemical circulation of the elements in nature for which there are several review articles (2,3) will not be discussed. Air pollution (4,5), except radioactive fall-out, will not be included either. The structure and composition of the atmosphere, chemical reactions in the chemosphere and some of the phenomena of the sky will be discussed briefly together with the radioactivity of the atmosphere which has been of special interest in recent years.

II. THE STRUCTURE OF THE ATMOSPHERE (6)

The earth's atmosphere is a mixture of gases surrounding the earth's surface to a height of about 1000 km. The mass of the entire atmosphere is calculated to be 51.17×10^{20} g. or somewhat less than a millionth the mass of the earth itself. The air becomes racefied with increasing altitude so rapidly that half of it by weight is within 5 km from sea level. At heights greater than 1000 km the atmosphere gradually thins out into planetary space. The upper limit is set where the gas molecules no longer follow the earth in its movement along its orbit.

The lower part of the atmosphere, in which convection is prominent, is known as the troposphere, above this is the stratosphere, so named because it appears to be stratified in a number of layers between which no strong verticle circulation seems to exist. The boundary between the troposphere and the stratosphere is called tropopause and varies both with the latitude and season, but can be placed at a height of about 10-15 km. In the troposphere the temperature decreases with increasing height. Whereas in the stratosphere the temperature is independent of altitude. The ozonosphere, where ozone is formed by action of the sun's ultraviolet radiation on ordinary oxygen molecule, is situated mainly in the lower part of the stratosphere. Above about 80 km the stratosphere passes into the ionosphere: in this region the atmosphere is rendered conducting by ionization induced by ultraviolet radiation from the sun. At least three apparent layers are recognized in the ionosphere, the E layer and F_1 and F_2 layers; they are characterized by their specific absorption and reflective properties toward radiowaves. Starting from the lower part of the ozonosphere up to the 120 km level, different atmospheric constituents - atomic oxygen, atomic nitrogen, molecular oxygen, molecular-nitrogen and ozone react chemically with one another. The chemical activity has led to the designation of this region as the chemosphere (7) and of the study of these reactions as chemical aeronomy which will be discussed later.

III. THE COMPOSITION OF THE ATMOSPHERE

A classical table of the average composition of the atmosphere was prepared by Paneth (8) with some more recent data as follows:

Table 1. The Average Composition of the Atmosphere

Gas	Composition by volume ppm	Composition by weight ppm	Total Mass ($x10^{20}g$)
N_2	780,900	755,100	38.648
O_2	209,500	231,500	11.841
A	9,300	12,800	0.655
CO_2	300	460	0.0233
Ne	18	12.5	0.000636
He	5.2	0.72	0.000037
CH_4	1.5	0.9	0.000045
Kr	1	2.9	0.000146
N_2O	0.5	0.8	0.000040
H_2	0.5	0.03	0.000002
O_3*	0.4	0.6	0.000031
Xe	0.08	0.36	0.000018

*variable

Tables showing the isotopic abundances of the elements in the atmosphere were prepared by Asimov (9). Isotopic argon, Ar^{40}, is useful for determination of the age of the earth (10). From Table 1, it can be seen that the atmosphere is rather simple in composition, being made up almost entirely of three elements, nitrogen, oxygen and argon. However, the minor constituents are highly important (11). Carbon dioxide provides the raw material for plant life and ozone plays a vital part in that it is responsible for absorption of solar ultraviolet radiation, thus protecting most forms of life on earth. The ozonosphere is also of some consequence in reducing the escape of terrestrial heat by radiation into space.

In addition to the atmospheric components listed by Paneth, alkali metals exist in the upper atmosphere, at about 85-130 km. Lithium was observed in the twilight airglow (12). The presence of sodium was found by the absorption of the D lines in twilight about twenty years ago (13). The determination and the study of behavior of sodium in the atmosphere was conducted in recent years (14) and it is believed that sodium takes part in the night airglow. Potassium is also detected in the spectra of light of night sky and its concentration is estimated to be 1/50 of the sodium concentration (15). The existence of magnesium and calcium ions in the upper atmosphere was also reported (16).

Radon(Rn), thoron(Tn) and actinon (An), the decay products of the three naturally occuring radioactive series, and their decay products are found in the atmosphere (17). The content varies with time and place (18).

There are also temporary constituents such as the industrially produced SO_2, NO_2, I_2, NH_3 and CO in the atmosphere.

IV. CHEMICAL REACTIONS IN THE CHEMOSPHERE

Chemical reactions in the atmosphere are a consequence of solar ultraviolet radiation. Although the sum is 93 million miles away from us, it encompasses the earth by its immense radiation(19). This is why Chapman said "the earth is in the sun's atmosphere"(20). When the sun is in its quietest condition, it emits 10^2 to 10^3 particles/cm^3 at a velocity of 500 km/sec toward the earth. In its more active stage, the velocity increases to 1500 km/sec and the density becomes 10^5 particles/cm^3 (21). The absorption of solar ultraviolet radiation by the atmospheric gases causes different chemical reactions and various phenomena in the sky.

(1) The formation of atmospheric ozone.

Molecular oxygen has three absorptions in the ultraviolet region, the Herzberg bands near 2400 Å , the Schumann-Runge continuum beginning at 1760 Å and the Schumann-Runge absorption bands beginning at about 1925 A and coverage to 1760 Å. The last one is believed to be responsible for the formation of ozone at about 35 to 40 km heights by the following reactions (22)

$$O_2 + h\nu \rightarrow O_2^* \qquad (1)$$

$$O_2^* + O_2 \rightarrow (O_2+O)+O = O_3+O \qquad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (3)$$

The first reaction means that simultaneously with the dissociatio one of the oxygen atoms produced combines with the reacting O_2 to produce O_3. The other oxygen atom then combines with O_2 by a three body collision process. [Reaction (3)].

The region in which ozone is formed, according to the above estimates, is higher than the region of maximum concentration of ozone. Studies show that ozone may be produced in the high region and carried down to lower levels by convection (23,.

(2) Chemistry of an oxygen-nitrogen atmosphere

Much work has been done concerning the reactions occuring in the atmosphere around 75 km (23 to 27). Barth and Kaplan (24) called these "the interactions in an oxygen-mitrogen atmosphere". The dominant atmospheric reactions between atomic nitrogen and atomic oxygen produced by solar radiation and their various molecular forms are described by the following nine equations:

$$N + N + M \xrightarrow{k_1} N_2 + M \qquad (4)$$

$$N + O + M \xrightarrow{k_2} NO + M \qquad (5)$$

$$O + O + M \xrightarrow{k_3} O_2 + M \qquad (6)$$

$$N + NO \xrightarrow{k_4} N_2 + O \qquad (7)$$

$$N + O_2 \xrightarrow{k_5} NO + O \qquad (8)$$

$$O + O_2 + M \xrightarrow{k_6} O_3 + M \qquad (9)$$

$$O + O_3 \xrightarrow{k_7} O_2 + O_2 \qquad (10)$$

$$NO + O + M \xrightarrow{k_8} NO_2 + M \qquad (11)$$

$$NO_2 + O \xrightarrow{k_9} NO + O_2 \qquad (12)$$

These reactions were studied by simulating upper atmospheric conditions in the laboratory (28). The results of the rate constants were interpreted as follows:

A. The rate of loss of atomic nitrogen is governed by its reaction with molecular oxygen, reaction (8).

B. The concentration of nitric oxide is determined by reaction (8) and the reaction of atomic nitrogen with nitric oxide, reaction (7). Then the density of nitric oxide is much less than, and proportional to, the density of the molecular oxygen present.

$$[NO] = k_5/k_4 \, [O_2]$$

C. The concentration of nitrogen dioxide in the upper atmosphere is governed by the reactions of atomic oxygen with nitric oxide and nitrogen dioxide, reactions (11) and (12). The density of nitrogen dioxide is less than and proportional to, the density of nitric oxide

$$[NO_2] = [k_8/k_9][M][NO].$$

(3) The airglow.

The airglow is the term applied to radiation emitted from the earth's upper atmosphere, excluding auroras. The total night airglow, although feeble, is comparable to the total emission of the stars. Chemical processes were believed to be responsible for the airglow (29). Two types of reactions lead to chemiluminesent processes:

$$A + B + C \rightarrow AB' + C'$$
$$A + BC \rightarrow AB' + C_1$$

The primes indicating that the species concerned may be in an excited state.

A number of possibilities were suggested for the excitation mechanisms of the spectrum. For example, the green atomic line of the airglow may be due to the process (30)

$$O + O + O \rightarrow O_2 + O\ (^1S).$$

The yellow doublet may be due to the oxidation-reduction cycle of sodium (31)

$$Na + O + M \rightarrow NaO + M$$

or $\quad Na + O_3 \rightarrow NaO + O_2$

followed by $\quad NaO + O \rightarrow Na\ (^2P) + O_2.$

Other possibilities are (32)

$$NaH + O \rightarrow Na\ (^2P) + OH$$

and

$$NaH + H \rightarrow Na(^2P) + H_2$$

The formation of sodium hydride involved might take place through

$$Na + O_2 + M \rightarrow NaO_2 + M$$
$$NaO_2 + H \rightarrow NaH + O_2$$

Experiments in the laboratory will be needed to prove the mechanisms responsible for the different lines and bands of the spectrum.

V. RADIOACTIVITY OF THE ATMOSPHERE

Suess grouped the radioactive nuclear species that occur in the atmosphere into three classes (33) : primary and secondary radio nucledes, cosmic ray produced radioactivities, and man-made radioactive substances.

(1) Extremely long lived species that have survived from the time when the elements formed are called primary radionuclides. Their daughter products, secondary radionuclides, form a minor constituent of the atmosphere indicated earlier.

(2) The number of radioactive particles produced by cosmic-ray event is proportional to the incoming cosmic ray flux and shows the same dependence on geomagnetic latitude as does the cosmic ray intensity. The average number of primary cosmic ray particles that hit the earth is of the order of one per cm^2 per sec.

A. Carbon-14

In 1948, Libby found the occurence of carbon-14 in nature (34). It is produced by the (n,p) reaction on N^{14} and is then oxidized in the atmosphere to molecular CO_2. Harteck (35) found that this oxidation is slow and that the C^{14} remains in the form of carbon monoxide for many years before the oxidation is completed. Wolfgang and co-workers (36) investigated the $N^{14}(n,p)\ c^{14}$ process of the upper atmosphere. They demonstrated that the recoil C^{14} from this process reacted with N_2-O_2 mixtures under a variety of conditions and that CO^{14} accounted for 90-100 per cent of the C^{14} produced.

B. Tritium

Tritium produced by cosmic radiation in the atmosphere has been shown to be present both in atmospheric hydrogen and in water vapor. Faltings and Harteck (39) found that atmospheric free hydrogen contains over a thousand times more tritium than the water vapor in air. Harteck (38) attempted to explain the high tritium concentration in the free H_2 by considering the various thermal reactions possible for tritium in the atmosphere, while Suess(33) considered only the physical conditions of the atmosphere. Rowland (39) showed that the high tritium content of free hydrogen was due to a hot atom reaction of the tritium recoiling from nuclear processes in the atmosphere.

C. Beryllium-7

The natural occurence of Be^7 was discovered by Arnold and Al-Sali (40). Because of the lack of stratospheric-tropospheric mixing, Be^7 is retained in the stratosphere for periods in excess of 53 days, its half-life.

D. Other cosmic ray produced radionuclides along with carbon-14, tritium and beryllium-7 are listed in Table II.

Table II. Cosmic-ray produced radioactive isotropy

Isotope	$T_{1/2}$	d/m per liter rain	atoms per c.c. rain	Q=atoms per minute per cm^2 Total	Troposphere	Ref.
T	12.3y	5 to 100	50000 to 10^6	100	60	42
Be^7	53d	10 to 60	2000 to 6000	6.3	1.3	40,43
C^{14}	5570y	spec.mod.carbon activity 14.7±0.5d/m		150		
Na^{22}	2.6y	$\sim$0.02	$\sim$40			45
P^{32}	14.5d	$\sim$1	$\sim$40			46,47
P^{33}	25d	$\sim$0.5	$\sim$30			47
S^{35}	87d	$\sim$2	$\sim$400			48
Cl^{39}	55 min.	$\sim$50	$\sim$2.5			49

(3) Artificially Produced radioactivities in the Atmosphere

A. Fission products of U^{235} and Pu^{239} from atomic weapons.

Libby (50) distinguishes three types of fall-out from atomic weapons: (a) local fall-out (b) tropospheric fall-out (c) Stratospheric fall-out. The local fall-out is mainly caused by settling of large-sized particles and covers considerable areas near the points of detonation. The second type is due to relatively small-sized particles that remain in the atmosphere until they settle out or are brought down by rains. This type of fall-out tends to remain in the same general latitude as the point of origin, but may circle the earth several times before it is precipitated. The stratospheric fall-out amounts to about half or more of the total activity produced and is the part that produces world wide effects. Libby finds that the average time this material stays in the stratosphere is of the order of 10 years. Only about 10 per cent of stratospheric radioactivities descend per year into the tropopause, where they are washed out within a few weeks by rain.

Stratospheric strontium-90 fall out have been studied extensively For example, Libby (57) estimated for December 1957 a total world wide stratospheric fall-out of $Sr^{90}$of the order of 0.25 d/m per cm^2.

B. Artificial tritium

After 1954, the tritium content in nature increased many times as a consequence of the H-bomb tests. After the 1957 castle test, Begeman and Libby (42) estimated that an average of 10^9 tritium atoms (corresponding to 100 d/m of tritium) per cm^2 have been deposited on the northern hemisphere, mostly in the troposphere.

C. Artificial carbon-14

According to Libby, most of the neutrons which escape into the surrounding atmosphere from an atomic or thermo-nuclear explosion interact with the nitrogen of the atmosphere to produce C^{14} through the nuclear reaction N^{14} (n,p)C^{14}. "Man-made" carbon 14 has increased the C^{14} content of the atmosphere in recent years. (52)

D. Other radioactive isotopes such as Co^{57} (59) in the atmosphere produced by thermonuclear tests are also detected.

VI. ATMOSPHERES OF OTHER PLANETS

Of the eight other known planets in our solar system, Mercury probably does not possess any atmosphere, a fact due partly to its small mass and partly to its high surface temperature. Saturn, Uranus and Neptune very closely resemble Jupiter while Pluto is so distant that virtually little is known of its atmosphere. Therefore, when we talk about the atmosphere of other planets only Venus, Mars and Jupiter are concerned.

(1) Venus - Venus has a deep atmosphere above the visible surface of clouds surrounding the planet. In 1932 Adams and Dunkam (55) found from infrared spectra of Venus that carbon dioxide is very abundant there while free oxygen and water are very rare.

Because of this difference from the earth's atmosphere, the main photochemical reaction believed to take place in the atmosphere of Venus is (56)

$$CO_2 + h\nu \rightarrow CO + O$$

The most important secondary reaction would be

$$O + O \rightarrow O_2$$

which would be followed by the rapid photochemical dissociation of the oxygen molecules. Finally carbon monoxide would be reoxidized to the dioxide.

Kuiper (54) from his polarization measurements in the infrared, concludes that Venus cloud cover is not composed of water droplets nor of dust, but probably of polymerized carbon suboxide, C_3O_2, formed by action of solar ultraviolet radiation on the abundant carbon dioxide.

(2) Mars

The atmosphere of Mars is rarer than the earth's. According to Hess (57) the mass of Martian atmosphere is some 20 percent of the mass of the earth's atmosphere and it is 100 km deep. Nitrogen forms the bulk of the Martian atmosphere. Carbon dioxide is slightly more abundant in the Martian atmosphere than in that of the earth. Adams and Dunham (58) estimated that the amount of oxygen must be less than 0.1 percent of the amount of oxygen in the terrestrial atmosphere. However, it is possible that the atmosphere of Mars once contained free oxygen or ozone, which has been consumed in the oxidation of iron, hence the red color of vast areas of the surface of the planet.

(3) Jupiter

Because of its large mass, this giant planet has been able to retain most of the original constituent of its atmosphere including much of the hydrogen and helium originally present. In the present composition, the atmosphere is characterized by the abundance of hydrogen compounds, helium, nitrogen, carbon dioxide, and small amounts of inert gases, and some compounds of the halogens and of sulfur. According to Russell, (6) carbon dioxide reacted with hydrogen to produce methane and water vapor:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O.$$

At temperatures below 300°C. practically all of the carbon dioxide was converted into methane. Nitrogen reacted with hydrogen to produce ammonia at low temperatures and pressures.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

VII. CONCLUSION

The study of the atmosphere is a joint effort of many branches of science. It has been the purpose of this seminar to introduce some of the more interesting chemical aspects of atmospheric phenomena.

Literature Cited

1. Bert Bolin, Proc. Natl. Acad. Sci. U.S. 45, 1663-72 (1959).
2. Papers in Natl. Acad. Sci. Natl. Research Council. Pub. No. 400, (1956).
3. Erik Eriksson. Svensk. Kem. Tidskr., 71, 15-12 (1959).
4. For example, Scientific America 1961, Oct. 49.
5. James P. Lodge, Jr. ed. "Atmospheric Chemistry of Chlorine and Sulfur Compounds" American Geophysical Union, 1959.
6. See for example, K. Rankama and Th.G. Sakama, "Geochemistry" The University of Chicag o Press, 1950. Chapter 7 or Brian Mason, "Principles of Geochemistry" 2nd ed. John Wiley and Sons, 1958.
7. Joseph Kaplan, "The Chemosphere" in Physics and Med. of the Upper Atmosphere, ed. C.S. White and O. O. Benson, Jr. University of New Mexico Press, 1953. Chapter 7.
8. F. A. Paneth, Quart. J. Roy. Meterorol. Soc. 63, 433 (1937).
9. Issac Asimov, J. Chem. Ed. 32, 633 (1955).
10. H. A. Shillibeer and R. D. Russell, Geochim. et Cosmochim Acta, 8, 16-21 (1958).
11. John W. Townsend, Jr., Proc. Intern. Symposium phys. Med. Atmosphere Space. Ind. San Antonio 1958, 112-33 (Pub. 1960).
12. A. Vallance Jones, Nature, 183, 1305-11 (1959).
13. F. E. Roach, Pub. Astron, Soc. Pacific 61, 184-5 (1949).
14. T. M. Donahue, et al., phys. Rev. 104, 873-9 (1956); J. A. Serin gev and D. M. Hunten, Nature 178, 753-4 (1956). T. M. Donahue and Jacques Emile Blamont, Compt. rend. 247, 498-8 (1958); T. M. Donahue phys. Rev. Letters 1, 287-8 (1958); T. M. Donahue Nature 183, 1480-1 (1959); Bullock. W. R. and Hunter D. M. Can. J. phys. 39, 976-82 (1961).
15. E. A. Lytle and D. M. Hunter, J. Atm. and Ten. phys., 16, 236-45 (1959).
16. V. G. Istomin, Doklady Akad. Nauk S.S.S.R. 136, 166-8(1961).
17. H. Israel, Boston American Meterological Society, Compendium of Meteorology, 1951, p. 155.
18. W. Anderson, W. V. Mayneord, and R. C. Turner. Nature 174, 424-6 (1954). F. Barreira, Nature, 190, 1092-1 (1961).
19. Joseph Kaplan and Charles A. Barth, Proc. Natl. Acad. Sic. U. S., 44. 105-12 (1958).
20. Sydney Chapman, Scientific America, 1959, Oct. 64.
21. L. Reiffel, Nature 185 , 229 (1960).
22. See for example, S. K. Mittka, "The Upper Atmosphere, The Asiatic Society, Calcutta, India, 1952, Chapter 9.
23. H. K. Poctgold, J. atm. Tenest. phys. 7, 128-40 (1955).
24. Papers in Theshold of Space, Proc. Conf. Chem. Aeron. 1956, (Pub. 1957).
25. Marcel Nicolet, Proc. Intern. Symposium phys. Med. Atmosphere Space, Ind. San Antonio 1958, 14-47 (Pub. 1960).
26. I. D. Bates and H.S.W. Massey, Proc. Roy. Soc. (London) A187, 261-96 (1946).
27. Marcel Nicolet, J. atm. and Tessest. phys., 7, 152-69 (1955).
28. Joseph Kaplan, W. J. Schale a and Charles A. Barth., Can. J. Chem. 38, 1688-92 (1960).
29. P. R. Bates, Theshold of Space, Proc. Conf. Chem. Aeron. 1956, 14-21 (Pub. 1957).

30. S. Chapman Proc. Roy Soc. A132, 353 (1931),
31. S. Chapman, Astrophys. J. 90, 309 (1939).
32. D. R. Bates and M. Nicolet, J. Geophys. Ras 55, 235;
Dr.R. Bates, "The Earth as a Planet", G. P. Kuiper ed. University of Chicago Press, Chicago, 1954.
33. Hans E. Suess, Ann. Rev. Nuclear Sicence 8, 243 (1958).
34. W. F. Libby, "Radiocafbonating" University of Chicago Press, Chicago, 1952.
35. P. Harteck. Proc. Nuclear Sci. Meeting, Houston, 1957.
36. M. Pandow, C. Mackay and R. Wolfgang, J. Inorg. Nucl. Chem. 14, 153 (1960).
37. V. Faltings and P. Harteck, Z. Naturforsch 59, 438 (1950).
38. P. Harteck, J. Chem. Phys. 22, 1746 (1954).
39. F. S. Rowland, J. Chem. Phys. 30, 1098 (1959).
40. J. R. Arnold and H. Ali Al-Sali, Science 121, 451 (1955).
41. P. A. Benioff, Phys. Rev. 104, 1122 (1956).
42. F. Begemann and W. F. Libby, Geochim. et Cosmochim. Acta, 12, 277 (1957).
43. R. Thor and D. K. Zutski, Tellus 10, 99 (1958).
44. H. E. Suess, Science 122, 415 (1955).
45. L. Marquez, N. L. Costa, and I. G. Almeida, Nuoro cimento, 6, 1292 (1957).
46. L. Marquez and N. L. Costa, Nuovo cimento, 2, 1038 (1955).
47. D. Lal, N. Larasappya and P. K. Zutski, Nuclear Phys. 3, 69 (1957).
48. P.S. Geol. Nature, 178, 1458 (1956).
49. L. Winsberg, Geochim et Cosmochim. Acta, 9, 183 (1956).
50. W. F. Libby, Science 123, 657 (1956); Proc. Natl. acad. Sci. U.S. 42, 365 (1956).
51. W. F. Libby, Proc. Natl. Acid. Sci. U.S., 45, 959-76 (1959).
52. W. S. Broecker and A. Walton, Science 130, 309-14 (1959).
33. S. L. Hess, Science 128, 809-14 (1958).
54. G. Kuiper ed., "The Atmospheres of the Earth and Planets" Univ. of Chicago Press, Chicago, 1968,Chapter 7.
55. W. S. Adams and T. Dunham, Jr., Publs. Astron. Soc. Pacific 44, 243 (1932).
56. R. Wildt, Astrophys. J., 86, 312 (1937).
57. H. L. Hess, Publ. Astron. Soc. Pacific, 60, 289 (1948).
58. W. S. Adams and T. Dunham, Astrophys. J. 79, 308 (1934).
59. L. Marquez, N. L. Costa, and I. G. Almeida, Nuovo Cimento, 11, 111-12 (1959).

COORDINATION NUMBER FIVE

James George December 19, 1961

I. INTRODUCTION

Until recently, complex compounds with a coordination number of five were considered to be a rarity. However, work which has been carried out in the past 5-10 years has shown that they are much more prevalent than was earlier believed. Because of the great quantity of material which has been published, it has been necessary to limit the present discussion to recent advances in the chemistry of five-coordinated transition metal complexes. Earlier work may be found in CHEMISTRY OF THE COORDINATION COMPOUNDS, edited by Professor Bailar. It will further be necessary to eliminate material which deals with five-coordinated species which undoubtedly exist as intermediates or transition states in substitution reaction involving more common configurations. These have been well covered in MECHANISMS OF INORGANIC REACTIONS, by Basolo and Pearson.

The seminar will be divided roughly into two sections. The first will be primarily concerned with descriptive chemistry, structure, and the application of physical methods. The second will be a brief resume of the limited theoretical considerations which are used in correlating electronic configuration, geometrical configuration, and stability. As we shall see, these are quite inadequate.

II. DESCRIPTIVE CHEMISTRY

A. d^0---d^6 Cases (See Table 1)

Few five-coordinate compounds in which the central metal atom has six or less electrons have been reported. Those which have, have not been well characterized. These are listed in Table 1, along with the available evidence (empirical formula, magnetic moment, conductivity, etc.).

The pentahalides of tantalum, niobium, and molybdenum have been shown to exist, in the gas phase, as trigonal bipyramids(1). In the solid state they are dimeric, consisting of an octahedral arrangement with a common edge (2).

The compounds of the type $Re(Base)_2Cl_3$ are of some interest in that they all show an absorption peak at 750 mμ. The author claims that this peak is characteristic of five-coordinated compounds of this type (3).

Some theoretical basis can be given for the existence of the paramagnetic ($4e^-$) d^4 compounds. Valence bond theory shows that there are five readily available orbitals which may be employed in forming a set of dsp^3 hybrid orbitals.

B. $\underline{d}^7$ Cases

The valence bond picture just considered may also be applied to indicate the existence of diamagnetic $\underline{d}^8$ and paramagnetic ($1e^-$) $\underline{d}^7$ compounds. Since the chemistry of these two families is nearly analogous, only brief mention will be made of the $\underline{d}^7$ cases. These have been compiled in Table 2.

Jensen and Nygaard prepared $Ni(Et_3P)_2Cl_3$ and showed that it is monomeric in benzene and has a magnetic moment corresponding to one unpaired electron. On the basis of its dipole moment (2.5 Debye), they concluded that it has a tetragonal (square) pyramidal structure. Unfortunately, the compound was too unstable for X-Ray analysis (4).

Alderman and Owston prepared the rather interesting compound $[(CH_3)_2NCS_2]_2CoNO$ and showed by X-Ray analysis that it is also of the tetragonal pyramid type (5). It has three interesting characteristics:

1. The cobalt atom is raised 0.5 A. above the plane formed by the four sulfur atoms.

2. The nitric oxide molecule is tipped at an angle of 135°

3. The compound is diamagnetic, indicating that the unpaired electron on the cobalt atom and the odd electron on the nitric oxide molecule have become paired. It should probably be considered as a $\underline{d}^8$ case.

C. $\underline{d}^8$ cases (See Table 3)

Most of the five-coordinate compounds described belong to the $\underline{d}^8$ class. These extend from compounds of dinegative chromium to those of tripositive gold.

All of the pentacarbonyl compounds are thought to have the same structure since they are isoelectronic. King and Lippincott(6) and Stammreich, Sola, and Tavates (7) studied the I.R. and Raman spectra of $Fe(CO)_5$ and showed that their results agreed with a D_3h symmetry (trigonal bipyramid) but not C_4v (tetragonal pyramid). Cotton and Parish investigated a number of substituted iron complexes with the results indicated below (8).

TYPE OF COMPOUND: $Fe(CO)_4L$

THEORETICAL

Structure	Point Group	I.R. active modes CN str.	 CO str.
	C_4v	1	2
	Cs	1	4
	C_3v	1	3
	C_2v	1	4

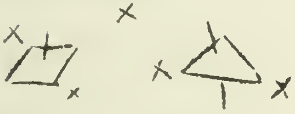
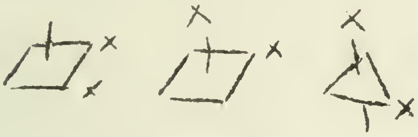
EXPERIMENTAL

	Compound	CN str.(CM.$^{-1}$)	CO str. (CM.$^{-1}$)
L=	Ph_3P	----	2006m 1980m 1940s
	CH_3NC	2218m	2072m 1996m 1967s
	Me_3CNC	2160m	2067m 2000m 1970s
	PhNC	2172w	2065m 2004m 1974s

This would indicate a C_3v structure but would not eliminate either C_s or C_{2v}.

TYPE OF COMPOUND: $Fe(CO)_3L_2$

THEORETICAL

Structure	Point Group	I. R. active modes CN str.	CO str.
	D_3h	1	1
	C_2v	2	3
	C_s	2	3

EXPERIMENTAL

	Compound	CN str.(Cm.$^{-1}$)	CO str.(Cm.$^{-1}$)
L =	Ph_3P	____	1886s
	CH_3NC	2165m	2009w 1926s
	Me_3CNC	2135m	2007w 1924s
	EtNC	2150m	2008w 1930s

Again it is not conclusive, but a D_3h symmetry is indicated. The weak band at 2000 cm.$^{-1}$ is thought to be an overtone or combination band with an increased intensity as a result of Fermi Resonance (8).

The most extensive work has been carried out on the nickel-palladium-platinum triad. When the $K_2Ni(CN)_4$ is dissolved in water and potassium cyanide is added to the solution, a definite color change from yellow to red occurs. Evaporation of this solution results in the isolation of the original starting materials. Recently this reaction has been studied using I.R. and visible spectrophotometric techniques (36). The I.R. spectrum shows peaks at 2050 cm.$^{-1}$ and 2150 cm.$^{-1}$ for the CN^- and $Ni(CN)_4^{-2}$ ions, respectively. As the concentration of potassium cyanide is increased, a new peak appears at 2100 cm^{-1}.

The intensity of this peak increases until an equimolar concentration of cyanide ion has been added. Then no further change can be observed. Application of the method of continuous variations, in the visible region indicates a maximum absorbance with a 1:1 ratio. Both of these serve to indicate the existence of a five-coordinate complex in the solution, but unfortunately they do not eliminate the possibility of six coordination.

Nyholm and his coworkers have studied coordination compounds of the type, $M^{II}(AsAs)_2XY$ in which M^{II} = Ni, Pd or Pt and X = Cl^-, Br^-, I^-, or SCN^- and Y = X or ClO_4^- (9,10,11,12,13,14,15). The ligand referred to as (AsAs) and all subsequent ligands may be found in Table 6. The results of this investigation are listed below.

1. Conductivities

Compound	Molar Cond. 10^{-3}M. in CH_3NO_2	Type	Spectra Mas.Absorb.( )	Intensity( )
$Ni(AsAs)_2(ClO_4)_2$	157	1:2	433	470
$[Ni(AsAs)_2X]X$	73-80	1:1	475-485	1120-1200
$[Ni(AsAs)_2X]ClO_4$	80-83	1:1	475	1110-1170
$Pt(AsAs)_2(ClO_4)_2$	175	1:2	----	----
$[Pt(AsAs)_2X]X$	73-76	1:1	----	----
$[Pt(AsAs)_2X]ClO_4$	73-104	1:1+	----	----

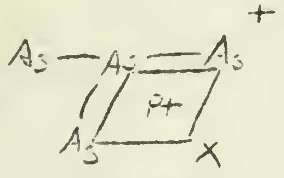
2. Continuous variations ($Ni(AsAs)_2(ClO_4)_2 + X^-$) shows a maximum absorbance at a 1:1 ratio.

3. Conductometric titration indicates a significant increase in the specific conductance after an equi-molar concentration of halide ion has been added.

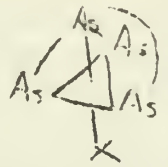
4. The X-Ray powder patterns are of two distinct types. The compound $Pt(AsAs)_2I_2$ has been investigated by single crystal methods, and apparently the platinum is an elongated octahedron. The compounds of the type $[M(AsAS)_2X]ClO_4$ have powder patterns that are quite distinctive. Preliminary work has shown that there are 8 molecules per unit cell. This indicates a much lower symmetry and eliminates the possibility of octahedral coordination. The authors feel that these are probably true five-coordinate compounds (11).

Complete X-Ray analysis has been carried out on $Ni(AsAsAs)Br_2$, and the structure is interpreted as being a distorted tetragonal pyramid(16). All three of the arsenic atoms lie on the bas ; however, one bromide ion is considerably below the plane.

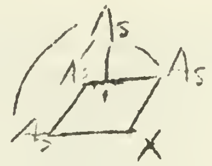
Recently, complexes have been made of a tetra-arsine compound which can have only a tetrahedral configuration if it is to act as a quadridentate ligand. The complex $[Pt(AsAsAsAs)X]X$ has been prepared and shown to be a 1:1 electrolyte in $PhNO_2$. There are three possible configurations which should be considered.



Coplanar



Trigonal Bipyramid



Tetragonal Pyramid

The first of these structures has been eliminated because there is no evidence for a free arsine group.

1. No quaternary arsonium salt can be formed.

2. The spectra are different from these for similiar compounds which are known to be coplanar.

3. The ligand has been quadridentate in all of the other cases which were studied.

4. The arsine groups are not easily oxidized.

The evidence for five-coordination is excellent.

1. $[Pt(AsAsAsAs)(SCN)]$ SCN shows two CN stretching frequencies in the I.R.. One occurs at 2120 $cm.^{-1}$ and corresponds to a coordinated thiocyanate; the other is at 2060 $cm.^{-1}$ and is in the ionic region.

2. Complex X-Ray analysis indicates a trigonal bipyramid with the bromine atom in an axial position (17,18).

Very little has been done on compounds of the type $Au(AsAs)_2X_3$. There is some evidence from conductance measurements that some of these may be five-coordinate (19).

Compoundm	Spec. Cond. $2x10^{-4}M$ in $PhNO_2$	Indication
$[Au(AsAs)_2I_2]I$	28.0	1:1
$[Au(AsAs)I_2]ClO_4$	27.9	1:1
$[Au(AsAs)I](ClO_4)_2$	40.9	1:2

In aqueous solution all are 1:3 electrolytes.

D. $\underline{d}^9$ Cases (Table 4)

Most of the work on $\underline{d}^9$ complexe has been X-Ray analysis. The complexes of dimethylglyoxime (DMG) with Ni(II) and Cu(II) have been studied (20). The nickel complex is highly insoluble because of metal-metal bonding, which leads to a polymeric material. The copper complex, on the other hand, has been shown to be dimeric. Each copper ion is coordinated to four nitrogen atoms lying in a plane and also to an oxygen atom of a third DMG molecule. The Cu-O distance (2.4 A.) indicates a considerable amount of bonding.

A number of other compounds, including the anhydrous copper carboxylates and complexes of Schiff bases, have been shown to have a similiar type of structures (21,22, 23).

E. d^{10} Cases (Table 5)

The compounds $Zn(AsAc)_2H_2O$ and $Zn(Terpy)Cl_2$ have both been investigated and have trigonal bipyramidal structures with the H_2O and both Cl^-, respectively, being found in the trigonal plane (24,25). Steric limitations of terpyridine cause distortions. The compound $Zn(Sal)H_2O$ has a square pyramidal structure with a Zn-O distance of 2.13 A.(26).

III. THEORETICAL CONSIDERATIONS

A. Electronic Configurations

Valence -bond considerations, as we have seen, indicate that spin-free d^4 and spin-paired d^7 and d^8 configurations should be applicable to the formation of five-coordinate compounds because of the availability of five orbitals for hybrid bond formation and the resulting inert-gas configuration.

Crystal-field theory is of little use since no absolute relationship is known which relates the electronic configuration to the coordination number. It has been observed, however, that the existence of a stable complex can often be correlated with the the magnitude of the crystal-field stabilization energy. If this were true, one might expect to find the square pyramidal configuration in the cases of d^4 and d^9 in a weak field and d^8 in a strong field. The trigonal bipyramidal structure would indicate d^3 and d^8 in the first case and d^6 in the second.

B. Geometrical Configuration

None of the present theories is adequate to explain the observed configurations. Kimball(27) showed on the basis of group theory and symmetry considerations that two hybridizations, dsp^3 and d^3sp, would lead to trigonal bipyramids and found. d^2sp^2, d^4s, d^4p and d^2p^3, would lead to tetragonal pyramids. Daudel (28) claims that dsp^3 will be a trigonal bipyramid only when an outer d orbital is involved. Others maintain that dsp^3 will be a trigonal bipyramid only when d_{z^2} is used.

Nyholm has pointed out that, in a given isoelectronic family, the compounds in which the charge on the central metal atom is low will usually have a symmetrical configuration (trigonal bipyramid) and that the bonding must be primarily covalent. Inversely, in the cases in which the electrostatic forces are predominate, the tetragonal pyramid will be favored (13).

C. Stability

For a given isoelectronic family, Nyholm has noted two general stability trends and attributes both of these to the effective nuclear charge. The higher the positive charge on the central metal atom, the less stable the compounds will be relative to the four-coordinated compound ($Cr^{=} > Mn^{-} > Fe > Co^{I} > Ni^{II} > Au^{III}$). For a given triad, he concluded that $Ni^{II} > Pd^{II} > Pt^{II}$ will be the order of stability. Unfortunately in his considerations he is concerned only with the energy required for hybridization and is not concerned with the magnitude of the energy received by the formation of the resulting bonds (14).

IV. CONCLUSION

Although work is far from completed in this field, a considerable amount of insight has already been gained. Primarily because of this work, a number of guides have been obtained which enable the chemist to select the compounds which are most likely to give him the configuration which he desires. For example, in trying to prepare compounds which are seven-coordinate, the most likely compounds would be ones in which the central metal atom has a low charge and a $\underline{d}^4$ configuration, which would allow for the hybridization of seven orbitals and the obtaining of an inert-gas configuration.

