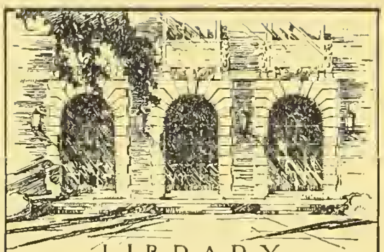

INORGANIC SEMINARS

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ISOTOPIC TRACER INVESTIGATIONS OF THE SOLVENT SULFUR DIOXIDE

David Lydy September 27, 1960

I. INTRODUCTION

The use of isotopic tracers to examine inorganic reaction mechanisms will be illustrated by a summary of investigations of the solvent sulfur dioxide.

II. ISOTOPIC EXCHANGE REACTIONS

An exchange reaction occurs when atoms of a given element interchange between two or more chemical forms of this element. The term "isotopic exchange reaction" arises since such a process can only be detected by isotopic labeling methods. A typical isotopic exchange may be described by the chemical equation:

$$\overset{*}{S}O_2 + SO_3^{=} \rightleftarrows \overset{*}{S}O_3^{=} + SO_2 \qquad (1)$$

III. HISTORY

In 1936, Jander (1-3) studied the chemistry of substances dissolved in liquid sulfur dioxide and compared it with that of the same substances dissolved in water and liquid ammonia. In explaining the results of these experiments, he assumed for the solvent, liquid sulfur dioxide, the following dissociation mechanism:

$$2\ SO_2 \rightleftarrows SO^{++} + SO_3^{=} \qquad (2)$$

Thionyl compounds and sulfites were therefore considered, respectively, as acids and bases, hypothetically ionizing to some extent according to such equilibria as the following to give "characteristic" cations and anions:

$$SOCl_2 \rightleftarrows SO^{++} + 2\ Cl^{-} \qquad (3)$$

$$(Me_4N)_2SO_3 \rightleftarrows 2\ Me_4N^{+} + SO_3^{=} \qquad (4)$$

Bateman, Hughes and Ingold (4) rejected Jander's proof for the sulfito theory. They found his experimental work to be non-conclusive and in part incorrect due to a calculational error. Their results have been confirmed by Herber and Norris (5).

Isotopic tracers provide means for testing the validity of the solvent system equilibria 2, 3 and 4. If these are important, a relatively rapid exchange should follow the labeling either of solvent or solute with an isotopic tracer (radiosulfur, radiochlorine, or oxygen-18).

IV. EXCHANGE REACTIONS

Grigg and Lauder (6) investigated the exchange of oxygen-18 between liquid sulfur dioxide and thionyl chloride. Their results

show that no detectable exchange occurs between the oxygen of the sulfur dioxide and that of the thionyl chloride. Jander's view, therefore, that both liquid sulfur dioxide and thionyl chloride are appreciably ionized to form thionyl ions cannot be correct.

Jander (7) also reported that a solution of sulfur trioxide in liquid sulfur dioxide has appreciable electrical conductivity. This may be due to an oxidation-reduction interaction of the two compounds which could be represented by the example:

$$2\ SO_2 \rightleftarrows SO^{++} + SO_3^{=} \tag{2}$$

$$SO_3 + SO_3^{=} \rightleftarrows S_2O_6^{=} \tag{5}$$

If this process, or any other involving transfer of an oxygen <u>atom</u> from sulfur trioxide to sulfur dioxide should occur, isotopic interchange would be detectable with either tracer oxygen or sulfur. Nakata (8) proposed this mechanism to explain his observed rapid oxygen-18 exchange for sulfur dioxide dissolved in excess liquid sulfur trioxide.

Alternatively the two substances may react as a Lewis acid and Lewis base, the sulfur in each maintaining its oxidation state. For example:

$$SO_2 + SO_3 \rightleftarrows SO^{++} + SO_4^{=} \tag{6}$$

or

$$SO_2 + 2\ SO_3 \rightleftarrows SO^{++} + S_2O_7^{=} \tag{7}$$

Jander offered this mechanism in explaination of the observed conductivity, though with little supporting evidence. Interaction of this sort, with transfer of an oxide <u>ion</u>, would yield a detectable isotopic exchange with tracer oxygen but not with tracer sulfur.

Huston (9) found no isotopic exchange of sulfur occurs at room temperature when sulfur trioxide is dissolved in liquid sulfur dioxide or when sulfur dioxide is dissolved in liquid sulfur trioxide. It is suggested on the basis of these results and on the work of Nakata that the two compounds undergo rapid exchange of oxide ions at room temperature, interacting as a Lewis acid and a Lewis base.

Johnson, Norris, and Huston (10) carried out exchange experiments with sulfur dioxide solutions of the feebly conducting "acids," thionyl chloride and thionyl bromide and with the more strongly conducting and relatively soluble "base," tetramethylammonium pyrosulfite.

The exchange of the"base," tetramethylammonium pyrosulfite with the solvent is extremely rapid, even close to dry ice temperatures. The most reasonable interpretation of the observed complete exchange appears to be to assume: a) that sulfite ion is formed in the solution by the equilibrium:

$$S_2O_5^{=} \rightleftarrows SO_3^{=} + SO_2 \tag{8}$$

and b) that this sulfite ion itself exchanges rapidly with the solvent in an equilibrium such as:

$$SO_3^{=} + \overset{*}{S}O_2 \leftrightarrows \overset{*}{S}O_3^{=} + SO_2 \qquad (1)$$

Johnson, et al., also demonstrated the absence of exchange with sulfur dioxide solutions of the "acids," thionyl chloride and thionyl bromide. The conclusion seems clear that there can be but little ionization according to equation 2 and hence but little SO^{++} formed in solution from these compounds.

Whereas in pure liquid sulfur dioxide, the thionyl halides do not exchange sulfur-35 at a significant rate with the solvent, it has been found that similar solutions containing certain soluble salts exhibit a rapid exchange.

Herber, Norris and Huston (11) found that addition of tetramethylammonium bromide to the SO_2-$SOBr_2$ system produces a strong catalysis of the exchange.

A rapid sulfur-35 exchange was also observed by Masters and Norris (12) for the tetramethylammonium chloride-catalyzed reaction in the SO_2-$SOCl_2$ system. Their results show marked similarities to those for the catalysis of the SO_2-$SOBr_2$ exchange. The principal difference between the two sets of results is the present finding of a first-order dependence of thionyl chloride in contrast to zero order for the bromide.

To test for the possible species $SOCl^+$, Masters, Potter, Asher, and Norris (13) studied the radiochlorine exchange between thionyl chloride and tetramethylammonium chloride, dissolved together in liquid sulfur dioxide. The authors found the exchange to be rapid, complete even in five minutes at - 20°. They proposed two distinct types of ionic processes which would give the observed rapid activity randomization: a) self-ionization giving solvent cations and chloride ions; e.g.

$$SOCl_2 \leftrightarrows SOCl^+ + Cl^- \qquad (9)$$

b) simple addition equilibria of solute chloride ions adding to unionized solvent molecules; e.g.

$$SOCl_2 + Cl^- \leftrightarrows SOCl_3^- \qquad (10)$$

Exchange systems involving both tetramethylammonium chloride and antimony trichloride, respectively, dissolved in thionyl chloride were also studied, and rapid exchange was found to occur in both. The same two ionic processes postulated for the previous exchange could result in the observed exchange in these systems.

Johnson and Norris (14) attempted to distinguish between the two ionic processes: self-ionization and association. They studied the radiosulfur exchange between thionyl chloride and thionyl bromide at - 20 and - 50°, both in liquid sulfur dioxide

solution and in the two pure mixed compounds. They found the exchange was rapid and complete, except for the pure compounds at - 50°, where a measurable rate was observed. The rapidity of the exchange appears to support, at least so far as sulfur dioxide solutions are concerned, the probable formation of the dissociated ionic species, SOX^+.

A study has been made by Burge and Norris (15) of the kinetics of catalysis by antimony pentachloride of the radiosulfur exchange between thionyl chloride and liquid sulfur dioxide. The process is interpreted as a case of acid catalysis in contrast to the previously investigated basic chloride catalysis.

Burge and Norris (16) also studied the mixed acidic and basic catalysis of the sulfur-35 exchange between SO_2-$SOCl_2$. They found that antimony pentachloride has a pronounced inhibiting effect on the catalysis by tetramethylammonium chloride of the radiosulfur exchange reaction between thionyl chloride and liquid sulfur dioxide.

V. CONCLUSION

Jander's concepts, at least as far as thionyl chloride is concerned, are in need of modification. As has been pointed out, an ionization equilibrium for thionyl chloride that is intrinsically more likely than equation 2 would be:

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^- \qquad (9)$$

In general it seems clear that Jander placed too great emphasis on strictly ionic mechanisms for his reactions in liquid sulfur dioxide. It seems likely that the concept of mobile oxide ions might be more fruitful for the understanding of chemical reactions in this solvent.

VI. ISOTOPIC TRACERS

The isotopic tracers used in this study were oxygen-18, sulfur-35 and chlorine-36. The radiochemical properties of these species are summarized in the following table:

Nuclide	Half-life	Decay Mode and Energy
O^{18}	stable	----
S^{35}	87.1 days	Beta 0.167 Mev.
Cl^{36}	4.4×10^5 years	Beta 0.714 Mev.