Table 1 $\underline{d}^0$-$\underline{d}^6$ Complexes

Spin Free

Compound	Configuration	Magnetic Moment(BM)	e⁻	Other Information	Ref.
$V(Me_3N)_2Cl_3$	d^2	2,69,2.75	2	M.W.283,254(275)	28
M^IMnF_5	d^3	3.88-3.90	3		29
Na_2MnF_5					29
$[Mn(AsAs)Cl_2H_2O]ClO_4$		5.1	4	1:1 electrolyte (PhNO$_2$)	30
$(Et_4N)_2MnCl_5$	d^4		4		13
Spin-Paired Complexes					
$TaBr_5$, $NbCl_5$	d^0	0	0	Trigonal Bipyramid	1
$Ti(Me_3N)_2Cl_3$	d^1	1.68	1		31
$MoCl_5$(gas)	d^1		1	Trigonal Bipyramid	1
K $Mo(CN)_5$	d^2	Dia.		1:1 electrolyte	32
$Re(Ph_3P)_2Cl_3$	d^4	Dia.		All are non-conductors in PhNO$_2$.Molecular weights	3
$Re(But_3P)_2Cl_3$	d^4	Dia.			3
$Re(AsAs)Cl_3$8	d^4	Dia.			3
K_2IrBr_5	d^6				33
$Ir(CO)_2Br_3$	d^6			Poor conductor	33

Table 2 - d^7 Complexes

Compound	Type	Mag.Mom.(BM)	e	Other Information	Ref.
$Mn(CO)_4(Ph_3P)$	Mn^0			Non-conductor	13
$Fe(CO)_2(AsAs)$ I	Fe(I)	2.18	1	Monomeric	39
$Co(CNR)_5(ClO_4)_2$	CO(II)		1	1:1 electrolyte	35
$Co(AsAsAs)I_2$			1	Poor conductor-M.W.	13
$[(CH_3)_2NNCS_2]_2CoNO$			0	X-Ray	5
$Ni(Et_3P)_2Br_3$	Ni(III)	1.72-1.90	1	Monomeric-Dipole Moment	4

Table 3-d^8 Complexes

Compound	Type	Mag.Mom.(BM)	e$^-$	Other Information	Ref.
Na$_2$Cr(CO)$_5$	Cr^{-2}				34
		All			14
Na$_2$Mo(CO)$_5$		Dia.			14
Na$_2$W(CO)$_5$					
NaMn(CO)$_5$	Mn^{-1}				14
		All			14
HMn(CO)$_5$		Dia.			14
Na(Re(CO)$_5$					
Fe(CO)$_5$	Fe^0			IR,Raman	6,7
		All			
Fe(CO)$_x$(L)$_{5-x}$		Dia.		I.R.	8
Ru(CO)$_5$					14
Os(CO)$_5$					14
Co(CNR)$_5$ClO$_4$	Co(I)	Dia.		1:1 electrolyte	35
Co(CNR)$_5$I		Dia.		1:1 electrolyte	35
[Co(CO)$_3$(Ph$_3$P)$_2$]X		Dia.			-
Rh(CNR)$_5$ X					14
K$_2$Ni(CN)$_5$	Ni(II)	Dia.		IR and Visible techniques	36
[M(AsAs)$_2$X]Y		Dia.		X-ray, others	9-15
M(AsAsAs)X$_2$		Dia.		X-Ray	16
[M(AsAsAsAs)X]Y		Dia.		X-Ray	17,1
[Au(AsAs)$_2$I](ClO$_4$)$_2$		Dia.		1:2 electrolyte	19

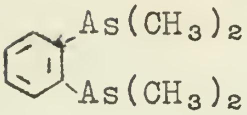
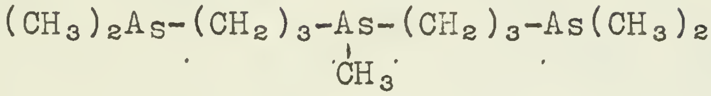
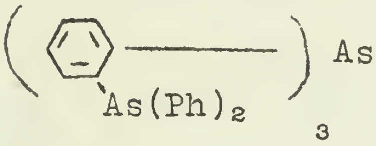
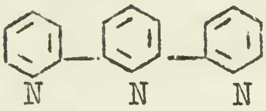
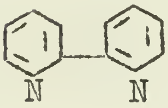
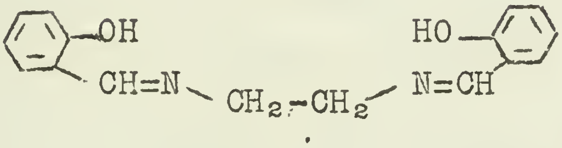
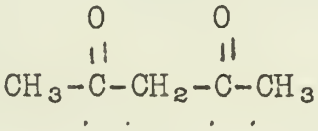
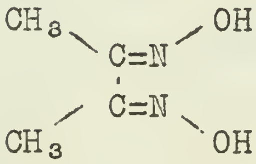
Table 4 - d^9 Complexes

Compound	Evidence	Ref.
Cu(Terpy)Cl$_2$	X-Ray	24
Cu(DMG)$_2$	X-Ray	20
Cu(DMG)$_2$H$_2$O		20
Cu(Sal) and Cu(Sal) H$_2$O	X-Ray	21,22
Cu(HCO$_2$)$_4$	X-Ray	23

Table 5 - d^{10} Complexes

Compound	Evidence	Ref.
Zn(Terpy)Cl$_2$	X-Ray	24
Cd(Terpy)Cl$_2$	Powder pattern	24
Cu(AsS)$_2$X		37
Cu(Bipy)$_2$I		38
Zn(Sal)H$_2$O	X-Ray	26
Zn(AcAc)$_2$H$_2$O	X-Ray	25

Table 6 - Key to Ligands

AsAs	
AsAsAs	 $(CH_3)_2As-(CH_2)_3-\underset{\displaystyle CH_3}{\underset{\vert}{As}}-(CH_2)_3-As(CH_3)_2$
AsAsAsAs	
Terpy	
Bipy	
Sal	
AeAe	 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_2-\overset{\overset{O}{\Vert}}{C}-CH_3$
DMG	

Bibliography

1. J. W. Cable, R. S. Nyholm, and R. K. Sheline, *J. Am. Chem. Soc.*, *76*, 3376 (1954).
2. D. E. Sands and A. Zalkin, *Acta Cryst.*, 732(1959).
3. F. A. Cotton, R. Levitus, and G. Wilkinson, *J. Chem. Soc.*, 4121,196
4. K. A. Jensen and B. Nygaard, *Acta, Chem. Scand.*, *3*, 474(1949).
5. P. R. H. Alderman, and P. G. Owston, *Nature*, *178*, 1071 (1956).
6. F. T. King and E. R. Lippincott, *J. Am. Chem. Soc.*, *78*, 4193(1956).
7. H. Stammreich, A. Sola, and Y. Tavares, *J. Chem. Phys.*, *32*, 856 (1960).
8. F. A. Cotton, and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).
9. G. M. Harris, R. S. Nyholm, and N. G. Stephenson, *Nature*, *177*, 1126 (1956).
10. G. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).
11. G. M. Harris, R. S. Nyholm, and N. G. Stephenson, *Nature*, *177*, 1126 (1956).
12. G. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).
13. R. S. Nyholm, American Chemical Society Meeting, Chicago,1961.
14. R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).
15. G. A. Barclay and R. S. Nyholm, *Chem. and Ind.*, 378 (1953).
16. G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).
17. J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J. Chem. Soc.* 3699 (1961).
18. G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961).
19. G. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, *63* (1957).
20. E. Frasson, K. Bardi, and S. Bezzi, *Acta. Cryst.*, *12*, 201 (1959).
21. D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).
22. F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 2639 (1960).
23. G. A. Barclay and C. H. L. Kinnard, *J. Chem. Soc.*, 3289(1961).
24. D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594(1956).
25. E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, 4996 (1960).
26. D. Hall and F. A. Moore, *Proc. Chem. Soc.*, 256 (1960).
27. G. E. Kimball, *J. Chem. Phys.*, *8*, 188 (1940).
28. G. W. A. Fowles and C. M. Please, *Chem. and Ind.*, 1793 (1955).
29. V. R. Hoppe, W. Liebe and W. Dahne, *Z. anorg. allgem. Chem.*, *307*, 276 (1961).
30. R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 564(1958).
31. M. Antler and A. W. Laubengayer, *J. Am. Chem. Soc.*, *77*, 5350(1955).
32. M. C. Steele, Aust. J. Chem., 10, 404 (1957).
33. L. Malatesta and F. Cauziani, *J. Inorg. Nuclear Chem.* *19*,81(1961).
34. H. Podall, H. B. Prestridge, and H. Shapiro, *J. Am. Chem. Soc.*, *83*, 2057 (1961).
35. L. Malatesta and A. Sacco, *Z. anorg. allgem. Chem.*, *273*,249(1953).
36. D. L. McCullough, L. H. Jones, and R. A. Penneman, *J. Inorg. Nuclear Chem.*, 286 (1960).
37. B. Chiswell and S. E. Livingstone, *J. Chem. Soc.*, 2931 (1959).
38. G. A. Barclay and C. H. L. Kinnard, Nature (In Press).
39. R. S. Nyholm, *J. Chem. Soc.*, 1397 (1959).
40. R. S. Nyholm, *Chem. Revs.*, *53*, 263(1953).

COVALENT BONDING IN SOME FIRST-ROW TRANSITION-METAL COMPLEXES

Anastas G. Karipides January 9, 1962

The properties and electronic structures of the ions of the transition metals have offered interesting and valuable correlations of theory and experiment. Pauling was among the first to study the shapes and magnetic moments of transition metal complexes. In fact, the magnetic properties of ML_n complexes have long been employed as a guide to the nature of bonding between M and L (1,2). In recent years application of crystal-field theory and molecular-orbital theory has met with some success in elucidating the type of bonding in complexes (3,4). Along with these theories have developed sensitive techniques for obtaining more quantitative data regarding the bonding between metal and ligand.

Pauling's theory deals with the ground state of the complex, and the orbitals of the complex are designated in terms of the orbita of the central ion (1,2). Thus, $Co(H_2O)_6^{+3}$ is represented as a $\underline{d^2sp^3}$ complex. Pauling was also the first to suggest that the anomalously low magnetic moment and total electronic spin of complexes (i.e., $Fe(CN)_6^{-3}$ or $Co(H_2O)_6^{+3}$) was evidence for covalent bonding. On this basis of "spin criterion", bonds in many complexes have been classified as being ionic or covalent (5,6). Accordingly, $Co(H_3O)_6^{+3}$ is diamagnetic and is called a "covalent" complex whereas $Co(H_2O)_3F_3$ is paramagnetic (4.47 BM) and is considered an "ionic" complex. However, this is a qualitative picture, and it does not tell us how much covalency there is in the $Co-H_2O$ bond in each compound (7,8).

The magnetic properties of the hydrated iron-group ions can be accounted for by the crystal-field theory of Van Vleck and Schlapp and Penney and others to a very good approximation (9,10,11). However, Abragam and Pryce were first to point out that an analysis of the optical and magnetic data for $Co(H_2O)_6^{+3}$ and $Cu(H_2O)_6^{+2}$ leads to discrepancies between experiment and theory (12). Griffiths and Owen showed that the same is true for $Ni(H_2O)_6^{+2}$(13). These discrepancies occur systematically for most hydrated iron-group salts and can be accounted for by introducing some charge transfer between the paramagnetic ion and the water molecules (14,15,16,17).

Thus it is necessary to obtain an estimate of the electron distribution over the complex, and this can only be found by the measurement of properties which give detailed information about the orbits of the electrons and not by the measurement of the total spin. The paramagnetic resonance method is well suited for this purpose of getting electron distributions, since it gives very precise information both about the orbital magnetic moment of the unpaired $\underline{d}$-electrons and any nuclei with non-zero spin which are bonded to the metal (6,14,18,19,20,21).

COVALENT BONDING IN SOME [illegible] TRANSITION-METAL COMPOUNDS

Thaddeus S. Lardiner January 1, 1964

[illegible]

[illegible]

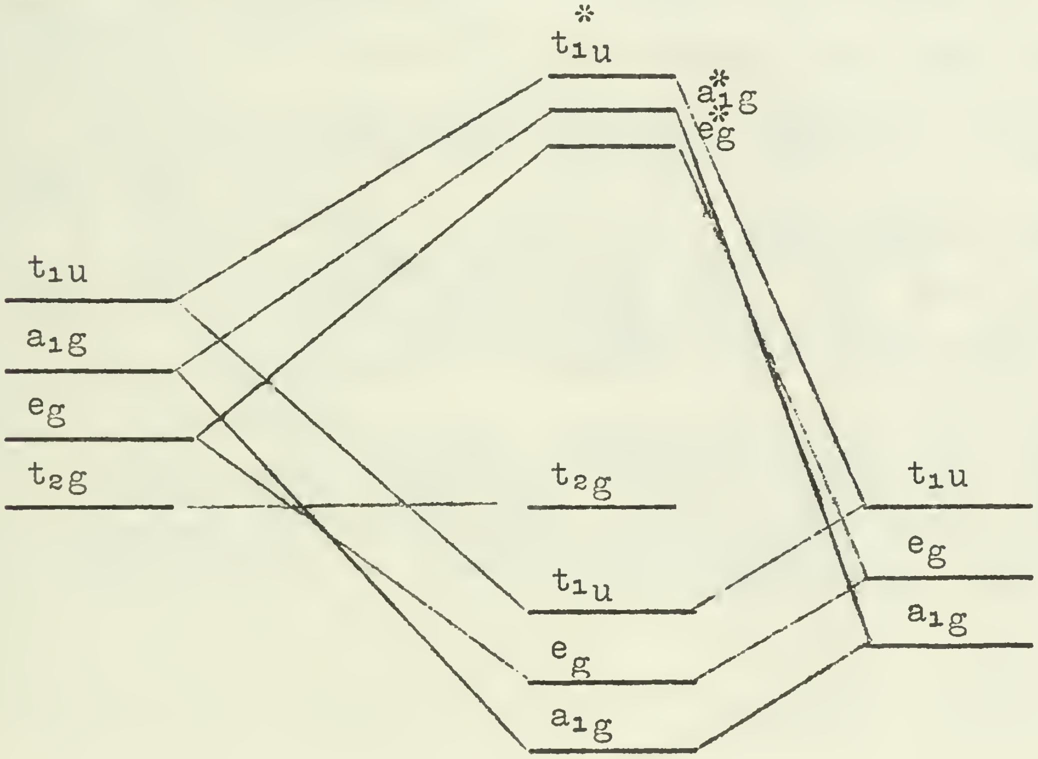
[illegible]

[illegible]

[illegible]

In particular, it is found that the spin-orbit coupling and the hyperfine interaction in a crystal differ from those obtained for a free ion (14,20). For example, the g factor for Ni^{++} in the cubic field of MgO is 2.227. The optical separation of the triplet $T_{2g}(F)$ and the lowest singlet A_{2g} measured on the same crystal is 8600 cm^{-1}. Since $g = 2.00 - 8\lambda''/\Delta$, we find that $\lambda'' = -245$ cm^{-1}. The spin-orbit coupling parameter in a free ion is -324 $cm.^{-1}$. Consequently, there is an apparent 25% reduction of λ (spin-orbit coupling constant) in the crystal (19). As a result, one as forced to reconsider the basic assumptions of the theory based on the static crystalline field. The central assumption made is that one can regard the surrounding ions as point charges. This is not entirely correct since d wave functions overlap the wave functions of the surrounding water ligands to some extent (19).

By using the molecular orbitals introduced by Van Vleck (11) and considering only σ-bonding orbitals of the oxygens, the following energy level diagram may be constructed.

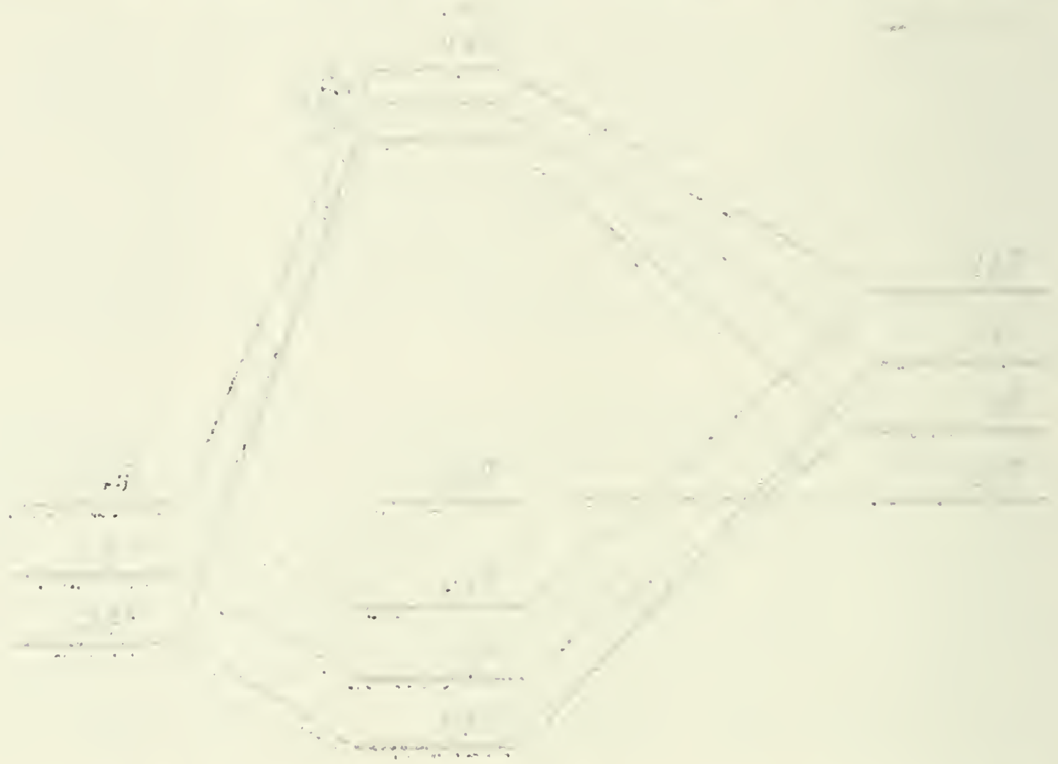


The e_g molecular orbital is now an admixture of metal and oxygen orbitals rather than pure d_{z^2} and $d_{x^2-y^2}$ orbitals, as is assumed in crystal-field theory.

Tinkham has also used this approach to explain the observed hyperfine structure in the iron-group fluorides (22,23). The hyperfine splitting from the surrounding ligands may be observed if one or more of the surrounding diamagnetic ligands has a nuclear magnetic moment. The order of magnitude of the hyperfine splitting is given by the product of the hyperfine structure of the free metal ion and the probability of finding the unpaired electron on the ligand. This effect was first observed by Owen and Stevens in ammonium hexachloroiridate (IV) (24). Recently, the ESR of $K_3Cr(CN)_5NO$ has been examined, and the observed hyperfine splittings indicate the presence of considerable covalent bonding (25).

[illegible]

[illegible]



[illegible]

[illegible]

REFERENCES

1. L. Pauling, "Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, N.Y. (1960).
2. J. W. Linnett, *Disc. Faraday Soc.*, *26*, 7 (1958).
3. L. E. Orgel, "An Introduction to Transition-Metal Chemistry", John Wiley and Sons, New York (1960).
4. T. M. Dunn, "The Visible and Ultraviolet Spectra of Complex Compounds" in "Modern Coordination Chemistry", Edited by J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York (1960).
5. L. Pauling, *J. Am. Chem. Soc.*, *53*, 1367 (1931).
6. J. Owen, *Disc. Faraday Soc.*, *19*, 127 (1955).
7. H. C. Clark, *J. Chem. Soc.*, 4132 (1957).
8. H. L. Friedman, *J. Am. Chem. Soc.*, *68*, 605 (1946).
9. J. H. Van Vleck, *Phys. Rev.*, *41*, 208 (1932).
10. W. C. Penney and R. Schlapp, *Phys. Rev.*, *41*, 194 (1932).
11. J. H. Van Vleck, *J. Chem. Phys.*, *3*, 807 (1935).
12. A. Abragam and H. M. L. Pryce, *Proc. Roy. Soc.* (*London*), *A206*, 173 (1951).
13. J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.* (*London*), *A213* 459 (195).
14. J. Owen, *Proc. Roy. Soc.*, (*London*), *A227*, 183 (1954).
15. A. Abragam and H. M. L. Pryce, *Proc. Roy. Soc.*, (*London*), *A206*, 164 (1951).
16. O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, *26*. 1686(1957).
17. L. E. Orgel, *J. Chem. Phys.*, *23*, 1004 (1955).
18. Bowens and J. Owen, *Rept. Prog. Phys.*, *18*, 304 (1955).
19. Bleaney and J.W.H. Stevens, *Rept. Prog. Phys.*, *16*, 108(1953).
20. W. Low, "Paramagnetic Resonance in Solids", Academic Press, New York (1960).
21. J. H. E. Griffiths, *Disc. Faraday Soc.*, *19*, 106 (1955).
22. M. Tinkham, *Proc. Roy Soc.* (London), *A236*, 535 (1956).
23. M. Tinkham, *Proc. Roy. Soc.* (London), *A236*, 549 (1956).
24. J. Owen and J.W. H. Stevens, *Nature*, *171*, 836 (1953).
25. I. Bernal and S. E. Harrison, *J. Chem. Phys.*, *34*, 102 (1961).

MECHANISMS OF OXY-ANION REACTIONS IN AQUEOUS SOLUTION

Robert L. Carlson

January 16, 1962

Information about the mechanisms of oxy-anion reactions has been obtained mainly from kinetic studies, isotope exchange studies, and the isolation of intermediates. Since a mechanism is a model developed to explain experimental facts, there are generally several such models which may exist. If only a single mechanism can be thought of to explain a given process, this does not necessarily mean that it is the correct one, but rather it may mean that not enough experiments have been performed to show it to be in error.

The simplest reaction that oxy-anions can undergo in aqueous solution is exchange with water. Numerous anions have been shown (1) to be quite stable with respect to oxygen exchange with water. In such cases the constitution of the anion is known. The isotopic oxygen exchanges of halate ions with water have been studied and the order of the exchange rate found to be $ClO_3^- < BrO_3^- < IO_3^-$. The exchange of chlorate with water follows (2) the rate law $k[H^+]^2[ClO_3^-]$. When the exchange is considered first order in water it is possible to postulate a mechanism similar to that for reduction by halide ion. The latter process follows (3) the kinetic law $k[H^+]^2[ClO_3^-][Cl^-]$. The following equations have been suggested (4) to explain both the exchange and reduction processes.

$$H^+ + ClO_3^- = HClO_3$$

$$H^+ + HClO_3 = H_2ClO_3^+ \quad \text{(rapid and reversible)}$$

$$X + H_2ClO_3^+ \rightarrow XClO_2^+ + H_2O \text{ (slow)}$$

where X can be a halide ion or water. Kinetic studies in deuterium oxide show that the exchange rate is greater in this medium. Since weak acids are less dissociated in deuterium oxide than in ordinary water (5), one would expect this from the above postulated equilibria. The bromate-water exchange (6) and the bromate-bromide reaction (7) obey similar kinetic laws.

A relationship

$$\log k/ko = \alpha E_n + BH$$

has been proposed (8) to correlate the relative rates of halide and water substitution in bimolecular reactions. E_n and H are nucleophilicity and basicity constants respectively. Good agreement between the calculated and experimental specific rate constants is obtained for the chlorate and bromate reactions.

The very rapid iodate-water exchange has recently been measured (9) and found to be both general acid- and general base(10) catalyzed. Since the iodate ion is believed (11) to exist mainly in a hydrated form, the acid dependence of the exchange can be explained by the following equations:

$$H_2IO_4^- = H^+ + HIO_4^=$$

$$H_2IO_4^- = H_2O + IO_3^-$$

The general base catalysis appears to be an S_N2 type process.

$$HIO_4^= + B = BIO_3^- + OH^-$$

Complexes of the type BIO_3^-, where $B=NH_3$, py, and F^-, have been characterized (12,13) in support of this mechanism. The overall rate expression for the exchange reaction can be given as

$$R = \underline{k}_1 [H_2IO_4^-] + \underline{k}_A [HA][HIO_4^=] + \underline{k}_B [B][HIO_4^=]$$

The difference in the exchange rates of iodate and bromate can then be explained by the ability of iodine to assume a coordination number greater than three.

The isotopic exchange of oxygen between hypochlorite and water (14) follows a rate law which indicates the importance of the species HOCl. The exchange is catalyzed by chloride ions, suggesting the equation

$$HOCl + Cl^- = HO^- + Cl_2$$

Exchange of chlorine between ClO^- and Cl^- occurs at a slower rate than the water exchange, however, indicating that an unsymmetrical intermediate may exist. The specific rate constant for the uncatalyzed water exchange is much greater than that for a kinetically similar term in the reaction of HOCl with phenol (15) but similar to that obtained (16) for the reaction of HOCl with acetic acid. Thus it appears that the reaction of HOCl with water is a bimolecular process. The Br^- catalyzed exchange of HOCl with water has a specific rate constant (17) nearly twenty times as great as the Cl^- catalyzed exchange. This suggests that Br^- attacks oxygen in preference to chlorine in HOCl. Halogen exchange studies support this mechanism.

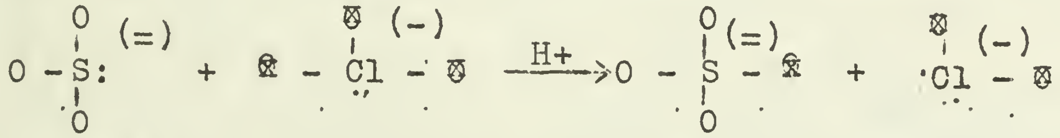
An oxidation-reduction reaction in which the oxidized anion gains in oxygen content can occur with the oxygen coming from either the oxidizing agent or water. In the latter case, electrons are transferred from the reducing agent to the oxidizing agent. The sulfite-nitrite reaction proceeds by such a mechanism. The net changes involved in this reaction are

$$2H^+ + NO_2^- + 2SO_3^= + H_2O = NH_3OH^+ + 2SO_4^=$$

$$2H^+ + NO_2^- + 3SO_3^= + H_2O = NH_4^+ + 3SO_4^=$$

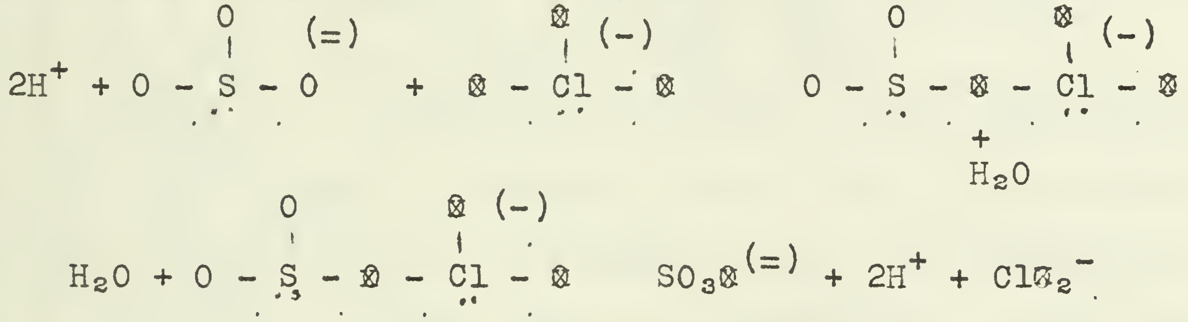
The intermediates of the reaction, $(KSO_3)_2NOH$ and $(KSO_3)_3N \cdot 2H_2O$, were prepared (18) and hydrolyzed in water of different oxygen isotope composition from that of the compounds. The results indicate that the oxygen added to SO_3^- comes from the solvent. Since sulfite exchanges quite rapidly with water a S-N bond in the complex is implied.

A reaction in which oxygen is transferred from one anion to another during the oxidation-reduction process is that between chlorate and sulfite. The rate law (19) for this reaction is $k[ClO_3^-][H_2SO_3]$. Complete transfer of oxygen is believed to occur during the $ClO_3^- \rightarrow ClO_2^-$ and $ClO_2^- \rightarrow ClO^-$ steps. In this case an S-Cl bond is ruled out. One possible mechanism is replacement on oxygen, $SO_3^=$ replacing ClO_2^- as



$$O-\overset{O}{\underset{O}{S}}{:}^{(=)} + \otimes-\overset{\otimes}{Cl}-\otimes^{(-)} \xrightarrow{H+} O-\overset{O}{\underset{O}{S}}-\otimes^{(=)} + \overset{\otimes}{Cl}-\otimes^{(-)}$$

The other is analogous to the mechanism proposed (20) for the oxidation of isopropyl alcohol by acid chromate.



$$2H^+ + O-\overset{O}{S}-O^{(=)} + \otimes-\overset{\otimes}{Cl}-\otimes^{(-)} \quad O-\overset{O}{S}-\otimes-\overset{\otimes}{Cl}-\otimes^{(-)} + H_2O$$

$$H_2O + O-\overset{O}{S}-\otimes-\overset{\otimes}{Cl}-\otimes^{(-)} \quad SO_3\otimes^{(=)} + 2H^+ + Cl\otimes_2^-$$

The rapid exchange of $SO_3^=$ with water makes it impossible to distinguish between the two mechanisms.

The rate law (21) for the nitrite-water exchange in acid solution suggests a unimolecular process

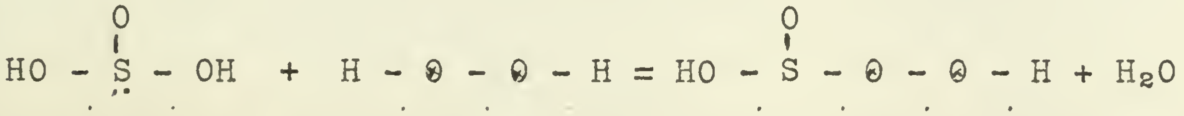
$$H_2NO_2^+ = H_2O + NO^+$$

The presence of hydrogen peroxide inhibits this exchange through the formation of a peroxynitrite intermediate (22). Tracer studies indicate that ONOOH derives two oxygen atoms from the peroxide and reacts by competing paths

$$ON\otimes\otimes H \rightarrow \otimes_2NO^- + H^+$$

$$ON\otimes\otimes H + NO_2^- \rightarrow ON\otimes^- + O_2N\otimes^- + H^+$$

The reaction of sulfite with hydrogen peroxide in acid medium (23) to form sulfate results in the transfer of two oxygen atoms from hydrogen peroxide although only one is needed. The



$$HO-\overset{O}{S}-OH + H-\otimes-\otimes-H = HO-\overset{O}{S}-\otimes-\otimes-H + H_2O$$

doubly labeled sulfate supposedly forms during an intramolecular rearrangement. In alkaline medium, only one oxygen atom (24) is transferred from peroxide for each $SO_4^=$ formed. This indicates the importance of protons to labilize $SO_3^=$ for substitution.

References

1. H. Taube, Ann. Rev. Nuclear Sci., 6, 280 (1956).
2. T. C. Hoering, F. T. Ishimeri, and H. O. McDonald, J. Am. Chem. Soc., 80, 3876 (1958).
3. A. Skrabal and H. Schreiner, Monatsh., 65, 213 (1955).
4. E. O. Edwards, Chem. Revs., 50, 455 (1952).
5. K. Wiberg, Chem. Revs., 55, 721 (1955).
6. T. C. Hoering, R. C. Butler, and H. O. McDonald, J. Am. Chem. Soc., 78, 4829 (1956).
7. M. Anbar and S. Gutmann, J. Am. Chem. Soc., 83, 4741 (1961).
8. E. O. Edwards, J. Am. Chem. Soc., 76, 1540 (1954).
9. M. Anbar and S. Guttmann, J. Am. Chem. Soc., 83, 781 (1961).
10. R. P. Bell, "The Proton in Chemistry", Chapt. 9, Cornell University Press, New York, N.Y. 1959.
11. N. V. Sidgwick, "The Chemical Elements and their Compounds", Oxford Press, New York, N.Y. 1950, p. 1229.
12. W. Hückel, "Structural Chemistry of Inorganic Compounds", Elsevier Publishing Co., Houston Texas, 1958, pp. 182-4.
13. A. Ray and G. Mitra, J. Indian Chem. Soc., 35, 211 (1958).
14. M. Anbar and H. Taube, J. Am. Chem. Soc., 80, 1073 (1958).
15. P. B. D. de la Mare, A. D. Ketley, and C. A. Vernon, J. Am. Chem. Soc., Volume 76, 1290 (1954).
16. M. Anbar and I. Dostrovsky, J. Chem. Soc., 1094 (1954).
17. L. Farkas, M. L. Lewin, and R. Block, J. Am. Chem. Soc., 71, 1988 (1949).
18. A. C. Rutenberg, J. Halperin, and H. Taube, J. Am. Chem. Soc., 73, 4487 (1951).
19. A. C. Nixon and K. B. Kravskopf, J. Am. Chem. Soc., 54, 4606 (1932).
20. F. Holloway, M. Cohen, and F. H. Westheimer, J. Am. Chem. Soc., 73, 65 (1951).
21. M. Anbar and H. Taube, J. Am. Chem. Soc., 76, 6243 (1954).
22. K. Glen, Z. anorg. allgem. Chem., 223, 305 (1952).
23. J. Halperin and H. Taube, J. Am. Chem. Soc., 74, 380 (1952).
24. H. Taube, Record of Chem. Progress, 17, 25 (1956).

NUCLEAR MAGNETIC RESONANCE MEASUREMENT OF REACTION RATES

J. T. Donoghue

January 17, 1962.

I. INTRODUCTION

The study of rapid reaction kinetics has received great impetus within the last few years. The progress in this area has been largely spurred by the appearance of new techniques for measurement of rate constants of reactions the half-lives of which are as small as 10^{-9} sec. The general topic has been adequately reviewed recently by Eigen and Johnson(1), Bell(2), and Eigen(3). The great part of the work in this area has been performed using various forms of relaxation spectrometry. This work has been recently reviewed by Eigen and coworkers (4,5). Non-resonance techniques, such as flash photolysis, shock tube studies and relaxation methods, have been described by Porter(6) and Button and Cole (7).

The NMh method for determination of kinetics of rapid reactions saw its greatest period of development in the period 1957-1960. One short review by Meiboom(8) is the only non-mathematical description of the technique which is offered in the literature.

The appearance of NMR in the 1940 s has been followed by a period of steady and rapid development, as is evidenced by the very large number of NMR papers in the current literature. The use of NMR as a structural tool is its most common application. No attempts to discuss this application of the method will be made here. The reader is referred to several selected reviews and papers in the bibliography (9-22). Instead, this discussion will concern itself with the determination of rapid reaction kinetics by means of the NMR method.

The most obvious manner in which kinetics could be studied by this method would be the measurement of the rate(s) of appearance or disappearance of NMR signals characteristic of reaction product(s) or reactant(s). However, in practice, much less conventional, though simpler, methods are used.

II. GENERAL CONSIDERATIONS

As an example of a type of kinetic analysis used, let us consider the system acetic acid-water(23). The NMR spectra of the separate components are represented below.

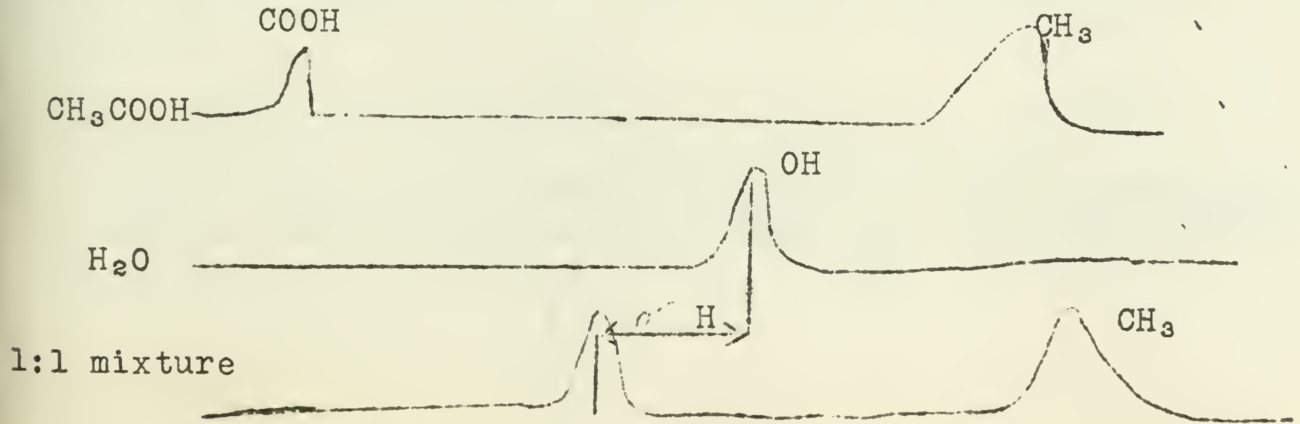


Fig. 1 - NMR spectra of CH_3COOH, H_2O, and a 1:1 mixture

It will be noted that the spectrum of the mixture does not show two separate OH resonances, but rather a single peak the position of which is intermediate between those of the separate OH signals. The position of this average OH resonance is an exactly linear function of mole% CH_3COOH in the mixture.

The occurrence of the average resonance serves to point out an important difference between NMR and the more conventional forms of spectroscopy. The single line is a consequence of rapid chemical exchange between the OH protons of water and acetic acid. It represents both sets of protons in a time averaged environment. Recall that in U.V., etc., the excitation time is always short compared with rotations or vibrations undergone by the molecule. However, in NMR, the radiation which excites nuclear transitions is of very low frequency and the transition time is frequently longer than the time required for a vibration and even long compared with rapid chemical reactions undergone by the molecule.

As for the specific example just cited (i.e. CH_3COOH-H_2O), the exchange is always too rapid to give anything but an average OH resonance; thus the kinetics cannot be measured by means of measurements of changes in line positions. However, it does illustrate the effect exerted on the spectrum by rapid exchange between two chemically non-equivalent sites.

III. EFFECTS OF CHEMICAL EXCHANGE ON CHEMICAL SHIFT AND SPIN-SPIN SPLITTING

The appearance of a resonance due to an exchanging magnetic nucleus in a particular chemical environment will generally change as the lifetime of the nucleus in that state is decreased. Consider the simple case of a nucleus exchanging between states A and B in each of which it spends, on the average, equal lengths of time. When the mean lifetime τ_A or τ_B is long compared with transition time, the spectrum shows two separate sharp resonances separated by $\delta_{AB}H$. When τ_A is short compared with transition time then a single sharp line is obtained at 1/2 $(\delta_A H + \delta_B H)$. When τ_A is approximately the same as transition time, then an intermediate broad line is observed.

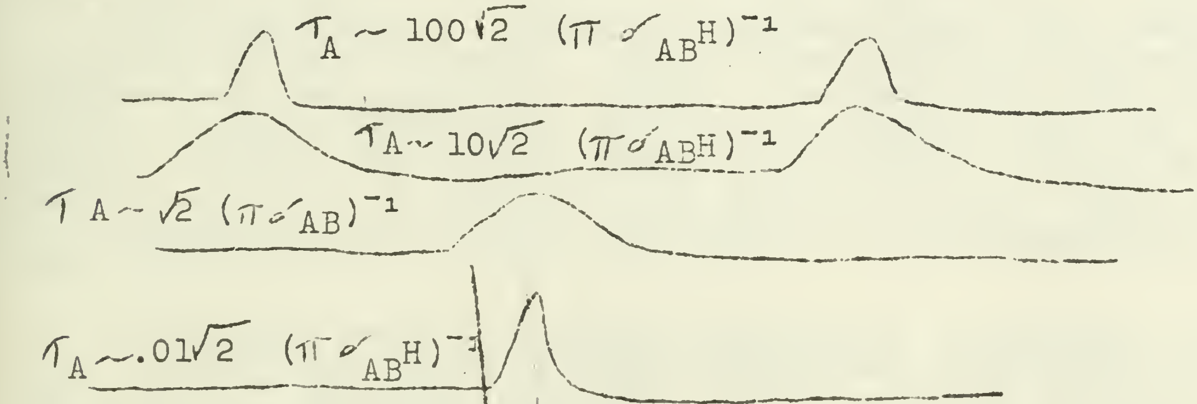


Fig. 2 - Theoretical NMR spectrum for nucleus exchanging between environments A and B when $\frac{[A]}{[B]} = 1$. See reference(24)

Gutowsky (24) has shown that for the above system, the point at which the separate lines just coalesce corresponds to $\tau_A = \sqrt{2}\ (\pi \delta_{AB} H)^{-1}$ sec. When $\delta_{AB}H$ is in c.p.s. Thus k, the specific rate constant for A-B is given by $1/\tau_A$. The above derivations based on proton chemical shifts which range from 5 to several hundred c.p.s. are most useful for processes having mean lifetimes between 0.1 and 0.0005 sec. Other indirect methods based on comparison of theoretical line shapes with observed shapes allow determination of rate constants of the order of $10^8 - 10^{11}$, etc. These other methods are discussed more fully in a later section.

Weinberg and Zimmerman (25) have studied exchange in ethanol-water mixtures. The results are qualitative. However, they will be discussed briefly since they illustrate the combined use of chemical shift and spin-spin splitting data to deduce kinetic information. Solutions containing 30% H_2O show three resonances: the two at higher fields corresponding to the ethyl protons and the lower frequency peak attributable to an average OH resonance. Thus at these concentrations there is rapid exchange. In mixtures containing 5% water, there are two OH resonances, separated by 32 c.p.s. The alcoholic OH resonance is split into a triplet.

When rapid exchange sets in, the splitting disappears before the two OH lines merge. This is because a separation of ~5 c.p.s will be averaged to zero by a process whose mean proton lifetime is <0.07 sec. The two OH resonances separated by 30 c.p.s. will not be averaged until τ_A is <0.015 sec.

In essence then, kinetic information is deduced by studying line positions and separation of spin-spin multiplets as a function of water concentration. Other semi-qualitative studies of this type are given in the bibliography (26-32). These studies are concerned with rates of rotation about CON bonds in amides(26-29), restricted rotation in ethane derivatives (30), and nitrogen inversion frequencies in cyclic amines (31, 32).

IV. PROTON EXCHANGE IN AMMONIA AND AMMONIUM IONS

Semi-qualitative exchange experiments have been carried out in ammonia-water mixtures. The studies show only one sharp resonance in such mixtures (33,34). Exhaustively dried ammonia shows a triplet resonance (33) due to coupling with the ^{14}N nucleus (I=1). When minute amounts of water or amide ion are added, splitting is washed out by rapid exchange. Mean lifetime of a proton on any nitrogen was found to be substantially less than 0.007 sec.

In aqueous NH_4NO_3 solutions containing enough NH_3 to preserve near neutrality, only an average resonance is obtained. The NH_3, H_2O, and NH_4^+ exchange processes are so rapid as to give only a single resonance. On acidification with HNO_3, the spectrum shows a triplet corresponding to the three spin orientations of ^{14}N and a large single proton resonance due to H_2O (35).

V. QUANTITATIVE STUDIES-LINE SHAPE AS A FUNCTION OF EXCHANGE RATES

Protolysis Kinetics of Substituted Ammonium Ions

Most of the recent quantitative work in this area has concerned itself with the protolysis kinetics of aqueous solutions of R_4N+ compounds (36). The methods used depend on study of resonance line shape as a function of exchange rate. Theories of the effect have been offered by Gutowsky (37,38) and extended by McConnell (39) and others (36).

Previous work on similar systems indicated that the half-life for exchange in ND_4^+ was of the order of several minutes (40,41). Swain and coworkers (42) found that exchange rates of NR_4+ with ROH were inversely proportional to the concentration of added mineral acid. Eigen and Schön (5), by the electrical impulse method, found $\underline{k}=3\times10^{10}$ for the reaction $NH_4+ + OH^- \rightarrow NH_3+H_2O$ at 20°C.

Consider the NMR spectra obtained by Meiboom, et al (36) for a 4.47<u>M</u> CH_3NH_3Cl solution at 31.65 Mc/sec.

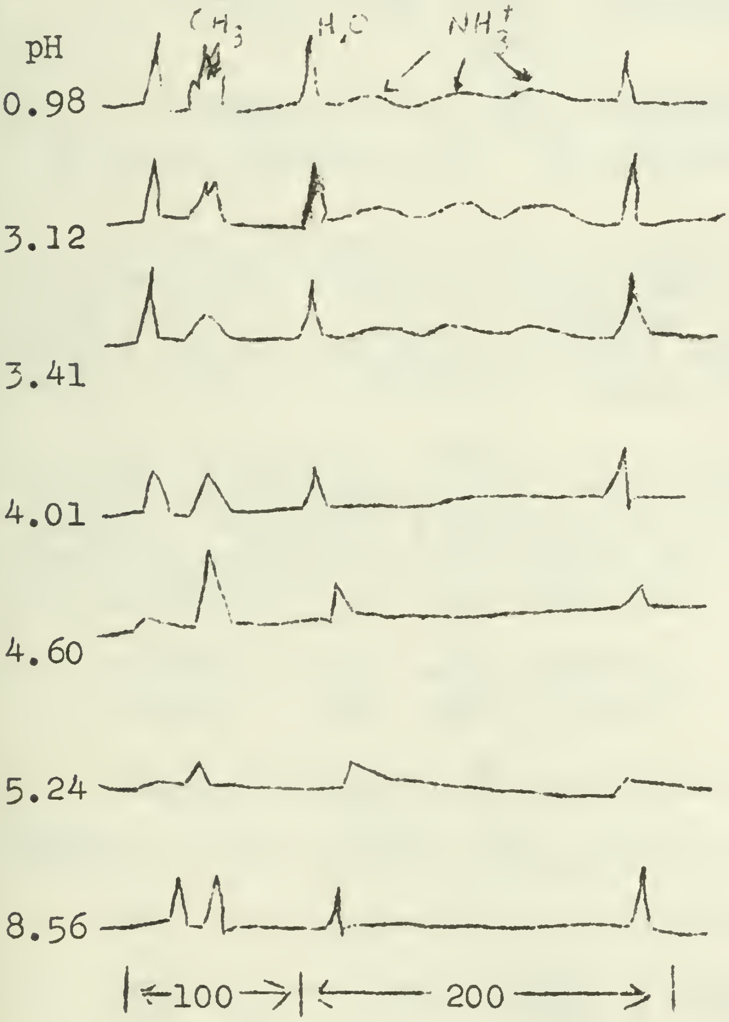


Fig. 3 - NMR spectrum of 4.47M CH_3NH_3Cl as a function of pN. Spectra run at 31.65 Mc/sec. After Meiboom, et al (36)

The spectra are interpreted as follows. The methyl resonance displays a quartet structure due to spin interaction with the NH_3+ protons. The NH_3+ resonance, by a mutual interaction should show quartet splitting. However quadrupole coupling gives an additional triplet structure. Resultant q'pole broadening is severe enough almost to obliterate the quadruplet sub structure. At pH = 0.98, there is no visible indication of exchange. As pH is increased, the components of the CH_3 quartet broaden until they coalesce to a single broad line which upon further increase in pH narrows. The NH_3+ triplet broadens and disappears at higher pH values while shifting slightly. The water signal broadens and narrows again.

On the basis of the gross spectral features, the reactions considered for protolysis of the NH_3+ group were of the types 1,2 and 3.

$$CH_3NH_3^+ + B \xrightarrow[\text{slow}]{k_1} CH_3NH_2 + BH \qquad (1)$$

$$CH_3NH_2 + BH^1 \xrightarrow[\text{fast}]{k_2} CH_3NH_2H^1 + B \qquad (2)$$

$$CH_3NH_2 + B \xrightarrow{k_3} CH_3NHH + B^1 \qquad (3)$$

$B = H_2O,\ CH_3NH_2,\ OH^-$. B^1 indicates replacement of H.

In any mechanism to be considered, CH_3NH_2 is a short lived intermediate, due to its very low concentration under experimental conditions ($< 10^{-6}$ M). Reaction 3 embodies all mechanisms which do not include $CH_3NH_3^+$. Brodski (44) states that (3) could be rapid since it involves an unshared pair on nitrogen.

In this study, rates were deduced from changes in the CH_3 quartet, broadening in the water line, and broadening of the NH_3^+ triplet. Assuming reaction (3) to be negligible compared with (2) (later proved to be the case), the mechanisms for reaction (1) are represented by equations 4-7.

$$CH_3NH_3^+ + OH_2 \xrightarrow{k_4} CH_3NH_2 + HOH_2^+ \qquad (4)$$

$$CH_3NH_3^+ + OH^- \xrightarrow{k_5} CH_3NH_3 + HOH \qquad (5)$$

$$CH_3NH_3^+ + H_2NCH_3 \xrightarrow{k_6} CH_3NH_2 + H_3\overset{+}{N}CH_3 \qquad (6)$$

$$CH_3\overset{+}{N}H_2H + \overset{H}{O}H + HH_2NCH_3 \xrightarrow{k_7} CH_3NH_2H + H\overset{H}{O} + HH_2\overset{+}{N}CH_3 \quad (7)$$

The total rate for $\underline{k}_1$ is given by

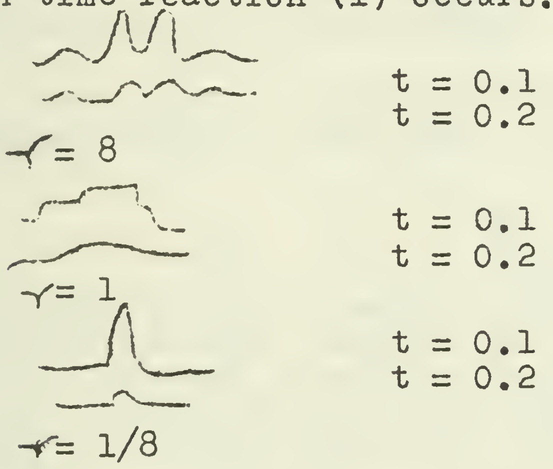
$$\frac{\text{rate}}{[CH_3NH_3^+]} = \underline{k}_4 + \frac{\underline{k}_5\ Kw}{[H^+]} + (\underline{k}_6+\underline{k}_7)K_A\,\frac{[CH_3NH_3^+]}{[H^+]} \qquad (8)$$

Measurements on the CH_3 quadruplet at various pH and $CH_3^+NH_3$ concentration values yielded values for k_4, k_5 and (k_6+k_7). Measurements on broadening of the NH_3+ resonance gave the magnitude of the contribution of reaction (3) to the total protolysis. Measurements of water-line broadening gave values for k_6 and k_7 separately. Preliminary values for k_4, based on the work of Brodski (40), can be estimated. The constant, k_4 should have a value less than 0.02 $sec.^{-1}$ for $CH_3NH_3^+$ (40,45). Thus k_4 was considered negligible. This contention is supported by the sharpness of the CH_3 quadruplet at pH = 0.96. The constant k_5 can be estimated via the Onsager equation. The calculated value for NH_4+ agrees well with Eigen's experimental value (5). The values calculated in this manner for CH_3NH_3+ at 25° and 19° respectively are 3.81 and 1.99 for $10^4 k_5 K_w$.

The values calculated are an order of magnitude greater than observed; so reactions like (6) and (7) are concluded to be important.

Analysis using the CH_3 quadruplet.

The theory of Gutowsky (37,38) was used to calculate line shape as a function of exchange rate of the NH_3^+ protons. In the calculations, k_3 was assumed negligible compared to k_2. These two reactions determine the numbers of protons replaced each time reaction (1) occurs.



$\tau = 2\pi\delta w$, $t = 1/T_2\,\delta w$.

Fig. 4 - Line Shape of CH_3 resonance as function of exchange rate. After Meiboom (36) δw = 1/2 frequency spacing in absence of exchange; T_2 is the transverse relaxation time in the absence of exchange; τ is mean time interval between exchanges on NH_3^+.

Since the change in spin configuration of NH_3^+ protons is a first-order process in $CH_3NH_3^+$, we can use τ to calculate a first order rate constant from (10)

$$\frac{(\text{rate})_1}{[CH_3NH_3+]} = k = \frac{1}{\tau} = \frac{2\delta w}{\tau} \qquad (10)$$

τ is evaluated by comparing observed line shape with the calculated shapes.

Rate Dependence on $[H^+]$

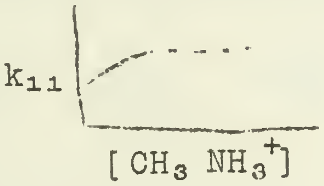
The relationship is inverse. There is a constancy in $\underline{k}[H^+]$, and $\underline{k}_4$ is assumed negligible. To estimate its upper limit, total rate was measured for 4.47M CH_3NH_3+ at $[H^+]=0.108$ M. The upper limit set was 0.02 sec^{-1}.

Rate Dependence on $[CH_3NH_3+]$

Neglecting $\underline{k}_4$ equation (8) is rewritten as:

$$\underline{k}_{11} = \underline{k}[H+] = \underline{k}_5K_W + (\underline{k}_6 + \underline{k}_7)\, K_A[CH_3N^+H_3]. \qquad (11)$$

The plot of $\underline{k}_{11}$ vs. $[CH_3NH_3+]$



At low concentrations (small salt effects) the data are linear. The intercept, $\underline{k}_5K_w$, is close to the origin. The value is of such magnitude compared to the calculated value that it is concluded that $\underline{k}_5$ makes a small contribution to the total protolysis.

Analysis Using the Water Line

Reaction (5) was assumed to be the primary cause of the broadening with contributions from others such as (7).

For cases in which exchange is so slow there is no appreciable overlap, equation (12) can be used

$$\frac{1}{T_2{}^1_1} = \frac{1}{T_2} + \frac{1}{\tau_{H_2O}} \qquad (12)$$

The quantity T_2 is measured directly, T_2 is measured on an unbroadened water sample, and T^1, the mean life of an NH_3+ group before transfer to water, is given by eq. (13). The fraction of protolysis involving direct transfer is given by eq. (14), and $\underline{k}$ is obtained from the CH_3 quadruplet at the same pH and $[CH_3NH_3+]$.

$$\tau^1 = \tau_{H_2O}\ \frac{[CH_3NH_3+]}{2[H_2O]} \qquad (13)$$

$$p = 1/k\tau^1 \qquad (14)$$

At 19°, p was found to be 0.58 and at 25° p was 0.60.

The measured value of p is too large to reconcile with $\underline{k}_5$ representing the only direct mechanism.

Using p = 0.02 for the fraction of protolysis via. $\underline{k}_5$, the following is obtained.

$$\frac{\underline{k}_7}{\underline{k}_6+\underline{k}_7} = 0.58 \text{ in } 4\underline{M}\ CH_3NH_3Cl.$$

Rate Measurements Using the NH_3+ Triplet

There is less accuracy here due to large quadrupclar broadening. As an approximation the superposed quartet substructure was ignored. Equation (15) was used to relate the increase in δ with increasing pH to the decrease in τ^1, the mean life of H on a N of a given spin,

$$\pi(\delta f_2 - \delta f_1) = \frac{1}{T_2^{11}} - \frac{1}{T_1^{11}} \qquad (15)$$

δ = full width at half the maximum height.

$$\frac{1}{T_2^{11}} - \frac{1}{T_1^{11}} = k_{16} \left(\frac{1}{(H+)_2} - \frac{1}{(H+)_1}\right) \qquad (16)$$

$$k_{16} = 3.2 \pm 0.3$$

If, as assumed, reaction (3) is negligible, k_{16} should be a function of k_{11} and p(only). For p = 1, $k_{16} = \frac{k_{11}}{3}$; for p=0 $k_{16} = \frac{2k_{11}}{9}$. For the general case, then:

$$\frac{3k_{16}}{k_{11}} = p + \frac{2}{3}(1 - P) \qquad (17)$$

The results of Meiboom and coworkers are summarized in Table I.

Table I. - Protolysis Kinetics for Substituted Ammonium Ions.

Reference	Compound	k_4	k_5	k_6	k_7
60	NH_4+	$\leq 0.6 \times 10^{-2}$	$\leq 10^{12}$	$(10.6 \pm 1.0) \times 10^8$	$(0.9 \pm 0.1) \times 10^8$
36	$CH_3NH_3^+$	$\leq 0.4 \times 10^{-2}$	$\leq 10^{11}$	2.5×10^8	3.4×10^8
59	$(CH_3)_2NH_2$+	$\leq 0.4 \times 10^{-2}$	$\leq 10^{11}$	0.4×10^8	5.6×10^8
59	$(CH_3)_3NH$+	5.5×10^{-2}	$\leq 10^{11}$	0.0×10^8	3.1×10^8

VI. OTHER QUANTITATIVE STUDIES

Further work by these investigators on H_2O_2 (62), H_2O (66), and N-methyl acetamide (61) will not be discussed due to limitations of time. Further work for NH_4+ in aqueous acid established diffusion control for the reaction corresponding to k_{-4}(67). These workers also obtained infinite dilution values for k_6 and k_7 for $CH_3NH_3^+$(65) and calculated the mean life of the amine-water hydrogen bond in aqueous NH_4+ (64). Activation energies of reactions of NH_4+ and CH_3NH_3+ in water have been calculated (63).

Interesting work in association equilibria has been performed by Hertz (68,73). The technique employed was similar to those previously described. Broadening of ^{79}Br, ^{81}Br, and ^{127}I

resonances, to calculate rate constants for reactions of the type:

$$MeX_{i-1} + X^- \underset{\underline{k}_{2i}}{\overset{\underline{k}_i}{\rightleftharpoons}} MeX_i$$ in aqueous solution.

Me = Zn, Cd, Hg X = Br, I

The species present in solution were Me^{2+}, MeX^+, MeX_2, MeX_3^-, and MeX_4^{2-}. The broadening was studied as a function of excess halide concentration. The ΔC of the free halide concentration was related to $\beta_i = \frac{1}{K_i^*} = \frac{\underline{k}_{11}}{\underline{k}_{21}}$ etc. The results of Hertz are summarized in Table II.

VII. SUMMARY

Limitations of time have necessarily caused this presentation to be very sketcky in nature, and complete discussion of the applications of kinetics studies by NMR in the present literature is impossible. As a consequence, much important and interesting wrk was neglected in the discussion. In as far as is possible, an attempt will now be made to cite some of the more important work, in summary fashion.

A great deal of work has been done on protonation of amides (69, 71, 72). Studies of rotational isomerism and tautomerism still form an important part of the rate studies by NMR (70, 74, 77, 81). NMR studies of exchange phenomena in CH_3CHO-H_2O have been made by Lombarde (82).

In the area of coordination compounds, Gasser and Richards(80) have studied Co nuclear resonance to obtain rate constants for various rate processes. The work of Hertz has been cited (68, 73). Taube and coworkers (75,76) have studied rates of hydration of transition metal ions and complexes by means of the NMR technique. Other work of this type has been done by Pearson (79) and Carrington (78).

Table II - Kinetics of halo complex formation after Hertz

Substance	k_{11}°	k_{12}°	k_{13}°	k_{14}°	k_{21}	k_{22}	k_{23}	k_{24}
$CdBr_2$	1.4×10^9	1.4×10^8	1.4×10^7	1.2×10^7	1.0×10^7	1.4×10^6	7.0×10^6	6.0×10^6
$HgBr_2$	----	----	$>4.7\times10^9<6.4\times10^9$	$>4.6\times10^8<1.4\times10^9$	----	----	2.5×10^7	2.5×10^7
$ZnBr_2$	5×10^5	5×10^5	5×10^5	8×10^7	$5\times10^5\leq k_{21}\sim k_{22}\sim k_{23}\leq 7\times10^6$			2.0×10^7
CdI_2	5×10^9	----	----	$>1.5\times10^8<7\times10^8$	2×10^7	---	------	1.5×10^7
ZnI_2	5×10^5	5×10^5	5×10^5	7×10^6	3×10^8	$5\times10^4<k_{22}\sim k_{23}<5\times10^5$		3×10^7

REFERENCES

1. M. Eigen and J. S. Johnson, Ann. REv. Phys. Chem., 2, 307 (1960).
2. R. P. Bell, Quart. Revs., 13, 169 (1959).
3. M. Eigen, Disc. Faraday Soc., 17, 194 (1954).
4. M. Eigen, Suomen Kem., 34A, 25 (1961).
5. M. Eigen and J. Schön, Z. Elektrochem., 59, 483 (1955).
6. G. Porter, Proc. Roy Inst, London, 38, 375 (1960).
7. D. Button and R. M. Cole, J. Phys. Chem., 65, 1302 (1961).
8. S. Meiboom, Z. Elektrochem., 64, 50 (1960).
9. R. Bershon, Ann. Rev. Phys. Chem., 2, 369 (1960).
10. E. R. Andrew, Nuclear Magnetic Resonance, Cambridge Univ. Press, N. Y., 1955.
11. J. T. Arnold, Phys. Rev., 102, 136 (1956).
12. S. Brownstein, Chem. REvs., 58, 463 (1959).
13. S. Alexander, J. Chem. Phys., 34, 106 (1961).
14. S. Castellano and J. S. Waugh, ibid, 34, 295 (1961).
15. M. Fexman, ibid., 35, 679 (1961).
16. J. E. Wertz, Chem. Revs., 55, 829-955 (1955). (627 references).
17. R. E. Richards, Quart. Revs., 10, 450 (1956).
18. J. A. Smith, ibid, 7, 279 (1953).
19. J. D. Roberts, Nuclear Magnetic Resonance, McGraw-Hill, N.Y., 1959.
20. L. M. Jackman, Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, N.Y., 1959.
21. J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, N.Y., 1959,
22. J. D. Roberts, An Introduction to Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance, W. A. Benjamin Inc, N.Y., 1961.
23. H. S. Gutowsky and A. Saika, J. Chem. Phys., 21, 1688 (1954).
24. H. S. Gutowsky and C. H. Holm, ibid, 25, 1228 (1957).
25. I. Weinberg and J. R. Zimmerman, ibid., 23, 748 (1955).
26. W. D. Phillips, Ann. N.Y. Acad. Sci., 70, 817 (1958).
27. W. D. Phillips, J. Chem. Phys., 23, 1363 (1955).
28. J. N. Shoolery, Varian Associates Tech. Bull., 2, 7 (1957).
29. G. Fraenkel and C. Niemann, Proc. Nat. Acad. Sci., 44, 688(1958).
30. P. M. Nair and J. D. Roberts, J. Am. Chem. Soc., 79 , 4565(1957).
31. A. T. Bottem and J. D. Roberts, ibid., 78 , 5126 (1956).
32. A. T. Bottem and J. D. Roberts, ibid, 80, 5203 (1958).
33. R. A. Ogg, Jr., J. Chem. Phys., 22, 560 (1954).
34. H. S. Gutowsky and S. Fujiwara, ibid., 22, 1782 (1954).
35. R. A. Ogg, Jr, Disc. Faraday Soc., 17 , 215 (1954).
36. E. Grinwald, A. Lowenstein, and S. Meiboom, J. Chem. Phys., 27, 630 (1957).
37. H. S. Gutowsky, D. W. McCall, and C. C. Slichter, ibid., 21, 279 (1953).
38. H. S. Gutowsky and A. Saika, ibid., 21, 1688 (1953).
39. H. M. McConnell, ibid., 28, 430 (1958).
40. A. I. Brodske and L. V. Sulima, Doklady Akad. Nauk. S.S.S.R., 74, 513 (1950).
41. L. Kaplan and K. E. Welzbach, J. Am. Chem. Soc., 76, 4243 (1954).
42. G. C. Swain, J. T. McKnight, M.M. Labes, and V.P. Kreiter, ibid., 76, 4243 (1954).
43. R. G. Pearson and R. L. Dillon, ibid., 75, 2439 (1953).
44. A. I. Brodski, Zhur. Obschei. Khim., 24, 413 (1954); C.A. 48, 8621 g, (1954).
45. N. F. Hall and M. R. Sprinkle, J. Am. Chem. Soc., 54, 3478 (1932).

46. A. Hantzsch and K. S. Caldwell, Z. physik. Chem., 58, 575 (1907).
47. E. Huckel, Z. Elektrochem., 34, 546 (1928).
48. J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933).
49. A. E. Stearn and H. Eyring, ibid., 5, 113 (1937).
50. S. Glasstone, K. J. Laidler, and H. Eyring, Theory of Rate Processe McGraw/Hill, N.Y., 1941.
51. S. Zaromb, J. Chem. Phys., 25, 350 (1956).
52. J. Hudes and R. W. Dodson, J. Am. Chem. Soc., 78, 911 (1956).
53. G. H. Hagges, J. B. Hasted and T. J. Buchanan, J. Chem. Phys., 20, 1452 (1952).
54. F. H. Westheimer and M. W. Shookoff, J. Am. Chem. Soc., 61, 555 (1939).
55. E. Rabenowetch, Trans. Faraday Soc., 33, 1225 (1937).
56. P. Walden, Z. Elektrochem., 26, 72 (1920).
57. L. P. Hammett, Physical Organic Chemistry, McGraw-Hill, N.Y., 1940.
58. J. E. Leffler, Science, 117, 3039 (1953).
59. A. Lowenstein and S. Meiboom, J. Chem. Phys., 27, 1067 (1957).
60. S. Meiboom, A. Lowenstein, and S. Alexander, ibid., 29, 969(1958).
61. A. Berger, A. Lowenstein, and S. Meiboom, J. Am. Chem. Soc., 81, 62 (1959).
62. M. Anbar, A. Lowenstein, and S. Meiboom, ibid., 80, 2630(1958).
63. T. M. Connor and A. Lowenstein, ibid., 83, 560 (1961).
64. M. T. Emerson, E. Grinwald, M. L. Kaplan, and R. A. Krumhout, ibid., 82, 6307 (1960).
65. E. Gruinwald, P. J. Karabatsos, R. A. Krumhout, and E. L. Purlee, J. Chem. Phys., 33, 556 (1960).
66. S. Meiboom, ibid., 34, 375 (1961).
67. M. T. Emerson, E. Gruinwald and R. A. Krumh out, ibid., 33, 547 (1960).
68. H. G. Hertz, Z. Elektrochem., 65, 36 (1961).
69. A. Saika, J. Am. Chem. Soc., 82, 3540 (1960).
70. G. Claeson, G. M. Androes, and M. J. Calven, ibid., 82, 4428(1960).
71. C. Franconi and G. Fraenkel, ibid., 82, 4478 (1960).
72. M. Lakeda and E. O. Strzskal, ibid., 82, 25 (1960).
73. H. G. Hertz, Z. Elektrochem., 64, 53 (1960).
74. J. P. Kokko, J. H. Goldstein, and L. Mandell, J. Am. Chem. Soc., 83, 2909 (1961).
75. J. A. Jackson, J. F. Lemons, and H. Taube, J. Chem. Phys., 32, 553 (1960).
76. J. P. Hunt and H. Taube, ibid., 19, 602 (1951).
77. L. W. Reeves and K. O. Stromme, Trans. Faraday Soc., 57, 390 (1961).
78. A. Carrengton, F. Dravineks, and M. R. Symons, Mol. Phys., 3, 174 (1960).
79. R. G. Pearson, J. Palmer, A. L. Allred, and M. M. Anderson, Z. Elektrochem., 64, 110 (1960).
80. R. P. H. Gasser and R. E. Richards, Mol. Phys, 3, 163 (1960).
81. R. J. Abraham and H. J. Bernstein, Can. J. Chem., 39, 39(1961).
82. E. Lombardi and P. B. Sogo, J. Chem. Phys., 32, 635 (1960).
83. S. Kinastkowski and Z. Oajak, Compt. rend., 252, 1774 (1961).

STABILIZATION OF VALENCE STATES OF TRANSITION METALS

R. C. Burrows January 13, 1962

I. INTRODUCTION

The existence of compounds in which some elements, notably the transition metals, exhibit unusual valences, has intrigued chemists for many years. Two manifestations of this interest are the accumulation of a large number of examples of such compounds and the continuing reviews on the subject (1-9). It is the purpose of this seminar to consider some of the means by which unusual valence states have been produced and to point out some progress which has been made in correlating the results.

Although the terms "valence" and "stability" have had much misuse and ought to be precisely defined, any definition seems to be deficient. "Valence" is used here in the sense of oxidation number, i.e., the apparent charge on the metal atom when the other atoms in the molecule or ion are assigned their conventional oxidation numbers. This is recognized as a purely formal definition since there is usually little relationship between valence and the charge actually carried by the atom. The "normal" valence state of a metal is arbitrarily taken to be that which the metal displays in acidic aqueous solutions at room temperature (7). All other states are relatively high or low. A valence state is considered to be "stabilized" in a given species if that species is thermodynamically more resistant to oxidation or reduction than the corresponding aquated ion is. It is often the case, however, that this relative stability cannot be properly assessed because the valence state considered does not exist under the reference conditions. Consequently, the mere preparation of such a valence state is frequently taken as evidence that it has been stabilized. This criterion is clearly different from the thermodynamic one.

II. THERMODYNAMIC CONSIDERATIONS (1,10,11)

The standard oxidation potential, $\underline{E}°$, for the half-reaction,

$$M^{m+}_{(aq)} = M^{n+}_{(aq)} + (n-m)\underline{e}^- ,$$

where $\underline{n} > \underline{m} \geq o$ and the species are in their standard states, is a measure of the difference in free energy between these two states relative to the difference in free energy between the oxidized and reduced states of the reference half-reaction,

$$1/2\ H_2 = H^+ + \underline{e}^- .$$

Where the concentration (activities) are not unity, ideally the electrode potential is obtained from the Nernst equation,

$$\underline{E} = \underline{E}^{\circ} - \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M^{m+}]}$$

Then any influence which affects the concentration of one of the species more than the other will alter the value of E and stabilize one state over the other.

In the case where m=o, i.e., where the pure metal is being oxidized, the qualitative effect of any reagent which combines with the oxidized state is clearly to increase the oxidation potential. Because M° does not usually enter into chemical combination, it provides a reference state. Formation of insoluble materials, weak electrolytes, or complex ions is the common cause of such stabilization.

When one considers the case where $m \neq o$, the effects are not quite so obvious. If the addition of a certain ligand results in an increase in the oxidation potential, it reduces the concentration of M^{n+} more than it reduces the concentration of M^{m+}. The higher valence state in the complex is thus stabilized relative to the lower valence state in the complex, but the ligand may very well stabilize both states relative to the corresponding aquo cations.

Consideration of simple thermodynamics thus emphasizes that stabilization of valence is a very general phenomenon since any effect which alters the relative concentrations of the reactants stabilizes either the high or the low state. A quantitative measure of the degree of stabilization can be obtained from the appropriate electrode potentials. This approach has limited usefulness, however, because the potential data, where they are available, necessarily refer to reversible reactions and to fixed temperatures. The unusual experimental conditions under which many high- and low-valent species must be prepared and maintained usually preclude measurement of the oxidation potentials. Another important objection is that although one state may be thermodynamically favored over another state, the reaction may proceed at an impractically slow rate or by such a mechanism that a still more stable intermediate state is reached (9).

In order to obtain an understanding of the fundamentals involved in those cases for which suitable potentials cannot be obtained, empirical correlations have been sought among the examples of extreme valency. Particular interest has centered on the bonding properties of the ligands which tend to stabilize one state over another. Although many factors are undoubtedly involved in valence stabilization, enthalpy differences due to bonding effects are likely to be most important in the extreme cases.

III. HIGH VALENCE STATES

High valence states of simple cations in aqueous solutions are limited by the tendency of water to be oxidized,

$$4M^{n+} + 2(n-m)H_2O \rightarrow 4M^{m+} + 4(n-m)H^+ + (n-m)O_2$$

One might expect from this reaction that an acid medium would stabilize M^{n+}. In practice, however, the valence states of major interest are too high for this method to be effective. Advantage is usually taken of the acidic nature of these highly charged cations by preparing them in an alkaline medium. The Lewis salt which is formed under these conditions retains the high valence of the metal but protects it from the reducing environment. A great many oxo complexes are produced in this manner.

Oxide and fluoride, the most electronegative simple anions, appear most frequently as ligands for the transition metals in their high valence states. Because of their strong tendency both to gain electrons and to hold them, oxygen and fluorine are often used in the dual capacity of oxidizing agent and stabilizing ligand. That oxide is generally more effective than fluoride indicates, however, there is not a simple relationship between the resistance of a ligand to oxidation and its ability to stabilize oxidizing ions.

The use of periodic acid and orthotelluric acid to stabilize the trivalent coinage metals (13,14) has recently been extended to include manganese(IV)and nickel IV)(15). Although these acids are fairly strong oxidizing agents, the highest metal valences can be reached only with an auxiliary oxidant such as persulfate or hypochlorite. The subsequent formation of the complex periodates and orthotellurates then stabilizes the oxidized ions.

A number of examples of high valence-state stabilization of particular ions have been reported in which the donor atom of the ligand is nitrogen, phosphorus, arsenic, or sulfur, frequently in a chelate ring. The cyanide ion also appears in many complex ions in which the metal exhibits a higher valence than normal. A few of these compounds are shown in Table I.

III. LOW VALENCE STATES

One of the factors limiting the existence of uncombined metals in their low valences in aqueous solutions is the oxidizing action of water,

$$2M^{m+} + 2(n-m)\ H_2O \rightarrow 2M^{n+} + 2(n-m)OH^- + (n-m)\ H_2$$

Reducing the concentration of the hydrogen ion should enhance the stability of the low valence state in this system. Use of a more basic medium, such as liquid ammonia, should have a similar effect. In practice low-valence compounds are frequently prepared in a strongly reducing, alkaline environment.

Except for those in the metal carbonyls, low valence states usually are formed by reduction of cationic species rather than directly from the element. This reaction may be effected by alkali metals in liquid ammonia, but frequently less vigorous conditions are sufficient. For example, the ligand itself may act as the reducing agent,

$$Pd(CNR)_2I_2 + RNC + 2KOH \rightarrow Pd(CNR)_2 + RNCO + 2KI + H_2O \quad (32),$$

the metal salt may disproportionate,

$$3Cr(C_2H_3O_2)_2 + 18\phi NC \rightarrow Cr(CN\phi)_6 + 2[Cr(CN\phi)_6](C_2H_3O_2)_3 \quad (33),$$

or a mild reducing agent may be intentionally added,

$$V(dipy)_3{}^{2+} + Zn \rightarrow V(dipy)_3 + Zn^{2+} \quad (34).$$

Some of the ligands which have been used in the preparation of low valence states are shown in Table II. Although the complexes with ammonia and ethylenediamine are very easily destroyed, many of the carbonyls, nitrosyls, and cyclopentadienyls are quite resistant to oxidation. The cyanide ion, the isocyanides, the phosphines, the arsines, dipyridyl, and 1,10-phenanthroline usually give compounds of intermediate stability.

V. BONDING CONSIDERATIONS

Consideration of these compounds in which extreme valence states exist has led to the conclusion that there are features of some ligands which seem to promote either high or low valences independent of the particular metal involved (7,9,35).

The ligands which stabilize high valence states most strongly, vis., O^{2-}, F^- and OH^-, are those which possess lone-pair electrons that can interact with the non-bonding $\underline{t}_{2g}$ orbitals of the transition metal. Since the bonding molecular orbitals which result from this interaction are occupied by the ligand electrons, only the higher energy antibonding orbitals are available to the electrons of the metal, which are consequently more easily removed by oxidizing agents. Reduction of the high valence states is also made more difficult since these antibonding orbitals are less attractive to outside electrons.

Conversely, in order for a ligand to stabilize low valence states, it must have available unfilled $\underline{d}_\pi$ or $\underline{p}_\pi$ orbitals which are at such energy levels that they can interact appreciably with the $\underline{t}_{2g}$ orbitals of the metal. The bonding molecular orbitals which are now formed can be occupied by $\underline{d}$ electrons of the metal and by electrons supplied by reducing agent, whereas the antibonding orbitals remain unoccupied.

The ligands which possess both lone-pair electrons and empty π-bonding orbitals may act either as donors or acceptors, depending on the reaction conditions and the demands of the metal atom. In general they are not especially effective in stabilizing extreme valence states. There are ligands which seem to stabilize both high and low states. They are usually the strongly coordinating chelating agents, such as o-phenylene bis(dimethylarsine), dipyridyl, and 1,10-phenanthroline. High-valence stabilization with these ligands seems to be associated with the electronic configuration of the specific metal involved.

The phenomenon of valence-state stabilization by formation of insoluble products, by valence inductivity (36), and by isomorphous replacement (37) clearly lies outside these considerations and has to be explained in terms of energies of the solid state.

Table I. Ligands Which Stabilize High Valence States

Ligand	Examples
oxide	Highest known valences for all metals
fluoride	V(V),Cu(IV),Fe(III),Ru(V),etc
hydroxide	Mn(III),Fe(III),Co(III),etc.
cyanide	Mo(V),W(V),Co(III),Fe(III),et
periodic, telluric acids(13-15)	Cu(III),Ag(III),Au(III),Ni(IV Mn(IV)
ethylenedibiguanide(16)	Ag(III)
dipyridyl	Ag(II)
triethylphosphine(18)	Ni(III)
o-aminothiophenol (19)	Ni(IV)
o-phenylenebis(dimethylarsine)(20-23)	Ni(III),Ni(IV),Tc(V),Re(V)

Table II. Ligands Which Stabilize Low Valence States

Ligand	Example	
carbon monoxide	$V(CO)_6$	(24)
nitric oxide	$Fe(CO)_2\ (NO)_2$	
aromatic hydrocarbons	$Cr(C_6H_6)_2$	
olefinic hydrocarbons	$[Pt.C_2H_4\cdot Cl_3]^{1-}$	
acetylenic hydrocarbons	$Pt\cdot C_2H_2\cdot(\varnothing_3P)_2$	(25)
cyanide	$[Ni(CN)_4]^{4-}$	(26)
isocyanides	$[Mn(CNR)_6]^{1+}$	(27)
phosphine derivatives	$Pt.diph_2$*	(28)
arsine derivatives	$Pt.\varnothing_3P.diar$**	(25)
heterocyclic amines	$Ti(dipy)_3$	(29)
ammonia	$Ir(NH_3)_5$	(30)
amines	$Pt\ en_2$	(31)

* diph = ethylenebis(diphenylphosphine)
** diar = o-phenylenebis(dimethylarsine)

Bibliography

1. M. J. Copley, L. S. Foster, and J. C. Bailar, Jr., Chem. Revs., 30, 227 (1942).
2. J. Kleinberg, Unfamiliar Oxidation States and Their Stabilization, University of Kansas Press, 1951.
3. J. Kleinberg, J. Chem. Education, 27, 32(1950); ibid., 29, 324 (1952); ibid., 33, 73 (1956).
4. B. E. Douglas, J. Chem. Education, 29, 119 (1952).
5. W. Klemm, Angew. Chem., 66, 468 (1954).
6. R. Scholder, Angew. Chem., 66, 461 (1954).
7. J. Chatt, J. Inorg. Nucl. Chem., 8, 515 (1958).
8. W. Klemm, J. Inorg. Nucl. Chem., 8, 532 (1958).
9. G. W. Watt, J. Electrochem. Soc., 108, 423 (1961).
10. T. Moeller, Inorganic Chemistry, John Wiley and Sons, Inc., New York, 1952, p. 300.
11. H. A. Laitinen, Chemical Analysis, McGraw-Hill Book Co., Inc., New York, 1960, p. 286.
12. H. J. Emeléus and J. S. Anderson, Modern Aspects of Inorganic Chemistry, D. Van Nostrand Co., Inc., New York 3rd Ed. 1960, p.198.
13. L. Malatesta, Gazz. chim. ital., 71, 467, 580 (1941).
14. M. W. Lister, Can. J. Chem., 31, 638 (1953).
15. M. W. Lister, Can. J. Chem., 39, 2330 (1961).
16. P. Rây, Nature, 151, 643 (1943).
17. G. T. Morgan and F. H. Burstall, J. Chem. Soc., 1930, 2594.
18. K. A. Jensen and B. Nygaard, Acta Chem. Scand., 3, 474(1949).
19. W. Hieber and R. Bruck, Naturwissenschaften, 36, 312 (1949).
20. R. S. Nyholm, J. Chem. Soc., 1950, 2061.
21. R. S. Nyholm, J. Chem. Soc., 1951, 2602.
22. J. E. Fergusson and R. S. Nyholm, Chem. and Ind., 1960, 347.
23. J. E. Fergusson and R. S. Nyholm, Chem. and Ind., 1958, 1555.
24. R. Ercoli, F. Calderazzo, and A. Alberola, J. Am. Chem. Soc., 82, 2966 (1960).
25. J. Chatt, G. A. Rowe, and A. A. Williams, Proc. Chem. Soc., 1957, 208.
26. J. W. Eastes and W. M. Burgess, J. Am. Chem. Soc., 64, 1187(1942).
27. L. Malatesta, "Isocyanide Complexes of Metals", Progress in Inorganic Chemistry, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, Vol. 1, 1959, p. 283.
28. J. Chatt, Nature, 191, 1191 (1961).
29. S. Herzog and R. Taube, Z. anorg. u. allgem. Chem., 306, 159 (1960).
30. G. W. Watt and P. I. Mayfield, J. Am. Chem. Soc., 75, 6178 (1953).
31. G. W. Watt, R. E. McCarley, and J. W. Dawes, J. Am. Chem. Soc., 79, 5163 (1957).
32. L. Malatesta, J. Chem. Soc., 1955, 3924.
33. L. Malatesta and A. Sacco, Ann. Chem., 43, 622 (1953).
34. S. Herzog, Naturwissenschaften, 43, 35 (1956).
35. L. E. Orgel, An Introduction to Transition-Metal Chemistry, John Wiley and Sons, Inc., New York, 1960, p. 132.
36. P. Selwood, J. Am. Chem. Soc., 70, 883 (1948).
37. B. Mohai, Vesz premi Vegyipari Egyetem Közlemenyei, 2, 185 (1958); through C.A., 55, 3237g (1961).
38. J. E. Huheey, Inorganic Seminars, University of Illinois, Nov. 3, 1958.