VII. BIBLIOGRAPHY

1. Jander, G., "Die Chemie in Wasserähnlichen Lösungmitteln," Springer-Verlag, Berlin, 1949, pp. 209-307.
2. Jander, G., and K. Wickert, Z. physik. Chem. A, *178*, 57 (1936).
3. Jander, G., and W. Ruppolt, *ibid*., *179*, 43 (1937).
4. Bateman, L. C., E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 243 (1944).
5. Herber, R. H., and T. H. Norris, J. Am. Chem. Soc., *76*, 3849 (1954).
6. Grigg, E. C. M., and I. Lauder, Trans. Faraday Soc., *46*, 1039 (1950).
7. Jander, G., Naturwissenschaften, *26*, 795 (1938).
8. Nakata, S., J. Chem. Soc. Japan, *64*, 635 (1943).
9. Huston, J. L., J. Am. Chem. Soc., *73*, 3049 (1951).
10. Johnson, R. E., T. H. Norris, and J. L. Huston, *ibid*., *73*, 3052 (1951).
11. Herber, R. H., T. H. Norris, and J. L. Huston, *ibid*., *76*, 2015 (1954).
12. Masters, B. J., and T. H. Norris, *ibid*., *77*, 1346 (1955).
13. Masters, B. J., N. D. Potter, D. R. Asher, and T. H. Norris, *ibid*., *78*, 4252 (1956).
14. Johnson, Jr., L. F., and T. H. Norris, *ibid*., *79*, 1584 (1957).
15. Burge, D. E., and T. H. Norris, *ibid*., *81*, 2324 (1959).
16. Burge, D. E., and T. H. Norris, *ibid*., *81*, 2329 (1959).

THE SULFURIC ACID SOLVENT SYSTEM

Melvin D. Joesten October 4, 1960

I. INTRODUCTION

The pioneer work with anhydrous sulfuric acid as a solvent was done by Hantzsch(20) in the early 1900's. In 1920, Kendall and coworkers(22,23) investigated the solubility relationships of the alkali metal sulfates in sulfuric acid. In the 1930's, Hammett(18,19) improved the accuracy of existing experimental methods in his determination of the acidity function of sulfuric acid. In the past ten years, Gillespie and coworkers have made great progress in elucidating the behavior of various compounds in sulfuric acid by making cryoscopic and conductometric measurements.

Excellent reviews(9,11) have appeared in the past year on the sulfuric acid solvent system.

II. PREPARATION

Anhydrous sulfuric acid is obtained by adding concentrated sulfuric acid to oleum (fuming sulfuric acid) until a maximum freezing point of 10.37°C. is reached.

III. STRUCTURE

X-ray studies(26) of sulfuric acid crystals have shown their structure to consist of layers of sulfuric acid molecules. Each molecule is held by hydrogen bonding to four other molecules.

IV. SOLVENT PROPERTIES

A. Conductance

The high specific conductance of sulfuric acid, 1.04×10^{-2} ohm^{-1} $cm.^{-1}$, is explained by the extensive self-dissociation of sulfuric acid and the high mobilities of the $H_3SO_4^+$ and HSO_4^- ions. The mobilities of metal ions are very small because of the high viscosity of sulfuric acid. The $H_3SO_4^+$ and HSO_4^- ions are not affected by the high viscosity because they conduct by a proton transfer mechanism similar to that generally accepted to explain the high mobilities of the H_3O^+ and OH^- ions in water(13,16,24). This proton transfer occurs along hydrogen bonds, eliminating the need for actual diffusion of ions through the solution. Because of the negligible mobilities of other ions in sulfuric acid, conductivity measurements will give directly an indication of the number of $H_3SO_4^+$ or HSO_4^- ions produced.

B. Cryoscopy

Sulfuric acid is a good solvent for cryoscopic measurements because of its large cryoscopic constant, 6.12, together with the ideal behavior of ionic and nonionic solutes dissolved in it. At higher concentrations of ionic solutes, the non-ideal behavior is attributed to the effects of ion solvation and ion size(2). In the

correct concentration range, cryoscopic measurements will give the total number of ions produced.

C. Nuclear Magnetic Resonance

Gillespie and White(14) have recently extended earlier studies by other investigators(17, 21) on the proton magnetic resonance shifts in the sulfuric acid solvent system. They found that monovalent metal ions cause a shift in the proton resonance of sulfuric acid in addition to that produced by the hydrogen sulfate ion. The greater the extent of solvation of a monovalent ion, the greater is the shift to higher field. This shift to higher field is attributed to the structure-breaking effect of the solvated ion. The shift produced by HSO_4^- is calculated by measuring the proton resonance of a thallium sulfate solution in sulfuric acid. A value of -13.9 for $\delta_{HSO_4^-}$ is obtained if it is assumed that the extent of solvation is small for the thallium ion. This large shift to lower field is tentatively explained as being due to hydrogen bonding and polarization effects between the HSO_4^- ion and sulfuric acid molecules.

D. Solubility Trends(1,11)

Sulfuric acid is a poor solvent for nonelectrolytes. Sulfuryl chloride and picric acid are among the few nonelectrolytes that are soluble in sulfuric acid.

The high dielectric constant of sulfuric acid(100) makes it a good solvent for electrolytes. The alkali metal hydrogen sulfates dissolve in sulfuric acid as fully ionized electrolytes, analogous to the hydroxides in water. The normal sulfates of the alkali metals are converted to hydrogen sulfates, analogous to the metal oxides in water. The solubility of metal sulfates in sulfuric acid parallels the solubility of the corresponding hydroxides in water.

Sulfuric acid is also a good solvent for most organic compounds, except aliphatic hydrocarbons and some aromatic hydrocarbons.

V. ACID-BASE RELATIONSHIPS

A. Dissociation Equilibria

Sulfuric acid is an example of an amphoteric solvent, exhibiting both acid and base properties. Various self-dissociation equilibria may be written for sulfuric acid, all of which may be summarized by the following two equations(8,10):

Autoprotolysis: $2\ H_2SO_4 \leftrightarrows H_3SO_4^+ + HSO_4^-$

Ionic Dehydration: $2\ H_2SO_4 \rightleftarrows H_3O^+ + HS_2O_7^-$

The four equilibrium constants listed in Table 1 for the self-dissociation reactions of sulfuric acid give a more complete picture. The strongest acid in sulfuric acid will be the solvated proton, $H_3SO_4^+$, and the strongest base will be the HSO_4^- ion. The autoprotolysis constant of sulfuric acid is larger than that of any other solvent.

B. Bases

Many compounds act as strong bases in sulfuric acid by producing the HSO_4^- ion. The alkali metal sulfates have already been mentioned. Some other compounds that act as bases in sulfuric acid are Ph_3P, Ph_3N, H_3PO_4, HOCl, and SeO_2. Many organic compounds (e.g., ketones, amides, carboxylic acids) behave as strong bases in sulfuric acid (5,11).

The extent of sulfation increases with decreasing electronegativity, with compounds intermediate between the sulfates and hydrogen sulfates being formed in the case of the more electronegative metals. The sulfato compound formed may be a nonelectrolyte or a polymer, or it may ionize as an acid or a base(11).

C. Acids

The acidity function of sulfuric acid is -10.89(4), which means that the combining power of sulfuric acid with a given base is approximately 10^{17} times that of water. Because of the high acidity of sulfuric acid, most aqueous acids are bases in sulfuric acid.

The addition of sulfur(VI) oxide increases the acidity of sulfuric acid by combining with the HSO_4^- ion to form higher polysulfuric acids(25). These polysulfuric acids (e.g., $H_2S_2O_7$, $H_2S_3O_{10}$) and the complex hydrogensulfate acids [e.g., $HAs(HSO_4)_4$] account for most of the acids in the sulfuric acid system. The strongest acid known at the present time in sulfuric acid is tetra (hydrogensulfato) boric acid, $HB(HSO_4)_4$. Table 2 lists the dissociation constants of several acids for comparison.

VI. SELECTED SOLUTES IN SULFURIC ACID

Much more work remains to be done in the study of the behavior of inorganic compounds in sulfuric acid. The behavior of some of the more thoroughly studied compounds is included in this report.

A. Boron Compounds

Before the work of Flowers, et al.(6), it was believed that $B(HSO_4)_3$ existed in sulfuric acid. Their cryoscopic and conductometric measurements gave evidence for the formation of the $B(HSO_4)_4^-$ ion. By dissolving boric acid in oleum, solutions of tetra(hydrogensulfato) boric acid can be obtained. This acid can be titrated conductometrically with a strong base, such as $KHSO_4$.

Boron trichloride reacts vigorously with sulfuric acid to form $B(HSO_4)_3$, a white deliquescent powder which forms the $B(HSO_4)_4^-$ ion in sulfuric acid(15).

B. Silicon Compounds

Work done with the monoalkylsilanols and their derivatives(11 indicates that no more than two hydrogen sulfates become attached to the silicon atom. Beyond this point oxysulfato compounds are formed.

C. Tin Compounds

All the tin compounds that have been investigated are completely converted to the corresponding sulfato compounds, which is consistent with the smaller electronegativity of tin. Evidence for $H_2Sn(HSO_4)_6$ has been obtained from cryoscopic and conductometric measurements on Ph_4Sn.

D. Lead Compounds

Lead(II) salts are generally converted to lead di(hydrogen sulfate), which is fully ionized as a strong base.

The only soluble compound of Pb(IV) that has been studied is lead tetra-acetate. Cryoscopic and conductometric measurements(12) made on solutions of lead tetra-acetate in sulfuric acid indicate the formation of $H_2Pb(HSO_4)_6$.

E. Nitrogen Compounds

Nitric acid, metallic nitrates, and nitrogen(V) are all converted to nitronium hydrogen sulfate, which is fully ionized as a base,

$$N_2O_5 + 3\ H_2SO_4 \leftrightarrows 2\ NO_2^+ + H_3O^+ + 3\ HSO_4^-$$

Metallic nitrites and nitrogen(III) oxide produce the nitrosyl ion, and nitrogen(IV) oxide produces both the nitronium and the nitrosyl ions,

$$NaNO_2 + 3\ H_2SO_4 \leftrightarrows Na^+ + NO^+ + H_3O^+ + 3\ HSO_4^-$$

$$N_2O_4 + 3\ H_2SO_4 \leftrightarrows NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

The presence of the HSO_4^- ion has been proven by Raman spectra(27). The nitronium and nitrosyl ion can exist only in a very weakly basic solvent or an inert solvent because of their highly electrophilic character. Since sulfuric acid is a good solvent for electrolytes, relatively concentrated solutions of these ions can be obtained. This finds application in aromatic nitration reactions.