SEXACOVALENT COORDINATION COMPOUNDS CONTAINING SIX DIFFERENT MONODENTATE LIGANDS

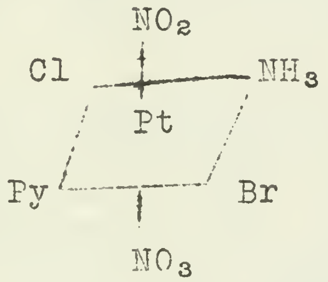
Thomas A. Donovan February 20, 1962

I. INTRODUCTION

The number of stereoisomers associated with any sexacovalent coordination compound becomes extremely large as the degree of complexity of the molecule increases. Thus, a compound of the type [Mabcdef] may exist in thirty different forms (fifteen sets of geometrically isomeric mirror image pairs). It is understandable, therefore, that very little information is available regarding compounds more complex than [M(AA)a_2b_2]. This seminar will provide a discussion of some recent work involving the synthesis and characterization of sexacovalent coordination compounds containing six different monodentate ligands, i.e., compounds of the type [Mabcdef].

II. BROMO-CHLORO-NITRO-NITRATO-AMMINE-PYRIDINE-PLATINUM(IV)

Gel'man and Essen(1) have reported the synthesis of [Pt(py)(NH_3)(NO_3)(NO_2)ClBr], I.



(I)

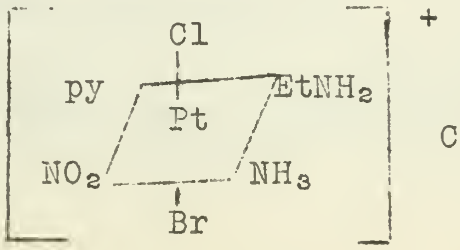
The properties of this compound are outlined in Table II.

III. BROMO-CHLORO-IODO-NITRO-AMMINE-PYRIDINE-PLATINUM(IV)

The compound [Pt(py)(NH_3)(NO_2)IClBr] may exist in any one of the fifteen geometric forms outlined in Table I. Five of these isomers, f, i, j, k, l, have been prepared and characterized by Essen and his coworkers (2,3,4). The properties of these compounds are outlined in Table II.

III. CATIONIC COMPLEXES

Essen and Alekseeva (5) have recently reported the synthesis of bromo-chloro-nitro-ammine-pyridine-ethylamine-platinum(IV) chloride, II.

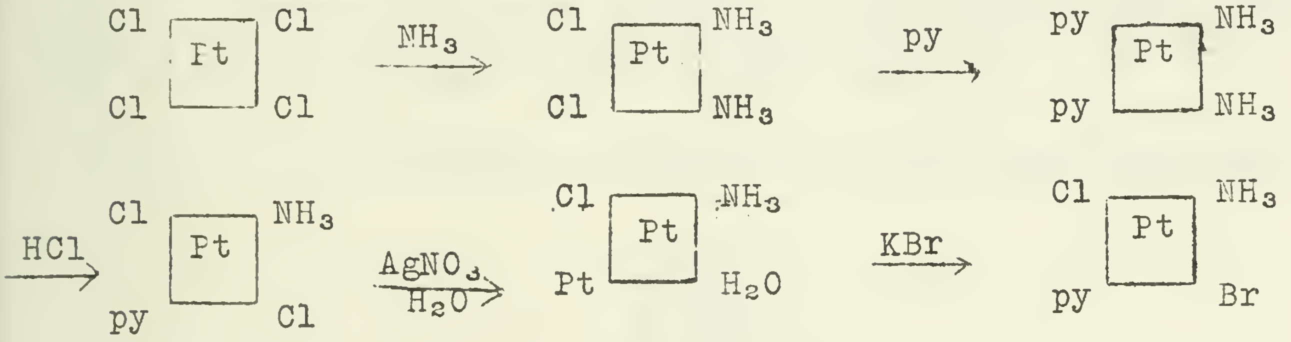


Cl$^-$ (II)

The corresponding complex containing methylamine was similarly prepared. Bromide salts of these cations were also isolated. The properties of these compounds are outlined in Table II.

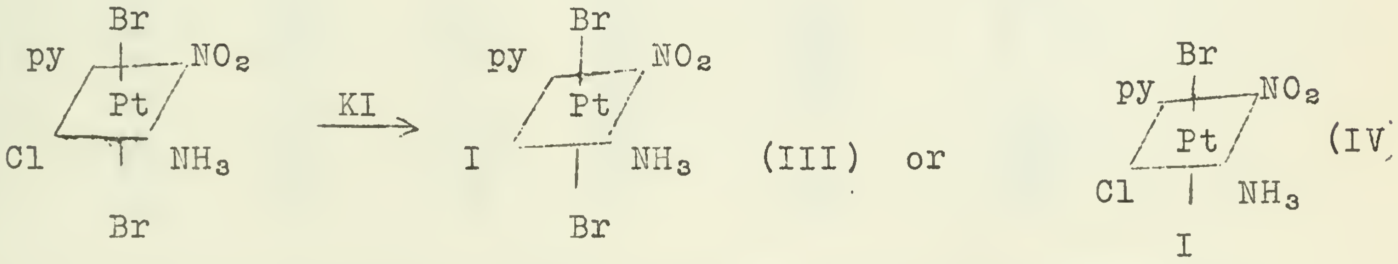
V. EXPERIMENTAL AND THEORETICAL CONSIDERATIONS

The synthesis of I was based to a large degree upon a careful application of the "trans-effect" rule first elucidated by Chernyaev(6). Thus, the first four steps of the reaction sequence, i.e.,



are so arranged as to place the halogens in trans positions. The final step, oxidation with nitric acid, give the trans-nitro-nitrato-platinum(IV) compound directly.

Proceeding directly from I to isomer *f* of [Pt(py)(NH₃)(NO₂)IClBr merely involves the direct replacement of a nitrate ion by an iodide ion and the reaction would appear to proceed as a result of the trans-effect of the nitro group. Further work, however, has led Essen and his coworkers to the conclusion that the nitro group, which has a considerable trans-effect in divalent platinum compounds, has only an insiginificant effect in platinum(IV) compounds. Thus, the reaction



should, if the trans-effect rule is valid for platinum(IV) compounds, give III as a product. In fact, however, IV is the resultant complex(2).

VI. AREAS OPEN TO FURTHER INVESTIGATION

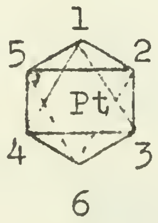
The compounds discussed in this seminar are apparently the first known examples of their type. Hence, the opportunities for further investigation are numerous. From a synthetic standpoint,

we might well expect the synthesis of further isomers of bromo-chloro-iodo-nitro-ammine-pyridine-platinum(IV) as well as numerous cationic and anionic species.

The resolution of any of these compounds would be a particularly interesting task with perhaps the greatest hope for success lying with the cationic or anionc species.

The theoretical chemist should find suitable material to tax his capabilities in an analysis of the spectra and optical rotatory powers of these species as a function of the nature and relative locations of the various ligands.

TABLE I: THE GEOMETRIC ISOMERS OF [PtBrClI(NO_2)(NH_3)(py)]



Isomer	Position of Ligand 1	2	3	4	5	6
a	Br	Cl	I	NO_2	NH_3	py
b	Br	Cl	NO_2	I	NH_3	py
c	Br	Cl	NO_2	NH_3	I	py
d	Br	py	I	NO_2	NH_3	Cl
e	Br	py	NO_2	I	NH_3	Cl
f*	Br	py	NO_2	NH_3	I	Cl
g	Br	py	I	Cl	NH_3	NO_2
h	Br	py	Cl	I	NH_3	NO_2
i*	Br	py	Cl	NH_3	I	NO_2
j*	Br	py	NO_2	Cl	NH_3	I
k*	Br	py	Cl	NO_2	NH_3	I
l*	Br	py	Cl	NH_3	NO_2	I
m	Br	py	NO_2	Cl	I	NH_3
n	Br	py	Cl	NO_2	I	NH_3
o	Br	py	Cl	I	NO_2	NH_3

*Known

VII. SUMMARY

The synthesis and characterization of a number of sexa-covalent platinum complexes containing six different monodentate ligands has been discussed. Some opportunities for further research in this area have been indicated.

TABLE II: PHYSICAL PROPERTIES OF SOME SEXACOVALENT COORDINATION COMPOUNDS CONTAINING SIX DIFFERENT MONODENTATE LIGANDS

Compound	Appearance	m.p.	Solubility
$[PtBrCl(NO_2)(NO_3)(NH_3)(py)$	bright yellow	200°	0.003g./100g. H_2O at 100°
$[PtBrClI(NO_2)(NH_3)(py)]$ -f	dark lustrous needles	223°d.	0.013g./100g. H_2O at 25°
" -i	dark shiny needles	---	———
" -j	dark brown powder	200°d.	———
" -k	brown crystals	232°	0.079g./100g. H_2O at 25°
" -l	dark brown needles	207°	0.059g./100g. H_2O at 25°
$[PtBrCl(NO_2)(NH_3)(CH_3NH_2)(py)]Cl$	orange	210°	0.023g./100g. H_2O at 25°
$[PtBrCl(NO_2)(NH_3)(CH_3NH_2)(py)]Br$	orange	250°d.	0.008g./100g. H_2O at 25°
$[PtBrCl(NO_2)(NH_3)(EtNH_2)(py)]Cl$	yellow	220°	0.013g./100g.H_2O at 25°
$[PtBrCl(NO_2)(NH_3)(EtNH_2)(py)]Br$	orange	250°d.	0.007g./100g. H_2O at 25°

VIII. BIBLIOGRAPHY

1. A. D. Gel'man and L. N. Essen: Doklady Akad. Nauk S.S.S.R., 75, 693-5 (1950); C.A., 45, 3279i (1951).
2. L. N. Essen and A. D. Gel'man: Proc. Acad. Sci. U.S.S.R. Chem. Sect., 108, 309-12 (1956).
3. L. N. Essen and A. D. Gel'man: Zhur. Neorg. Khim., 1, 2475-87 (1956); C.A., 51, 12732c(1957); 55, 21954i (1961).
4. L. N. Essen, F. A. Zakharova, and A. D. Gel man: Zhur. Neorg. Khim., 3, 2654-61 (1958); C.A., 55, 21955d, 24353b(1961).
5. L. N. Essen and D. P. Alekseeva: Zhur. Neorg. Khim., 6, 857-62 (1961); C.A., 55, 24364i(1961).
6. I. I. Chernyaev: Ann. Inst. Plat. U.S.S.R., 4, 243(1926).

THEORY OF METAL-AMMONIA SOLUTIONS

R. L. Middaugh February 27, 1962

INTRODUCTION

Alkali and alkaline earth metals dissolve in liquid ammonia, amines, and certain ethers to give deeply colored blue solutions. Electrolysis of solutions of alkali amides gives the same blue solutions. Concentrated solutions of alkali metals in liquid ammonia have a bronze-like metallic color. The metals are dissolved without chemical reaction and can be recovered pure by evaporation of the solvent. There are several recent reviews on the subject of solutions of metals in ammonia, amines, and other solvents(1,2,3).

The apparent molecular weight of sodium in liquid ammonia is 23 at 0.1 N, slightly higher in more concentrated solution, slightly lower in more dilute solutions (4).

The electrical behavior of such solutions at infinite dilution is remarkable. The conductance is characteristic of a nearly completely dissociated 1:1 electrolyte, with the anionic conductance being about seven times the cationic conductance (4). At a concentration of about 0.05 N the equivalent conductance passes through a minimum value about half that of its value at infinite dilution and then increases rapidly to a value characteristic of metallic conductance (5,6). Any theory attempting to describe metal-ammonia solutions must include dissociation of an electron from the atom with the formation of discreet one-electron anionic centers and independent cations. In more concentrated solutions, these bound electrons become "free" and move in conductance bands similar to those of metals.

Another striking property of these solutions is their magnetic susceptibility behavior. As the concentration approaches infinite dilution, the molar susceptibility approaches that of Avogadro's number of unpaired spins; in concentrated solutions, it is on the order of the bulk susceptibilities of the pure metals (7,8,9).

Metal-ammonia solutions are less dense than either of their pure components(10). There is an increase in volume of about 40 cm.^{3}/gm-atom of sodium more than the sum of the volumes of the pure components.

TWO MODELS FOR DILUTE SOLUTIONS

The cavity model, developed by Ogg, considers two equilibria in solution:

$$M \rightleftharpoons M^+ + e^-$$

$$2e^- \rightleftharpoons e_2^- \ .$$

The metal atom dissociates into a solvated metal cation and an electron in a cavity in the solvent. Two electrons can be in the same cavity with their spins opposed, giving a diamagnetic species (11,12,13).

The expanded metal model, proposed by Becker, Lindquist, and Alder (BLA), considers four species (I-IV) in equilibrium in dilute solution:

$$M^+ + e^- \rightleftharpoons M$$

$$M \rightleftharpoons \frac{1}{2} M_2$$

I, the monomer M, or expanded metal atom, consisting of the metal cation solvated probably by six ammonia molecules, with the electron circulating about the hydrogens of the coordinated ammonia molecules, II and III, the solvated cation and electron from the dissociation of the monomer, and IV, a dimer consisting of two monomers held together largely by exchange forces. The dimer is a pseudo-hydrogen molecule, with a pair of electrons circulating about all the hydrogens of the two monomer centers(14). This model was suggested by the formation of solid ammoniates of some metals in liquid ammonia, such as $Ca(NH_3)_6$, which display metallic properties.

CORRELATION OF THE MODELS WITH EXPERIMENTAL DATA

Neither model as presented fits all the observed data. Refinements of the cavity model have been made by Lipscomb(15), Kaplan and Kittel(16), and Jortner(17); Douthit and Dye(18) have proposed a model retaining some features of both models. Details and refinements of these models will be discussed in the light of experimental data.

Electrical Properties

Ogg observed photoconductivity in dilute (10^{-5} N) solutions(11). Treating the electron in the cavity as a particle in a box and using the energy of radiation needed to produce photoconductivity, he calculated the size of the cavity. Lipscomb modified this treatment and calculated a cavity radius of 4.8 Å, in better agreement with the volume increase which predicts a cavity of 3.2Å radius (15). Another group was unable to reproduce Ogg s observation of photoconductivity (19). The mechanism of conductance is thought to be quantum-mechanical tunneling of the electron in a cavity to another site, leaving behind the polarization energy required to form the cavity and giving a negative heat of transport(2 Jortner has calculated the energy necessary to orient the dipoles of four ammonia molecules to form a cavity or potential well to hold the electron (17).

Equilibrium constants K_1 and K_2 for the ion-pairing and dimerization equilibria of the BLA model can be calculated from conductances. Good agreement is found with values obtained from ion transference numbers and from activity coefficients determined from transference numbers and emf s of concentration cells(21,22,23). For solutions of sodium in ammonia to which sodium chloride has been added, conductances, which agree well with experimental values are calculated, using the Onsager-Kim theory for mixed electrolytes, and the following equilibria:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + e^- \rightleftharpoons M$$

$$M \rightleftharpoons \frac{1}{2} M_2 \qquad (24).$$

Magnetic Susceptibility

In addition to the magnetic properties stated above, it is of interest that the susceptibility curves for sodium and potassium solutions are identical at the boiling point of ammonia, but at higher temperatures, the susceptibilities of sodium solutions are greater than those of potassium solutions of the same concentration (9). This is more easily explained by the BLA model than by the cavity model (14,21).

Paramagnetic Resonance

The outstanding featuee of the single paramagnetic resonance line is its very narrow width of 0.03 gauss(16,9). The extreme narrowness has been attributed to hyperfine interaction with nitrogen nuclei of ammonia molecules, and to motional narrowing due to tunneling (16,9,25,26,27). In more concentrated solutions, spin-orbit interactions account for relaxation times(27). All measurements are for concentrations at which there is appreciable ion pairing or monomer formation. Hyperfine coupling with hydrogen nuclei has been ruled out by the finding that relaxation times are the same in NH_3 and ND_3, and by NMR evidence which will be discussed below (27).

Nuclear Magnetic Resonance

A large Knight shift for the ^{14}N resonance and a small shift for the ^{23}Na resonance are observed in solutions of sodium in liquid ammonia, but none is observed for the ^{1}H resonance(28). Pitzer suggested that the wave function describing the interaction of the electron with an ammonia molecule could have 3s character at the nitrogen atom and 2p character with a node at the hydrogen nucleus (29). Blumberg and Das have calculated expected Knight shifts for ^{14}N, ^{23}Na, and ^{1}H resonances by two different methods, using a multipole expansion of the potential (MEP) and a distributed charge development of the potential (DCP) to calculate wave functions for the electron on a BLA monomer (30). Good agreement with observed Knight shifts was derived for ^{14}N by the MEP method and for ^{23}Na by the DCP method. Both methods predict a proton Knight shift less than the experimental uncertainty of the measurements.

Volume Expansion

In a recent study, the molar volume expansion ΔV, was plotted as a function of concentration where

$$\Delta V = \frac{(\text{volume of solution}) - (\text{volume of constituents})}{\text{gm-atoms Na}} \quad (31).$$

A minimum in the curve was found at the same concentration at which the conductance minimum occurs, suggesting that the molecules and atoms are not of the BLA expanded type.

Visible and Infrared Spectra

Solutions of metals in ammonia and amines have one or both of two absorption bands, depending on the metal, the solvent and the temperature (32,33,34). They are at approximately 6800 $cm.^{-1}$ in the infrared region and 15,000 $cm.^{-1}$ in the visible region. Ogg attributed these to the ejection of electrons from e^- and $e_2^=$ cavities, respectively, to conduction bands (12). Becker, Lindquist, and Alder explained the infrared absorption by an angular momentum transition of the bound electron on the monomer(14). Fowles, McGregor, and Symons found that solutions with only visible absorption are diamagnetic, but that solutions with only the infrared or with both absorptions are paramagnetic (34). Thus the infrared absorption is due to a one-electron center and the visible, to a two-electron center. Energy calculations based on the refined cavity model indicate the infrared absorption is due to an energy transition within the cavity, not the ejection of the electron from the cavity (34,35). In support of the cavity theory, Clark, Horsfield, and Symons have found the high oscillator strength of the infrared band cannot be explained by the concentration of BLA monomer predicted on the basis of the equilibrium constants calculated earlier (25). However, they were able to detect a new band at 12,500 $cm.^{-1}$ by the addition of excess sodium iodide to a sodium solution, and they tentatively assigned this absorption to the BLA monomer. The infrared absorption is assigned to the solvated electron, and the visible band to a dimer.

Douthit and Dye have summarized the spectral behavior of sodium and potassium solutions (18). The line shape of the infrared absorption is the same for Na and K, and is independent of concentration up to 0.01 N. The band shifts to lower energies with increasing temperature, in agreement with the effect expected for the Jortner cavity model as a result of the temperature dependence of dielectric constant and cavity size. Sodium obeys Beer's Law, but K displays a negative deviation, attributed to a greater tendency to form monomers or dimers. As the concentration increases, the peak shifts to lower energies. There is a good correlation between the peak shift and the concentration of ion pairs calculated from conductance data. Because of the close correspondence of the visible absorption frequency to a strong transition in gaseous Na_2 at 15,000 $cm.^{-1}$, it is proposed that the dimer is a solvated Na_2 molecule rather than a BLA expanded molecule.

The composite model of Douthit and Dye is as follows:

(1) $Na^+(am) + e^-(am) \rightleftharpoons Na^+e^-$ ion pair

(2) Na^+e^- ion pair $\rightleftharpoons M$

(3) $M \rightleftharpoons \frac{1}{2}\, Na_2\ (am)$.

(1) In very dilute solutions the main species present are solvated metal cations, electrons in solvent cavities resulting from orientation and polarization of solvent dipoles by the electrons themselves, and ion pairs.
(2) As the concentration increases, some of the electrons escape from their cavities and are bound in BLA monomers.
(3) When a small concentration of monomers is present, they dimerize to form a solvated Na_2 molecule.

X-Ray Scattering

Small-angle X-ray scattering by lithium and sodium solutions of intermediate concentrations is characteristic of centers of about 15 Å diameter, near that predicted for the BLA model. Other centers larger than 3 Å in diameter were not observed (36).

CONCLUSION

The structure of dilute metal-ammonia solutions is still not known with certainty. No model is consistent with current interpretations of all the available data. Metal-ammonia solutions remain of interest because they are systems in which the transition from electrolytic to metallic properties can be studied.

BIBLIOGRAPHY

1. W. L. Jolly, Progr. Inorg. Chem., 1, 235 (1959).
2. M. C. R. Symons, Quart. Revs., 13, 99 (1959).
3. E. C. Evers, J. Chem. Ed., 38, 590 (1961).
4. C. A. Kraus , J. Franklin Inst., 212, 537 (1931).
5. C. A. Kraus, J. Chem. Ed., 30, 83 (1953).
6. C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc., 43, 2529 (1921).
7. E. Huster, Ann. Physik, 33, 477 (1938).
8. S. Freed and N. Sugarman, J. Chem. Phys., 11, 354 (1943).
9. C. A. Hutchison, Jr., and R. C. Pastor, ibid., 21, 1959(1953).
10. C. A. Kraus, E. S. Carney, and W. C. Johnson, J. Am. Chem. Soc., 49, 2206 (1927).
11. R. A. Ogg, Jr., ibid., 68, 155 (1946).
12. R. A. Ogg, Jr., J. Chem. Phys., 14, 114 (1946).
13. R. A. Ogg, Jr., ibid., 14, 295 (1946).
14. E. Becker, R. H. Lindquist, and B. J. Alder, ibid., 25, 971 (1956).
15. W. N. Lipscomb, ibid., 21, 52 (1953).
16. J. Kaplan and C. Kittel, ibid., 21, 1429 (1953).
17. J. Jortner, ibid., 27, 823 (1957).
18. R. C. Douthit and J. L. Dye, J. Am. Chem. Soc., 82, 4472 (1960).
19. R. L. Potter, R. G. Shores, and J. L. Dye, J. Chem. Phys., 35, 1907 (1961).
20. G. Lepoutre and J. F. Dewald, J. Am. Chem. Soc., 78, 2953, 2956 (1956).
21. E. C. Evers and P. W. Frank, Jr., J. Chem. Phys., 30, 61(1959).
22. J. L. Dye, R. F. Sankuer, and G. E. Smith, J. Am. Chem. Soc., 82, 4797 (1960).
23. J. L. Dye, G. E. Smith, and R. F. Sankuer, ibid., 82, 4803 (1960).
24. D. S. Berns, G. Lepoutre, and E. A. Bockelman, J. Chem. Phys., 35, 1820 (1961).

25. H. C. Clark, A. Horsfield, and M. C. R. Symons, J. Chem. Soc., 1959, 2478.
26. V. L. Pollak, J. Chem. Phys., 34, 864 (1961).
27. D. E. O Reilly, ibid., 35, 1856 (1961).
28. H. M. McConnell and C. H. Holm, ibid., 26, 1517 (1957).
29. K. S. Pitzer, ibid., 29, 453 (1958).
30. W. E. Blumberg and T. P. Das, ibid., 30, 251 (1959).
31. E. C. Evers and A. M. Filbert, J. Am. Chem. Soc., 83, 3337 (1961).
32. H. Blades and J. W. Hodgins, Can. J. Chem., 33, 411 (1955).
33. G. Hohlstein and U. Wannagat, Z. anorg. u. allgem. Chem., 288, 193 (1956).
34. G. W. A. Fowles, W. R. McGregor, and M. C. R. Symons, J. Chem. Soc., 1957, 3329.
35. J. Jortner, J. Chem. Phys., 30, 839 (1959).
36. P. W. Schmidt, ibid., 27, 23 (1957).

FUSED SALTS

William J. Randall March 6, 1962

INTRODUCTION

Reviews discussing the chemistry[1] of "fused salts", "melts", "molten salts", or "ionic melts" emphasize the versatility[2] of these "solvents" for problems in coordination[3], synthetic[4], electro[5,6], and reactor[7] chemistry. The application of spectrophotometric methods[8] to fused salts is growing. Investigations of physical properties and structures[9] of fused salt solutions rely heavily on diffraction and conduction techniques. Fused salts are applicable to difficult problems in the study of acid--base reactions, which defy investigations that are confined to liquid solvent systems.[10] The literature of fused salt chemistry is expanding rapidly as seen in a recent bibliography[11] covering both domestic and international journals from 1900 to 1960 which included some two thousand references, most of them dated later than 1950.

PHYSICAL PROPERTIES AND STRUCTURE[12,13]

Even though extended crystal lattices are not possible in molten systems, the properties of such systems do suggest some short-range ion-core and ion-coulomb interactions.[14] These data are gained by x-ray and neutron diffraction[15,16], densitometry[17], heat and entropy of fusion[15,18], cryoscopy[5], viscosity[5], and conductance[4,5,19,20,21,22,23] measurements.

X-ray studies definitely indicate some type of collapsed structure. This supports the lacunar nature of molten halides in that the holes are cracks fluctuating between clusters of ions[16]. In alkali halides the number of ions retained around a given central ion in a statistical fashion varies inversely with the atomic number. Fourier analyses for x-ray spectra of molten fluorides show that the series of first interatomic distances of the crystal (short-range order) is conserved in the liquid state, that the coordination number of the crystal species is smaller than in the ionic lattice, and that the coordination number decreases rapidly as the temperature increases, explaining the corresponding decrease in density.[24]

Spectrometric methods have been used to describe some properties of high temperature systems.[1,7,25,26,27,28] An adaptation of a Cary Model 14 spectrophotometer to these systems has been described.[28,29] Applications to several halide systems (for example: $ZnCl_2$[27]; $VCl_{2,3,4,}$ and $_5$[28]; $PbCl_2$, AgCl; and $Ni(ClO_4)_2$ in fused perchlorates[32,33]) indicate an increase in the frequency of the absorption maximum as the temperature in increased.

Melt densities are necessary to correlate conductivity, viscosity, and diffusivity measurements. The coefficients of thermal expansion for mercuric halides are from two to three times greater than those for alkali halides and alkaline-earth halides, but are less than those for typical non-polar liquids; implying that the cohesive forces in mercury halide melts are

weaker than the coulombic forces predominating in simple ionic melts, but are greater than the London dispersion forces acting in purely non-polar liquids. Therefore, mercuric halides are polar solvents.[15]

INTERACTIONS IN IONIC MOLTEN SALTS

Theoretical interpretations of ionic melts deal particularly with the difference between an ordered solid and a disordered liquid.[34,35,36,37,38,39] Considering anions and cations randomly distributed among themselves (disregarding valency, but with anions surrounded by cations and vice versa) is useful thermodynamically[40] for predicting the behavior of ideal melts. Deviations from ideality result partially from the heat of mixing and entropy of mixing or other phenomena.

The activities of molten solutions[41] are analogous to those in aqueous systems, particularly of ions in melts containing large oxy-anions such as carbonate and nitrate. In contrast to this interpretation is one which proposes that deviations from ideality, particularly for systems which are measured electrometrically, constitute evidence for complex-ion formation.[45] A theory of simple ionic melts, which predicts that short-range ion-core interactions drive ions into close-packed lattice-like arrangements, contains the Debye limiting law as a special case for extremely high temperatures, or for very low ion-number densities.[44] Activities of reciprocal salt melts are determined by deviations from ideality as a function of concentration.[45,46] Several investigators have found that the negative deviations from ideality of the activities of salts the type MCl_2 decreased in alkali chloride solutions as the size of the solvent cation decreased.[33,43,47]

Analytical investigations[3] use the methods of cryoscopy,[48] solubility[49,50] electromotive force,[51,52,53] and kinetics[54,55] to evaluate the ion-associations or coordination equilibria of solute species in molten systems. Equilibrium constants vary linearly in mixed reciprocal salt solutions with respect to mole fraction of salt.[56] Table I summarizes the formation constant data of a number of metal halide species. An alternate explanation is based on the "quasi-lattice" theory, which does not allow any structural inference of the complex-ion type. Using this concept, Blander has been able to explain activity data quantitatively without a particular complex-ion species and feels that no structural conclusions should be inferred from purely thermodynamic data.[53]

Activation energy[57] plays a major role in determining reaction rates at low and moderate temperatures, but at high temperatures the activation energy term becomes less important in the Arrhenius equation. If no factors other than molecular collisions and a constant activation energy were involved, reaction rates would not vary greatly among bimolecular reactions at 2000°K. and above. In condensed phases, the rate of reaction is controlled by the rate of diffusion.

F.R. Duke and coworkers[10,58,58,60] have studied the rate of the reactions of pyrosulfate and dichromate with nitrate using a eutectic mixture of potassium nitrate and sodium nitrate as their solvent. The resultspermitted evaluation of the equilibrium constants for the reactions

$$M_2O_7^{=} \quad + \quad NO_3^{-} \quad \overset{K_M}{\rightleftarrows} \quad MO_4^{=} \quad + \quad NO_2^{+} \ (M=S,Cr) \qquad (1)$$

and the rate constant for the reaction

$$NO_2^{+} + NO_3^{-} \xrightarrow{k} 2NO_2 \quad + \quad 1/2\ O_2 \qquad (2)$$

The equilibrium constants, K_M, are separable from the rate constant, k, because the rate of equation (2) was found to be independent of M.

The decomposition of bromate, catalysed by metal ions[54,55] gave rate expressions that were first order in bromate ion and first order in metal ion. The order of the bromide ion in the rate expression was not a simple integer. The mechanism which fits the data best, as measured at equivalent concentrations of metal ion and bromide ion which were greater than the concentration of bromate ion, involves a series of complex metal-bromide-bromate equilibria. This work clearifies some of the results obtained in a similar studies using water as a solvent medium (reviewed in ref. 60).

Cryoscopic investigations reveal some interesting compounds. Their structures, however, must be elucidated by diffraction studies on quenched samples, or solid precipitates. Phase diagrams of alkali fluorides with cerium fluoride[61], plutonium fluoride[62], and thorium fluoride[63] show several similar characteristics which are attributed mainly to radius ratio phenomena.[63]

The bismuth-bismuth halide systems (chloride, bromide, and iodide) have been investigated by spectrophotometric, electromotive force, and vapor pressure studies.[65,66,67,68,69] The solubility of bismuth in bimuth chloride is increased by the addition of the acid aluminum trichloride, whereas the solubility of bismuth in bismuth triiodide is decreased upon the addition of aluminum triiodide. Several other systems have been studied by J. D. Corbett and his coworkers.[71,72,73,74] Bredig also has published data for the cerium-cerium tribromide and potassium-potassium halide systems.[75,76,77,78] Other results and interpretations of conductivities show the need for more data [75,79,80,81,82,83] and cannot be explained by simple compound formation.

Fused salt media have been used to prepare compounds that have not been synthesized in ordinary solvent systems.[4] Some examples are the tetrafluorohalates of cesium, rubidium, and potassium;[84] cesium trichloronickelate(II) and cesium pentachloronickelate(II);[85] potassium tetracyanonickelate(0), potassium tetracyanonickelate(I), and potassium tetracyanonickelate(II);[86] and sodium hexatitanate (using solid potassium hexatitanate and moltem sodium chloride).[87] The nitration of propane was accomplished in molten sodium nitrate- potassium nitrate eutectic at 372°C by allowing propyl iodide to react

with gaseous nitric acid.[88]

The application of fused salts to industrial and reactor technologies[89,90,91,92] is an application of their physical properties rather than their solvent or chemical properties.

CONCLUSION

In summary it should be emphasized that the chemistry of fused salts offers versatile methods for the inorganic chemist who is interested in higher temperarure systems. If the increased interest during the last decade is indicative, the next decade should see a rapid expansion in all phases of this very interesting area of chemistry.

Table I: Formation Constants, $K_n = \frac{MX_n}{MX_{n-1}}$, for Complex Species

Complex	Solvent[a]	T, °K.	K_n	Method	Ref.
$CdCl_2$	A	579	$K_1.K_2=320$	Freezing point	48
$CdCl_4^{=}$	A	579	$K_3.K_4=0.25$	Freezing point	48
$CdCl^+$	B	523	20	Solubility	48
$CdBr_2$	A	579	$K_1.K_2=3000$	Freezing point	48
$CdBr^+$	B	529	108	E M F	51
$CdBr^+$	B	547	95	E M F	51
$CdBr^+$	B	571	75	E M F	51
$CdBr_2$	B	529	51	E M F	51
$CdBr_2$	B	547	47	E M F	51
$CdBr_3$	B	529	10	E M F	51
$CdBr_3^-$	B	547	2.5	E M F	51
$PbCl_2$	A	579	$K_1.K_2=30$	Freezing point	48
$PbCl^+$	B	523	18	Solubility	53
$PbCl^+$	B	573	11	Solubility	53
$PbCl_2$	B	523	2	Solubility	53
$PbCl_2$	B	573	3	Solubility	53
$PbBr^+$	B	523	18	Solubility	53
$PbBr^+$	B	548	13	Solubility	53
$PbBr^+$	B	528	18	E M F	51
$PbBr_2$	B	573	2	Solubility	53
$PbBr_2$	B	579	6	E M F	51
$ZnCl_2$	A	579	$K_1.K_2=400$	Freezing point	48
$ZnCl_4^{=}$	A	579	$K_3.K_4=0.2$	Freezing point	48
$ZnBr^+$	B	523	250	Kinetics	55
$ZnBrO_3^+$	B	523	1.3	Kinetics	54
AgCl	A	647	17.7	E M F	52
$AgCl_2^-$	A	647	6.78	E M F	52
AgCl	C	647	28.0	E M F	52
$AgCl_2^-$	C	647	8.93	E M F	52
AgCl	D	647	44.9	E M F	53
$AgCl_2^-$	D	647	18.0	E M F	53
AgCl	D	709	28.5	E M F	53
$AgCl_2^-$	D	709	12.5	E M F	53
AgBr	B	649	93.5	E M F	50
AbBr	B	687	72.3	E M F	50
$AgBr_2^-$	B	647	33.3	E M F	50
$AgBr_2^-$	B	687	18.4	E M F	50

[a] A is $NaNO_3$; B is a eutectic mixture of KNO_3 and $NaNO_3$; C is 47% KNO_3 and 53% $NaNO_3$; D is KNO_3.

BIBLIOGRAPHY

1. D. M. Gruen, S. Fried, F. Graf, and R. L. McBeth, *Proc. U.N. Intern. Conf. Peaceful uses of Atomic Energy*, 2nd Geneva, 28, 112 (1958).
2. R. W. Laity, J. Chem., Education 39, 56(1962).
3. F. R. Duke, "Complex Ions in Fused Salts," *Advances in the Chemistry of Coordination Compounds,* Proceedings of the Sixth International Conference on Coordination Chemistry, S. Kirschner, Ed., p. 227, The MacMillan Company, New York (1961).
4. H. Bloom, Revs. Pure Applied Chem. (Australia), 9, 139(1959).
5. H. J. Janz, C. Solomons, and H. J. Gardner, Chem. Revs., 58, 461 (1958).
6. R. W. Laity, J. Chem. Education, 39, 67 (1962).
7. H. G. MacPherson, *Abstracts of Papers 139th Meeting,* American Chemical Society, 6F (1961).
8. D. M. Gruen, *Abstracts of Papers 139th Meeting*, American Chemical Society, 3F (1961).
9. G. J. Janz, J. Chem. Education, 39, 59 (1962).
10. F. R. Duke, J. Chem. Education, 39, 57 (1962).
11. G. J. Janz, *Bibliography of Molten Salts,* Rensselaer Polytechnic Institute Technical Publication, Troy, New York (1960).
12. G. Watelle-Marion, J. chim. phys., 56, 302 (1959).
13. Anon., Angew. Chem., 73, 739 (1961).
14. J. G. Kirkwood, "The Structure of Liquids," *Science in Progress*, vol. III, Yale University Press, New Haven (1942).
15. A. G. McLellan, Proc. Roy. Soc. (London), A210, 509(1951).
16. G. Zarzycki, J. phys., radium, 19, 13A (1958).
17. H. A. Levy, P. A. Agron, M. A. Breding, and M. D. Danford, Ann. N. Y. Acad. Sci., 79, 762 (1960).
18. A. R. Ubbelhohde, "Melting Mechanisms of Ionic Crystals," *The Structure of Electrolytic Solutions,* John Wiley and Sons, New York (1959); A. R. Ubbelhohde, Proc. Chem. Soc., 332(1960).
19. W. Biltz and A. Klemm, Z. anorg. u. allgem. Chem., 152, 267(1926).
20. H. Bloom and J. O M. Bockris, *Modern Aspects of Electrochemistry*, vol. II, New York (1959).
21. E. R. van Artsdalen and I. S. Yaffe, J. Phys. Chem., 59, 118 (1955).
22. J. O M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards, Proc. Roy. Soc. (London), A255, 558 (1960).
23. G. J. Janz and M. R. Lorenz, J. Electrochem. Soc., 108, 1052 (1961).
24. G. Zarzycki, J. phys. radium, 18, 65A(1957); C.A., 52, 14269e (1958).
25. W. Bues, Z. anorg. u. allgem. Chem., 279, 104 (1955).
26. I. Greenberg and L. H. Hallgren, J. Chem. Phys., 33, 900(1960).
27. J. D. MacKenzie and W. K. Murphy, J. Chem. Phys., 33,366(1960).
28. D. M. Gruen and R. L. McBeth, J. Phys. Chem., 66, 57 (1962).
29. J. R. Morrly and A. W. Marton, Rev. of Sci. Instruments, 32, 799 (1961).
30. K. Sakai, Nippon Kagaku Zasshi, 78, 1108 (1957); C.A., 52, 6924d (1958).
31. K. Sakai, Nippon Kagaku Zasshi, 78, 1257 (1957); C.A. 52, 5151e (1958).
32. D. M. Gruen, J. Inorg. Nuclear Chem., 4, 74 (1957).
33. D. M. Gruen and R. L. McBeth, J. Phys. Chem., 63, 393(1959).
34. J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc.(London) A169, 317 (1938).