F. Arsenic Compounds(11)

Dilute solutions of arsenic(III) oxide in sulfuric acid give the first evidence of the AsO^+ ion. At higher concentrations a polymeric cation is indicated.

$$\begin{array}{lllll} As_2O_3 + 3\ H_2SO_4 & \rightleftarrows & 2\ AsOHSO_4 & + H_3O^+ & + HSO_4^- \\ & & \Big\updownarrow\!\longrightarrow & AsO^+ & + HSO_4^- \end{array}$$

By dissolving arsenic(III) oxide in oleum, it can be further sulfated to give $As(HSO_4)_3$ or $HAs(HSO_4)_4$.

G. Selenium Compounds(7)

Selenium(IV) oxide acts as a weak base in sulfuric acid, partially ionizing to give the $HSeO_2^+$ ion. Polymeric ions such as $HSe_2O_4^+$ are also present in these solutions. It appears that the unionized portion of SeO_2 forms addition compounds with sulfuric acid in the form of: $H_2SO_4 \cdot SeO_2$, $H_2SO_4 \cdot Se_2O_4$, $H_2S_2O_7 \cdot SeO_2$.

Table 1(3)

At 10° C.

$$K_{ap} = (H_3SO_4^+)(HSO_4^-) = 1.7 \times 10^{-4}$$

$$K_{id} = (H_3O^+)(HS_2O_7^-) = 3.5 \times 10^{-5}$$

$$K_a = \frac{(H_3SO_4^+)(HS_2O_7^-)}{(H_2S_2O_7)} = 1.4 \times 10^{-2}$$

$$K_b = \frac{(H_3O^+)(HSO_4^-)}{(H_2O)} = 1$$

Table 2(11)

Acids	K_a
H_2SO_4	1.7×10^{-5}(10°C)
$HClO_4$	very weak
$HPb(HSO_4)_6^-$	1.8×10^{-3}(10°C)
HSO_3F	3.0×10^{-3}(25°C)
$H_2Pb(HSO_4)_6$	1.1×10^{-2}(10°C)
$H_2S_2O_7$	1.4×10^{-2}(10°C)
$HB(HSO_4)_4$	strong (3×10^{-1})

REFERENCES

1. L. F. Audrieth and J. Kleinberg, Nonaqueous Solvents, Wiley and Sons, New York (1953), pp. 172-180.

2. S. J. Bass, R. J. Gillespie and J. V. Oubridge, J. Chem. Soc., 837 (1960).

3. S. J. Bass, R. J. Gillespie and E. A. Robinson, J. Chem. Soc., 821 (1960).

4. J. C. Brand, J. Chem. Soc., 997 (1950).

5. J. A. Duffy and J. A. Leisten, J. Chem. Soc., 545 (1960).

6. R. M. Flowers, R. J. Gillespie and J. V. Oubridge, J. Chem. Soc., 1925 (1956).

7. R. M. Flowers, R. J. Gillespie and E. A. Robinson, J. Inorg Nucl. Chem., 9, 155 (1959).

8. R. H. Flowers, R. J. Gillespie and E. A. Robinson, Can. J. Chem., 38, 1363 (1960).

9. R. J. Gillespie, Revs. Pure Appl. Chem., 9, 1 (1959).

10. R. J. Gillespie and J. V. Oubridge, J. Chem. Soc., 80 (1956).

11. R. J. Gillespie and E. A. Robinson, *Advances in Inorganic Chemistry and Radiochemistry*, Academic Press, New York (1959), Vol. 1, pp. 385-421.

12. R. J. Gillespie and E. A. Robinson, Proc. Chem. Soc., 145 (1957).

13. R. J. Gillespie and S. Wasif, J. Chem. Soc., 209, 221 (1953).

14. R. J. Gillespie and R. F. M. White, Can. J. Chem., 38, 1371 (1960)

15. N. N. Greenwood and A. Thompson, J. Chem. Soc., 3643 (1959).

16. N. N. Greenwood and A. Thompson, J. Chem. Soc., 3474 (1959).

17. H. S. Gutowsky and A. Saika, J. Chem. Phys., 21, 1688 (1953).

18. L. P. Hammett and A. J. Deyrup, J. Am. Chem. Soc., 55, 1900 (1933)

19. L. P. Hammett and F. A. Lowenheim, J. Am. Chem. Soc., 56, 2620 (1934).

20. A. Hantzsch, Z. physik. Chem., 61, 257 (1907).

21. G. C. Hood and C. A. Reilly, J. Chem. Phys., 27, 1126 (1957).

22. J. Kendall and A. W. Davidson, J. Am. Chem. Soc., 43, 979 (1921).

23. J. Kendall and M. L. Landon, J. Am. Chem. Soc., 42, 2131 (1920).

24. M. Kilpatrick, *The Structure of Electrolytic Solutions*, Wiley and Sons, New York (1959), p. 291.

25. M. Kilpatrick, J. Chem. Ed., 37, 403 (1960).

26. R. Pascard, Compt. Rend., 240, 2162 (1955).

27. T. F. Young, L. F. Maranville and H. M. Smith, *The Structure of Electrolytic Solutions*, Wiley and Sons, New York (1959), p. 48

THE DETERMINATION OF FORMATION CONSTANTS OF COMPLEXES FROM POLAROGRAPHIC MEASUREMENTS

Robert L. Gerteis October 11, 1960

I. INTRODUCTION

Polarography is an eletroanalytical technique based on the unique properties of the dropping mercury electrode and a diffusion controlled limiting current which is proportional to the concentration of the electroactive species. The decomposition potential of the solution is characteristic of the electroactive species; thus making polarography simultaneously both a qualitative and quantitative method of analysis. Most metals in concentrations ranging from 10^{-4} to 10^{-2} molar can be analyzed, either separately or in mixtures, and their concentrations determined within ±1% accuracy.[1]

The polarograph consists of (1) the dropping mercury electrode; (2) a current measuring device; and (3) a potentiometer. The dropping mercury electrode consists of a vertically placed glass capillary from which mercury issues dropwise. The drop-time, usually about four seconds, is controlled by the height of the mercury reservoir. The tip of the capillary is immersed in a test solution containing 0.1 molar indifferent electrolyte, which prevents any current arising from electrical migration. The test solution is connected to a standard calomel reference electrode by a salt bridge. The mercury electrode is polarized by a potentiometer the terminals of which are connected to the mercury reservoir and the reference electrode.

The pen of an automatic recording polarograph traces a saw-tooth current-potential wave which rapidly rises to a plateau as the decomposition potential is reached. The saw-tooth trace is due to the growth of the mercury drop and its subsequent fall. The potential

at which the current is equal to one-half the diffusion current is defined as the half-wave potential and is characteristic of the electroactive species. The half-wave potential of the simple metal ion is shifted when the metal ion is complexed. Since dissolved oxygen in the test solution is reduced by potentials more negative than 0.1 volt and, consequently, masks any curve due to the reduction of a metal-ion, it must be first removed by bubbling nitrogen through the test solution for several minutes.

II. THE ILKOVIC EQUATION

A limiting current results whenever the rate of the electrode reaction is governed by the rate of supply of the electroactive species to the electrode surface. The rate of supply depends on electrical migration, convection or diffusion mass transfer processes or a combination of these. In the case of polarography, the relatively high concentration of the indifferent electrolyte as compared to the unknown eliminate mass transfer caused by electrical migration. Thus, at a potential where the electroactive species is immediately used up on arrival at the electrode surface, the rate of supply is controlled entirely by diffusion provided the electrode reaction is rapid and there is no stirring of the test solution.

Fourteen years after Heyrovský[2] discovered polarographic analysis in 1920, Ilkovič[3] succeeded in deriving the equation for the diffusion current. This equation is

$$i_d = 607nCD^{1/2}m^{2/3}t^{1/6} \qquad (1)$$

where i_d is the average diffusion current in microamperes during the drop life, n is the number of faradays per mole of electrode reaction, C is the concentration of the electroactive species in millimoles/liter, D is the diffusion coefficient in cm.^{2}/sec., m is the rate of flow

of mercury in mg./sec. and t is the drop-time in seconds. The constant given in the above equation is slightly temperature dependent; the number given is for 25°. For a derivation and further discussion of this equation, see reference (4).

III. THE EQUATIONS OF POLAROGRAPHIC WAVES

A. Simple metal-ion reduction

Consider the simplest case in which a metal-ion is reduced to a soluble species either in solution or in the amalgam. The electrode reaction may be represented by

$$\mathrm{Ox} + ne = \mathrm{Red}$$

The Nernst equation, neglecting the activities, is

$$E = E^{o} + RT/nF \ln C^{o}_{ox}/C^{o}_{red} \qquad (2)$$

where the C^{o},s stand for the molar concentrations at the electrode surface. From the Ilkovic equation, we can derive the following equations

$$C^{o}_{ox} = (i_d - i)/k_{ox}$$

$$C^{o}_{red} = i/k_{red}$$

Substitution into the Nernst equation gives

$$E = E^{o} + RT/nF \ln k_{red}/k_{ox} + RT/nF \ln (i_d - i)/i \qquad (5)$$

Since the half-wave potential, $E_{1/2}$, is defined as that potential when the current equals half the diffusion current, equation (5) becomes

$$E = (E_{1/2})_s + RT/nF \ln (i_d - i)/i \qquad (6)$$

where the subscript s stands for simple metal-ion. The reversibility of the electrode reaction may be checked by plotting E vs. $\log (i_d - i)/i$ which yields a straight line having a slope of $0.059/n$ if the electrode reaction is reversible.

B. Complex metal-ion reduction

When complex ions are involved, the electrode reaction becomes

somewhat more complicated. Consider the reversible electrode reaction

$$MX_q + ne = MX_r$$

where q is the number of X ligands per molecule of the oxidized form and r is the number per molecule of the reduced form. Assuming that the final complex of a series of complexes is by far more stable than any of the preceding complexes, their respective formation constants are

$$K_{ox} = \frac{[MX_q]}{[M][X]^q}$$

$$K_{red} = \frac{[MX_r]}{[M][X]^r}$$

Substitution of the concentrations of the oxidized species and the reduced species into equation (2) and the subsequent substitution of the current relationships of the oxidized and reduced complexes gives the final result

$$E = (E_{1/2})_c + RT/nF \ln K_{red}/K_{ox} + (r-q)RT/nF \ln X + RT/nF \ln(i_d-1)/i \qquad (7)$$

The difference between equations (6) and (7) is equal to the degree of shift between the polarographic waves of the complex metal-ion and the simple metal-ion.

$$\Delta E_{1/2} = (E_{1/2})_c - (E_{1/2})_s = (r-q)RT/nF \ln X + RT/nF \ln K_{red}/K_{ox} \qquad (8)$$

The unknowns r, q, K_{red}, and K_{ox} can be determined by varying the concentration of the ligand. Examples using this method for the determination of formation constants are found in references(5),(6), and (7).