35. J. Frenkel, *Kinetic Theory of Liquids*, Clarenden Press, Oxford (1946).
36. J. G. Kirkwood, J. Chem. Phys., 3, 300 (1935).
37. J. G. Kirkwood, J. Chem. Phys., 7, 19 (1939).
38. J. G. Kirkwood, J. Chem. Phys., 14, 80(1946).
39. H. Eyring, Proc. Nat. Acad. Sci. U.S., 44, 683(1958).
40. M. Temkin, Acta Physiochim. URSS(Eng), 20, 411 (1945).
41. G. N. Lewis and M. Randall, Thermodynamics, Revised by K.S.Pitzer and L. Brewer, 2nd Ed., p. 565, McGraw-Hill Book Company, Inc. New York (1961).
42. M. Blander and J. Bronstein, Ann. N. Y. Acad. Sci., 79, 838 (1960).
43. O. J. Kleppa, J. Phys. Chem., 64, 1937 (1960).
44. F. H. Stillinger, J. G. Kirkwood, and P. Wojtowicz, J. Chem. Phys., 32, 1937 (1960).
45. H. Bloom and B. J. Welch, Trans. Faraday Soc., 57, 61 (1961).
46. K. Grojotheim, C. Krohra, and J. M. Taguri, Trans. Faraday Soc., 57, 1949 (1961).
47. J. L. Dahl and F. R. Duke, J. Phys. Chem., 62, 1498(1958).
48. E. R. van Artsdalen J. Phys. Chem., 60, 172 (1956).
49. F. R. Duke and M. L. Iverson, J. Phys. Chem., 62, 417(1958).
50. F. R. Duke and M. L. Iverson, J. Phys. Chem., 65, 1627(1961).
51. F. R. Duke and H. M. Garfinkel, J. Phys. Chem., 65, 461(1961).
52. F. R. Duke and H. M. Garfinkel, J. Phys. Chem., 65, 461 (1961).
53. M. Blander, F. F. Blankenship, and R. F. Newton, J. Phys. Chem., 63, 1259 (1959).
54. F. R. Duke and W. W. Lawrence, J. Am. Chem. Soc., 83, 1269(1961).
55. F. R. Duke and W. W. Lawrence, J. Am. Chem. Soc., 83, 1271(1961).
56. H. M. Garfinkel and F. R. Duke, J. Phys. Chem., 65, 1629(1961).
57. E. R. van Artsdalen, "Kinetic Considerations about Fused Salts", *Proc. Symposium High Temperature*, p. 133, Berkeley (1956); C.A., 52, 9731f (1958).
58. F. R. Duke and M. L. Iverson, J. Am. Chem. Soc., 80, 5061(1958).
59. F. R. Duke and S. Yamamoto, J. Am. Chem. Soc., 81, 6378(1959).
60. R. L. Carlson, "Mechanisms of Oxy-Anion Reactions in Aqueous Solution", *Inorganic Seminars*, p. 120, University of Illinois (January 16, 1962).
61. C. J. Barton, J. D. Redman, and R. A. Strehlow, J. Inorg. Nuclear Chem., 20, 45 (1961).
62. C. J. Barton and R. A. Strehlow, J. Inorg. Nuclear Chem., 18, 143 (1961).
63. R. E. Thoma and T. S. Carlton, J. Inorg. Nuclear Chem., 17, 88 (1961).
64. P. H. L. Waller, J. Kleinberg, and E. Griswold, J. Inorg. Nuclear Chem., 19, 223 (1961).
65. S. J. Yosum, L. D. Ranson, R. A. Sallack, and L. E. Topol, J. Phys. Chem., 66, 28 (1962).
66. C. R. Boston and G. P. Smith, Ann. Prog. Rept., Metallurgy Division, Oak Ridge National Laboratory ORNL--2988, 9(July,1960).
67. L. E. Topol, S. J. Yosum, and R. A. Osteryoung, J. Phys. Chem., 65, 1511 (1961).
68. D. Cubicciotti and F. J. Keneshea, Jr., J. Phys. Chem., 62, 999 (1958).
69. D. Cubicciotti and F. F. Keneshea, Jr., J. Phys. Chem., 63, 295 (1959).
70. J. D. Corbett and R. K. McMullan, J. Am. Chem. Soc., 78, 2906 (1956).
71. J. D. Corbett, L. F. Druding, and C. B. Lindahl, J. Inorg. Nucl, Chem., 17, 176 (1961).

72. J. D. Corbett, W. J. Burkanrd, and L. F. Druding, J. Am. Chem. Soc., 83, 76 (1961).
73. L. F. Druding and J. D. Corbett, J. Am. Chem. Soc., 83, 2462 (1961).
74. L. F. Druding and J. D. Corbett, J. Am. Chem. Soc., 81, 5512 (1959).
75. H. R. Bronstein, A. S. Dworkin, and M. A. Bredig, J. Phys. Chem., 66, 44 (1962).
76. H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc., 80, 2077 (1958).
77. H. R. Bronstein and M. A. Bredig, J. Phys. Chem., 65, 1220(1961).
78. J. W. Johnson and M. A. Bredig, J. Phys. Chem., 62, 604(1958).
79. G. W. Mellors and S. Senderoff, J. Phys. Chem., 64, 294(1960).
80. S. Senderoff and G. W. Mellor, J. Electrochem. Soc., 105, 224 (1958).
81. G. W. Mellors and S. Senderoff, J. Phys. Chem., 63 , 1111(1959).
82. D. Cubicciotti, J. Am. Chem. Soc., 4119 (1949).
83. M. A. Bredig, Abstracts of Papers 139th Meeting, American Chemical Society, 5F (1961).
84. L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, J. Am. Chem. Soc., 83, 2955 (1961).
85. E. Iberson, R. Gut, and D. M. Gruen, J. Phys. Chem., 66, 65 (1962).
86. S. vonWinbrush, E. Griswold, and J. Kleinberg, J. Am. Chem. Soc., 83, 3197 (1961).
87. A. L. Plumley and W. C. Orr, J. Am. Chem. Soc., 83, 1289(1961).
88. D. C. Coldiron, L. F. Albright, and L. G. Alexander, Ind. Eng. Chem., 50, 991 (1958).
89. E. I. Gurovich, J. Applied Chem. U.S.S.R., 33, 2064 (1960).
90. Metallhütte Mark A.G. (Wilhelm Dantzenberg, Inventor), German patent 895, 059 (October 29, 1953); C.A. 52, 6133i (1958).
91. E. R. Marshall and L. A. Monson, U. S. patent 2,845,341 (July 29, 1958; C.A., 52, 18157b (1958).
92. T. L. Roach and D. M. Himmelblau, J. Inorg. Nuclear Chem., 17, 373 (1961).

SELECTED TOPICS OF ALKYLIDENE PHOSPHORANE CHEMISTRY

Gerald R. Feistel March 13, 1962

INTRODUCTION

Tri-phenyl phosphine methylene, or methylene triphenylphosphorane, was first prepared by Staudinger and Hauser(13) in 1921. They used it in reactions with organic compounds containing a carbonyl functional group. Wittig enlarged the scope of the reaction to make it a general method for the replacement of oxygen in carbonyl functional groups by a =CRR' group. The reaction is illustrated below.

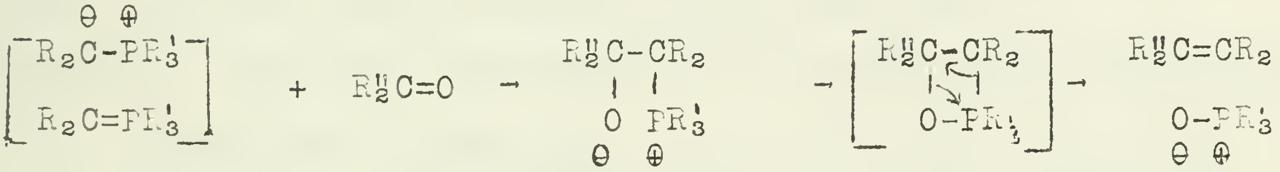
$$RR'CO + (C_6H_5)_3P{=}CR''R''' \rightarrow RR'C{=}CR''R''' + (C_6H_5)_3P{=}O$$

The electronic structure of methylene triphenylphosphorane is usually represented as the resonance hybrid

$$(C_6H_5)_3P{=}CH_2 \longleftrightarrow (C_6H_5)_3\overset{\oplus\ominus}{P\ddot{C}}H_2$$

In terms of the contributing resonance structures, it might be expected that compounds of this type are polar and therefore act as nucleophiles in reactions. This has been found to be true. In fact, they also act as Lewis bases toward certain reagents.

A mechanism which has been proposed for the Wittig reaction is given below.



Although this mechanisms has not been proven, it seems reasonable. On the basis of this mechanism it seems possible that methylene triphenylphosphorane might react with organometallic halides to give a new class of compounds.

Some of the reactions of alkylidene phosphoranes and their analogs with Group IIB, IIIA, IVA, and VA compounds will be discussed. Some coordination chemistry of the products will also be mentioned and extensions thereof emphasized.

The Wittig reaction itself has been reviewed recently(12) and, therefore, will not be discussed in detail in this seminar.

PREPARATION OF ALKYLIDENE PHOSPHORANES

An alkylidene phosphorane can be prepared by treatment of the quaternary phosphonium halide with phenyl lithium in ether. This method works with a wide variety of phosphonium salts, and therefore the reactions mentioned later using these phosphoranes are presumably very general, although they have been demonstrated for only the simple analogs. The general reaction sequence is

$$R_3P + R'R''CHX \rightarrow (R_3PCHR'R'')^{+} X^{-}$$

$$(R_3PCHR'R'')^{+} X^{-} + C_6H_5Li \rightarrow R_3P{=}CR'R'' + LiX + C_6H_6$$

It has also been found that certain alkylidene phosphoranes can be prepared by the reaction of the tertiary phosphine with a carbene. This may be capable of extention to a more general reactions. One example is given below (10,11).

$$CH_2Cl_2 + C_4H_9Li \rightarrow :CHCl + LiCl + C_4H_{10}$$

$$:CHCl + (C_6H_5)P \rightarrow (C_6H_5)_3P{=}CHCl$$

The alkylidene phosphoranes are not isolated but are used directly for the subsequent reaction. The solutions are yellow, which is characteristic of alkylidene phosphoranes. This serves as a useful guide for their formation and disappearance in reactions. Care must be taken in these syntheses to exclude oxygen and water, for the alkylidene phosphoranes are easily oxidized and hydrolyzed.

Methylene triphenylarsenane, and methylene triphenylstibane can be made from phenyllithium and the -onium salt in a manner similar to the preparation of methylene triphenylphosphorane (4). However, the corresponding bismuth compound has not been synthesized because it was not possible to form an -onium salt of bismuth. Perhaps it can be synthesized by the second procedure using a carbene, but this does not seem to have been tried.

REACTIONS OF ALKYLIDENE PHOSPHORANES WITH ORGANOMETALLIC COMPOUNDS

A. Displacement Reactions.

An example of a displacement reaction is the reaction of methylene triphenylphosphorane with trimethylsiliconbromide.(1,5,6,9)

$$(C_6H_5)_3P{=}CH_2 + (CH_3)_3SiBr \rightarrow [(C_6H_5)_3\overset{\oplus}{P}CH_2Si(CH_3)_3]\ Br^{\ominus}$$

This type of reaction is typical and may be carried out also with mercuric halides, organogermanium, organotin, organoantimony, organophosphorus, and organosilicon halides. In some cases, both monohalo and dihalo compounds have been used, although some complications do arise. Only seldom can the compound be isolated as the simple halide salt pictured in the equation above. They are usually recovered pure only as the Reinekate, bromomercurate, or tetraphenylborate. A rather unusual bromomercurate complex is formed, as well as a salt of a methylbromo tin complex anion.

B. Acid-Base Adducts.

Methylene triphenyl phosphorane reacts with BF_3 to give an acid-base adduct as follows:

$$(C_6H_5)_3P{=}CH_2 + BF_3 \rightarrow (C_6H_5)_3\overset{\oplus}{P}CH_2\overset{\ominus}{B}F_3$$

Other boron compounds, e.g., BCl_3, $(BH_3)_2$, $B_{10}H_{14}$, and alkyl- or aryl-substituted boranes, also give this reaction (2,3,8).

The halo compounds, $(C_6H_5)\overset{\oplus}{P}CH_2\overset{\ominus}{B}X_3$, react with Grignard reagents to yield substituents on the boron atom. The mechanism of this reaction is in doubt but is being investigated. One possibility is that the boron halide may be released before it is alkylated and that the product may then add to give the final compound.,

C. Methylene Triphenylarsenanes.

These react in a manner similar to the phosphorus compounds(7). Two reaction~~s~~ are given below to illustrate this.

$$(C_6H_5)_3As{=}CH_2 + (CH_3)_3SiBr \text{ ---- } [(C_6H_5)_3\overset{\oplus}{As}CH_2Si(CH_3)_3]\ Br^{\ominus}$$

$$(C_6H_5)_3As{=}CH_2 + BF_3 \text{ ----- } (C_6H_5)_3\overset{\oplus}{As}CH_2\overset{\ominus}{B}F_3$$

CONCLUSION

It is obvious that the reactions outlined above are general. This method of synthesis may permit the syntheses of new types of ligands and ~~many~~ other various mixed organometallic compounds.

REFERENCES

1. S. O. Grim and D. Seyferth, Chem. and Ind., 849 (1959).
2. M. F. Hawthorn, J. Am. Chem. Soc., 80, 3480 (1958).
3. M. F. Hawthorn, J. Am. Chem. Soc., 83, 367 (1961).
4. M. C. Henry and G. Wittig, J. Am. Chem. Soc., 82, 563(1960).
5. D. Seyferth, Angew. Chem., 72, 36 (1960).
6. D. Seyferth and K. A. Brandle, J. Am. Chem. Soc., 83, 2055(1961).
7. D. Seyferth and H. M. Gohen, J. Inorg. Nucl. Chem., 20, 73(1961).
8. D. Seyferth and S. O. Grim, J. Am. Chem. Soc., 83, 1613(1961).
9. D. Seyferth and S. O. Grim, J. Am. Chem. Soc., 83, 1610 (1961).
10. D. Seyferth, S. O. Grim, and T. O. Read, J. Am. Chem. Soc., 82, 1510 (1960).
11. D. Seyferth, S. O. Grim, and T. O. Read, J. Am. Chem. Soc., 83, 1617 (1961).
12. R. C. Slagel, University of Illinois Organic Seminar Abstracts, 92, (1960-61).
13. H. Staudinger and E. Hauser, Helv. Chim. Acta, 4, 86 (1921).
14. G. Wittig, Angew. Chem., 70, 65 (1958).

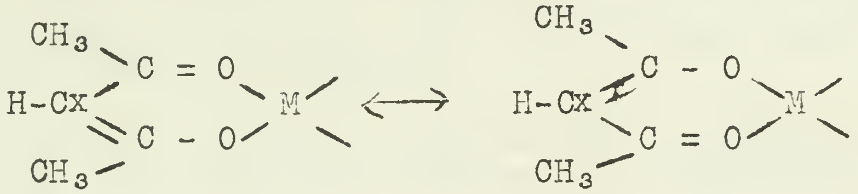
AROMATIC BEHAVIOR OF METAL-CHELATE COMPOUNDS

J. H. Incremona March 20, 1962

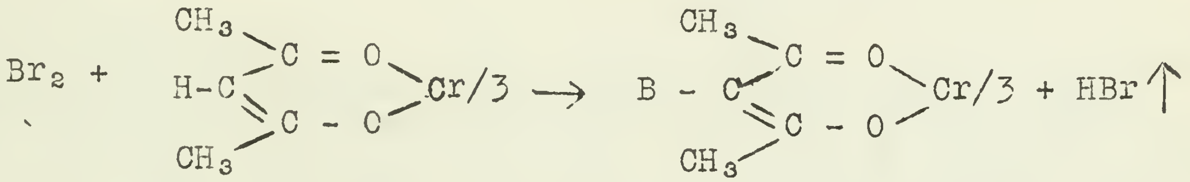
As early as 1914, Morgan and Moss recognized the aromatic behavior of metal β-diketones, as exemplified by their unusually high melting points, hydrolytic reactivity, etc. (1,2,3). More recently, R. B. Roof has submitted evidence for the coplanarity of the chelate ring and has found that the C-C and C-O bond distances are 1.38Å and 1.28Å respectively(4). Both of these distances represent intermediate values between single- and double-bond distances. Developments such as these have led to a greater study of the aromatic properties of various metal chelates. This paper deals with the more recent developments in the study of the aromatic behavior of the metal chelates and includes arguments presented for and against benzenoid aromaticity.

ELECTROPHILIC SUBSTITUTION REACTIONS

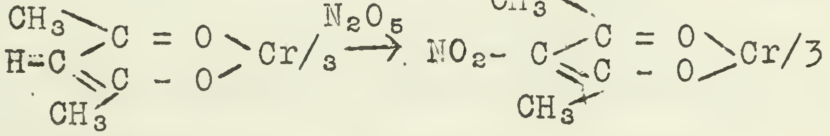
The proposed resonance existing in the chelate ring, as illustrated below, suggested the probability of electrophilic attack at the central carbon atom, Cx(5).



One of the first of such reactions was reported in 1925 by Reihen and coworkers and involves the bromination of chromium(III)-acetylacetonate by the action of bromine in chloroform (6),



Another extension of this treatment involved the reaction of N_2O_5 and bis-(2,4-pentanediono copper(II) to yield bis-(3-nitro-2,4-pentanediono) copper(II) (7,8).



The reactions illustrated above are not general. Whereas many chromium complexes tend to be stable in some moderately acidic solutions, copper chelates are unstable. Hence, where the production of strong acids is possible, copper and other acid-labile chelates will decompose (9,10,11). The latter concept has been found useful in the synthesis of some β-diketones(12).

When tris-(1,3-diphenyl-propanediono)chromium(III) was treated with bromine in chloroform under the same conditions as those indicated for chromium(III)-acetylacetonate, no substitution occurred (13). It has been found, however, that halogenation can be accomplished if N-bromosuccinimide, NBS, is used as the brominating agent. NXS, where X=Cl,Br or I, has been found to be a very general halogenating agent for pentanedionates and has been used successfully with other compounds, as is illustrated in Tables A and B.

Table A

Synthesis of Metal Chelates of the type $M(R'COCR''COR''')_n$

	R'	R"	R"'	M	M.p.,°C.	Reagent
1.	Me	Br	Me	Al	215.5-216	NBS
2.	Me	Br	Me	Be	177-179	NBS
3.	Me	Br	OEt	Al	132-134	NBS
4.	Me	Br	Ph	Cu	208-210	NBS
5.	Me	Br	Me	Cu	200	NBS
6.	Me	NO_2	Me	Ni	248	HNO_2 (8)

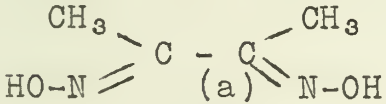
Table B

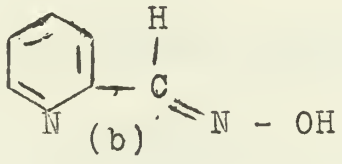
Bromination of Schiff Base Complexes

	Complex	M.p.of brominated species,°C
1.	Bis-(2,4-pentanediono)-ethylene diamine-copper(II)	135
2.	Bis-N-n-butylsalicylimine-nickel(II)	193-194

The success of NXS is believed to be related to its tendency to avoid strongly acidic by-products. This is evidenced by the success of syntheses 4 and 5 in Table A.

In addition to the β-diketones, Krause and coworkers studied the nickel, palladium, and platinum complexes of dimethylglyoxime (a) and 2-pyridinaldoxime (b) (15).


(HDMG)


(HPOX)

It might be expected that an oxime oxygen would be readily attacked by an acyl halide to form the corresponding oxime ester. These reactions are known. However attempted acylation of the HDMG chelates of nickel, platinum, and palladium gave no acylated chelate products. Rather all of these chelates were found to undergo stepwise cleavage of the coordinated rings as is indicated in equation 1.

$$[Ni(DMG)_2] + 2CH_3COCl \rightarrow [Ni(HDMG)Cl_2] + DMG(COCH_3)_2$$

$$[Ni(HDMG)Cl_2] + 2CH_3COCl \rightarrow NiCl_2 + DMG(COCH_3)_2 + 2HCl \qquad (1)$$

Attempts to synthesize the mono or diacylated chelate of nickel using as starting materials mono and diacylated dimethylgloxime and $NiCl_2$ in absolute alcohol failed.

$$[DMG(CO_2CH_3)_2] + NiCl_2 \xrightarrow[HCl]{EtOH} [Ni(HDMG)_2Cl_2] \qquad (2)$$

On the contrary, reactions involving palladium and platinum complexes of pyridinaldoxime were found to yield acylated chelates. The case for platinum is cited below. The presence of an infra-red band at 1790 cm.$^{-1}$ supports equation 3.

$$[Pt(POX)_2] + 2CH_3COCl \rightarrow [Pt(POX\text{-}COCH_3)_2]Cl_2 \qquad (3)$$

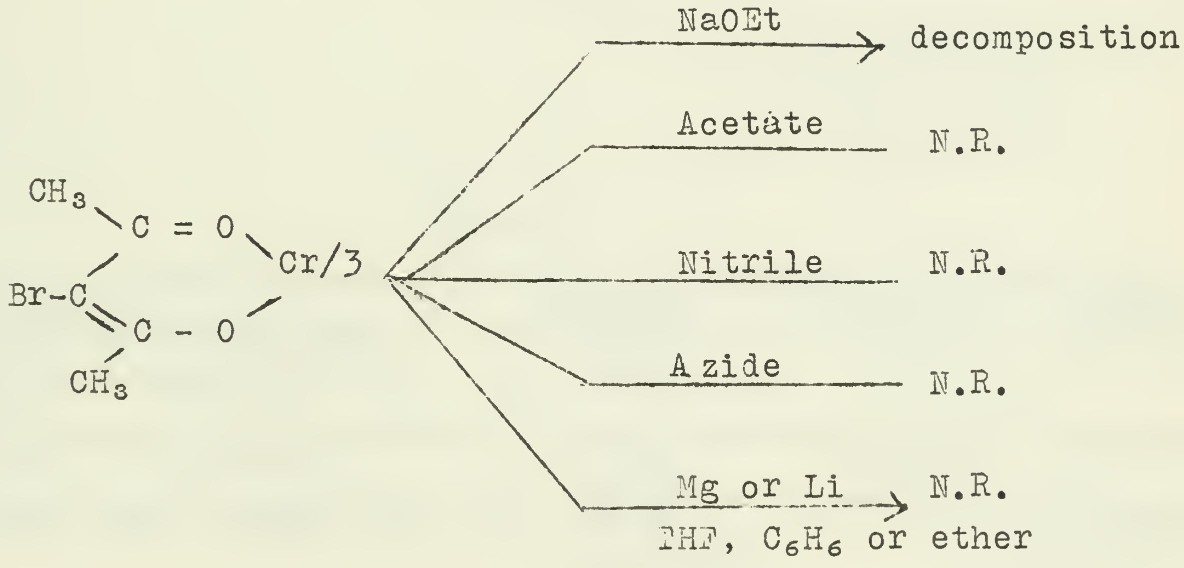
STRUCTURE OF THE HALOGENATED CHELATES

Various experimental and spectroscopic techniques have been employed in an attempt to ascertain the structures of the halogenated chelates. One such experiment involved a comparison of the physical properties of the product obtained in one case from the reaction of N-chlorosuccinimide with copper acetylacetonate and the products obtained from the reaction of 3-chloro-2,4-pentadione and $CuCl_2$. Both products proved to be identical. Another experiment involved the reaction of chromium(III)-acetylacetonate with bromine. A quantitative study of this reaction indicated that one mole of bromine was consumed per chelate ring. This conclusion lends support to the proposed structure and completely dismisses the possibility of halogenation of the methyl groups.

Further evidence in the elucidation of the chelate structure is provided by infra-red spectroscopy. It has been noted that the infra-red spectra of the halogenated β-diketones of different metals are very similar. Moreover, the same pattern of spectral changes is observed upon comparison of the unhalogenated species. Whereas metal acetylacetonates yield two bands from 1500 cm.$^{-1}$ to 1600 cm.$^{-1}$, the halogenated species exhibit a single band at 1550 cm.$^{-1}$ (16,17,18).

ATTEMPTED SUBSTITUTION REACTIONS ON THE HALOGENATED PENTANEDIONATES

Attempts to carry out other typically aromatic reactions on chelate rings failed. Krause and coworkers (15), using tris-(3-bromo-2,4-pentanediono)chromium(III), attempted to carry out the following reactions:



MECHANISM OF THE PROPOSED ELECTROPHILIC SUBSTITUTION REACTIONS

Kluiber has suggested the following five possible mechanisms (Table C) to explain the proposed electrophilic substitution reactions on the chelates of β-diketones (14). In an attempt to elucidate the correct mechanism, Kluiber speculated that if any ring opening occurred in the mechanism, it should be possible to witness exchange in various experimental runs. The experimental work carried out is shown in Table D. As indicated, all runs were carried out using tris-(2,4-pentadiono) chromium(III), since it exhibited little exchange in step e. Results indicate that no exchange occurred using the chromium chelates, and it was concluded that mechanism b was the most likely. Mechanism c is also probable since halogenation of the pentanedionate proved to be faster than halogenation of the diketone, and the suggested ring closure occurred faster with the halogenated species than with the unhalogenated one. This possibility is eliminated through the results obtained in experiments a-d.

Table C

Mechanisms for the Bromination of Metal Pentanedionates

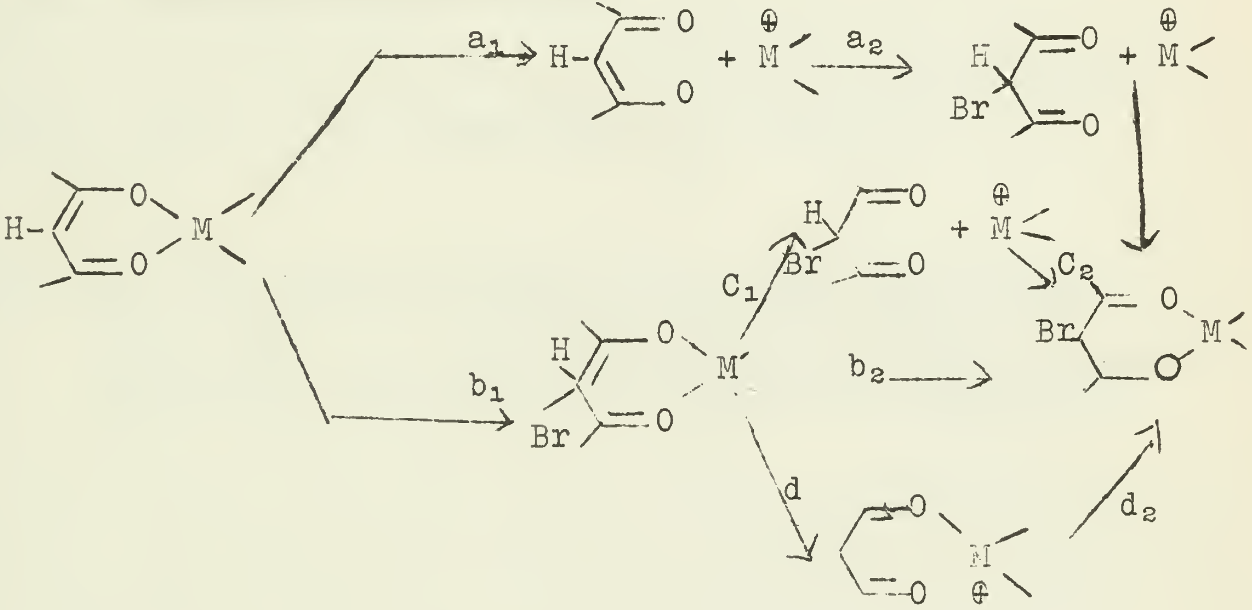


Table D

Competitive Reactions of Tris-(2,4-pentanediono) Chromium(III)

	Reactants	Solvent	Products	Conclusion
(a)	10 meq. A, 10 Meq. NBS. After five minutes B is added	10 ml chloroform	C and B	No Exchang
(b)	10 meq. D, 10 meq. A.	10 ml benzene	D and A	No Exchange
(c)	10 meq. NBS, 10 meq. B.	10 ml chloroform	D	Stochiometry of reaction confirmed
(d)	10meq.A, 10meq.B, 10meq.NBS	10 ml chloro - form	D and C; 54.6% of available bromine entering chelate	Rates of(19) bromination(20) equivalent(21)
(e)	10meq.labelled A,10meq.B.	10 ml chloro- form	~10meq. labelled A, ~10meq. B	<1%Exchange
(f)	10meq.labelled A,10meq.B, 20meq.NBS.	----	~10meq.labelled C, ~10meq. D	< 1% Exchange

A = 2,4-pentanedione B=tris-(2,4-pentanediono)chromium (III)
C = 3-bromo-2,4-pentanedione D=tris-(3-bromo-2,4-pentanediono) chromium(III)

[illegible]

[illegible]

[illegible]

[illegible]

CORRECTIONS

PAGE-163-

Paragraph 2-line 7-for N_2O_5 read N_2O_4 .

Paragraph 2-in the example immediately following line 9 change Cr to Cu.

PAGE-165-

Paragraph 2-for nitrile read nitrite.

PAGE-166-

Paragraph 1-line 12-change since to if .

Table C-note errors in the structures following steps b_1 and d .

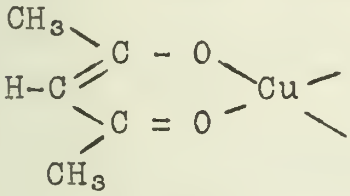
Table D-section e-for <1% exchange read 1% exchange.

PAGE-167-

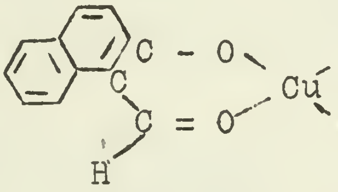
Paragraph 3---the last sentence should read---This observation, however, is not conclusive evidence against aromaticity since the chemical shift of heterocyclic compounds containing two or more hetero-atoms has not yet been determined.

AROMATIC BEHAVIOR IN METAL CHELATES

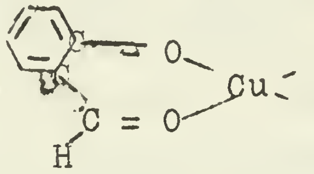
Calvin and Wilson proposed that if some correlation could be obtained between the stability constants for metal chelates and the assigned ease with which the ring could support aromaticity, this might confirm the presence of benzenoid aromaticity(22). The compounds investigated by Calvin and Wilson are indicated below. Pauling's assigned values, N, which designate the relative aromaticity in the chelate ring, are given with each compound (23,24).



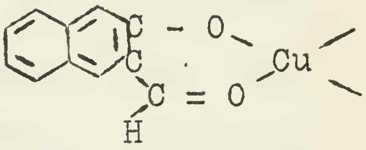
N=2.00



N = 1.67



N = 1.50



N = 1.33

Good correlation was observed between the stability constants as found by Calvin and Wilson and the values assigned these compounds by Pauling. Calvin and Wilson suggest these results can possibly be justified by two means. One of these is a resonance situation as illustrated in Figure 1, or a completely conjugated system as illustrated in Figure 2.

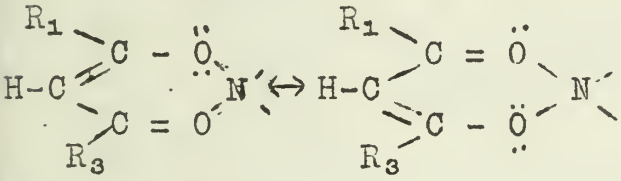


Figure 1

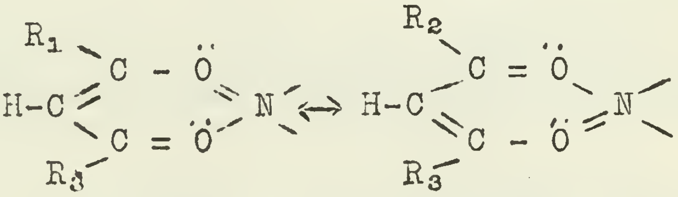


Figure 2

Through the use of NMR and molecular-orbital considerations, Cotton and Holm dismiss the possibility of benzenoid resonance and give support to the resonance situation as exemplified in Figure 1. The known charge separation in the chelate ring would not support π-bonding between the metal and oxygen atoms since any such bonding would only increase the charge separation(5).

Nuclear magnetic resonance data obtained from a study of the center carbon atom indicates that the chemical shift of the proton in the ring is very different from that of a typical proton in the benzene ring. This observation, however, is not conclusive evidence against aromaticity since the chemical shift of heterocyclic compounds has not yet been determined.

CONCLUSION

It can be concluded from the above studies that metal - β-diketone compounds, although undergoing some typically aromatic substitution reactions do not possess benzenoid resonance. Rather resonance occurring as illustrated in Figure 3 is at present more representative of the known experimental and theoretical data.

BIBLIOGRAPHY

1. G. T. Morgan and H. W. Moss, J. Chem. Soc., 105, 189 (1914).
2. A. N. Nesmeyanov, D. N. Kursanov, T. A. Simolina and Z. N. Parnes, Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk. 598 (1949).
3. W. Gerrard, M. F. Lappart and R. Shafferman, Chem. and Ind. (London), 722 (1958).
4. R. B. Roof, Jr., Acta Cryst., 9, 781 (1956).
5. R. H. Holm and F. A. Cotton, J. Am. Chem. Soc., 80, 5658(1958).
6. H. Reihlen, R. Illig and R. Wittig, Ber., 58, 12 (1925).
7. C. Djordjevic, J. Lewis and R. S. Nyholm, Chem. and Ind.(London), 122 (1959).
8. J. P. Collman, R. A. Moss, S. D. Golby and W. Trahanovsky, Chem. and Ind.,(London). 1213 (1960).
9. K. V. Auwers and E. Aufferbery, Ber., 50, 29 (1917).
10. A. Micheal and G. H. Carlson, J. Am. Chem. Soc., 58, 353(1936).
11. V. Vaillant, Compt. rend., 119 , 648 (1894).
12. W. J. Barry, J. Chem. Soc., 670 (1960).
13. J. P. Collman, R. A. Moss, Henry Maltz and C. C. Heindel, J. Am. Chem. Soc., 83, 531 (1961).
14. R. W. Kluiber, J. Am. Chem. Soc., 82, 4839 (1960).
15. R. A. Krause, D. C. Jicha, D. H. Busch, J. Am. Chem. Soc., 83, 528 (1961).
16. L. Birckenbach, K. Kellermann and W. Stein, Ber., 65B, 1071(1932).
17. R. P. Deyden and A. Winston, J. Phys. Chem., 62, 635(1958).
18. F. A. Cotton, "Modern Coordination Chemistry", edited by Lewis and Wilkins, Interscience Publishers Inc., New York, N.Y., p. 379, 1960.
19. W. C. Fernelius, M. Shamma, L. A. Davis, D. E. Goldberg, B.B. Martin, D. F. Martin, F.D. Thomas, 11, WADC Technical Report 56-203, part 111.
20. R. W. Taft, Jr. and E. H. Cook, J. Am. Chem. Soc., 81, 46(1959).
21. H. Taube, Chem. Revs., 50, 69 (1952).
22. M. Calvin and K. W. Wilson, J. Am. Chem. Soc., 67, 2003 (1945).
23. L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1939.
24. G. E. Branch and M. Calvin, "The Theory of Organic Chemistry", Prentice-Hall Inc., New York, N.Y., p. 113, 1941.

RECENT STUDIES OF THE METAL DERIVATIVES OF THE β-DIKETONES

R. A. Palmer March 27, 1962

The metal β-diketonates are complexes which lend themselves quite conveniently to a variety of experimental and theoretical treatments. They are generally stable and relatively easy to prepare. Their non-electrolyte character and consequent solubility in non-polar solvents suits them to the fields of chromatography, dipole moment measurement, and solvent extraction. Among the transition metals, β-diketonates have afforded a rich field for spectral analysis and magnetic studies in terms of ligand-field and molecular-orbital theories. This seminar will concern itself with the recent work in the investigation of these inner complexes, particularly that concerning the nature of the M-O bond and the characterization of the nickel(II) and copper(II) derivatives, with a brief survey of the other literature from January 1959.

THE NATURE OF THE M-O BOND

In view of the generally high stability of the β-diketonates and the resonance effects observed in the chelate ring (1), the nature of the M-O bond is naturally of considerable interest. Work in this area has centered around stability-constant evaluation, electron-spin resonance, nuclear magnetic resonance, and visible, UV, and IR spectral analysis.

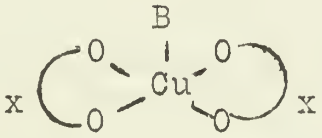
Among recently reported work, the attempts of Nakamoto and co-workers (2,3,4) and of Dismukes, Jones, and Bailar (5) at the analysis of the IR spectra of the simple acetylacetonates are of note. Both groups found the unambiguous assignment of the bands in the 1400-1600 cm^{-1} region impossible due to mixing effects. Nakamoto and co-workers were able, however, (by means of theoretical calculation of vibrational frequencies based on a normal coordinate treatment of bis-acetylacetonato-copper(II), Cu(acac)$_2$) to assign one band to the virtually pure M-O stretching vibration. This was supported by correlation of the metal-dependent shift of this band with the independently determined heat of formation of the M-O bond. Bailar and co-workers find this relationship holds only for the series of divalent metals from cobalt to copper. Other recent work in IR spectra includes that of Charette and co-workers(6) and that of Forman and Orgel (7), who interpreted the spectrum of Mn(acac)$_3$ in terms of Jahn-Teller distortion.

The visible and UV spectra of β-diketonates have been interpreted by several investigators (8,9,10,11,12,13), in relationship to the extent and nature of π-bonding between the metal and the chelate ring. Recent work in solution (11) and polarized crystal (9,10,13) spectra, support the conclusion that there is a definite amount of dπ- O$p\pi$ interaction dependent on the nature of the metal orbitals available. The most quantitative evaluation of the π-bonding has been reported by Maki and McGarvey (14,15). These workers analyzed the electron-spin resonance spectrum of Cu(acac)$_2$ and concluded that,

though there is extensive σ- and in-plane π-bonding, the out-of-plane π-bonding is extremely slight.(a)

COPPER(II) β-DIKETONATES

In a recent series of papers, Graddon and Watton (16,17,18,19) have reported and characterized five-coordinate species of the type:



where B is pyridine, pipyridine, or picoline and X is acetylacetonate, (acac), benzoylacetonate, (bzac), or ethyl-acetylacetonate, (acest), in various solvents of low coordinating power. The five-coordinate structure is supported by analysis of the visible and IR spectra and constancy of the equilibrium constant for the reaction:

$$Cu(acac)_2 + py \rightleftarrows Cu(acac)_2 \cdot py \ .$$

A Jahn-Teller distortion effect is offered as the reason for the tendency to form a five-coordinate species instead of six. (cf. nickel(II) below)

Holm and Cotton (20) have used dipole moment measurements in a study of beryllium(II), copper(II), and cobalt(II) bis-trifluoroacetylacetonates. They find that the moments of the latter two complexes indicate equilibria between *cis* and *trans* isomers, with the *cis* predominating 3:2.

Ni(II) β-DIKETONATES

The key to the magnetic anomalies of nickel(II) β-diketonates was found some years ago in Bullen's X-ray crystal structure determination for Ni(acac)$_2$ (21). However, the detailed analysis of the trimeric structure (22) was just published last year.

Fackler and Cotton (23,24,25,26) have investigated the molecular association of Ni(acac)$_2$, as well as other β-diketones of nickel(II), in solvents of low coordinating power. They have explained the spectral and magnetic properties of these compounds as functions of molecular association and solvent association, which

---

(a) Barnum(48) has recently published an extensive analysis of the IR, visible, and UV spectra of a series of tri-valent metal acetylacetonates (M(III)(acac)$_3$). His results indicate that the π-π^* transition energy, which increases from titanium(III) to cobalt(III), is due to metal-ligand π-interaction. He proposes that the π-interaction occurs between the metal $d\varepsilon$- orbitals and both higher, empty, π^*orbitals and lower, filled, πorbitals of the ligands.

are dependent in turn on temperature and steric effects. The species in solution is found to be essentially the same as that in the crystal. However, in the presence of pyridine or other bases, breakup of the trimer occurs. With pyridine, solvation occurs according to the equilibria:

$$2[Ni(acac)_2]_3 + 3py \rightleftharpoons 3[Ni(acac)_2]_2 \cdot py$$

$$[Ni(acac)_2]_2 \cdot py + 3py \rightleftharpoons 2[Ni(acac)_2 \cdot 2py] .$$

A solid of composition corresponding to the mono-solvated dimer was isolated and equilibrium constants for the two steps evaluated. (b)

In their work with sterically hindered β-diketonates, Fackler and Cotton (25) have reported the apparent polymerization of bis-(dibenzoylmethano)-nickel(II), induced at high temperatures:

$$\begin{array}{ccc} & 185°C & \\ 3Ni(DBM)_2 & \rightleftharpoons & [Ni(DBM)_2]_3 \\ \text{diamagnetic} & & \text{paramagnetic} \\ \text{red} & & \text{green} \end{array}$$

However, Wolf and co-workers (28) have reported almost exactly opposite spectral behavior of the same complex in xylene solution (i.e., the high temperature form is brown; the low, green). Magnetic data have not been reported by these workers.

OTHER RESEARCH INVOLVING β-DIKETONATES (January 1959--)

Papers concerning aromatic effects are referenced in the preceeding seminar (1). Other studies have included: ESR of $Ni(acac)_2$.p-dioxane (29), formation constants of M(II) β-diketonates(30 luminescence of $Cr(acac)_3$ (31), volatility of acetylacetonates (32), x-ray crystal structure of $Co(acac)_2 \cdot 2H_2O$ (33) and $Cr(acac)_3$ (34), and magnetic moment of $Ti(acac)_3$ and $Cr(acac)_3$ (35), and of $V(acac)_3$ (36). The analysis of polarized crystal spectra of $Co(acac)_3$(37) and of $Cr(acac)_3$ (38), as well as a number of other tri-valent metal

---

(b) Graddon and Watton (27) have reported the formation under similar conditions, of a 1:1 pyridine adduct of $Ni(acac)_2$ which they postulate to be five-coordinate (cf. Cu(II) above). Although they have evaluated equilibrium constants for the two-step solvation:

$$[Ni(acac)_2]_3 + 3py \rightleftharpoons 3Ni(acac)_2 \cdot py$$

$$Ni(acac)_2.py + py \rightleftharpoons Ni(acac)_2.2py ,$$

this scheme seems much less likely than that of Fackler and Cotton (vide supera) for the d^8 case, which favors octahedral or pseudo-octahedral coordination.

acetylacetonates[39] has also been carried out. NMR has been used to characterize the <u>cis</u> and <u>trans</u> isomers of tri-valent metal benzoyl acetonates (40) and trifluoroacetylacetonates (41), where the difference in other properties is too slight to distinguish between isomers.

Recent additional preparative work has included Pt(acac)$_2$ (42), Cr(bzac)$_2$2py (43) and an interesting five-coordinate species, Co(acac)$_2$NO (44). Wolf and co-workers have proposed a general method for the preparation of higher β-diketonates and have used it to prepare dibenzoyl-methane and p,p'-dinitro-dibenzoyl-methane chelates of iron(III), ruthenium(III) and rhenium(III) (45). The magnetic properties of the rare earth acetylacetonates, Ln(acac)$_3$, at very low temperatures (46) and the properties of the Ln(acac)$_3$ solvates have also been reported (47).

BIBLIOGRAPHY

1. J. H. Incremona, Inorganic Seminars, University of Illinois, Sp. 1962, p. 163-168.
2. K. Nakamoto and A. E. Martell, J. Chem. Phys., 32, 588 (1960).
3. K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, J. Am. Chem. Soc., 83, 1066 (1961).
4. K. Nakamoto, P. J. McCarthy, and A. E. Martell, J. Am. Chem. Soc., 83, 1272 (1961).
5. J. P. Dismukes, L. H. Jones, and J. C. Bailar, Jr., J. Phys. Chem., 65, 792 (1961).
6. J. Charette and Ph. Teyssié, Spectro. Chem. Acta., 16, 689(1960).
7. A. Forman and L. E. Orgel, Mol. Phys., 2, 362 (1959).
8. R. H. Holm and F. A. Cotton, J. Am. Chem. Soc., 80, 5658(1958).
9. J. Ferguson, J. Chem. Phys., 34, 1609 (1960).
10. J. Ferguson, J. Chem. Phys., 34, 2206 (1960).
11. J. Charette, G. Neirynck, and Ph. Teyssié, J. Phys. Chem., 65, 735 (1961).
12. L. E. Orgel, J. Chem. Soc., 3683 (1961).
13. R. L. Carlin and T. S. Piper, unpublished observations.
14. B. R. McGarvey, J. Phys. Chem., 60, 71 (1956).
15. A. H. Maki, and B. R. McGarvey, J. Chem. Phys., 29, 31 (1958).
16. D. P. Graddon, Nature, 183, 1610 (1959).
17. D. P. Graddon, J. Inorg. Nuclear Chem., 14, 161 (1960).
18. D. P. Graddon and E. C. Watton, Nature, 187, 1021 (1960).
19. D. P. Graddon and E. C. Watton, J. Inorg. Nuclear Chem. 21, 49 (1962).
20. R. H. Holm and F. A. Cotton, J. Inorg. Nuclear Chem., 15, 63 (1960).
21. G. J. Bullen, Nature, 177, 537 (1956).
22. G. J. Bullen, R. Mason and P. Pauling, Nature, 189, 291 (1961).
23. J. P. Fackler, Jr., and F. A. Cotton, J. Am. Chem. Soc., 82, 5005 (1960).
24. F. A. Cotton and J. P. Fackler, Jr., J. Am. Chem. Soc., 83, 2818 (1961).
25. J. P. Fackler, Jr. and F. A. Cotton, J. Am. Chem. Soc., 83, 3775 (1961).

26. J. P. Fackler, Jr., J. Am. Chem. Soc., 84, 24 (1962).
27. D. P. Graddon and E. C. Watton, Nature, 190, 906 (1961).
28. L. Wolf, E. Butler, and H. Weinelt, Naturwissenschaften, 48, 378 (1961).
29. M. Peter, Phys. Rev., 116, 1432 (1959).
30. G. A. Guter and G. S. Hammond, J. Am. Chem. Soc., 31, 4686(1959).
31. L. S. Forster and K. DeArmond, J. Chem. Phys., 33, 1208(1960).
32. E. W. Berg and J. T. Truemper, J. Phys. Chem., 64, 487 (1960).
33. G. J. Bullen, Acta. Cryst., 12, 703 (1959).
34. L. M. Shkol'nikova and E. A. Shugam, Kristallograpiya, 5, 32(1960).
35. R. L. Carlin and T. S. Piper, unpublished observations.
36. B. N. Figgis, J. Lewis, and F. Mabbs, J. Chem. Soc., 2480 (1960).
37. T. S. Piper, J. Chem. Phys., 35, 1240 (1961).
38. A. Chakravorty and S. Basu, J. Chem. Phys., 33, 1266 (1961).
39. R. L. Carlin and T. S. Piper, unpublished observations.
40. R. C. Fay and T. S. Piper, J. Am. Chem. Soc., in press (1962).
41. R. C. Fay and T. S. Piper, unpublished observations.
42. A. A. Grinberg, Zhur. Neorg. Khim., 4, 314 (1959).
43. R. Nast, Chem. Ber., 93, 2329 (1960).
44. R. Nast, Chem. Ber. 92, 1858 (1959).
45. L. Wolf, E. Butler, and H. Weinelt, Z. anorg. u. allgem. Chem., 306, 87 (1960).
46. G. W. Pope, J. F. Steinbach, and W. F. Wagner, J. Inorg. Nuclear Chem., 20, 304 (1962).
47. J. J. Fritz, P. E. Field, and I. Grenthe, J. Phys. Chem., 65, 2070 (1961).
48. D. W. Barnum, J. Inorg. Nuclear Chem., 21, 221 (1962).

HOMOGENEOUS CATALYZED REACTIONS OF MOLECULAR HYDROGEN

G. D. Shier April 3, 1962

INTRODUCTION

The first unambiguous case of homogeneous activation of molecular hydrogen in solution was reported by Calvin (1) in 1938. Since then, and particularly after 1953, much work has been done to elucidate the scope and mechanism of activation of molecular hydrogen in various solvents and by various catalysts. This discussion will rather arbitrarily exclude the reactions of molecular hydrogen with cobalt and its complexes, since this is an extensive subject in itself. Homogeneous catalysis is intrinsically simpler to study than heterogeneous catalysis, and therefore, it was thought that an elucidation of its mechanism might have a bearing on the general problem of catalysis. Insofar as practical application of the subject is concerned, powders of the nobler metals can be produced on a commerical scale by hydrogen reduction, and recently (3) some olefinic compounds were reported to have been hydrogenated by molecular hydrogen and a ruthenium(II) catalyst.

COPPER SALTS

Calvin's first work (1,2) was with the reduction of capric salts and quinone in quinoline solution. He showed that cupric salts were reduced to cuprous salts autocatalytically, and that quinone could be reduced to hydroquinone by hydrogenation with a cuprous catalyst.

Additional work on copper catalyzed reduction in quinoline has been done recently (4,5,6,7,8) and has shown that for the reduction of copper(II) acetate in quinoline, the rate law is of the form:

$$\text{rate} = K[H_2][Cu(I)]^2$$

Investigation of the rate in the temperature interval 25 to 60° has shown that K is given by:

$$K = 1.62 \times 10^8 \exp(-13{,}000/RT)\ M^{-1}\ sec^{-1}$$

The form of the rate law raises the question of whether the catalytic species is dimeric copper(I). Some evidence(8) has been advanced for this, but the conditions under which this evidence was obtained have been criticized, and at present there seems to be no justification for assuming a catalytically active dimeric species. In the case of cuprous catalysis in heptanoic acid (9), it has been shown that a dimeric cuprous species is formed and that the dimer is catalytically inactive. However, the kinetics of hydrogenation in this case, are first order in copper(I) instead of second-order as in quinoline.

Activation of hydrogen by copper compounds has been studied in pyridine, dodecylamine(10), heptanoic acid(9,11), and aqueous solution (12,13,14,15,16,17), plus some qualitative studies in other solvents. Cuprous salts activate in pyridine and dodecylamine and cupric salts activate in water. Both cuprous and cupric heptanoate activate in heptanoic acid. The rate law for both cuprous and cupric activation in all solvents except quinoline is first-irder in copper ion. Additional data on these systems are given in Table I.

SILVER SALTS

Silver(I) salts are reduced to metallic silver in aqueous solution (18,19,20), pyridine (10,22), and heptanoic acid (23). The rate laws are first order in both silver ion and hydrogen for all solvents except water, where a third-order rate law becomes important at high silver concentration and low temperature. The silver-catalyzed reduction of dichromate ion was extensively studied in aqueous perchlorate solution and the kinetics were shown to follow the rate law

$$\text{Rate} = K[Ag^+]^2[H_2] + \frac{K_1[Ag^+]^2[H_2]}{(K_{-1}/K_2)[H^+]+[Ag^+]}$$

This rate law accounts for the observed acid retardation of the kinetics, and lack of an appreciable salt effect. The mechanisms proposed for this kinetic law are given in Table I. Both metallic silver and acetic acid markedly change the kinetic behavior of silver acetate in pyridine. The effect of metallic silver may be due to the hetrogeneous decomposition of AgH, which is postulated to be an intermediate.

MERCURY SALTS

The reduction of mercuric salts has been studied principally in aqueous solution (24,25,26,27), but also in heptanoic acid(23). The hydrogen reduction of mercury proceeds in two stages, corresponding to the reduction of mercuric to mercurous compounds, and mercurous compounds to metallic mercury. Both mercury(II) and mercury(I) activate hydrogen, giving a rather complicated rate expression after integration. However, the experimental values correspond very well to the values calculated from the integrated rate constant.

OTHER HOMOGENEOUS REDUCTION SYSTEMS

The reduction of permanganate ion in acidic or neutral aqueous solutions gives manganese(IV) oxide as the sole product of the reaction(28). The product in basic solution is the manganate ion. The permanganate ion itself acts as the hydrogen activator in these solutions, and the rate is unaffected by the species $NaClO_4$, Cu^{++},

Co^{++}, or VO_2^{++}. The rate increased slightly with perchloric acid addition and the precipitated manganse(IV) oxide affected the rate somewhat. In basic solution, there is no salt effect, and manganate ion is not an activating species. When silver ion is added to an acidic permanganate solution, the rate is faster than can be explained on the basis of a combination of permanganate and silver ion activation. It has been shown that the rate law for the silver-permanganate system has a third order term that is first-order in hydrogen, permanganate, and silver.

The reduction of iron(III)to iron(II) in 3M hydrochloric acid is catalized by the ion $[PdCl_4]^=$ (29). The reaction is first order in hydrogen and palladium(II), has no salt effect, and is independent of acid concentration above 3M. On a qualitative basis, the catalytic activity of palladium(II) ion, the lower chloride complexes, and the ethylenediammine complex is lower than that of the $PdCl_4^=$ ion.

Ruthenium(III) catalyzes the hydrogen reduction of Ruthenium(IV) and iron(III) in aqueous hydrochloric acid under mild conditions (30). Ruthenium (IV) showed no catalytic activity, and solutions containing an oxidant to keep the ruthenium in the higher oxidation state were completely unreactive. The rate law is first-order in hydrogen and in Ruthenium(III), and the hydrochloric acid -dependency of the rate suggests that the catalytic species are the anionic chloride complexes.

Rhodium(III) catalyzes the reduction of iron(III) to iron(II) in 3M HCl (31), with a rate expression first-order in rhodium(III) and in hydrogen. The rate-dependency on hydrochloric acid indicates that the $[RhCl_6]^=$ ion is probably the catalytic species.

Maleic, fumaric, and acrylic acids have been hydrogenated using chlororuthenate(II) complexes (3) in aqueous hydrochloric acid. The rate-determining step is postulated to be the bimolecular reaction of a hydrogen molecule and a chlororuthenate·olefin complex. In the case of maleic acid, formation of a 1:1 complex of ruthenium(II), with a stability constant of $5x10^3$(3M HCl, 20°), has been confirmed spectrophotometrically.

MECHANISM AND THE EFFECT OF COMPLEXING

The catalytic reactions which have been discussed can be divided into two classes: those involving heterolytic splitting of the hydrogen molecule, and those involving homolytic splitting. As may be seen in Table I, the homolytic path is less common and has a lower activation energy, but it has a much higher entropy of activation. It is favored by high metal-ion concentrations and low temperature. Other metal ions which have been tested for catalytic activity are Ca^{++}, Mg^{++}, Zn^{++}, Co^{++}, Cd^{++}, Pb^{++}, Al^{+3}, Fe^{+2}, Cr^{+3}, Tl^{+3}, Ce^{+4}, UO_2^{+2}, VO_3^- and CrO_4^{-2} (32).

Most of the experimental data for homogeneous activation of hydrogen can be rationalized on the basis of a four-center mechanism, (32,34) with the activated complex

$$\begin{array}{lcccc} X_{(n-1)} & M^{+2} & - & X \\ & \vdots & & \vdots \\ & H^{-} & - & H^{+} \end{array}$$

This indicates that the reactivity of a given metal ion should depend directly on the M-H and X-H bond strengths, and inversely on the M-X bond strength, all of which vary with X. Most complexation effects (Table II) can be explained on this basis. Excessive electron displacement from ligand to metal also may contribute by lowering the M-H bond strength. The implication of this, expressed in valence-bond language is that the unfilled orbitals of the metal atom, needed for bonding with hydrogen, are less available because of their participation in covalent bonding with the ligands. In terms of the ligand-field theory, this effect can correspondingly be ascribed to promotion of those orbitals, due to high ligand-field intensity, in these complexes (32). Thermodynamic arguments (33) have been used to support the existence of a hydride intermediate.

Both cuprous and cupric heptanoate activate hydrogen hetrolytically in heptanoic acid, diphenyl, and octadecane, but the rate is much lower than for carboxylate salts in water. This is due to the greater energy of charge separation of the M-X bond in nonpolar solvents. The magnitude of the solvent effect should depend inversely on the ionic charge of the metal atom. This is shown by the ratio of copper(I)- activation to copper(II)-activation, since cuprous salts have not been observed to activate hydrogen in aqueous solution but to activate it in several non-aqueous solvents. The reason for apparent homolytic splitting by copper(I) in quinoline is not clear, particularly when contrasted to heterolytic splitting in pyridine and dodecylamine. Thus far, there has been no reasonable explanation of this anomaly.

ELECTRONIC STRUCTURE AND REACTIVITY

Halpern (32,34) has pointed out that almost all the simple metal ions that exhibit catalytic activity have nearly filled or just filled "d" shells. This leaves mercury (I), which Halpern ignores, as the apparent exception. Halpern goes on to correlate catalytic activity with electron affinity, the energy separation of the (N-1)d levels and (n)s levels, and the fact that these simple metal ions (Cu^{++}, Cu^{+}, Ag^{+}, Hg^{++}) are isoelectronic with metals of great catalytic activity (Co, Ni, Pd, Pt). Using these concepts, he is able to rationalize the behavior of the simple metal ions quite nicely, but that leaves mercury(I), MnO_4^-, palladium(II), ruthenium(II), ruthenium(III), and rhodium(III) to be explained.

It seems obvious that the catalytic species must have available orbitals to form bonds with hydrogen and that it must be reasonably electrophilic.

Either very strong electrophiles such as copper(II) or very strong nucleophiles such as NH_2^- ion can catalyze hydrogen-deuterium exchange reactions. It is perhaps enlightening to consider the case of the $Hg(en)_2^{++}$ ion, for which the added anions acetate, carbonate, and hydroxide increase the rate of activation in the order listed (26). If this effect is due to ion-pairing, it may be considered, a good example of combination acid-base interaction with hydrogen. Ruthenium(III), rhodium(III), and palladium(II) all show catalytic activity as their chloro-complexes. Since these complexes are anionic, M-X bond scission is eased, giving the chloro complex an advantage over the corresponding cationic aquo complex. If these chloro complexes are spin-paired, as is probable in second transition-series complexes, a hydrogen molecular displacing one of the chloride ions in the coordination sphere of the complex would come into close proximity with a highly charged and lightly shielded positive center.

CONCLUSION

It is obvious that the factors governing the homogeneous catalytic activation of molecular hydrogen are complex, and much more work must be done before they are sufficiently clarified.

BIBLIOGRAPHY

1. M. Calvin: Trans. Faraday Soc., 34, 1181 (1938).
2. M. Calvin: J. Am. Chem. Soc., 61, 2230 (1939).
3. J. Halpern, J. F. Harrod, and B. R. James: ibid., 83, 754(1961).
4. W. K. Wilmarth, M. K. Barsh, and S. S. Dharmatti: ibid., 74, 5035 (1952).
5. W. K. Wilmarth and M. K. Barsh: ibid., 75, 2237 (1953).
6. M. Calvin and W. K. Wilmarth: ibid., 78, 1301 (1956).
7. W. K. Wilmarth and M. K. Barsh: ibid., 78, 1305 (1956).
8. . Weller and G. A. Mills: ibid., 75, 769 (1953).
9. A. J. Chalk and J. Halpern: ibid., 81, 5846 (1959).
10. L. W. Wright, S. Weller, and G. A. Mills: J. Phys. Chem., 59, 1060 (1955).
11. A. J. Chalk and J. Halpern: J. Am. Chem. Soc., 81, 5852 (1959).
12. J. Halpern and R. G. Dakers: J. Chem. Phys., 22, 1272 (1954).
13. R. G. Dakers and J. Halpern: Canad. J. Chem., 32, 969(1954).
14. E. Peters and J. Halpern: ibid., 33, 356 (1955).
15. E. Peters and J. Halpern: J. Phys. Chem., 59, 793 (1955).
16. J. Halpern, E. R. Macgregor and E. Peters: ibid., 60, 1455(1956).
17. E. Peters and J. Halpern: Canad. J. Chem., 34, 554 (1956).
18. A. H. Webster and J. Halpern: J. Phys. Chem., 60, 280 (1956).
19. A. H. Webster and J. Halpern: ibid., 61, 1239 (1957).
20. A. H. Webster and J. Halpern: ibid., 61, 1245 (1957).
21. L. W. Wright and S. Weller: J. Am. Chem. Soc., 76, 3345(1954).
22. W. K. Wilmarth and A. F. Kapauan: ibid., 78, 1308 (1956).
23. A. J. Chalk, J. Halpern, and A. C. Harkness: ibid., 81, 5874 (1959).
24. J. Halpern, G. J. Korinek and E. Peters: Research London, 7, S61 (1954).
25. J. Halpern and E. Peters: J. Chem. Phys., 23, 605 (1955).
26. G. J. Korinek and J. Halpern: Canad. J. Chem., 34, 1372(1956).
27. G. J. Korinek and J. Halpern: J. Phys. Chem., 60, 285 (1956).
28. A. H. Webster and J. Halpern: Trans. Faraday Soc., 53, 51(1957).

29. J. Halpern, J. F. Harrod, and P. E. Potter: Canad. J. Chem., 37, 1446 (1959).
30. J. F. Harrod, S. Ciccone and J. Halpern: ibid., 39, 1372(1961).
31. J. F. Harrod and J. Halpern: ibid., 37, 1933 (1955).
32. J. Halpern: J. Phys. Chem., 63, 398 (1959).
33. J. Halpern: Advances in Catalysis, 9, 302 (1957).
34. J. Halpern: ibid., 11, 301 (1959).
35. J. Halpern: Quart. Revs., 10, 463 (1956).

Table I
Kinetics of Activation

Catalytic Species	Solvent	T, °C.	Rate Law	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Mechanism	Ref
Cu^{++}	H_2O	80-140°	$K[H_2][Cu^{++}]$	26	-10	$Cu^{++} + H_2 \rightarrow$ $CuH^{+} + H^{+}$	16
$CuAc_2$	H_2O	80-140	$K[H_2][CuAc_2]$	24	-7	$CuAc_2 + H_2 \rightarrow$ $(CuH)Ac + HAc$	13
CuAc	Quinoline	25-117	$K[H_2][CuAc]^2$	13-16	(-20)	$2CuAc + H_2 \rightarrow$ $2CuHAc$	7
$CuHp_2$	Heptanoic Acid	125-155	(1)$K[H_2][CuHp_2]$ (2)$K[H_2][CuH_p]$	29 20	-2 -15	$CuHp_2 + H_2 \rightarrow$ $(CuH)(Hp) + HHp$ $CuHp + H_2 \rightarrow$ $(CuH)C + HHp$	11
Ag^{+}	H_2O	30-120	(1)$K[H_2][Ag^{+}]^2$ (2)$K[H_2][Ag^{+}]$	14 23	-25 -6	$2Ag^{+} + H_2 \rightarrow$ $2AgH^{+}$ $Ag^{+} + H_2 \rightarrow$ $AgH + H^{+}$	19
AgAc	Pyridine	25-78	$K[H_2][AgAc]$	12-14	(-25)	$AgAc + H_2 \rightarrow$ $AgH + HAc$	22
$Ag^{+} + MnO_4^{-}$	H_2O	30-60	$K[H_2][Ag^{+}][MnO_4^{-}]$	9	-26	$Ag + MnO_4^{-} + H_2 \rightarrow$ $AgH^{+} + MnO_4^{=} + H^{+}$	28
Hg^{++}	H_2O	65-100°	$K[H_2][Hg^{++}]$	18	-12	$Hg^{++} + H_2 \rightarrow$ $Hg^{\circ} + 2H^{+}$ or $Hg^{++} + H_2 \rightarrow$ $HgH^{+} + H^{+}$	27
Hg_2^{++}	H_2O	65-100°	$K[H_2][Hg_2^{++}]$	20	-10	$Hg_2^{++} + H_2 \rightarrow$ $Hg_2 + 2H^{+}$ or $Hg_2^{++} + H_2 \rightarrow 2HgH^{+}$	27
MnO_4^{-}	H_2O	30-70	$K[H_2][MnO_4^{-}]$	14	-17	$MnO_4^{-} + H_2 \rightarrow$ MnV	28
$PdCl_4^{=}$	H_2O	66-87.5	$K[H_2][PdCl_4^{=}]$	$E_a = 20$	-6.3	$PdCl_4^{=} + H_2 \rightarrow$ $HPdCl_3^{=} + HCl$	29

Table I (Continued)

Kinetics of Activation

Catalytic Species	Solvent	T, °C.	Rate Law	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Mechanism	Ref
Ru III	3M HCl	65-85	$K[H_2][RuIII]$	23.1	+6	$RuX_n^{3-n} + H_2 \rightarrow HRuX_{n-1}^{3-n} + HCl$	30
RhIII	3M HCl	61.5-85	$K[H_2][RhIII]$	$E_a=25.2$	+9	$RhX_n^{3-n} + H_2 \rightarrow HRhX_{n-1}^{3-n} + HCl$	31
RuII	3M HCl	70-90	$K[H_2][RuII.olefin]$	19	-2	$RuII{=}olefin \xrightarrow{fast} RuII.olefin$ $RuII.olefin + H_2 \xrightarrow{K} RuII +$ saturated compd.	3

Table II

Effect of Complexing on Activity (32)

Complex	Mean Formation Constant*	Relative Activity
Cu(II) Butyrate	--	150
Cu(II) Propionate	--	150
Cu(II) Acetate	30	120
$CuSO_4$	100	6.5
$CuCl_4^=$	1	2.5
Cu^{++}	--	1
Cu(II) Glycinate	$5x10^7$	0.5
$Cu(en)_2^{++}$	$1x10^{10}$	0.1
$HgSO_4$	22	1.8
Hg^{++}	--	1
Hg(II) Acetate	$1.6x10^4$	$4x10^{-2}$
Hg(II) Propionate	--	$4x10^{-2}$
$HgCl_4^=$	$6x10^3$	$3.2x10^{-3}$
$HgCl_2$	$4x10^6$	$2.5x10^{-3}$
$HgBr_2$	$3.5x10^7$	$1.7x10^{-3}$
$Hg(en)_2^{++}$	$1.5x10^{11}$	$1x10^{-3}$
Ag Acetate	3	80
$Ag(en)_2^+$	$7x10^3$	25
Ag^+	--	1
$Ag(CN)_2^-$	$2.4x10^9$	No Reaction

* $M.F.C = \sqrt[n]{K_n}$ $K_n = \frac{[MX_n]}{[M][X]^n}$

INFRARED STUDIES OF CYANIDE COMPLEXES

F. L. Khalil April 24, 1962

INTRODUCTION

During the last few years infrared spectroscopy has been extensively applied in many structural determinations. The purpose of this seminar is to outline some of the important results of infrared spectroscopy as applied to the study of cyanide complexes in the solid state. Some applications of infrared techniques to the study of complex ions in aqueous solution will also be considered.

METAL-CARBON LINKAGE IN CYANIDE COMPLEXES

The structure of $KAg(CN)_2$ was determined by Hoard(1) from x-ray diffraction studies. However, Hoard could not distinguish between the nitrogen and carbon positions.

Jones(2) ruled out the structure N-C-Ag-N-C, since in the normal species there is only one strong infrared CN frequency and one strong Raman frequency, separated by about 6 $cm.^{-1}$, whereas in the monosubstituted isotopic species $N-{}^{13}C-Ag-{}^{12}C-N$ and ${}^{15}N-C-Ag-C-{}^{14}N$ there are two strong infrared CN frequencies. Force constants were evaluated using Wilson's FG matrix method(3) to fit the observed fundamental frequencies for the two possible structures N-C-Ag-C-N or C-N-Ag-N-C, as shown in Table I.

Table I

Force Constants Calculated for $KAg(CN)_2$ (F=millidynes/angstrom)

	N-C-Ag-C-N	C-N-Ag-N-C
F_{CN}	17.04 ± 0.25	18.51 ± 0.21
F_{Ag-x}	1.826 ± 0.05	1.810 ± 0.05
F_{12}	0.08 ± 0.22	1.56 ± 0.24

Assuming the C-N-Ag-N-C structure, the high C-N force constant appears to be incompatible with the high Ag-N, N-C interaction constant F_{12}. The structure N-C-Ag-C-N gives much more favorable results. (The CN force constant in HCN is about 18.5 md/angstrom. (4)). The foregoing data and discussion are presented as strong, though not completely conclusive, evidence that in $KAg(CN)_2$, the cyanide groups are bonded to the silver atoms through the carbon atoms. Similar results have been obtained also in determination of the structure of $Hg(CN)_2$ (5) and $KAu(CN)_2$ (6).

THE NATURE OF THE METAL-CARBON BOND IN CYANIDE COMPLEXES

Pauling(7) interpreted the short metal-carbon bond distances and the stabilities of the transition metal-cyanide complexes as indicating some double bond character in the metal-ligand bonds.

Cagliotí, Sartori and Scrocco(8) studied the influence of the oxidation state of the metal on the M-C and C-N frequencies for iron, chromium, and manganese cyanide complexes, as shown in Table II.

Table II

The Influence of the Oxidation State of the Metal on the Frequencies

Compound	Electronic state	C-N frequency $cm.^{-1}$	M-C frequency $cm.^{-1}$
$[Fe(CN)_6]^{-3}$	d^5	2125	505
$[Fe(CN)_6]^{-4}$	d^6	2047	584
$[Mn(CN)_6]^{-3}$	d^4	2125	514
$[Mn(CN)_6]^{-4}$	d^5	2060	-
$[Mn(CN)_6]^{-5}$	d^6	2048	-
$[Cr(CN)_6]^{-3}$	d^3	2127	457

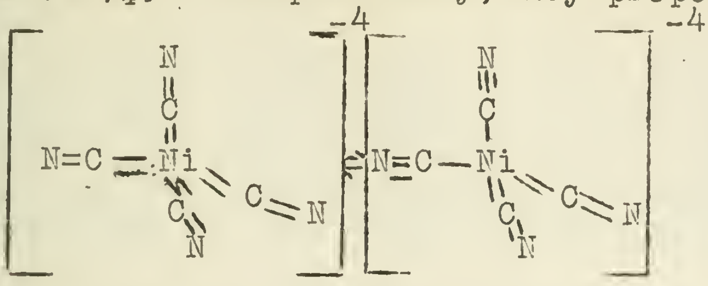
They explained these results on the basis of ligand-field and molecular-orbital theories and showed that the capacity of a metal to form M-L π bonds depends upon the number of filled d_ϵ orbitals in the central atom(9). Thus the ferric ion (d^5) should have less tendency to form π-bonds with the CN groups than the ferrous ion (d^6) as was shown by its lower M-C infrared frequency.

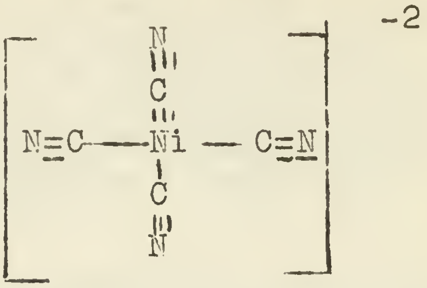
STRUCTURE OF $[Ni(CN)_4]^{-4}$ AND $[Ni(CN)_4]^{-2}$

The structure of $Ni(CO)_4$, in which the four (Co) groups are arranged tetrahedrally around the nickel atoms, has been proven by both electron diffraction (10) and spectroscopic means(11). Since $[Ni(CN)_4]^{-4}$ is isoelectronic with $Ni(Co)_4$, it was predicted (12,13) to have a similar structure. X-ray analysis has not been carried out for $[Ni(CN)_4]^{-4}$, mainly because of its instability.

El-Sayed and Sheline (14) observed that $[Ni(CN)_4]_4^{-4}$ absorbs at 1985 $cm.^{-1}$ whereas $[Ni(CN)_4]^{-2}$ absorbs at 2130 $cm.^{-1}$ in the infrared. The low value of the C-N frequency in $[Ni(CN)_4]^{-4}$, as compared with that in $[Ni(CN)_4]^{-2}$, can be explained semiquantitatively on the basis of Pauling's principle of electrical neutrality (15).

Calculating the contribution (x) of the pure single-bonded form in the Ni-C bonds to be 1/3 and 3/4 for $[Ni(CN)_4]^{-4}$ and $[Ni(CN)_4]^{-2}$ respectively, they proposed the following structures:





Structure of $[Ni(CN)_4]^{-4}$

[Similar to that of $Ni(Co)_4$ (16).]

Structure of $[Ni(CN)_4]^{-2}$

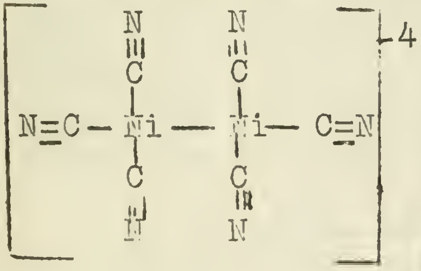
CYANIDE COMPLEXES INVOLVING METAL-METAL BONDS

In 1919, Bellucci and Corelli (17) observed that when $K_2[Ni(CN)_4]$ is reduced by sodium or potassium amalgam, a red color develops and a red crystalline compound having the emperical formula $K_2[Ni(CN)_3]$ may be isolated. Since then, the structure of this complex ion has been the subject of a great amount of discussion.

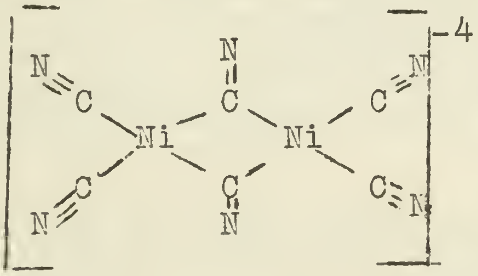
Mellor and Craig (18) (1942) suggested structure I on the basis of magnetic moment measurements which indicated that the complex is diamagnetic and therefore dimeric.

Nast and Pfab (19) (1952) suggested structure II as a result of a preliminary x-ray analysis which showed that the anion is dimeric and planar, involving bridiging CN groups.

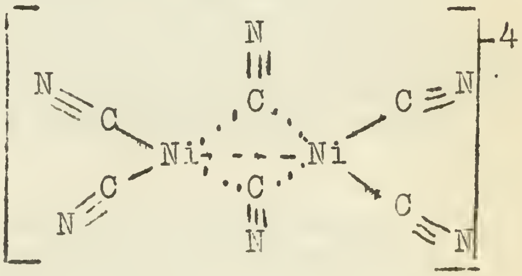
El-Sayed and Sheline (20) (1955), as a result of observing the presence of infrared absorption bands in the C≡N region only (2130, 2079, and 2055 cm^{-1}), suggested structure III, in which the dotted lines represent half-bonds which form the C≡N bridge (21,22) and the broken line represents the spin coupling of the two odd electrons on the two nickel(I) ions. They attributed the 2130 cm^{-1} band to the bridged CN groups.



Structure I



Structure II



Structure III

Griffith and Wilkinson (23) (1958), observing that all of the nickel and cobalt complexes have an intense absorption in the region of 2130 cm.$^{-1}$, concluded that it is much more reasonable to attribute absorption in this region to terminal cyanide groups than to bridging cyanide groups. In the absence of conclusive x-ray evidence to the contrary, Griffith accepted the Mellor and Craig structure I. El-Sayed and Sheline also pointed out that structure I is energetically favored over structure III by about 196.78 k. cal/mole.

From the above discussion, it may be concluded that structure III agrees with all the experimental results (dimeric, diamangetic, planar, bridged cyanides and presence of only C≡N groups) but is less energetically favorable, whereas structure I does not agree with x-rays conclusions, but is the most favorable structure from an energetic point of view. Consequently the need for a complete x-ray analysis giving bond distances and Fourier maps is quite obvious.

INFRARED SPECTROSCOPIC DETECTION OF BRIDGING CYANIDE GROUPS

Dows, Haim, and Wilmarth (24) studied the infrared spectra of some cyanide complexes and obtained the following results.

Table III

Infrared Spectra of Some Cyanide Complexes

Compound	Mull Absorption cm.$^{-1}$	Bonding
$K_3[Co(CN)_6]$	2130	Co-CN
$[Ag_2Co(CN)_5 1.5H_2O]_x$	2130,2170	Co-CN and Co-CN-Co
$Ag_3[Co(CN)_6]$	2130, 2170	Co-CN and Co-CN-Ag

In the two silver compounds it seems appropriate to assign the higher frequency to bridging cyanide groups. Dows and his coworkers explained this increase in the cyanide frequency on bridging by a simple vibrational analysis. They calculated the CN force constant and M-C force constant as well as the MC-CN interaction force constant, basing their calculations on $K_3[Co(CN)_6]$ where the terminal frequency is 2130 cm^{-1}. These force constants, when used in the secular determinant of the bridging case, yield higher CN frequencies (2170 cm.$^{-1}$).

L. H. Jones pointed out that under certain circumstances this vibrational analysis can lead to a decrease in CN frequency on bridging. A somewhat more detailed analysis shows that an approximate condition for an increase is that the M-N force constant must be at least four times the CN-NM interaction force constant.

INFRARED ABSORPTION STUDIES OF THE AQUEOUS CYANIDE COMPLEXES OF Cu(I), Ag(I) and Au(I)

The infrared spectral studies of L.H. Jones and Penneman have shown that increasing the ratio of the concentration of cyanide ion to metal ion in aqueous solution brings about the successive formation of $[Ag(CN)_2]^-$, $[Ag(CN)_3]^{-2}$, and $[Ag(CN)_4]^{-3}$ in the system $AgCN-KCN-H_2O$ (25); $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{-2}$, and $[Cu(CN)_4]^{-3}$ in the system $CuCN-KCN-H_2O$ (26); and only $[Au(CN)_2]^-$ in the gold system (25).

Because each of these species has an infrared-active CN stretching frequency at a different position from the others as shown in Table IV, the equilibrium constants and the constants for complete dissociation of the different species were measured as shown in Table V.

Table IV

Infrared Absorption Frequencies and Extinction Coefficients for Various Cyanide Complexes

Species	ν, $cm.^{-1}$	ϵ $moles^{-1}$ liters $cm.^{-1}$
$[Ag(CN)_2]^-$	2135 ± 1	264 ± 12
$[Ag(CN)_3]^{-2}$	2105 ± 1	397 ± 23
$[Ag(CN)_4]^{-3}$	2092 ± 1	556 ± 83
$[Cu(CN)_2]^-$	2125 ± 3	165 ± 25
$[Cu(CN)_3]^{-2}$	2094 ± 1	1090 ± 10
$[Cu(CN)_4]^{-3}$	2076 ± 1	1657 ± 15
$[Au(CN)_2]^-$	2147 ± 1	477 ± 25
CN^-	2080 ± 2	29 ± 1

Table V

Constants for Equilibria Among the Cyanide Complexes of Cu(I), Ag(I), and Au(I).