When more than one stable complex is formed, the method of DeFord and Hume[8] may be used. Consider the following series of

equations having k_1, $k_2, \ldots, k_j$ formation constants, respectively

$$M + X = MX \quad , k_1$$

$$MX + X = MX_2 \quad , k_2$$

$$\cdots$$

$$MX_{j-1} + X = MX_j \quad , k_j$$

The electrode reaction may be written as

$$MX_j + ne = M(Hg)_x + jX$$

Let $F_0(X)$ be the reciprocal of the fraction of the uncomplexed metal-ion in solution.

$$F_0(X) = c_m/[M] = K_0 + K_1(X) + K_2(X)^2 + \ldots + K_j(X)^j \qquad (9)$$

where C_m is the total concentration of the metal both complexed and uncomplexed, (X) is the molar concentration of the ligand and the K's are defined as follows

$$K_0 \equiv 1, \ K_j = \prod k_j$$

The difference between the half-wave potentials of the simple and complexed metal-ions is

$$\Delta E_1/_2 = (E_1/_2)_c - (E_1/_2)_s = - RT/nF \ln F_0(X) \qquad (10)$$

Now, define a series of F functions as follows

$$F_1(X) = \frac{F_0(X) - K_0}{(X)} = K_1 + K_2(X) + K_3(X)^2 + \ldots + K_j \qquad (11)$$

$$F_2(X) = \frac{F_1(X) - K_1}{(X)} = K_2 + K_3(X) + \ldots + K_j \qquad (12)$$

$$\cdots$$

$$F_j(X) = K_j \qquad (13)$$

The value of K_1 may be found from equation (11) by plotting $F_1(X)$ against (X) since the y-intercept equals the value of K_1. The remaining formation constants are determined similarly. This method has been successfully by a number of experimenters.[9,10,11]

IV. CONCLUSION

The polarographic technique for the investigation of complex ions is based of the fact that the half-wave potential of a simple metal-ion is shifted when the metal-ion concentration is decreased by complexation. By measuring this degree of shift, information about the formula of a complex and its stability can be determined. This method is limited to rapid, reversible electrode reactions.

V. REFERENCES

1. I. M. Kolthoff and J. J. Lingane, Polarography, Vol. 1, Interscience Publishers, Inc., New York, 2nd ed., p. 14
2. J. Heyrovsky, Chem. listy, 16, 256 (1922)
3. D. Ilkovic, Collection Czechoslov. Chem. Communs., 6, 498 (1934)
4. J. M. Markowitz and P. J. Elving, Chem. Revs., 58, 1047 (1958)
5. H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and S. Swann,Jr., J. Am. Chem. Soc., 71, 1550 (1949)
6. E. I. Onstott and H. A. Laitinen, J. Am. Chem. Soc., 72, 4724 (1950)
7. C. J. Nyman, E. W. Murbach, and G. B. Millard J. Am. Chem. Soc., 77, 4194 (1955)
8. D. D. DeFord and D. N. Hume, J. Am. Chem. Soc., 73, 5321 (1951)
9. D. N. Hume, D. D. DeFord, and G. C. B. Cave, J. Am. Chem. Soc., 73, 5323 (1951)
10. H. A. Laitinen and M. W. Grieb, J. Am. Chem. Soc., 77, 5201 (1955)
11. T. J. Lane, C. S. C., J. A. Ryan, and E. F. Britten, J. Am. Chem. Soc., 80, 315 (1958)

CHELATION AS A DRIVING FORCE IN SYNTHESIS

Soter G. Kokalis October 18, 1960

I. PRINCIPLES OF CHELATION:

A. Metal Ions as Electron Acceptors.

Various atoms coordinate with metal ions by electrostatic or covalent linkages in which the ligand atoms serve as electron donors to the metal ion. A recent nuclear magnetic resonance study has shown that the electron-withdrawing power of a metal is reduced when coordination to a ligand occurs (1). Thus the spectra of $GaEt_3$ and $AlEt_3$ and their respective etherates indicate an increase in the chemical shift values for the methylene protons once the metal is coordinated to the ether oxygen, reflecting an increase of electron shielding for the protons. In the phenomenon of chelation, at least two coordination sites of the metal ion are filled by donor atoms that are components of a single molecule. A heterocyclic ring is formed which includes the metal ion, the two donor atoms, and other atoms of the chelating molecule located between the two donor atoms. If both donor groups of a chelate molecule are negative, a larger energy of formation is needed, resulting in a less stable complex.

B. Chelate Stability.

The formation constants of metal chelates reflect their greater stability relative to metal complexes with non-chelating ligands The enhanced stability of chelates is explained in terms of a gain in translational entropy through chelate formation (2). Since the most random state is the most probable, reaction of a chelate ligand (L) with a solvated metal ion will increase the number of particles in the system by (n-1) for a net gain in entropy,

$$M(aq)n^{+q} + L \rightarrow Nag + ML^{+q}$$

The most stable chelate system occurs with the formation of the smallest ring which is still strain-free, usually the five-membered chelate ring. However, rings involving two double bonds can best be stabilized in the five- or six-membered structures. The majority of the known chelates are based upon five- or six-membered rings.

C. Influence of Chelation on the Catalytic Activity of Metals.

The important role chelation plays in affecting reaction rates and routes is becoming increasingly apparent. Thus, to cite an example, the rate of decomposition of H_2O_2 is enhanced through the presence of copper(II) chelates in contrast to free copper(II) ions (3).

II. CHELATES AS REACTION CATALYSTS:

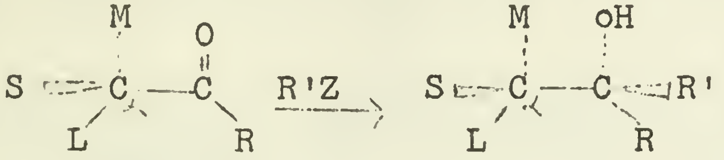
A. Enhancement of Yields.

In the reaction of benzaldehyde and pyrrole to produce tetraphenyl porphine (A) and tetraphenyl isoporphine (B), i.e., chlorin, zinc acetate was found to double the yields of A and B over those from the uncatalyzed reaction (4). The product was isolated in the former

case as the Zn-A chelate, illustrating the importance of chelation in the enhancement of yield.

B. Stereospecific Products.

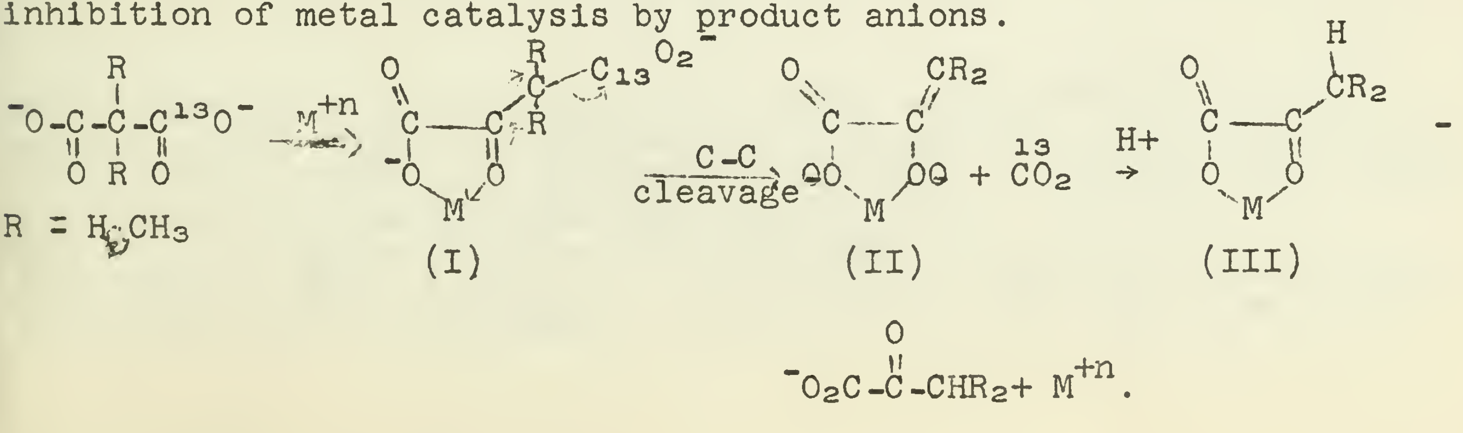
The presence of an asymmetric center in the substrate molecule can induce asymmetric synthesis. Often it appears that a metal chelate is the reaction intermediate (5). The relative bulk of substituents on an asymmetric carbon alpha to a carbonyl group under attack by a Grignard reagent, RMgX, by $LiALH_4$, or by $Al(OR)_3$ influences the stereospecificity of the attack:



The reduction of hindered ketones by Grignard reagents produces predominantly a stereoisomer predicted by a low energy six-membered chelate ring intermediate (6).