	K moles / liters
$[Cu(CN)_2]^- \rightleftharpoons Cu^+ + 2\,CN^-$	1×10^{-24}
$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$	8×10^{-22} (27)
$[Au(CN)_2]^- \rightleftharpoons Au^+ + 2CN^-$	5×10^{-39}
$[Cu(CN)_3]^{-2} \rightleftharpoons Cu^+ + 3CN^-$	2.6×10^{-29}
$[Ag(CN)_3]^{-2} \rightleftharpoons Ag^+ + 3CN^-$	1.6×10^{-22} (25, 27)
$[Cu(CN)_4]^{-3} \rightleftharpoons Cu^+ + 4CN^-$	5×10^{-31}
$[Ag(CN)_4]^{-3} \rightleftharpoons Ag^+ + 4CN^-$	2.3×10^{-21} (25, 27)

Of particular interest is the extreme stability of $[Au(CN)_2]^-$ and the complete lack of higher gold(I) cyanide complexes. All of the copper(I) cyanide complexes, and particularly the higher complexes, are more stable than the corresponding ones of silver(I). Thus in alkaline cyanide solution, copper(I) readily forms tetrahedral complexes, silver(I) does so less readily, and gold(I) does not do so at all. Apparently the availability of the sp^3 tetrahedral orbitals decreases in the order of $Cu(I) > Ag(I) > Au(I)$. In the case of gold(I), the extraordinary relative stability of the $[Au(CN)_2]^-$ ion may indicate some double-bond character of the Au-C bond.

INFRARED ABSORPTION STUDIES OF THE AQUEOUS CYANIDE COMPLEXES OF Hg, Cd, and Zn.

Characteristic infrared absorption bands were measured for several aqueous cyanide and mixed-ligand complexes of mercury, cadmium, and zinc (28). Characteristic absorption maxima in aqueous solutions are $[Hg(CN)_3]^-$, 2161 cm.$^{-1}$, $[Hg(CN)_4]^{-2}$, 2143 cm.$^{-1}$, ϵ = 113 mole^{-1} l. cm.$^{-1}$; $[Hg(CN)_2OH]^-$, 2180 cm.$^{-1}$; $[Hg(CN)_2Cl]^-$, 2189 cm.$^{-1}$; $[Hg(CN)_3Cl]^{-2}$, 2157 cm.$^{-1}$; $[Cd(CN)_3]^-$, 2148 cm.$^{-1}$; $[Cd(CN)_4]^{-2}$, 2140 cm.$^{-1}$ ϵ = 75 mole^{-1} l. cm.$^{-1}$; $[Cd(CN)_2Cl]^-$, 2147 cm.$^{-1}$; $[Cd(CN)_3Cl]^{-2}$, 2145 cm.$^{-1}$ and $[Zn(CN)_4]^{-2}$, 2149 cm.$^{-1}$, ϵ = 113 mole^{-1} l. cm.$^{-1}$.

Contrary to the interpretation of a polarographic study (29) involving $[Cd(CN)_4]^{-2}$ in excess potassiumcyanide, no infrared evidence for the formation of $[Cd(CN)_6]^{-4}$ was found. Concentrated solutions of $Hg(ClO_4)_2$ containing low CN/Hg ratios (0.1 to 1.2) showed infrared absorption from three species, two of which are shown to involve previously unknown polymeric species containing more than one metal ion per ligand.

INFRARED STUDY OF AQUEOUS CYANO AND CYANO-CHLORO COMPLEXES OF Ni(II) (30).

R. A. Penneman and L. H. Jones found that at CN/Ni ratios higher than 4/1, the infrared absorption of $[Ni(CN)_4]^{-2}$ at 2124 cm.$^{-1}$ diminishes and absorption from $[Ni(CN)_5]^{-3}$ appears at 2103 cm.$^{-1}$. The complex ion $[Ni(CN)_6]^{-4}$ is observed in saturated sodium cyanide and absorbs close to the position of $[Ni(CN)_5]^{-3}$. Stepwise formation constants were derived from quantitative infrared measurements. In aqueous solutions at ionic strength 4 at 25°C. the values are

$$[Ni(CN)_4]^{-2} + CN^- \rightleftharpoons [Ni(CN)_5]^{-3} \quad K_V = 0.279 \text{ mole}^{-1} \text{ liter}$$

$$[Ni(CN)_5]^{-3} + CN^- \rightleftharpoons [Ni(CN)_6]^{-4} \quad K_{VI} = 0.095 \text{ mole}^{-1} \text{ liter}$$

The formation constants in 2M ammonia are only slightly lower (0.256 and 0.087 respectively). The mixed-ligand complex $[Ni(CN)_5Cl]^{-4}$ is formed in solutions containing $[Ni(CN)_4]^{-2}$, NaCN, and NaCl. Its formation constant from $[Ni(CN)_5]^{-3}$ and Cl^- is 0.22 mole^{-1} liter.

BIBLIOGRAPHY

1. J. L. Hoard, Z. Krist., 84, 231 (1933).
2. L. H. Jones, J. Chem. Phys., 26, 1578 (1957).
3. E. B. Wilson, J. C. Decius, and P. C. Cross *Molecular Vibrations* (McGraw-Hill Book Company Inc. New York, 1955), Chapter 4.
4. Allen, Tidwell, and Plyler, J. Chem. Phys., 25, 302(1956).
5. L. H. Jones, J. Chem. Phys., 27, 665 (1957).
6. L. H. Jones, J. Chem. Phys., 27, 468 (k957).
7. L. Pauling, *The Nature of the Chemical Bond* (Cornell, 1939) p. 232.
8. V. Caglioti, G. Sartori, and M. Scrocco, J. Inorg. Nuclear Chem., 8, 87 (1958).
9. H. J. Emeléus, and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*,Routledge& Kegan Paul Ltd., 3rd Edition, 1960,p. 190.
10. L. O. Brockway and P. C. Cross, J. Chem. Phys., 3, 828(1935).
11. P. C. Cross, ibid. 6, 525 (1938).
12. Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules and the Chemical Bond*, Interscience Publishers Inc., New York, N. Y., 1950, p. 379.
13. R. S. Nyholm, Chem. Revs., 53, 303 (1953).
14. M. F. El-Sayed and R. K. Sheline,J. Am. Chem. Soc., 80, 2047 (1958).
15. L. Pauling, J. Chem. Soc., 1461 (1948).
16. J. W. Cable and R. K. Sheline, Chem. Revs., 56, 1 (1956).
17. I. Bellucci, Gazz. chim. ital., 49 [11] 70 (1919).
18. D. P. Mellor and D. P. Craig, Proc. Roy. Soc., N.S. Wales, 76, 281 (1942).
19. R. Nast and W. Pfab, Naturwissenschaften, 39, 300 (1952).
20. M. F. El-Sayed and R. K. Sheline, J. Am. Chem. Soc., 78, 702 (1956).
21. W. H. Eberhardt, B. Crawford, and W. N. Lipscomb, J. Chem. Phys., 22, 989 (1954).
22. G. H. Duffey,ibid., 19, 963 (1951).
23. W. P. Griffith and G. Wilkinson, J. Inorg. Nuclear Chem., 7, 295 (1958).
24. D. A. Dows, A. Haim, and W. K. Wilmarth, J. Inorg. Nuclear Chem. 21, 33 (1961).
25. L. H. Jones and R. A. Penneman, J. Chem. Phys., 22, 965(1954).
26. L. H. Jones and R. A. Penneman, J. Chem. Phys. 24, 293(1956).
27. R. Ga gin, J. Chim. Phys., 42, 28 (1945).
28. R. A. Penneman and L. H. Jones, J. Inorg. Nuclear Chem., 20, 19 (1961).
29. M. Prytz and T. Osterud, Acta Chem. Scand., 6, 1534(1952).
30. R. A. Penneman and L. H. Jones,Abstracts of the 141th American Chemical Society Meeting, March, 1962.

SPECTRAL STUDIES OF ISOMERS OF COORDINATION COMPOUNDS

James George May 1, 1962

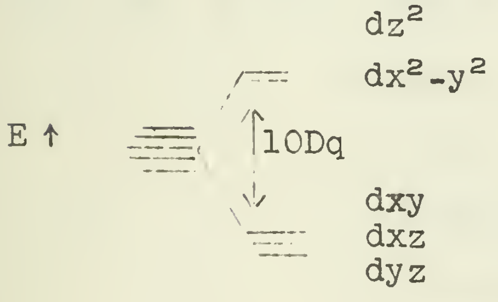
INTRODUCTION

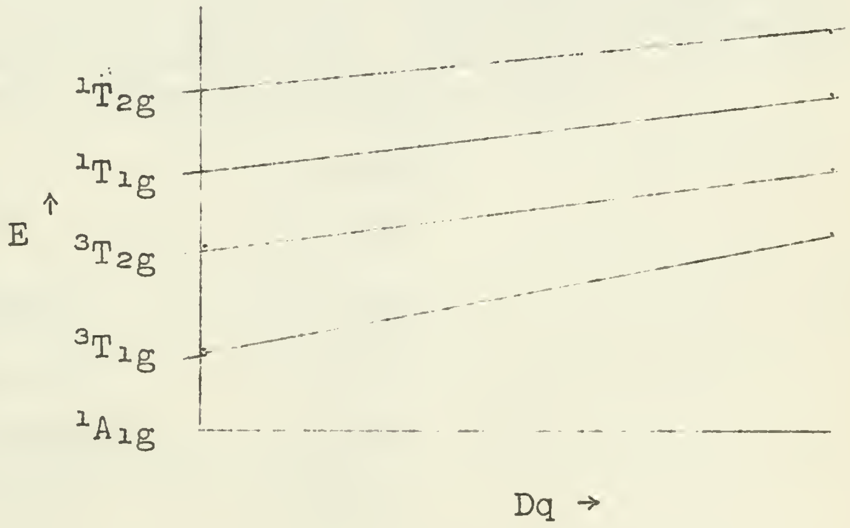
It is well known that there are many types of isomerism in coordination compounds (1). As a result, the coordination chemist is often faced with the perplexing problem of identifying or verifying the isomeric nature of a compound which he has prepared. Alfred Werner was among the first to use physical properties, in particular color, as means of identification. More recently, empirical and theoretical advances in ultraviolet and visible spectroscopy have greatly extended Werner's original "optical" method. These advances have been very nicely summarized in MODERN COORDINATION CHEMISTRY, edited by Lewis and Wilkins (2).

For the sake of simplifying the problem, only $\underline{d}^6$, strong-field complexes will be considered. The discussion, thus, will be applicable to the important cases of Co(III) and Pt(IV).

OCTAHEDRAL COMPOUNDS

If six identical ligands are placed octahedrally about a $\underline{d}^6$ metal ion, the $\underline{d}$ orbitals will be split into two levels: t_{2g} and e_g (3). The strong-field ground state, t^6_{2g}, can be described as $^1A_{1g}$. The first excited state, $t^5_{2g}\,e^1_g$, will give rise to four energy levels: $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$, and $^1T_{2g}$ (4).





The splitting of $^1T_{1g}$ and $^1T_{2g}$ or $^3T_{1g}$ and $^3T_{2g}$ is due to mutual repulsions of the electrons.

The spectrum of K_3IrCl_6 consists of five bands (5):

a. Two bands of very low intensity ($\varepsilon < 10$) and low energy, corresponding to the spin-forbidden ${}^1A_{1g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}$ transitions.

b. Two bands (crystal-field bands) of intermediate intensity ($\varepsilon = 10$-100) and intermediate energy, corresponding to ${}^1A_{1g} \rightarrow {}^1T_{2g}$, ${}^1T_{1g}$ transitions.

c. A very intense ($\varepsilon > 1,000$) charge-transfer band of higher energy. In most cobalt compounds the spin-forbidden transitions are not observed.

As the coordinating ability of the ligand increases, the separation between the ground and the first excited states also increases, and the crystal-field bands shift to higher energy. Tsuchida (6,7) and Fajans (8) have used this spectral shift to arrange the ligands in order of increasing magnitude of the shift. They found this spectrochemical series to be: $I^- < Br^- < SCN^- \sim Cl^- < NO_3^- < F^- <$ Urea $\sim$ - $OH^- \sim ONO^- \sim HCOO^- < C_2O_4^{=} < H_2O < NCS^- <$ Glycine$^- \sim EDTA^{4-} <$ Pyridine $\sim NH_3$ - $<$ Ethylenediamine $<$ Dipyridyl $< NO_2^- \ll CN^-$.

This has been a somewhat simplified presentation. The actual energy diagram for a d^6 ion is much more complicated (9). The above treatment neglects all excited states corresponding to two-electron and spin-forbidden transitions. It should be pointed out that as the strength of the field increases, the mutual repulsion of the electrons decreases as a result of delocalization onto the ligands, and the separations in the diagram tend to decrease.

SPECTRAL SHIFTS

The direction of the spectral shift in substituted compounds is determined by the relative positions of the ligands in the spectrochemical series. The greater the difference, the greater the shift will be. A few examples will serve to illustrate (10).

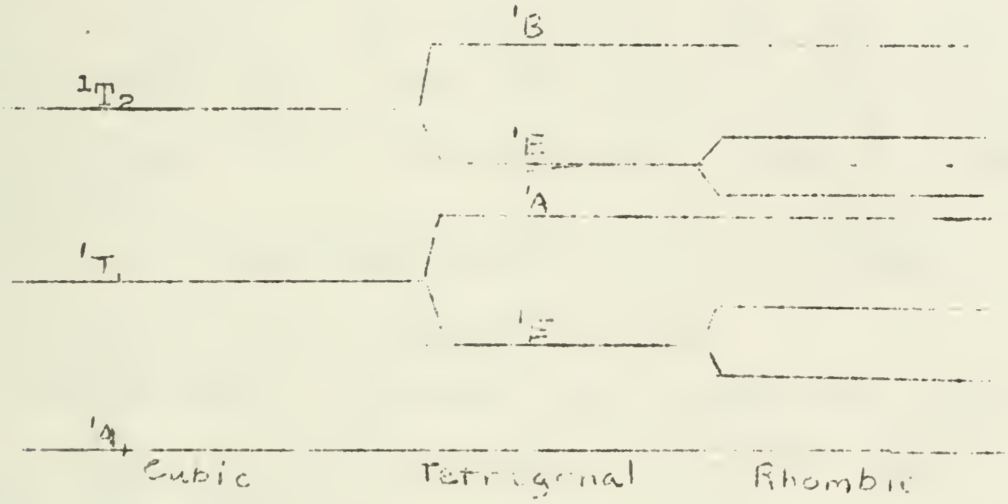
Complex	ν cm^{-1}
$Co(NH_3)_6^{+++}$	21,050
$[Co(NH_3)_5NO_2]^{++}$	21,800
$[Co(NH_3)_5NCS]^{++}$	20,200
$[Co(NH_3)_5HCOO]^{++}$	19,900
$[Co(NH_3)_5Cl]^{++}$	18,730

In some cases, the spectral shift can be used to differentiate between structural isomers (11) or to determine whether an anion is ionic or coordinated.

Jørgensen has formulated a "rule of average environment", according to which the position of a band for a substituted complex is determined by a weighted average of the fields of the ligands present provided the ligands do not differ greatly in the spectrochemical series (12). Shimura has studied a large number of cis and trans compounds of the type CoA_4B_2 and has shown that if "A" is lower than "B" in the spectrochemical series, the bands in the trans compound will appear at higher energy; the opposite is true if "A" is greater than "B" (13). It has also been pointed out that normally the bands in the cis compound are of greater intensity than those of the trans compounds.

SPLITTING IN NON-OCTAHEDRAL FIELDS

When a ligand in an octahedral complex is replaced by a second type of ligand, the symmetry of the complex is reduced. When this occurs, the triply degenerate levels (orbital degeneracy) will be split. The manner in which the energy levels split can be determined by the use of correlation tables (14). As a result, the bands in the spectra will split or become broadened.



The doubly degenerate levels in the tetragonal case will be of lower energy when the new ligand is more strongly bonding than the others present.

Jørgensen has presented a simple device for determining to which of the above symmetry systems a compound belongs (15). If μ is the dipole moment along a given axis, then the compound will belong to the cubic system when $\mu_x = \mu_y = \mu_z$, to the tetragonal when $\mu_x = \mu_y \neq \mu_z$, and to the rhombic when $\mu_x \neq \mu_y \neq \mu_z$. Quantitatively, he has shown that the splitting in the tetragonal complexes will be proportional to the difference in the dipole moments along the z and x axes.

A different approach has been developed by McClure (16). He describes the splitting in terms of two parameters, $\delta\sigma$ and $\delta\pi$, which represent the sigma and pi antibonding character of the ligands. The magnitude of the splitting is the same as by the method of Jørgensen, but in some cases the energy levels are inverted. The most important of these calculations shows that the splitting in the trans series of MA_4B_2 will be twice as large as in the cis series.

CONCLUSION

The use of visible and ultraviolet spectroscopy has been developed to the point where the chemist can use it as a tool for identifying isomers of coordination compounds. With a little ingenuity, he can now apply it to many new and different research problems.

BIBLIOGRAPHY

1. J. C. Bailar, Jr., Ed., The Chemistry of the Coordination Compounds, Reinhold Publishing Co., New York, 1956.
2. J. Lewis and R. G. Wilkens, Eds., Modern Coordination Chemistry, Interscience Publishers, Inc., New York, 1960.
3. L. Orgel, An Introduction to Transition Metal Chemistry: Ligand Field Theory, Methuen and Co., Ltd., London, 1960.
4. J. Lewis and R. G. Wilkens, p. 239.
5. C. K. Jørgensen, Acta Chem. Scand., 10, 500 (1956).
6. R. Tsuchida, Bull. Chem. Soc. Japan, 13, 388, 436, 471 (1938).
7. R. Tsuchida and M. Kobayashi, Bull. Chem. Soc. Japan, 13, 47 (1938).
8. K. Fajans, Naturwissenschaften, 11, 165 (1922).
9. J. Lewis and R. G. Wilkens, p. 250.
10. Y. Shimura and R. Tsuchida, Bull. Chem. Soc. Japan, 29, 311 (1956)
11. M. Linhard, H. Siebert, and M. Weigel, Z. anorg. u. allgem. Chem., 278, 287 (1955).
12. C. K. Jørgensen, Energy Levels of Complexes and Gaseous Ions, Gjellerups, Copenhagen, Denmark, 1957.
13. Y. Shimura, Bull. Chem. Soc. Japan, 25, 49 (1952).
14. E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill Book Co., 1955.
15. C. J. Ballhausen and C. K. Jørgensen, K. danske vidensk. Selsk., Mat. fys. medal., 29, 14 (1955).
16. D. S. McClure, in Advances in the Chemistry of Coordination Compounds, edited by S. Kirschner, Macmillan Co., New York, 1961.

ADDITIONAL SOURCES OF INFORMATION

1. F. Basolo, C. J. Ballhausen, and J. Bjerrum, Acta Chem. Scand., 9, 810 (1955).
2. J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, Acta Chem. Scand., 8, 1275 (1954).
3. C. K. Jørgensen, Acta Chem. Scand., 10, 500 (1956).
4. C. K. Jørgensen, Acta Chem. Scand., 11, 151 (1957).
5. V. M. Linhard and M. Weigel, Z. anorg. u. allgem. Chem., 264, 321 (1951).
6. V. M. Linhard and M. Weigel, Z. anorg. u. allgem. Chem., 266, 49 (1951).
7. V. M. Linhard and M. Weigel, Z. anorg. u. allgem. Chem., 267, 113, 121 (1951).
8. V. M. Linhard and M. Weigel, Z. anorg. u. allgem. Chem., 271, 101 (1952).
9. Y. Shimura, Bull. Chem. Soc. Japan, 25, 46 (1952).
10. M. Mori, M. Shibata, E. Kyuno, and T. Adachi, Bull. Chem. Soc. Japan, 29, 884 (1956).
11. M. Mori, M. Shibata, E. Kyuno, and T. Adachi, Bull. Chem. Soc. Japan, 31, 291 (1958).

REACTIONS AND EQUILIBRIA IN LIQUID HYDROGEN FLUORIDE

F. Y. Tsang May 8, 1962

I. INTRODUCTION

Liquid hydrogen fluoride is commonly regarded as the most "water-like" solvent. This undoubtedly is the result of similarities in structure (isoelectronic), degree of H-bonding, dielectric constant, and many other physical and chemical properties between the compound and water. Its chemistry would undoubtedly have been much more thoroughly investigated had it not been for the hazards involved in handling it, including its extremely corrosive and poisonous characteristics. It still is one of the most extensively studied non-aqueous inorganic solvents.

In spite of the fact that aqueous hydrogen fluoride is a weak acid, the anhydrous compound has an extremely negative Hammett acidity value. (<10.02 when pure) (1). Indeed, there is no known substance that can behave as a Brønsted acid in liquid hydrogen fluoride; even Lewis acids are very limited in number(2).

Hydrogen fluoride was first prepared and reported by Margraff in 1768 (3). Fremy(4) and Simon(5) developed the method of preparing the anhydrous material which is still followed extensively today, namely

$$KHF_2 \xrightarrow[\text{Cu or Ni vessel}]{\text{elec in}} \text{anhyd.}KHF_2 \xrightarrow[500°-600°C.]{\Delta} HF\uparrow + KF$$

II. REACTIONS

A. Inorganic reactions

Because of the highly acidic nature of liquid hydrogen fluoride, dissolution of a vast number of inorganic compounds is followed immediately by solvolytic or protonation reactions(6). This extreme solvolytic nature makes metathetical reactions in this solvent less feasible. For example:

$$AgF + NaCl\ (\text{fresh}) \xrightarrow[HF]{\text{Liq}} AgCl\ (c) + NaF$$

$$AgF + NaCl\ (\text{stand at } 10°C) \xrightarrow[HF]{\text{Liq}} \text{no reaction}$$

An extensive study had been carried out by Clifford and coworkers (2) on acid-base reactions in liquid hydrogen fluoride. The criterion of acidity is based upon the ability to react with bases of different strength. On this basis, the acids were

divided into eight categories in order of decreasing strength:

(1) dissolve CoF_3
(2) dissolve Cr, Mn
(3) dissolve Mg, or react with CoF_2, CuF_2, AgF_2
(4) form salt with AgF
(5) very weak (solution unstable)
(6) amphoteric
(7) neutral
(8) soluble strong base (alkali metal fluorides).

Table I summarizes the acidities of various fluorides.

Anhydrous silver(I) tetrafluoroborate, $AgBF_4$, was successfully prepared in liquid hydrogen fluoride (7). Complex formation in the solvent had also been studied (8). It was found, for example, that a solution of acetonitrile will dissolve zinc vigorously, nickel readily, and cobalt and iron slowly. Evaporation of the above solutions gives the adducts $MF_x(CH_3CN)_y$. Furthermore, $[Cu(H_2O)_x]^{++}$ could be formed in liquid HF, in analogy to $[Cu(NH_3)_x]^{++}$ in water.

B. Organic reactions (9-12)

Organic compounds, in general, are either insoluble or very soluble in liquid hydrogen fluoride. The soluble compounds (with but few exceptions) are those possessing substituents containing N, S, O, or C=C.

The above property, together with the high acidity and dehydrating power of the solvent, make it a reaction medium for many organic reactions (13), even on a commercial scale. Typical reactions are fluorination, nitration, sulfonation, and diazotization

III. EQUILIBRIA AND EQUILIBRIUM CONSTANTS

As mentioned before, certain fluorides act as Lewis acids in liquid hydrogen fluoride. The dissociation constant of the ion BF_4^-, a conjugate base, was measured conductometrically (14) and found to be about 5×10^{-3} at 20°C.,

From this value, and the equilibrium constant for the reaction represented as

$$BF_3 + 2HF \rightleftharpoons H_2F^+ + BF_4^-$$

measured in a similar fashion, the auto-ionization constant of hydrogen fluoride (to give H_2F^+ and F^-) was estimated to be $< 2 \times 10^{-10}$.

Another approach was used to compare acid strength in liquid hydrogen fluoride (15). An excess of the volatile acid is added to a solution of a base, say sodium fluoride in the solvent, and the solution evaporated. The resulting mixture is analyzed for metal and fluorine content, thereby establishing the extent of solvolysis of the conjugate base of that acid. Table II

summarizes the experimental results which led to the relationship

BF_3, AsF_5, PF_5, $SbF_5 > GeF_4 > TeF_6 > SeF_6$

As in the case of adding sulfur trioxide to 100% sulfuric acid to increase the magnitude of its Hammett acidity value, addition of antimony(V) fluoride to 100% hydrogen fluoride has a similar effect (16).

The solubility product constants for the salts $AgBF_4$, $TlSbF_6$, and CaF_2 were measured (17,18). From the solubility of calcium fluoride in hydrogen fluoride containing different quantities of water, the K_B for H_2O in HF can be estimated to be 0.55.

With the aid of spectrophotometric measurements, Kilpatrick and coworkers (16) showed that antimony(V) fluoride has the same order of acidic strength in hydrogen fluoride as the ion HSO_4^- is in water.

$$2HF + SbF_5 \underset{K=4.4x10^{-4}}{\rightleftharpoons} H_2F^+\ SbF_6^-$$

$$\underset{K=1.7x10^{2}}{\rightleftharpoons} H_2F^+ + SbF_6^-$$

IV. CONCLUSION

Despite its powerful solvolytic property, liquid hydrogen fluoride has many other specifically useful properties. It should prove to be useful as a medium for many other reactions in the near future.

V. REFERENCES

1. H. H. Hyman, M. Kilpatrick, and J. J. Katz, J. Am. Chem. Soc., 79, 3668 (1957).
2. A. F. Clifford, H. C. Beachell, and W. M. Jack, J. Inorg. Nucl. Chem., 5, 57 (1957).
3. J. Margraff, Memoires de Berlin, p. 3(1768).
4. M. E. Fremy, Ann. chim. et phys., [3], 47, 5 (1856).
5. J. Simons, J. Am. Chem. Soc., 46, 2179 (1924).
6. K. Fredenhagen, Z. Elektrochem., 37, 684 (1931).
7. A. F. Clifford and S. Kongpricha, J. Inorg. Nucl. Chem., 5, 76 (1957).
8. A. F. Clifford and J. Sargent, J. Am. Chem. Soc., 79, 4041 (1957).
9. V. W. Klatt, Z. anorg. u. allgem. Chem., 222, 225(1935).
10. V. W. Klatt, Z. anorg.u. allgem. Chem., 232, 293(1937).
11. V. W. Klatt, Z. anorg. u. allgem. Chem., 234, 189(1937).
12. K. Fredenhagen, Z. Physik. Chem., A164, 176(1933).
13. K. Wiechert in Newer Methods of Preparative Organic Chemistry, Interscience Publisher, New York, 1948.
14. M. Kilpatrick and F. E. Luborsky, J. Am. Chem. Soc., 76, 5863 (1954).
15. A. F. Clifford and A. G. Morris, J. Inorg. Nucl. Chem., 5,71(195
16. H. H. Hyman, L. A. Quaterman, M. Kilpatrick, and J. J. Katz, J. Phys. Chem., 65, 123 (1961).
17. S. Kongpricha and A. F. Clifford, J. Inorg. Nucl. Chem., 18, 270 (1961).
18. A. F. Clifford and S. Kongpricha,J.Inorg.Nucl.Chem.,20,147(1961).

Table I

Relative Strengths of Fluoroacids in HF

Periodic Group	Category (refer to IIA)						
	7	6	5	4	3	2	1
IIA		Be(II)					
IVA			Ti(IV)				
VA				Nb(V) Ta(V)	V(V)		
VIA		Cr(III)			Mo(VI) W(VI)		
VIIA					Re(VI)		
IIIB		Al(III)				B(III)	
IVB	C		Si(IV)	Ge(IV)	Sn(VI)		
VB	N	Sb(III)			P(V)	As(V)	Sb(V)
VIB	O S(VI)		Se(IV)	Te(VI)			
VIIB	F Cl(III)			I(V)			

Table II

Extent of Solvolysis of Various Fluoro Anions

Acid Used	Base Added		Product Obtained				
	Cmpd.	Wt.(g)	Wt.(g)	Theoretical for		%dev.	Solubility in HF
PF_5	AgF	0.5398	1.0777	1.0752g.	$AgPF_6$	+0.3	sol.
	BaF_2	0.4662	1.1088	1.1360	$Ba(PF_6)_2$	-2.4	sol.
	NaF	0.3312	1.2977	1.3247	$NaPF_6$	-1.9	sol.
AsF_5	BaF_2	0.1999	0.5991	0.5874	$Ba(AsF_6)_2$	+2.0	mod.sol.
	NaF	0.1913	0.9941	0.9652	$NaAsF_6$	+3.0	sl.sol.
TeF_6	AgF	0.1786	0.5313	0.5187	$AgTeF_7$	+2.4	mod.sol.
	BaF_2	0.2532	0.7869	0.6018	$BaTeF_8$	+30.7	sol.
				0.9492	$Ba(TeF_7)_2$	-17.3	
	CaF_2	0.1328	0.8010	0.5437	$CaTeF_8$	+47.3	sol.
				0.9544	$Ca(TeF_4)_2$	-16.1	
SeF_4	BaF_2 in 20ml.HF	0.1810	0.2308	0.3437	$BaSeF_6$	-32.9	sol.
				0.2017	$BaHF_3$		
	BaF_2 in 30ml.HF	0.1813	0.2174	0.3442	$BaSeF_6$	-36.9	
				0.2020	$BaHF_3$		
	NaF	0.1447	0.2423	0.6786	$NaSeF_5$	-64.3	sol.
				0.2136	$NaHF_2$		
IF_5	BaF_2	0.1937	0.3236	0.6832	$Ba(IF_6)_2$	-52.6	sol.
				0.4388	$BaFIF_6$	-26.3	
				0.2158	$BaHF_3$		
	NaF	0.1971	0.3150	1.2357	$NaIF_6$	-74.5	mod.sol.
				0.2910	$NaHF_2$		
GeF_4	BaF_2	0.1658	0.4110	0.4468	$Ba(GeF_5)_2$	-8.0	sol.
				0.3064	$BaGeF_6$	+25.5	
	NaF	0.2172	0.9248	0.9857	$NaGeF_5$	-8.3	sol.

SOME RECENT DEVELOPMENTS IN TETRAHEDRAL COMPLEXES

J. T. Donoghue May 15, 1962

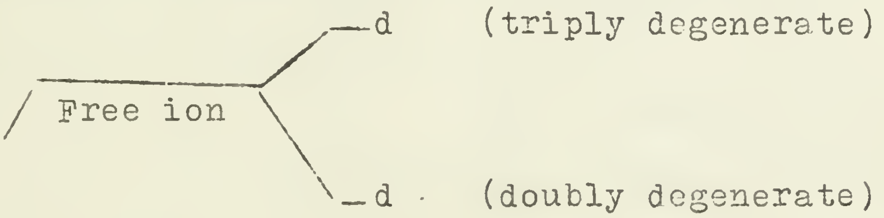
I. INTRODUCTION

Before 1950, many four coordinate complexes were assumed to possess square planar or tetrahedral symmetry solely on the basis of stoichiometry and considerations of the steric requirements of the ligand and metal ions, or as was the case in many instances, assignment of structure was based on magnetic criterion of bond type. Often, the possession of a particular color was associated with a particular geometrical arrangement of ligands about a metal ion. However, with developments in and the more general application of physical methods of investigation of structures of coordination compounds (particularly x-ray methods), many of the earlier geometrical studies have been shown to be incorrect.

Ligand field theory has yielded some useful results in modern investigations of structures of complexes. Spectral properties can often be predicted by its application and in many instances, x-ray work can be cited to vindicate assignments of structure made by analysis of the spectrum of the complex in question. The magnetic moment of the complex, although a somewhat less certain criterion than the spectrum, is also often characteristi of the gross symmetry of the ligand field which perturbs the central metal ion. There still remain many unresolved questions regarding assignment of structures from spectral and magnetic data, and many workers in the field are often at odds with one another on the validity of certain assumptions.

II. GENERAL

On the basis of simple electrostatic theory, one would predict that regular tetrahedral environments would be achieved most easily in complexes of the first series, the electronic configurations of which are represented by the following nonbonding arrangements of d electrons: d^0, d_{γ}^2, d_{γ}^2, d_{ϵ}^3, d_{γ}^4, d_{ϵ}^3, and d^{10}, where



The above configurations apply respectively to the following ions: Ca(II); Ti(II); Mn(II) and Fe(III); Co(II); Zn(II) and Cu(I).

It will be noted that for the above configurations the metal d electrons constitute filled, half-filled, or empty shells or subshells. Under these conditions, no distortions from regular tetrahedral symmetry are expected. However, arrangements other than the above, due to ground-state configurations which are

orbitally degenerate, could give rise to tetrahedral complexes in which the arrangement is distorted from regular symmetry by the operation of Jahn-Teller forces. These distortions might be either small or large depending on the nature of the configuration.

III. COBALT(II) - $\underline{d}^4_\gamma \underline{d}^3_\epsilon$

The cobalt(II) ion forms a large number of tetrahedral complexes which have been well characterized. Many crystal-structure determinations have been made, and it is thus possible to make a number of correlations between the known crystal structures and the associated spectral and magnetic properties. With this body of data available, it is thus possible to use spectral data to elucidate electronic structures for the cobalt(II) ion in many of its compounds.

The history of studies of the structures of the halo complexes of cobalt(II) is interesting and is typical of the work which has been done. The $CoCl_4^{-}$ ion has been found to be a discrete tetrahedral unit in the compounds: Cs_2CoCl_4 (2) and Cs_3CoCl_5 (3). In addition, Nyholm(1) has characterized the compound $[Et_4N]_2CoCl_4$ and found it to contain tetrahedral cobalt(II). The spectra of the compounds $[Et_4N]_2[CoX_4]$ in nitromethane have been studied by the latter authors, and the solution spectra are in accord with theoretical predictions for tetrahedral complexes. The visible electronic spectrum consists of a broad band which often has a great deal of fine structure and intensities that are very much greater than those usually observed for octahedral cobalt(II), (i.e. 400-2000 for T_d and 5- 20 for O_h). Cotton(4) has established that the solid-state spectra of these compounds are the same as the solution spectra, indicating that no gross changes have occurred in the solution process. Crystal-field theory predicts three spin-allowed transitions at 3000-5000 cm.$^{-1}$, 5000 - 6000 cm.$^{-1}$, and 16,000 - 17,000 cm.$^{-1}$, respectively. The first transition is often not observed due to ligand vibrational transitions or solvent absorption, though the other bands (ν_2 and ν_3) have been observed for many cobalt(II) complexes.

The following equations have been applied in calculating ligand-field parameters for cobalt(II) (5). They can be derived from the equations of Tanabe and Sugano(6).

$$\nu_1 = \Delta \qquad (1)$$

$$\nu_2 = 1.5\Delta + 7.5\ B' - Q \qquad (2)$$

$$\nu_3 = 1.5\Delta + 7.5\ B' + Q \qquad (3)$$

$$Q = 1/2[(0.6\Delta - 15B')^2 + 0.64\Delta^2]^{1/2} \qquad (4)$$

where Δ= ligand-field modulus, B' = Racah interelectronic repulsion parameter.

The value of Δ(10Dq') thus obtained can be used in conjunction with the magnetic moment to obtain a value for the spin-orbit

coupling constant λ^1, according to the relationship (5,7):

$$\mu = \mu_{So} - \frac{15.56\,\lambda^1}{\Delta} = 3.89 - \frac{15.56\,\lambda^1}{\Delta} \qquad (5)$$

where μ_{So} is the spin-only value of the moment.

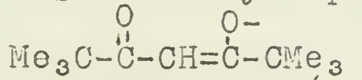
Figgis has predicted a range of magnetic moments consistent with tetrahedral cobalt(II) (8). The range is 4.3-4.8 B.M. The known or presumed cases of this stereochemistry fall in this range with but few exceptions (see Table I).

An interesting series of compounds formed by transition-metal halides with sulfoxides has been reported by several workers (9, 10, 11, 12). Cobalt forms a series for which it is generally agreed that CoX_4^- unit is present: (i.e. $CoCl_2.3DMSO = [Co(DMSO)_6][CoCl_4]$. The spectra of these compounds is the superposition of those which are obtained separately for the cation and anion. Also, the magnetic moment is very close to the root mean square average of the moments of the cation and anion.

Table I Spectral and Magnetic Data for Tetrahedral Cobalt(II)

Complexes

Complex	ν_2, Cm.$^{-1}$	ν_3, Cm.$^{-1}$	Δ, Cm.$^{-1}$	λ', Cm.$^{-1}$	μeff, B.M.,	Ref.
$CoCl_4^=$			3250		4.65	20,13
CoP or $_4^=$					4.75	13
$CoI_4^=$					4.88	13
$Co(N_3)_4^=$	6750	14900	3920	146	4.47	5
$Co(NCO)_4^=$	7150	16100	4150	115	4.32	5
$Co(\varnothing_3PO_4)^{+2}$					4.72	15

Cotton(15) has recently reported a 1:2 complex of cobalt(II) with the ligand  $Me_3C-\overset{O}{\overset{\|}{C}}-CH=\overset{O-}{\overset{|}{C}}-CMe_3$ (DPM). Partial single-crystal work indicates that the cobalt(II) is at the center of a distorted tetrahedron (i.e. - perhaps D_2d). The compound is unusual in that the spectrum gives a band of very low intensity compared with those of CoX_4^- ions. Further work on this compound should be reported shortly.

Isslieb (16) has prepared complexes of the type $[(Me_3NO)_4Co](ClO_4)_2$, $[(Me_3NO)_2CoX_2]$ and $[(Me_3NO)_3CoX]X$. The magnetic moments of these compounds are in accord with those expected for tetrahedral cobalt(II). No spectra were reported.

Mixed complexes of the types $CoX_2.2R$ have been prepared where R is $\varnothing_3PO$ (17,18), and $CoX_2.2R_3P$ and $[CoX_3.R_3P]^-$ have been prepared where R is C_6H_5 and cyclohexyl (13).

An interesting series of $MCl_2.2py$ compounds was studied by Nyholm(19). The cobalt(II) compound exists in two forms - red and blue. The red solid decomposes in solution to give the paramagnetic blue compound, which is unstable in the solid state. The violet form exhibits a magnetic moment in excess of 5 B.M. and gives a reflectance spectrum typical of octahedral cobalt(II) whereas the blue form gives a moment typical of tetrahedral cobalt (II) and a spectrum very similar to that of $CoCl_4^=$. It is thought that cobalt(II) achieves octahedral coordination in the red form by polymerization and that this polymer breaks down in solution to give a tetrahedral monomer.

Many studies of equilibria between various halo cobalt species in solution have been carried out. Buffagini and Dunn (20, 21) have demonstrated that in solutions of dipositive cobalt in solvents such as nitromethane and dimethylformamide (DMF), species other than $CoCl_4^=$ are present, and in support of this the species $[CoCl_3(DMF)]^-$ was isolated. They find that only when a large excess of chloride ion is present is all of the cobalt present as the tetrahalo ion. A similar study was carried out in acetone (22), and in this case conditions were favorable enough to demonstrate the existence of intermediates such as $[CoCl_2.2Ac]$, $[CoCl_3.Ac]^-$ in addition to $CoCl_4^=$. Equilibrium constants for the stepwise formation reactions were estimated. Finally, Cotton (13) has found that under ordinary conditions (up to 9$\underline{M}$ HCl) in aqueous solution, only a very small fraction of the cobalt is actually present as $CoCl_4^=$.

IV. Manganese $\underline{d}^2\gamma\ \underline{d}^3\epsilon$

No distortion from tetrahedral geometry is expected, and many complexes should be obtainable.