C. Influences upon Reaction Equilibria.

A kinetic study of the decarboxylation of oxaloacetate, $^-O_2CCOCH_2CO_2^-$, reveals an important reaction catalyzed by metal ions. The anion could form a five-, six-, seven-, or a five- and six-membered chelate ring system. Carbon-13 studies indicate the five-membered ring as most likely in the mechanism, with the non-chelated carboxylate group being lost during the reaction (7). Although the copper(II) catalyzed rate is sixty times that of the non-catalyzed rate, the enzyme rate is fifty thousand times the copper(II)-catalyzed rate of decarboxylation. Since exchange of D_2O for H_2O fails to affect the metal-catalyzed rate, it is indicated that the rate-determining step is cleavage of the C-C bond. In enzyme catalysis, proton transfer is indicated as the rate-determining step since the use of deuterim oxide alters the reaction rate. The enol intermediate(II) has been detected in the ultra violet spectra and by bromine titration (8). The decarboxylation of the mono-ethyl ester, $EtO_2CCOCMe_2COO^-$, is not catalyzed by metals, because of inhibition of formation of a chelate like (I). Moderate acidities, e.g., pH = 2.4, catalyze decarboxylation, whereas excess acid, e.g., pH=0, inhibits the reaction. A recent quantitative correlation of complex stability versus catalytic power for various transition metals refute the importance of chelation in the reaction (9). The most stable 1:1 chelate of oxaloacetate, i.e., the copper(II) compound proved to be the best decarboxylation catalyst. The lesser stability of the pyruvate chelate(III) relative to chelates of structure I prevents extensive inhibition of metal catalysis by product anions.



(I)

(II)

(III)

$$^-O_2C\overset{O}{\overset{\|}{C}}CHR_2 + M^{+n}.$$

The catalyzed auto-oxidation of cyclohexene is enhanced by the use of metal-N,N'-disalicylidene ethylenediamine chelates in contrast to the use of the uncomplexed metal ions (10). Copper(II) is exceptional, since reaction is retarded by the chelate, possibly due to the prevention of substrate entry into the coordination sphere of Cu^{II} since a quadridentate chelate is formed.

The irreversible auto-oxidation of metal-acetylacetonates reveals a variation of rate with metal ions (11). A metal of variable oxidation state is necessary for enhanced radical decomposition of the ligand. The stability constants of the chelates indicate that the most stable tend to yield the lowest rate of auto-oxidation.

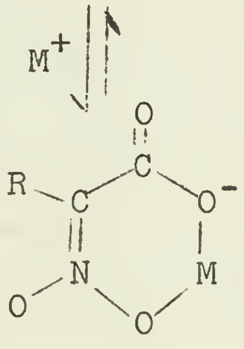
Employment of alkali carbonates in the methylation of acetylacetone reveals a definite influence of M^+ ion on the reaction rate due to chelation (12). A carbonium ion is attacked in the methylation reaction, whereas chelation stabilizes the ion and retards methylation. Hence, the rate of methylation correlates with the stability constants of chelates indicating a large rate for the weaker chelate, since this means a greater number of available carbonium ions. A more exhaustive study of metal-catalyzed reaction rates is urgently needed! This information will be valuable in classifying mechanisms for metallo-enzyme systems.

III. APPLICATION OF CHELATION TO REACTION MECHANISMS:

A. Synthesis of Molecules.

Chelation has been found vital in the synthesis of α-nitro acids from primary nitroalkanes and carbon dioxide (13). Decarboxylation of dibasic acids of the type $RCH(NO_2)COOH$ in the presence of metal ions or in alkaline media was very slow, due to resonance stabilization of the anion in the chelate, C, although evolution of CO_2 is very fast in acidic or weakly basic media.

$$RCH(NO_2)COOH \rightleftarrows RCH(NO_2)CO_2^{-1} \rightleftarrows [RC(NO_2)COO]^{-2} \rightleftarrows CO_2 + RCH_2NO_2.$$



C

The decarboxylation of nitroacetic acid is reversible, and the reaction of magnesium methoxide with carbon dioxide in the presence of nitromethane results in quantitative recovery of $Mg[CH(NO_2)CO_2]$ which yields the acid $CH_2(NO_2)COOH$ upon acidification. The influence of chelation on the equilibria involved permits the compound $Mg(OCOOCH_3)_2$(MMC) to serve as a carboxylating agent for nitroalkanes containing active hydroxygen. An extension of the use of MMC as a

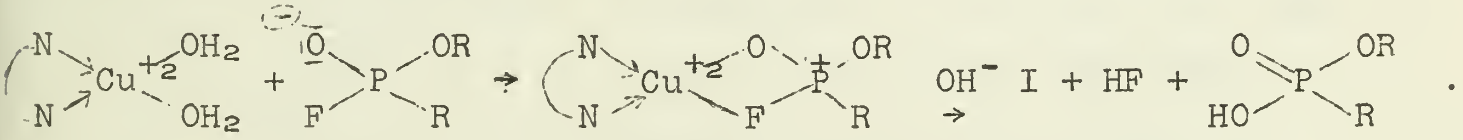
carboxylating agent permits the conversion of ketones to β-keto acids via a chelate intermediate (14). The importance of chelation is revealed by observation that the reaction of cyclohexanone with sodium ethyl carbonate, Na(OCCOEt), failed to produce the β-keto acid, whereas use of magnesium methyl carbonate gave a good yield of the 2,5-dicarboxylic keto acid. A new synthetic route for α-substituted β-keto esters employs the acylation of a magnesium chelate of ethyl hydrogen methyl malonate - following its decarboxylation - to form a new chelate (15).

B. Decomposition of Molecules.

An attempted synthesis of the copper(II) complex of the Schiff base, 2-thiophenol ethylenediamine, at a pH of 7 resulted only in the recovery of the bis-ethylenediamine copper(II) complex ion (16). The metal ion catalyzed hydrolysis of the C=N bond. A kinetic study showed the energy of activation for the copper(II)-catalyzed hydrolysis to be 11.3 Kcal., whereas when the nickel(II) chelate was used, it was 12.5 Kcal (17). Catalytic activity can be related to strength of the coordinate covalent bonds formed, since copper(II) ion is known to form stronger bonds to nitrogen atoms than nickel(II) ion. The stronger the bonding of the ligand to the metal ion, the greater the driving force for reaction because of the smaller energy of activation for bond rupture. The energy of activation should thus reflect the catalytic effect.

Chelate formation has been found to stabilize the C=N bond in the Schiff base, salicylal-glycine (18). The free Schiff base is dissociated at pH 3, whereas copper(II) ion forms a stable 1:1 chelate at pH 3. The formation of two chelate rings per ligand molecule enhances stability.

Transesterfication of the bis-salicylaldimine copper(II) complex proceeds by a new mechanism employing a lactone-chelate as the intermediate (19). Amidation of a Schiff base complex employs addition of the aliphatic amine to C=N bond and a reorientation of ligands. Catalysis of the hydrolysis of *i*-propyl methyl phosphonofluoridate, ROPO(CH_3)F, is maximal with copper(II) complexes (20). It is imperative that the coordination sphere of the metal ion be only partially filled by chelation and that at least two sites be filled by water molecules. Tridentately (e.g., with DIEN) and tetradentately (e.g., with TRIEN) chelated copper(II) ions are poor catalysts. Since a high hydroxyl ion concentration is needed for hydrolysis, the latter is inhibited by the chelate which maintains the metal ion in reasonable concentration in an aqueous system. The simple aquated metal ion could not exist in solution at higher pH values.



I II III

A model system for the metal-catalyzed decomposition of 6-succino aminopurine can elucidate a vital enzyme-catalyzed reaction (21). The hydrolyses of the 6-succino aminopurine to 6-aminopurine and fumaric acid was greatly enhanced by the presence of various metal salts at pH of 7. Chelation serves to labilize the C-N bond to proton attack.

Man is a long way from fully controlling reactions by metal-ion catalysis. A slow, but persistent, accumulation of knowledge in areas of simple chelation phenomenons will lead to a mastery of the most complex mechanism utilizing chelation as the driving force in synthesis. Many reactions must be rerun employing metal ions as catalysts; reaction kinetics data must be compiled and correlated with the metal ion and chelating ligand employed; and lastly, thermodynamic stability data must be evaluated to permit correlation of catalysis with chelate stability. Only then will reaction mechanisms be completely understood.

REFERENCES

1. S. Brownstein, B. C. Smith, G. Ehrlich, and A. W. Laubengayer, J. Am. Chem. Soc., 81, 3826 (1959).
2. G. Schwarzenbach, Anal. Chem., 32, 6 (1960).
3. G. Thuillier, Bull. Soc. Chim. France, No. 10, 1431 (1959).
4. R. H. Ball, G. D. Dorough and M. Calvin, J. Am. Chem. Soc., 68, 2278 (1946).
5. C. D. Mitchell, *University of Illinois Organic Chemistry Seminars*, p. 100 (Nov. 30, 1959).
6. W. M. Foley, F. J. Welch, E. LaCombe, and H. S. Mosher, J. Am. Chem. Soc., 81, 2779 (1959).
7. S. Seltzer, G. A. Hamilton, and F. H. Westheimer, J. Am. Chem. Soc Soc., 81, 4018 (1959).
8. R. Steinberger and F. H. Westheimer, J. Am. Chem. Soc., 73, 429 (1951).
9. E. Gelles, J. Inorg. Nucl. Chem., 8, 625 (1958).
10. A. S. Chalk and J. F. Smith, Nature, 174, 802 (1954).
11. M. Mendelsohn, E. M. Arnett, and H. Freiser, J. Phys. Chem., 64, 660 (1960).
12. A. Brändström, Arkiv. för Kemi, 2, 587 (1950).
13. M. Stiles and H. L. Finkbeiner, J. Am. Chem. Soc., 81, 505 (1959).
14. M. Stiles, J. Am. Chem. Soc., 81, 2598 (1959).
15. R. E. Ireland and J. A. Marshall, J. Am. Chem. Soc., 81, 2907 (1959).
16. G. L. Eichhorn and J. C. Bailar, Jr., J. Am. Chem. Soc., 75, 2905 (1953).
17. G. L. Eichhorn and I. M. Trachtenberg, J. Am. Chem. Soc., 76, 5183 (1954).
18. G. L. Eichhorn and N. D. Marchand, J. Am. Chem. Soc., 78, 2688 (1956).
19. H. S. Verter and A. E. Frost, J. Am. Chem. Soc., 82, 85 (1960).
20. R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hyytiainen, S. C. Chaberck, Jr., and A. E. Martell, J. Am. Chem. Soc., 79, 3030 (1957).
21. J. Baddiley, J. Buchanan, and J. Stephenson, Arch. Biochem. Biophys., 83, 54 (1959).