Jørgensen(23) has examined the spectrum of $[Et_4N]_2[MnBr_4]$ and has concluded that it is in accord with a tetrahedral arrangement around the manganese(II) ion. The electronic spectra of both tetrahedral and octahedral manganese(II) are similar in that both show a large number of electronic absorptions. The main difference lies in the intensities of absorption. As is generally observed, the tetrahedral species has intensities (0.2-2.0) much higher than those of the octahedral complex(0.001- 0.02). Nyholm and coworkers (1,24) have established from x-ray data that the $MnX_4^=$ ion is tetrahedral. They have examined the spectra of these compounds using solutions in nitromethane and obtained results similar to those of Jørgensen. Cotton(25) has established that no major structural changes accompany the solution process by an examintion of the mull and reflectance spectra of these compounds.

The ion $[Mn(\phi_3PO)_4]^{+2}$ has been reported (26); its x-ray diffraction diagram is somewhat different than those of the cobalt(II) and zinc(II) derivatives, which exhibit strict isomorphism. There is still some doubt concerning the structure of this ion.

Various other workers report the preparation and properties of MnX_4^- compounds, including spectral analyses (27,28,29,30,31, 32,33). It is now generally recognized that these compounds contain the tetrahedral MnX_4^- units.

As a result of the nature of the ground and excited-state configurations of manganese(II) in both tetrahedral and octahedral fields, no large orbital contributions to the magnetic moment are expected for either case. It is thus not possible to draw inferences from measurements of magnetism (34). It has been observed that the moments for all spin-free manganese(II) compounds are close to the spin-only value, regardless of stereochemical configuration.

Compounds of the type $MnX_2.2L$ have been reported where L is Me_3NO, py NO (16), $\varnothing_3PO$,$\varnothing_3AsO$ (35), and $\varnothing_3P$,$\varnothing_3As$ (33). The spectra of most of these compounds have been obtained and interpreted in terms of a tetrahedral structure.

The configuration $\underline{d}^2$ $\underline{d}^3$ is also characteristic of the complexes of Fe(III). The crystal structure of the ion $FeCl_4^-$ (Cs salt) shows that the iron is at the center of a flattened tetrahedron (36). The spectrum of this ion in several solvents has been recorded (37,38). The compound $[Fe(\varnothing_3PO)_4](ClO_4)_3$ has been reported (39,40) and its absorption spectrum is similar to that of $FeCl_4^-$. The compound $[FeCl_3.2PAr_3]$ (Ar is aryl) has been reported. It is thought that this species is dimeric and thus contains octahedral iron. The same author reports $[Ar_3PH]FeCl_4$ (41).

V. COPPER(II) $\underline{d}^4_{\gamma}$ $\underline{d}^5_{\epsilon}$

The ground state for copper(II) in a tetrahedral field is degenerate, and therefore, the tetrahedron should be distorted. Liehr (42) points out, however, that if spin-orbit coupling is accounted for, the ground-state degeneracy can be removed without the operation of the Jahn-Teller effect, and thus a tetrahedral copper(II) system should be possible. On the basis of these assumptions, Liehr has constructed an energy-level diagram for copper(II) in tetrahedral fields. Using typical values for Dq' and other electronic parameters, he calculates that tetrahedral copper(II) should show a transition at 5,000-7,000 $cm.^{-1}$ and no transitions in the visible region. Pappalardo has investigated the spectrum of copper(II) in ZnO lattices and has found the spectrum to be in good agreement with predictions (43). The spectrum of Cs_2CuCl_4 is also in reasonable agreement with these predictions. However, the crystal structure of this compound has been investigated, and it was found that the copper(II) is situated at the center of a grossly distorted tetrahedron (44) (i.e. halfway between a square plane and a regular tetrahedron). The fact that the $CuCl_4^-$ ion is so distorted would seem to indicate that spin orbit interaction is not sufficient in removing the degeneracy, and Jahn-Teller forces are operable. It is of interest to note that the spectrum of the $CuCl_4^-$ ion is significantly different in the solid state than in solution (10). Nyholm has reported the spectrum of $CuBr_4$ $[Et_4N]_2CuBr_4$ and found it to be somewhat similar to the spectrum of $[Et_4N]_2CuCl_4$ (1), and it is thus concluded that the structures of these ions are similar.

The compounds $[Cu(\emptyset_3PO)_2Cl_2]$ and $[Cu(\emptyset_3PO)_2Br_2]$ have been assigned pseudotetrahedral structures on the basis of their spectra (45), although no conclusions could be drawn relative to the magnitude of distortions if any are present.

Magnetism, per se, has been of little use in the elucidation of structures of copper(II) complexes, although it is thought that copper(II) in $\underline{T}_d$ fields should exhibit fairly large orbital contributions (1). The moment of the ion $CuCl_4^{=}$ has been found to be 1.9 - 2.0 B.M. This is not significantly different from those found for copper(II) in square-planar circumstances.

Other studies of copper(II) involved ligands that were designed to force a tetrahedral configuration on the cation (46).

VI. IRON(II) $\underline{d}^3$ $\underline{d}^3$

The difference in CFSE for tetrahedral and octahedral iron(II), calculated for the same ligand, is 3 kcal. in favor of the octahedral complex. Thus it should be possible to form tetrahedral complexes of iron(II). The Jahn-Teller theorem requires distortion, since the ground-state configuration is degenerate. The degeneracy, however, is in the lower level ($\underline{d}_{\gamma}$), and so distortion is not expected to be large. Gill(47) has prepared $[Et_4N]_2[FeCl_4]$, an almost colorless solid. The spectra of this compound and that of $[Et_4N]_2[FeBr_4]$ show no absorption, except for strong charge-transfer bands below about 450 mu. Although in mull, it appears that these compounds absorb at around 3000 cm.$^{-1}$, which is in the CH stretching region. The powder pattern of the chloro complex shows that it is isomorphous with the nickel(II), zinc(II), and cobalt (II) derivatives. This evidence supports a tetrahedral formulation for the iron(II) derivative. The magnetic moment of the compound is 5.3-5.4 B.M. (θ=C°); in the permissible range for $\underline{T}_d$ iron(II).

Complexes of the types $FeX_2.2\emptyset_3P$, $Fe(\emptyset_3P)_4^{+2}$, and $Fe(\emptyset_3As)_4^{+2}$ (48, 49) have been postulated to contain tetrahedral iron, as have the compounds $[Et_2PH]_2FeCl_2$ and $[\ C_6H_{11})_2PH\ _2FeCl_2]$ (49).

VII. CHROMIUM (II) $\underline{d}^2_{\gamma}\underline{d}^2_{\epsilon}$

The degeneracy in the ground state occurring in the higher triplet, would require very large distortions from regular tetrahedral symmetry. Crystal-field theory predicts that a square-planar or tetragonal six-coordinate complex should be favored. In support of this there seem to be very few known complexes of Cr(II) with tetrahedral symmetry.

The blue compounds $CrCl_2.2PR_3$ have been suggested to contain tetrahedral chromium(II)(50). In addition, the compounds $CrCl_2.2POR_3$ (51) have also been characterized. The latter compounds have dipole moments of approximately 5 D. This would seem to rule out trans planar structures, though not cis planar or distorted tetrahedral arrangements.

VIII. NICKEL(II) $\underline{d}_{\gamma}^{4}\underline{d}_{\epsilon}^{4}$

More uncertainty and controversy have characterized the tetrahedral complexes of nickel(II) than the complexes of any other metal ion. There have been many claims and counter claims; much heat having been generated and surprisingly little light.

Within very recent years, a complete theory of nickel(II) in tetrahedral fields, including spin-orbit coupling, has been worked out by Liehr and Ballhausen (52). Simple theory predicts that this cation in a tetrahedral field must be distorted from pure tetrahedral symmetry, the ground-state configuration being degenerate. However, Liehr contends (53) that if spin-orbit coupling is allowed for, the ground state is non-degenerate and Jahn Teller forces need not operate. He points out also, that the first excited state to higher energies is 3,000 cm.$^{-1}$, and thus no large pseudo Jahn-Teller distortions are to be expected.

About the safest thing to say about this area is that it is now recognized that there are very few tetrahedral complexes of nickel(II). Earlier it was believed that if stoichiometry suggested four-coordination and if the compound were paramagnetic, then the nickel(II) must be tetrahedrally coordinated. X-ray work has shown that much of this work was in error. A typical example is the compound $Nien_2(SCN)_2$, which has a deep blue color. X-ray (54) work showed that the NCS^- ion is within the coordination sphere and that coordination is *trans* octahedral. Thus, color as a criterion for stereochemistry fell into disrepute.

The first case of tetrahedral nickel(II) that was supported by actual structural investigations was reported by Venanzi(55,56). The compounds $NiX_2.2\phi_3P$ (X is halogen, NCS) were prepared and studied. The compounds for which X is halogen showed susceptibilities corresponding to moments of 3.1 - 3.3 B.M. (just greater than spin only values). The thiocyanato derivative was diamagnetic and gave a very low dipole moment in benzene. X-ray work showed the chloro derivative to be tetrahedral and the iodo and bromo derivatives to be not *trans* planar. Since these compounds had large dipole moments, it was concluded by inference that they contained tetrahedral nickel(II), whereas the thiocyanato compound is thought to be *trans* planar.

Further work by this group of investigators included studying the effects of successive substitution of alkyl groups for phenyl in the phosphine ligand. Again, the NCS^- compound was diamagnetic and showed a low dipole moment, regardless of ligand. The halo derivatives were found to be tetrahedral when the ligand contained only one alkyl group, i.e., $C_4H_9P\phi_2$, and diamagnetic planar when the ligand contained two butyl groups, e.g., $(C_4H_9)_2P\phi$ (57).

A third article by this group (58) describes complexes of nickel(II) with the ligands (*p*-tolyl)$_3$P and (*p*-MeO-C_6H_4)$_3$P. The results are similar to those stated above.

Ballhausen and Liehr's complete theory found a test in interpretation of the spectrum of nickel(II) trapped in silicate glasses (60,61). The agreement was quite good. Further support was gained from examination of the spectrum of nickel(II) - chloride systems in fused LiCl-KCL eutectic (62,63,64). Jørgensen (65) interpreted the spectrum and by allowing for the absorption of $NiCl_6^{4-}$ ion (estimated from the reflectance spectra of $MNiCl_3$ compounds (66)) deduced the positions of the bands of $NiCl_4^{-}$ in these melts. The assignments agree well with those reported by Nyholm (1) for the $NiCl_4^{-}$ ion in nitromethane.

Much work has been done on pseudotetrahedral nickel(II) compounds of the type $NiX_2.2L$ (L is $\emptyset_3PO$,$\emptyset_3AsO$) (67,69,70). Though the formal symmetry of these compounds can be no higher than C_{2v}, Cotton has successfully interpreted their spectra, with the aid of the average field approximation (68), in terms of a cubic tetrahedral field with a component of lower symmetry imposed on the cubic field. For many of the cases mentioned, the perturbing effects of the different ligands are not evident in the spectra. Other species successfully treated in this manner are $[Ni(\emptyset_3P)X_3]^-$ and $[Ni(\emptyset_3P)_2X_2]$, for which slight splittings of the absorption bands, presumably due to the noticeable perturbing effects of the lower symmetry components, are reported (71,72). The compound $[(\emptyset_3PO)_2Ni(NO_3)_2]$ has been described and its spectrum interpreted in terms of the nickel(II) being situated at the center of a grossly distorted tetrahedronn(i.e., D_{2d}). The spectrum for nickel(II) for this point group was predicted by Furlani (73,74) and was found to resemble very closely that of the nitrato compound.

Interesting work similar to that described by Venanzi, involves compounds of the type $NiX_2.2PR_3$, for which it is found that nickel(II) is tetrahedral only when R is predominantly aryl. For when R is cyclohexyl, the compounds are square planar (75), or when R is Me or Et the nickel ion is six coordinate (76).

As regards symmetrical (i.e., all four groups the same) tetrahedral complexes, it appears at present that the NiX_4^{-} ions are the only representatives. The characterization of these species in melts has already been described. A few years ago, Cotton (39) reported the compound $[Ni(\emptyset_3PO)_4](ClO_4)_2$ to contain tetrahedral nickel(II) on the basis of the magnetic moment. The spectrum could be interpreted in terms of a tetrahedral geometry if it was assumed that the term separations in the complex were not reduced relative to those in the free ion. However his conclusions were criticized on several counts ([illegible]), and in the meantime the paper by Ballhausen had appeared. Reinterpretation of the spectrum revealed that the compound could not be tetrahedral unless Dq had the value of 1750 $cm.^{-1}$; a value greater than those found for octahedral complexes. Also, intensities of absorption seem to rule out a T_d environment, and finally the powder pattern of this compound was somewhat different than those of the cobalt(II) and zinc(II) derivatives, which are strict isomorphs (40). It was then concluded that the species had D_{2d} symmetry. Subsequent to this paper, Furlani published a predicted spectrum of nickel(II) in D_{2d} fields. This agress very nicely with the spectrum published by Cotton (73,74).

Figgis (8,34) has predicted a permissible range of moments for nickel(II) in tetrahedral circumstances. It is thought that the magnitude of the orbital contribution, in these cases, should be a sensitive function of the deviation of the compound from regular tetrahedral stereochemistry. Thus the ion $NiCl_4^{2-}$ and dipositive nickel in silicate glasses, both of which show high moments, are thought to exhibit little distortion. The crystal structure of the compound $[Et_4N]_2[NiCl_4]$ is in agreement, and the results indicate that if there is any distortion of the tetrahedron in this case it is in the sense that three bonds are equivalent and the fourth slightly different (1,24). However, some of the mixed compounds that can not have T_d symmetry exhibit moments as large as those of the $NiX_4^=$ ions; so it is not known at present if this criterion is completely valid.

IX. MISCELLANEOUS COMPLEXES

The compounds $[Ag(\emptyset_3P)_4^+]ClO_4$ and $[Cu(\emptyset_3PO)_4]ClO_4$ have been described (78). No attempts at studying the structures of these species have been made.

Recent studies of Ni(β-diketone)$_2$ compounds (79,80,81), including a complete x-ray analysis (79), seem to have demonstrated the polymeric and octahedral nature of the complex $Ni(acac)_2$. Recent work on aldimine compounds seems to indicate planar arrangements in these compounds (82,83).

A very recent study of the species present in melts is of particular interest. Gruen (84) has studied the absorption spectra of halide-vanadium(II), vanadium(III), vanadium(IV), and vanadium(V) systems in LiCl-KCl eutectic, paying particular attention to octahedral- tetrahedral equilibria for the vanadium(II) and (III) systems. At high temperatures, the spectra can be interpreted in terms of the presence of tetrahedral VCl_4^- and VCl_4^- ions, respectively. A second paper in this series, reports the $NiCl_4^=$ ion in the compound Cs_3NiCl_5 and gives a literature survey of studies of this type (85).

X. DISCUSSION

Venanzi considers that the following is pertinent for the formation of tetrahedral $NiX_2.2L$ compounds. The difficulty involved is not the inherent instability of nickel(II) ion in tetrahedral surroundings, but the tendency to attain six-coordination by tetragonality or condensation. Thus the two factors considered as most important are: the field generated by the ligands should not be strong enough to give spin-pairing and the ligand bulky enough that the T_d arrangement is preferred.

Nyholm points out that the ligands that give T_d nickel(II) are polarizable species, and appreciable charge transfer can occur. So, less ligands should be required to satisfy the principle of electroneutrality. If any covalent bonding occurs the most readily available orbitals are $4s\,4p^3$ which, as in the ionic case, give rise to a tetrahedral arrangement.

XI. CONCLUSIONS AND SUMMARY

The current status of the research in the area of tetrahedral complexes has been briefly described. Only recently have the necessary theoretical calculations of spectral properties of ions in tetrahedral environments been made. In many cases it has been possible to compare crystallographic results with spectra of compounds thought to have tetrahedral stereochemistry. In many instances, the agreement is gratifying. However, at present, there seems to be no certain way to assess magnitudes of distortion from regular geometry on the basis of spectra and magnetic data. In this respect, further refinements are badly needed.

XII. REFERENCES

1. N. S. Gill and R. S. Nyholm, J. Chem. Soc., 1959, 3997.
2. A. Porai-Koshits, Kristallografiya, 1, 291 (1956).
3. H. M. Powell and A. F. Wells, J. Chem. Soc., 1935, 359.
4. R. H. Holm and F. A. Cotton, J. Chem. Phys., 31, 788 (1959).
5. F. A. Cotton and M. Goodgame, J. Am. Chem. Soc., 83, 1777 (1961).
6. Y. Tanabe and S. Sugano, J. Phys. Soc., Japan, 9, 753 (1954).
7. R. H. Holm and F. A. Cotton, J. Chem. Phys., 32, 1168 (1960).
8. B. N. Figgis and J. Lewis, In Modern Coordination Chemistry, J. Lewis and R. G. Wilkins, Eds. Interscience, New York, 1960.
9. F. A. Cotton and R. Francis, J. Am. Chem. Soc., 82, 2986(1960).
10. F. A. Cotton and R. Francis, J. Inorg. Nucl. Chem., 17, 62(1961).
11. D. W. Meek, D. K. Straub and R. S. Drago, J. Am. Chem. Soc., 82, 6013 (1960).
12. R. Francis and F. A. Cotton, J. Chem. Soc., 1961, 2078.
13. F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, J. Am. Chem. Soc., 83, 1780 (1961).
14. E. Bannister and F. A. Cotton, J. Chem. Soc., 1960, 1878.
15. F. A. Cotton and R. H. Soderberg, J. Am. Chem. Soc., 84, 872 (1962).
16. K. Issleib and A. Kreibich, Z. anorg. allgem. Chem., 313, 338 (1962).
17. D. J. Phillips and S. Y. Tyree, Jr., J. Am. Chem. Soc., 83, 1806 (1961).
18. F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, J. Am. Chem. Soc., 83, 4157 (1961).
19. N. S. Gill and R. S. Nyholm, J. Inorg. Nucl. Chem., 18, 88(1961).
20. S. Buffagini and T. M. Dunn, Nature, 188, 937 (1960).
21. S. Buffagini and T. M. Dunn, J. Chem. Soc., 1961, 5105.
22. D. A. Fine, J. Am. Chem. Soc., 84, 1139 (1962).
23. C. K. Jørgensen, Acta. Chem. Scand., 11, 53 (1957).
24. N. S. Gill, R. S. Nyholm, and P. Pauling, Nature, 182, 168 (1958).
25. F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, J. Am. Chem. Soc., 84, 167 (1962).
26. F. A. Cotton and E. Bannister, J. Chem. Soc., 1960, 1873.
27. C. Furlani and A. Furlani, J. Inorg. Nucl. Chem., 19, 51(1961).
28. A. G. Galinos, ibid., 19, 69 (1961).
29. H. Schlafer, Z. phys. Chem., N.F., 4, 116 (1955).
30. J. Lang and J. Millet, Bull. soc. chim. France, 1960, 867.
31. L. Naldini and A. Sacco, Gazzetta, 89, 2258 (1959).

32. S. Prasad and K. Prasad Kacker, J. Indian Chem. Soc., 35, 719, 722 (1958).
33. L. Naldini, Gazzetta, 90, 1337 (1960).
34. B. N. Figgis, Nature, 182, 1568 (1958).
35. D. M. L. Goodgame and F. A. Cotton, J. Chem. Soc., 1961, 3735.
36. B. Zaslow and R. E. Rundle, J. Phys. Chem., 61, 490 (1957).
37. H. L. Friedman, J. Am. Chem. Soc., 74, 5 (1952).
38. D. E. Metzler and R. J. Myers, ibid., 72, 3776 (1950).
39. F. A. Cotton, E. Bannister, R. Barnes, and R. H. Holm, Proc. Chem. Soc., 1959, 158.
40. F. A. Cotton and E. Bannister, J. Chem. Soc., 1960, 1878.
41. L. Naldini, Gazzetta, 90, 1231 (1960).
42. A. D. Liehr, J. Phys. Chem., 64, 43 (1960).
43. A. Pappalardo, Symposium on Molecular Structure and Spectroscopy, Ohio State Univ., Columbus, Ohio, June, 1960.
44. L. Helmholtz and R. F. Kruh, J. Am. Chem. Soc., 74,
45. D. M. L. Goodgame and F. A. Cotton, J. Chem. Soc., 1961, 2298.
46. F. Lions and K. V. Martin, J. Am. Chem. Soc., 79, 1273 (1957).
47. N. S. Gill, J. Chem. Soc., 1961, 3512.
48. L. Naldini, Gazzetta, 90, 361 (1960).
49. K. Isslieb and G. Doll, Z. anorg. allgem. Chem., 305, 1 (1960).
50. K. Isslieb and H. O. Frohlich, ibid., 298, 84 (1959).
51. K. Isslieb, A. Tzschach, and H. O. Frohlich, ibid., 298, 164 (1959).
52. C. J. Ballhausen and A. D. Liehr, Ann. Phys., 6, 134 (1959).
53. A. D. Liehr, 137th National Meeting of ACS, April 5-14, 1960, Cleveland.
54. E. C. Lingafelter, Nature, 182, 1730 (1958).
55. L. M. Venanzi, J. Chem. Soc., 1958, 719; J. Inorg. Nucl. Chem., 8 p. 37 (1958).
56. H. M. Powell and L. M. Venanzi, Proc. Chem. Soc., 1956, 6.
57. C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton and L. M. Venanzi, J. Chem. Soc., 1961, 2705.
58. M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton and L. M. Venanzi, ibid., 1961, 4816.
59. M. C. Browning, J. R. Mellor, D. J. Morgan, S.A. J. Pratt, L. E. Sutton, and L. M. Venanze, ibid., 1962, 693.
60. W. A. Weyl, Glastech. Ber., 11, 113 (1956); Quelques Probleme de Chimie Minerale, X Solvay Conseil, Bruxelles, 1956, pp. 400-458.
61. D. M. Gruen, J. Inorg. Nucl. Chem., 4, 74 (1957).
62. D. M. Gruen and R. L. McBeth, J. Phys. Chem. 63, 393 (1959).
63. C. R. Boston and G. P. Smith, ibid., 62, 409 (1958).
64. C. K. Jørgensen, Mol. Phys., 1, 410 (1958).
65. R. W. Asmussen and O. Bostrup, Acta. Chem. Scand., 11, 745 (1957).
66. D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, J. Am. Chem. Soc., 83, 4161 (1961).
67. C. K. Jørgensen, Acta. Chem. Scand., 10, 887 (1956).
68. F. A. Cotton and D. M. L. Goodgame, J. Am. Chem. Soc., 82, 5771 (1960).

69. D. M. L. Goodgame and F. A. Cotton, ibid., 82, 5775 (1960).
70. F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, ibid., 83,344 (1961).
71. F. A. Cotton and D. M. L. Goodgame, ibid., 82, 2967 (1960).
72. E. Bannister and F. A. Cotton, J. Chem. Soc., 1960, 2267.
73. C. Furlani and G. Sartori, J. Inorg. Nucl. Chem., 8, 127(1958).
74. C. Furlani, Gazzetta, 88, 279 (1958).
75. A. Turco, V. Scatturin, and G. Giacometti, Nature, 183, 601 (1959).
76. G. Giacometti and A. Turco, J. Inorg. Nucl. Chem., 15, 242 (1960).
77. C. Furlani and G. Morpurgo, Z. phys. Chem. (Frankfurt), 28, 93 (1961).
78. F. A. Cotton and D. M. L. Goodgame, J. Chem. Soc., 1960, 5267.
79. G. J. Bullen, R. Mason, and P. Pauling, Nature, 189, 291(1961).
80. G. J. Bullen, Nature, 177, 537(1956).
81. J. P. Fackler and F. A. Cotton, J. Am. Chem. Soc., 83, 3775(1961).
82. R. H. Holm, J. Am. Chem. Soc., 83, 4683 (1961).
83. J. Ferguson, J. Chem. Phys., 34, 611 (1960).
84. D. M. Gruen and R. L. McBeth, J. Phys. Chem., 66, 57(1962).
85. E. Iberson, R. Güt and D. M. Gruen, ibid., 66, 65 (1962).
86. C. M. Harris, S. L. Lenzer, and R. L. Martin, Australian J. Chem., 14, 420 (1961).

SUPPLEMENTARY PERTINENT REFERENCES

87. C. K. Jørgensen, Acta. Chem. Scand., 11, 399 (1957).
88. E. Bannister and F. A. Cotton, J. Chem. Soc., 1960, 1959.
89. K. Isslieb and B. Mitscherling, Z. anorg. Chem., 304, 73(1960).
90. C. Furlani and F. De Tella, Gazzetta, 90, 280 (1960).
91. L. I. Katzin, Nature, 183, 1672 (1955).
92. K. Isslieb and G. Bohn, Z. anorg. Chem., 301, 188 (1959).
93. N. S. Gill, Chem. and Ind., 1961, 989.
94. V. R. Apfel and R. Schaaf, Z. Naturforsch., 16b, 405 (1961).
95. M. M. Ray, Z. anorg. Chem., 306, 133 (1960).
96. R. S. Nyholm, J. Inorg. Nucl. Chem., 8, 401 (1958).
97. F. A. Cotton, J. Chem. Soc., 1960, 5269.
98. S. M. Nelson, Proc. Chem. Soc., 1961, 372.
99. A. Hantzsch, Z. anorg. allgem. Chem., 159, 273 (1926).
100. L. I. Katzin, Nature, 182, 1013 (1958).
101. B. Brehler, Z. Krist., 109, 68 (1957).
102. L. E. Orgel and J. D. Dunitz, Nature, 179, 462 (1957).
103. L. E. Orgel, Proc. Xth Solvay Congress, Brussels, 1956, p.308.
104. C. K. Jørgensen, ibid., 1956, 355.
105. R. S. Nyholm, ibid., 1956, 225.
106. L. Cambi, Gazzetta, 39, 361 (1909).
107. L. E. Orgel, J. Chem. Phys., 23, 1004 (1955).
108. C. J. Ballhausen and A. D. Liehr, J. Am. Chem. Soc., 81,538(1959)
109. R. S. Nyholm, Chem. Revs., 53, 263 (1953).
110. D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L.E. Sutton, J. Chem. Soc., 1954, 332.
111. P. Senise, J. Am. Chem. Soc., 81, 4196 (1959).
112. R. Stahl-Brada and W. Low, Phys. Rev., 113, 775 (1959).
113. C. J. Ballhausen and A. D. Liehr, J. Mol. Spectroscopy, 2, 342 (1958); ibid., 4, 190 (1960).

114. C. J. Ballhausen, Kg. Danske Videnskab., Selskab. mat fys. Medd., 29, no. 4 (1954).
115. W. Manch and W. C. Fernelius, J. Chem. Educ., 38, 201 (1961).
116. G. Maki, J. Chem. Phys., 28, 651 (1958).
117. G. Maki, ibid., 29, 1129 (1958).
118. G. Maki, ibid., 29, 162 (1958).
119. L. E. Orgel, J. Chem. Soc., 1952, 4756.
120. C. H. Brubaker, Jr., and C. E. Johnson, J. Am. Chem. Soc., 80, 5037 (1958).
121. A. Carrington and C. K. Jørgensen, Mol. Phys., 4, 395 (1961).
122. A. Carrington and D. S. Schonland, ibid., 3, 331 (1960).
123. D. R. Stephens and H. G. Drickamer, J. Chem. Phys., 35, 424, 427, 429 (1961).
124. O. Bostrup and C. K. Jørgensen, Acta. Chem. Scand., 11, 1223(1957).
125. R. W. Asmussen and O. Bostrup, ibid., 11, 1097 (1957).
126. A. D. Liehr, Ann. Phys., 1, 221 (1957).
127. G. Felsenfeld, Proc. Roy. Soc., 236A, 506 (1956).
128. R. J. P. Williams, J. Chem. Soc., 1956, 8.
129. B. N. Figgis and C. M. Harris, ibid., 1959, 855.
130. C. J. Ballhausen and C. K. Jørgensen, Acta Chem. Scand., 9, 397 (1955).
131. R. W. Asmussen and H. Soling, Z. anorg. Chem., 283, 3(1956).

GROWTH OF INORGANIC CRYSTALS UNDER UNUSUAL CONDITIONS

Gerald J. Tennenhouse　　　　May 22, 1962

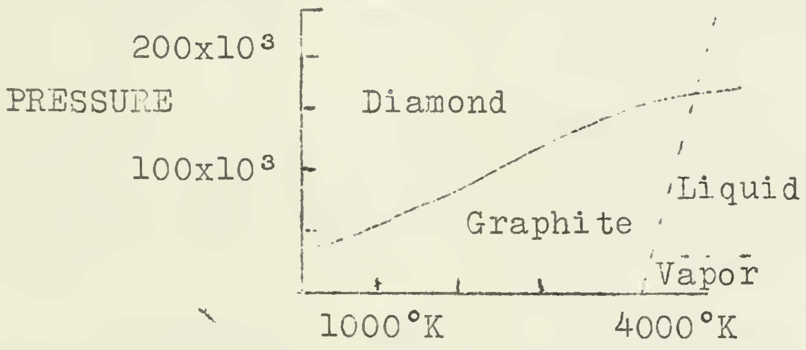
I. INTRODUCTION

After the Second World War, a great need developed for many crystals that had been either rare or unobtainable. Rubies and sapphires were needed for masers and jewel bearings; diamonds for cutting tools; large salt crystals for optical systems; and single crystals of germanium, silicon, and tin for semi-conductors.

Since most of these crystals were very difficult to prepare, several unusual and ingenious methods have been developed for their synthesis.

II. DIAMONDS

Diamond is simply an allotropic form of carbon. According to the phase diagram of carbon (1),

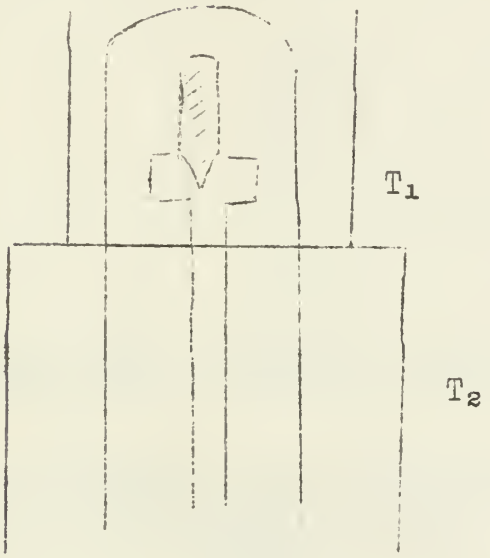


the preparation of diamond by recrystallizing graphite would require temperatures and pressures approaching 4,000° K. and 200,000 atmospheres. However, in the presence of certain transition metal catalysts, diamonds can be prepared under the comparatively mild conditions of 1,200°C - 2,400°C and 55,000 - 100,000 atmospheres (1). These reactions must be carried out in a specially constructed vessel (2).

III. GROWTH OF SINGLE CRYSTALS

It is only possible to grow crystals in a crucible when the melt does not react appreciably with the container.

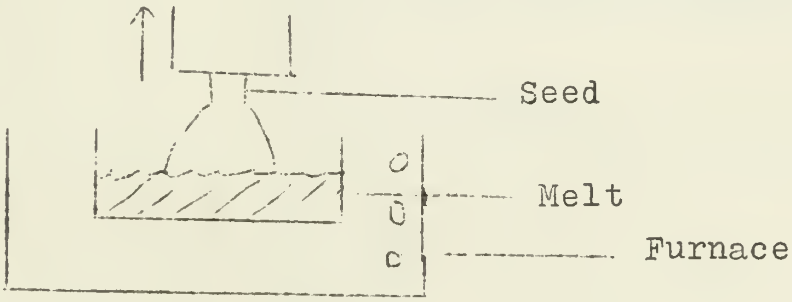
Large single crystals of lead selenide and lead telluride have been grown in tapered crucibles (3). The polycrystalline



material was melted in Furnace 1, and the crucible was very slowly lowered to Furnace 2 (which was kept at a temperature below the melting point of the compound). Calcium fluoride crystals of optical quality have also been prepared by this method (4).

A variation of this procedure involves the application of zone melting. Large germanium crystals have been prepared by heating a boat containing polycrystalline germanium so that only a narrow zone melted; as the molten zone was slowly moved the length of the sample, a single crystal was formed (5).

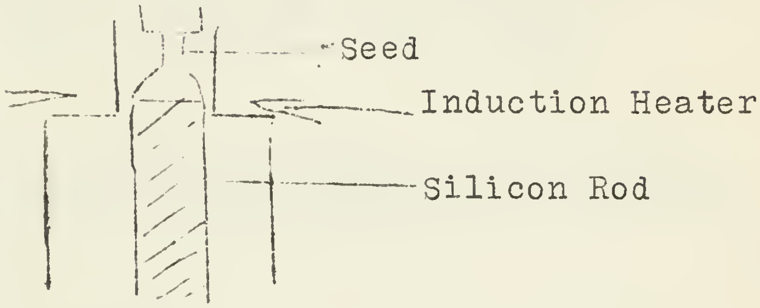
The technique of crystal pulling has also been used to grow single crystals, such as germanium (6). Polycrystalline



germanium was melted in a graphite crucible. A seed crystal was touched to the surface of the melt, and the temperature was lowered. As the melt crystallized on the seed, the seed was slowly raised, allowing the crystal to grow.

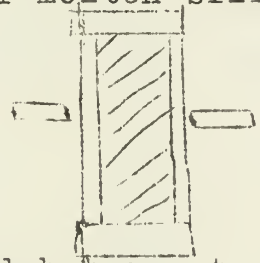
IV. CRYSTALS WITHOUT CRUCIBLES

The crystal-pulling technique has also been used to grow single crystals of silicon without the use of crucibles (7).



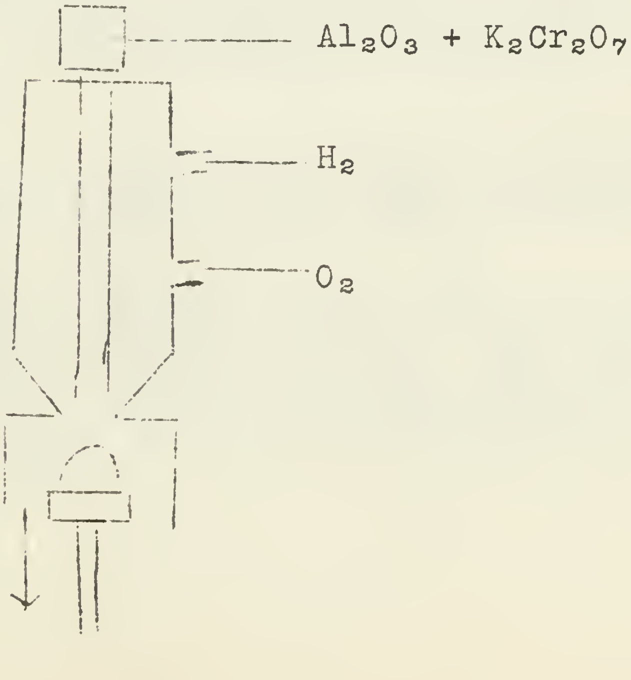
The top of a silicon rod was melted by an induction heater. A seed crystal was then used to pull a large single crystal from the melt.

An interesting variation of the technique makes use of the high surface tension of molten silicon.



A silicon rod was supported between two chucks, and an induction heater was used to melt a narrow zone at the top of the rod. The zone was very slowly moved along the length of the rod, forming a single crystal (8). The surface tension of the molten silicon kept the rod from collapsing.

The flame fusion process for growing crystals without the use of containers is well know. Verneuil first used this technique to synthesize rubies.



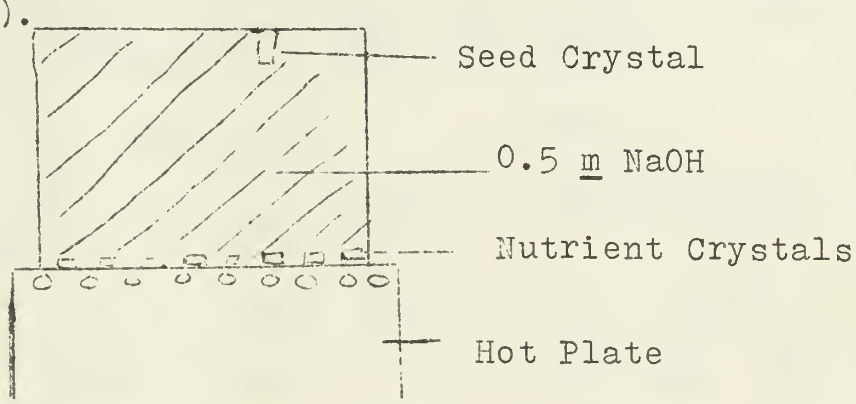
Powdered alumina and potassium dichromate were added to the gas stream of an oxy-hydrogen torch. When the gas mixture was ignited, the alumina melted and was deposited on a platform. As the molten boule grew, the platform was lowered to allow the lower part of the boule to crystallize and the crystal to grow. At the present time, the boule is grown on a seed crystal to prevent contamination and ensure the growth of a single crystal (10).

Large silicon crystals have been grown by a variation of this method (11). The heat source is provided by an induction coil; this allows crystallization to be carried out in a controlled atmosphere.

V. CRYSTALLIZATION FROM SOLUTION

Crystallization from aqueous solution may also have unusual aspects.

Crystals of quartz weighing as much as one kilogram have been prepared(12).



The bottom of a vessel containing a seed crystal, 0.5M NaOH, and small pieces of quartz was heated to 385°C. Some of the quartz dissolved and redeposited on the seed crystal suspended in the cooler part of the solution.

Sapphires and rubies have also been prepared in this way, using alumina in 1 - 2M NaOH or Na_2CO_3 (13), and a similar process has been used in the preparation of emeralds (10).

Other unusual solution techniques involve the use of non-aqueous solvents. Large single crystals of GaP, GaAs, GaSb, AlSb, and InP have been grown in molten gallium, aluminum, and indium, respectively (14). Large tin crystals have been grown in mercury solutions (15), and silicon crystals have been grown from gold solutions (16).

BIBLIOGRAPHY

1. Bovenkerk, H. P., Bundy, F. P., Hall, H. T., Strong, H. M., and Wentorf, R. H., Nature, 184, 1094 (1959).

2. Hall, H. T., Rev. Sci. Instr., 31, 125 (1960).

3. Lawson, W. D., J. Appl. Phys., 22, 1444 (1951).

4. Stockbarger, D. C., Disc. Faraday Soc., 5, 294 (1949).

5. Pfann. W. G., and Olsen, K. M., Phys. Rev., 89, 322 (1953).

6. Lehovec, K., Soled, J., Koch, R., MacDonald, A., and Stearns, C., Rev. Sci. Instr., 24, 652 (1953).

7. Hannay, N. B., Semiconductors, p. 115, New York, Reinhold Publishing Co., 1959.

8. Keck, P. H., Van Horn, W., Soled, J., and MacDonald, A., Rev. Sci. Instr., 25, 331 (1954).

9. Verneuil, A., Compt. Rend., 135, 791 (1902) as reported by White, E. A. D., Quart. Rev., XV, 13 (1961).

10. White, E. A. D., Quart. Rev., XV, 1 (1961).

11. Keck, P. H., Levin, S. B., Broder, J., and Leiberman, R., Rev. Sci. Instr., 25, 298 (1954).

12. Laudise, R. A., J. Am. Chem. Soc., 81, 562 (1959).

13. Laudise, R. A. and Ballman, A. A., J. Am. Chem. Soc., 80, 2655 (1955).

14. Keck, P. H. and Broder, J., Phys. Rev., 94, 753 (1954).

15. Tufte, O. N. and Ewald, A. W., J. Appl. Phys., 29, 1007 (1958).

16. Carman, J. N., Stello, P. E., and Bettman, C. A., J. Appl. Phys., 25, 543 (1954).