RECENT WORK ON THE STEREOCHEMISTRY OF PARAMAGNETIC NICKEL(II) COMPLEXES

Devon W. Meek October 25, 1960

I. INTRODUCTION

It is generally agreed that Ni(II) can exist in either the hexacoördinated or tetra-coördinated form; tetra-coördinated Ni(II) in turn has been thought to be found in either the planar or tetrahedral configuration.

According to Pauling's(1) valence bond approach to the stereochemistry of complex molecules, the four-coördinated paramagnetic complexes of Ni(II) must be tetrahedral($\underline{4s}\underline{4p}^3$) with two unpaired electrons, whereas the diamagnetic ones must have a square-planar arrangement ($3\underline{d}\underline{4s}\underline{4p}^2$ hybridization). Such correlations have not been proven, either theoretically by independent energy and bond type calculations, or experimentally by proofs of structures for pertinent compounds. Rather, information about structure and bonding has been inferred from magnetic moment data based on qualitative energy arguments. For Ni(II) complexes, those found to be paramagnetic were assumed to have ionic bonding with the most stable configuration predicted to be tetrahedral or octahedral for four- and six-coördinated complexes, respectively.

Recently, a flurry of research, both experimental and theoretical, has been initiated because of the absence of unequivocal experimental proof for the existence of the tetrahedral configuration in nickel(II) complexes(2).

II. FOUR-COVALENT CHELATE-TYPE COMPLEXES

The coördination compounds formed between nickel and various alkyl salicylaldimines are generally highly colored, diamagnetic solids with trans-planar configurations(3). These complexes, diamagnetic in the solid state, become paramagnetic even in "non-coördinating" solvents such as benzene and chloroform(4) and in the molten state(5). The paramagnetism in solution has been attributed to transformation from an "inner" to an "outer" orbital type(6), to an equilibrium between $\underline{sp}^3$ and $\underline{dsp}^2$ configurations(7), and to the formation of six-coördinate adducts with two molecules of strongly polar solvents such as pyridine(8).

It is now believed that diamagnetic to paramagnetic transitions in supposedly "planer" complexes are not due to a change in stereochemistry but to a change in the strength of the field associated with the ligands. The complexes are, in fact, pseudo-octahedral, the two apical ligands causing a perturbation from a singlet to a triplet ground state(9,10). This perturbation can also be effected merely by temperature changes(11).

III. NON-CHELATE NICKEL COMPLEXES

A. "Tetrahedral" Complexes Which Have Been Shown To Have Some Other Structure.

Contrary to the general belief, tetrahedral complexes of Ni(II) are rather uncommon. The usually accepted example of bis-(acetylacetonato)-Ni(II) is now known to be a trimer, almost certainly involving octahedrally coördinated nickel(12,13,14).

The reflection spectra of some tabulated, apparently tetrahedral complexes, e.g., $Ni(Py)_4(NCS)_2$, $Ni(tren)SO_4 \cdot 7H_2O$, $Ni(tren)SO_4$, show that in all cases three bands appear at approximately the same positions as for known octahedral complexes(15). X-ray diffraction studies have shown that the complexes $Ni(NH_3)_4(NO_3)_2$, $Ni(NH_3)_4(NCS)_2$, $Ni(Py)_4Cl_2$, $Ni(Py)_4Br_2$, and $Ni(Py)_4(NCS)_2$ are all octahedral, not tetrahedral(16).

At Copenhagen in 1953, $Ni(tren)(SCN)_2$ was mentioned as an example of a tetrahedral nickel complex(17). By using three-dimentional x-ray studies, Rasmaussen(18) and Hall and Woulfe(19) have shown that the complex has a slightly distorted octahedral structure, the thiocyanate groups being coördinated through the nitrogen atoms.

The complex $Ni(en)_2(NCS)_2$ is blue and paramagnetic, but coördination of the nickel ion is *trans*-octahedral, with Ni-N distances of 2.10 Å to the ethylenediamine and 2.15 Å to the isothiocyanate. A coördination octahedron also exists in $[Ni(en)(H_2O)_4](NO_3)_2$, which is again blue and paramagnetic(20). This would indicate that the visual blue color in paramagnetic nickel complexes in not indicative of tetrahedral coördination, as has been suggested(21)

B. Complexes That Have the Greatest Possibility of Being Tetrahedral.

It is known that the complexes $[(C_2H_5)_3P]_2NiX_2$(X=Cl,Br,I) are diamagnetic with *trans*-planar structures, whereas $[(C_2H_5)_3P]_2Ni(NO_3)_2$ is paramagnetic (μ=3.10 B.M.) and possibly tetrahedral(22,23). The high electric dipole moment value of the latter (8.85D) excludes the *trans*-planar configuration, but could be due to a *cis*-planar instead of a tetrahedral arrangement of ligands(2).

The complexes $(Ph_3P)_2NiX_2$(X = Cl, Br, I, NO_3) are paramagnetic with distorted tetrahedral structures*, although $(Ph_3P)_2Ni(SCN)_2$ is diamagnetic and probably *trans*-planar(25,26). The magnetic moment of this paramagnetic series ranges from 2.92 to 3.07 B.M., which is only slightly in excess of the spin-only value, 2.83 B.M. If the Ni(II) ion is surrounded by a regular tetrahedron of ligands, a large orbital contribution to the magnetic moment is expected because of the possibility of rearrangement of electrons in the three degenerate d_ε orbitals when a magnetic field is applied(27,28). Figgis(29) has calculated that regular tetrahedral Ni(II) complexes should have an effective magnetic moment of near 4.0 B.M. Thus, the magnetic moments for the above complexes support a non-tetrahedral configuration.

* Cited by Venanzi in 1957 (24) but no experimental x-ray results have been published.

An x-ray study on the complexes $[(C_6H_{11})_3P]_2NiBr_2$ and $[(C_6H_{11})_3P]_2Ni(SCN)_2$ showed a trans-planar arrangement of the four ligands about the nickel atom. The compounds are green and diamagnetic and have very small dipole moments. The diamagnetism of this series, compared to the paramagnetism of analogous phenylphosphine complexes, was attributed to an enhancement of the ligand field along the P-P axis in going from the aromatic to the alliphatic phosphines(30).

Secondary alkylphosphines also react with anhydrous nickel halides to form stable complexes of the types $[(C_2H_5)_2PH]_4NiX_2$ and $[(C_6H_{11})_2PH]_2NiX_2$ (X = Cl and Br). All of these complexes are red, diamagnetic, non-electrolytes, and monomeric in solution. The $[(C_2H_5)_2PH]_4NiBr_2$ compound has a dipole moment of 7.88 D and thus has a <u>cis</u>-octahedral structure. The dipole moment value of $[(C_6H_{11})_2PH]_2NiBr_2$ is nearly zero; thus it is probably <u>trans</u>-planar(30a). The diphenylphosphine reacts with anhydrous $NiBr_2$ in absolute ethanol according to the equation

$$NiBr_2 + 4(C_6H_5)_2PH \rightarrow [\{(C_6H_5)_2P\}_2Ni\{HP(C_6H_5)_2\}_2] + 2HBr.$$

The compound is yellow, diamagnetic, and stable in air. It has a planar structure(30b).

Tertiary phosphine oxides react with nickel salts to form complexes of the general composition $[(R_3PO)_2NiX_2]$(X=Cl, Br, I, NO_3) and $[(R_3PO)_4Ni](ClO_4)_2$ when the non-coördinating perchlorate anion is used(31-34). Cotton(31) first assigned a tetrahedral configuration to the $[(R_3PO)_4Ni]^{2+}$ cation on the basis of steric requirements of the ligand, magnetic susceptibility measurements, and visible absorption data, but detailed and "exact" calculations of the energy levels of Ni^{2+} in both octahedral and tetrahedral fields by Liehr and Ballhausen(35) required an alteration of this conclusion. The observed transition would require a D_q value of about 1700 cm.$^{-1}$, which seems unreasonable when one considers that the $[Ni(H_2O)_6]^{2+}$ has a D_q value of 850 cm.$^{-1}$. Steric requirements and the available x-ray data can be satisfied by either a tetrahedral configuration with linear Ni-O-P chains or a planar configuration with Ni-O-P angles $\leq 160^\circ$. The inconsistency between the spectral and the magnetic data leads Cotton and Bannister to suggest the possibility of a configuration intermediate between a regular tetrahedron and a square(33).

The tertiary phosphine oxide complexes of the type $(R_3PO)_2NiX_2$ (X = Cl, Br, I, NO_3; R = C_2H_5, C_6H_{11}, C_6H_5) dissolve in organic solvents like nitrobenzene and benzene as monomers and are undissociated(32,34). Again the hypothesis is suggested that because of crowding due to the very bulky phosphine oxide groups in $(Ph_3PO)_2$-$Ni(NO_3)_2$, the NiO_4 configuration may have D_{2d} symmetry(34),

COMPLEXES OF THE TYPE $(R_3P)_2NiX_2$ AND $(R_3PO)_2NiX_2$

Compound	Color	μ B.M.	μ D	Probable Coördination
$[(C_2H_5)_3P]_2NiX_2$ $(X=Cl,Br,I)$	Red	0.00	0.00	Trans-planar (x-ray)
$[(C_2H_5)_3P]_2Ni(NO_3)_2$	Green	3.10	8.85	Tetrahedral of Cis-planar
$[(C_6H_{11})_3P]_2NiX_2$ $(X=Cl,Br,SCN)$	Green	0.00	0.00	Trans-planar(x-ray)
$(Ph_3P)_2NiX_2$ $(X=Cl,Br,I,NO_3)$	Green-Blue	2.92-3.07	5.1-8.5	Distorted Tetrahedral
$(Ph_3P)_2Ni(SCN)_2$	Red	0.00	0.00	Trans-planar
$(Et_3PO)_2NiBr_2$	Blue	3.40	9.63	Distorted Tetrahedral
$[(C_6H_{11})_3PO]_2NiCl_2$	Blue	3.65	-	?
$[(C_6H_{11})_3PO]_2Ni(NO_3)_2$	Yellow	3.26	11.21	Distorted Tetrahedral
$(Ph_3PO)_2Ni(NO_3)_2$	Yellow	3.45	-	"
$[(Ph_3PO)_4Ni](ClO_4)_2$	Yellow	3.51	-	"
$[(C_2H_5)_2PH]_4NiBr_2$	Red	0.00	7.88	cis-Octahedral
$[(C_6H_{11})_2PH]_2NiBr_2$	Red	0.00	0.00	Trans-planar

The infrared spectrum of $Ni(NO)(OH)_3$ shows strong peaks at 1828 and 3500 cm^{-1}, typical of coördinating NO^+ and OH^- groups, respectively. A methanolic solution of the complex has a strong absorption peak at 650 mu, but no peak near 400 mu. On the basis of the blue color and the absence of a 400 mu peak, Griffith, et al., assign a probable tetrahedral configuration to this complex(36).

The absorption spectrum of $NiCl_2$ in LiCl/KCl eutectic at 400° has four d-d peaks at 510, 590, 625, and 695 mu(37). Jörgensen(38) concluded that the latter three were due to tetrahedrally coördinated Ni^{2+} and that the 510 peak was due to octahedrally coördinated Ni^{2+}. By means of a thoughtfully designed experiment, Gruen and McBeth(39) were able to obtain the spectrum of tetrahedrally coördinated $NiCl_4^{=}$ and to demonstrate that Ni(II) is tetrahedral in molten CsCl and molten pyridinium chloride. Gill and Nyholm(40) have prepared the tetrachloro-nickelates R_2NiCl_4 ($R=(C_2H_5)_4N^+$, Ph_3MeAs^+) from alcoholic solutions, and the magnetic moment of the $(Ph_3MeAs)_2NiCl_4$ compound is 3.89 B.M. This is unusually high for a Ni(II) complex and strongly supports a tetrahedral arrangement of the ligands. Moreover, for the orbital contribution to be so large, distortion from a regular tetrahedral arrangement is small. Also conductivity, spectroscopic, and crystallographic studies support a tetrahedral coördination about the nickel in these salts.

TETRAHALOGENO-NICKEL COMPLEXES

Compound	Color in Solid State	At 20°(B.M.)
$[Ph_3MeAs]_2[NiCl_4]$	Blue	3.89
$[(C_2H_5)_4N]_2[NiCl_4]$	Blue	3.87
$[(C_2H_5)_4N]_2[NiBr_4]$	Blue	3.79
$[Ph_3MeAs]_2[NiI_4]$	Red	3.49

C. Ligand Field Explanations for the Rare Occurrence of Tetrahedral Ni(II) Complexes.

Until recently, any proof that Ni(II) is ever tetrahedrally coördinated was lacking. Indeed, the apparent non-existence of such complexes was generally assumed to be in accord with simple ligand-field theory. The ligand-field treatment(2,41) predicts that the five-fold degenerate d-orbitals will be split into two sublevels of different energy by the octahedral and tetrahedral electrostatic fields. In an octahedral field the crystal-field stabilization energy is equal to 12 D_q, whereas that for a tetrahedral field is equal to 8 Dq'. The energy difference between the two fields is about 15-30 kcal. This would account, to a large extent, for the rare occurrence of tetrahedral nickel (II) complexes(25_a,28,41,42).

Also the Jahn-Teller effect will operate to distort the tetrahedral symmetry of nickel (II) complexes(25,43). In the tetrahedral configuration there are four electrons in the lower d_γ-level and four in the upper d_ϵ -level, and the energy of the system can be lowered by a Jahn-Teller distortion of the tetrahedron, thereby removing the degeneracy of the d_ϵ -level. The axial distortion may be about one-half of the distance observed(44) for the Jahn-Teller effect on Cu(II), e.g., 0.15 A(43). The lowest energy of the system will be attained if this distortion occurs and may explain the small orbital contribution to paramagnetic $(R_3P)_2NiX_2$ complexes.

IV. CONCLUSION

In summary, the following points should be emphasized:

1. Thus far no regular tetrahedral nickel complex structures have been unequivocally ascertained, but the magnetic moment of nickel in the $NiCl_4^=$ ion corresponds very closely to that expected for Ni(II) surrounded by a regular tetrahedron of negative charges. Preliminary x-ray studies indicate that the complexes $(Ph_3P)_2NiX_2$ (X=Cl,Br,I) may have distorted tetrahedral structures.

2. The delicate balance between the paramagnetic and the diamagnetic forms is easily influenced by such factors as solvent, nature of the ligands, changes in the environment, and temperature. There seems to be no clear relationship between color, magnetism, and structure for Ni(II) complexes.

3. The transition from paramagnetic to diamagnetic complexes is attributed to the force of the electrostatic field generated by the ligands. No abrupt change in the nature of the interaction, nor in the symmetry of the complex, need be postulated. Thus, no *a priori* correlation of magnetic moment and structure can be made!

4. Available data indicate that the formation of tetrahedral nickel complexes, instead of diamagnetic planar ones or paramagnetic octahedral ones, will occur only when the ligands do not have enough perturbing power to cause "spin pairing" and when a tetrahedral arrangement is forced by the steric requirements of the ligands(25,26).

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1. [illegible]

2. [illegible]

3. [illegible]

4. [illegible]

References

1. L. Pauling, Nature of the Chemical Bond, Cornell University Press, 3rd Ed., pp. 166-172 Ithaca, (1960).
2. R. S. Nyholm, Quelques Problemès de Chimie Minerale, "Report to the Tenth Solvay Council", pp. 225-287, Brussels (1956).
3. E. Frasson, C. Panattoni, and L. Sacconi, J. Phys. Chem., 63, 1908 (1959).
4. J. B. Willis and D. P. Mellor, J. Am. Chem. Soc., 69, 1237 (1947).
5. L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, J. Am. Chem. Soc., 82, 3487 (1960); L. Sacconi, R. Cini and F. Maggio, ibid., 79, 3993 (1957).
6. L. Sacconi, P. Paoletti, and G. DelRe, J. Am. Chem., 79, 4062 (1957); L. Sacconi, M. Ciampolini, F. Maggio and G. DelRe, ibid., 82, 815 (1960).
7. H. C. Clark and A. L. Odell, J. Chem. Soc., 3431 (1955).
8. F. Basolo and W. R. Matoush, J. Am. Chem. Soc., 75, 5663 (1953).
9. Gilda Maki, J. Chem. Phys., 29, 1129 (1958).
10. C. J. Ballhausen and A. D. Liehr, J. Am. Chem. Soc., 81, 538(1959).
11. H. C. Clark and R. G. O'Brien, Can. J. Chem., 37, 436 (1959).
12. S. Shibata, M. Kishita, and M. Kubo, Nature, 179, 320 (1957); S. Shibata, Bull. Chem. Soc. Japan, 30, 753 (1957).
13. G. J. Bullen, Nature, 177, 537 (1956).
14. J. P. Fackler, Jr., and F. A. Cotton, J. Am. Chem. Soc., 82, 5005 (1960).
15. R. W. Asmussen and O. Bostrup, Acta Chem. Scand., 11, 1097 (1957).
16. M. A. Porai-Koshits, Zhur. Neorg. Khim, 4, 730, (1959); Russian J. Inorg. Chem., 4, 332 (1959).
17. Proceedings of the Symposium on Coördination Chemistry, Copenhagen, 1953, P. 72.
18. S. E. Rasmaussen, Acta Chem. Scand ., 13, 2009 (1959
19. D. Hall and M. D. Woulfe, Proc. Chem. Soc., 346 (1956).
20. E. C. Lingafelter, Nature, 182, 1730 (1958); ibid., 183, 1673 (1959).
21. L. I. Katzin, Nature, 182, 1013 (1958); ibid., 1672 (1959).

[illegible]

1. [illegible]
2. [illegible]
3. [illegible]
4. [illegible]
5. [illegible]
6. [illegible]
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14. [illegible]
15. [illegible]
16. [illegible]
17. [illegible]
18. [illegible]
19. [illegible]
20. [illegible]

22. K. A. Jensen, Z. anorg. u. allgem. Chem., 229, 265 (1936).

23. R. W. Asmussen, A. Jensen, and H. Soling, Acta Chem. Scand., 9, 1391 (1955).

24. L. M. Venanzi, "International Symposium on the Chemistry of Coördination Compounds", Rome (Sept. 1957).

25. L. M. Venanzi, J. Chem. Soc., 719 (1958); Proc. Chem. Soc., 6 (1958).

26. L. M. Venanzi, J. Inorg. Nuclear Chem., 8, 137 (1958).

27. R. S. Nyholm, ibid., 8, 142 (1958).

28. N. S. Gill, R. S. Nyholm, and P. Pauling, Nature, 182, 168 (1958).

29. Figgis, quoted in ref. 28.

30. A. Turco, V. Scatturin, and G. Giacometti, Nature, 183, 601(1959).

30a. K. Issleib and G. Döll, Z. anorg u. allgem. Chem., 305, 1(1960).

30b. K. Issleib and E. Wenschuh, Z. anorg. u. allgem. Chem., 305, 15 (1960).

31. F. A. Cotton, E. Bannister, R. Barnes, and R. H. Holm, Proc. Chem. Soc., 158 (1959).

32. K. Issleib and B. Mitscherling, Z. Anorg. Allgem. Chem., 304, 73 (1960).

33. F. A. Cotton and E. Bannister, J. Chem. Soc., 1873 (1960).

34. E. Bannister and F. A. Cotton, ibid., 2276 (1960).

35. A. D. Liehr and C. J. Ballhausen, Ann. Phys., 6, 134 (1959).

36. W. P. Griffith, J. Lewis, and G. Wilkinson, J. Chem. Soc., 1775 (1959).

37. C. R. Boston and G. P. Smith, J. Phys. Chem., 62, 409 (1958).

38. C. K. Jörgensen, J. Mol. Phys., 1, 410 (1958).

39. D. M. Gruen and R. L. McBeth, J. Phys. Chem., 63, 393 (1959).

40. N. S. Gill and R. S. Nyholm, J. Chem. Soc., 3997 (1[illegible]

41. J. S. Griffith and L. E. Orgel, Quart. Revs., 11, 38[illegible] (1957).

42. R. A. Berg and Oktay Sinanoglu, J. Chem. Phys. 32, 1062 (1960).

43. T. S. Piper, Personal Communication (1960).

44. L. E. Orgel and J. D. Dunitz, Nature, 179, 462 (1957).

45. M. Kubota, Inorganic Seminars, University of Illinois, Feb. 25, 1958

THE APPLICATION OF MASS SPECTROMETRY TO INORGANIC CHEMISTRY

Donald A. Bafus November 1, 1960

I. INTRODUCTION

Thomson (1,2), in 1912, first introduced positive ray analysis into chemistry during his work on isotopes of elements and initiated the development of the modern day instruments.

In 1913, Aston (3-7) modified Thomson's instrument so that resolution of small differences of m/e could be determined in isotopic work. Aston's instrument produced deflections in the same plane, but in different directions, in contrast to Thomson's which produced deflections in planes at right angles to one another.

Dempster (8-10) in 1918 used a different method to focus the ion beam and to measure it. This method, known as direction focusing, depends on the production of ions having low kinetic energy and thus a high intensity spectrum is obtained which leads to more nearly precise measurements of the m/e value.

In the years following 1918, many changes and improvements were made on Dempster's instrument. However, in 1932, Bainbridge (11, 12) introduced an entirely new concept, that of velocity focusing rather than direction focusing. Velocity focusing gives a more accurate determination of the m/e value because of a linear relationship between the position of the line and the m/e value. This simplifies very considerably the accurate determination of the mass value, which can be estimated to 1 part in 10,000.

More recent forms of the mass spectrometer which employ both direction and velocity focusing have been developed. Those contributing were Dempster (13), Bainbridge and Jordan (14), and Mattauch and Herzog (15). These instruments give a high intensity spectrum and a linear mass scale, as well as good resolving power.

Another relatively simple but very accurate mass spectrometer employing the double focusing technique was developed by Nier (16) in 1940. The instrument is so designed that particles, all of which have the same momentum, enter and leave the magnetic field in directions perpendicular to the pole faces of the magnet. The ion source, the apex of the V-shaped field, and the point of focus are all co-linear.

Nier's instrument and variations of it are the most common type of the spectrometer in use at the present time.

II. MASS SPECTROMETRIC DATA AND ITS RELATION TO THERMODYNAMIC PROPERTIES OF MOLECULES.

The mass spectrum depends on the formation of ions in the gas phase. These ions can be produced by the following processes:

$$RX + e \longrightarrow RX^{+} + 2e \qquad (I)$$

$$RX + e \longrightarrow R^{+} + X + 2e \qquad (II)$$

These processes are not the only processes by which such ions can be produced, but they are the simplest processes by which ionization occurs upon electron bombardment.

Equation (I) shows a simple ionization of RX, and the energy of the process should be just the ionization potential of the molecule. However, equation (II) represents a somewhat more complex situation than does (I), since fragmentation occurs in addition to ionization to produce the R^+ ion and a neutral species. The energy for (II) is called the appearance potential of the R^+ ion.

If the molecule RX is bombarded by electrons according to (II), then the appearance potential of the R^+ ion, $A(R^+)$, may be given as

$$A(R^+) = D(R\text{-}X) + I(R) + E_k + E_e \qquad \text{(III)}$$

where $D(R\text{-}X)$ is the dissociation energy of the RX bond, $I(R)$ is the ionization potential of the radical R, E_k is the kinetic energy of the particles produced, and E_e is the excitational (electronic, vibrational, and rotational) energy of the fragment produced. The latter two terms are very small and may be neglected, thus

$$A(R^+) = D(R\text{-}X) + I(R) \qquad \text{(IV)}$$

If the ionization potential is known for the radical R, then the bond energy may be obtained by measuring $A(R^+)$.

The nature of the appearance potential can give information as to which of two or more possible processes is occurring, e.g.,

$$CH_4 + e \longrightarrow CH_2^+ + H_2 + e$$

or

$$CH_4 + e \longrightarrow CH_2^+ + 2H + 2e$$

Once the ion, R^+, has been produced in the ionization chamber of the spectrometer, it is accelerated, deflected, and collected in some type of an electrometer which is capable of recording ion current or ion intensity, (I^+).

The ion current, (I^+), can be related to the pressure of the ion if a Knudsen effusion cell is used as the sample holder, and takes the form

$$(I^+) = KP/T \qquad \text{(VA)}$$

This relationship may be deduced from Knudsen's effusion equation

$$Z = P\bar{v}\ \ /4RT \qquad \text{(VB)}$$

where Z is the rate of effusion of the molecules from the cell, $\bar{v}$ is the average velocity of the molecules, and   is the area of the orifice of the cell.

Since there is a direct relationship between the ion current, I^+, and the pressure, P, the Clausius-Clapeyron equation takes the form

$$d\ln(I^+)T/d(1/T) = -\Delta H/R \qquad \text{(VI)}$$

Thus a plot of $\ln(I^{+})T$ vs. $(1/T)$ will give the heat of sublimation.

In addition to the heat of sublimation, ΔH, changes in the free energy, ΔF, of dissociation may also be obtained as well as the ΔH of this dissociation.

III. APPLICATIONS TO INORGANIC SYSTEMS.

Many systems have been studied with the aid of a mass spectrometer and the above methods. A few of the systems that have been investigated are: Ta-Ta_2O_5 (17), VO-VO_2 (18), MoO_3 (19), Zr-ZrO_2 (20), $FeCl_2$ (21), MoO_2 (22), In-Sb (23), the transition metal(II) halides (24), H_2O--B_2O_3 (25), and H_2O-Li_2O (26).

The MoO_3 system will be considered as a representative example of the above systems and will be used to show how the mass spectrometer is applied to such a system.

The principal species found in the gas phase were the trimer, tetramer, and pentamer of MoO_3 with lesser amounts of the monomer and dimer which were shown to be due to fragmentation of the higher polymers of MoO_3.

The vapor pressure of the three primary species were determined, and the free energy change, the enthalpy change, and the entropy change of sublimation at 900°K were calculated for the species.

The change in entropy upon sublimation at 900°K determined in this experiment for the polymeric species combined with the entropy determined from third law calculations for solid MoO_3 at 900°K (27), allowed the calculation of the entropies of vaporization to be made for each. Assumptions made about the structure along with estimation of the Mo-O and Mo=O bonds lengths permitted the entropies of translation, vibration, and rotation to be calculated for each species.

From other thermochemical data and the heats of sublimation determined in the above experiment, the energy of atomization for each of the primary polymeric species were calculated.

REFERENCES

1. J. J. Thomson, Phil. Mag., 21, 225 (1911).
2. J. J. Thomson, ibid., 24, 209 (1912).
3. F. A. Aston, Proc. Roy. Soc., 89A, 440 (1914).
4. F. A. Aston, Phil. Mag., 38, 707 (1919).
5. F. A. Aston, ibid, 39, 449 (1920).
6. F. A. Aston, ibid., 42, 436 (1921).
7. F. A. Aston, Proc. Roy. Soc., 115A, 487 (1927).
8. A. J. Dempster, Phys. Rev., 11, 316 (1918).
9. A. J. Dempster, ibid., 18, 415 (1921).
10. A. J. Dempster, ibid., 20, 631 (1922).
11. K. T. Bainbridge, ibid., 39, 1021 (1932).
12. K. T. Bainbridge, ibid., 42, 1 (1932).

13. A. J. Dempster, ibid., 50, 98 (1936).
14. K. T. Bainbridge and E. B. Jordan, ibid., 51, 384 (1937).
15. J. Mattauch and R. Herzog, Phys. Z., 35, 567 (1934).
16. A. O. Nier, Rev. Sci. Inst., 11, 212 (1940).
17. M. G. Inghram, W. A. Chupka, and J. Berkowitz, J. Chem. Phys., 27, 569 (1957).
18. J. Berkowitz, W. A. Chupka, and M. G. Inghram, ibid., 27, 87 (1957).
19. J. Berkowitz, M. G. Inghram, and W. A. Chupka, ibid., 26, 842 (1957).
20. W. A. Chupka, J. Berkowitz, and M. G. Inghram, ibid., 26, 1207 (1957).
21. R. Schoonmaker and R. F. Porter, ibid., 29, 116 (1958).
22. R. Burns, G. E. DeMaria, J. Drowart, and C. E. Giese, ibid., 32, 1363 (1960).
23. G. E. DeMaria, J. Drowart, and M. G. Inghram, ibid., 31, 1076 (1959).
24. R. Schoonmaker, A. Friedman, and R. F. Porter, ibid., 31, 1586 (1959).
25. D. J. Meschi, W. A. Chupka, and J. Berkowitz, ibid., 33, 530 (1960).
26. J. Berkowitz, D. J. Meschi, W. A. Chupka, ibid., 33, 533 (1960).
27. L. F. Cosgrove and P. Snyder, J. Am. Chem. Soc., 75, 1227 (1952).

MATRIX INCLUSION SPECTROSCOPY

George L. Morgan November 8, 1960

I. INTRODUCTION

Forty years ago, Vegard(1) began a study of the luminescence of solid nitrogen which had been bombarded with electrons and positive ions. It was found that if the solid were allowed to warm up from 21°K., it would emit light for a short period of time. This was obviously a result of the trapping of some active species in a solid inert matrix. Upon diffusion, this solid then underwent reaction.

In 1954, several separate laboratories published notes describing attempts to study free radicals in some sort of a matrix (2,3,4,5,6,7). It is the purpose of this report to outline the advantages and problems of isolating reactive species for investigation.

II. PRINCIPLES OF MATRIX INCLUSION

A. Production and Detection

After the original experiments, various investigations used a number of methods to prepare and detect unstable species in an inert matrix(8). Among these are

<u>Production</u>:
1. Electron Bombardment
   - a. Cathode ray
   - b. Beta ray
   - c. "Tesla Coil" ion
2. Positive ion bombardment
   - a. Canal ray
   - b. Alpha ray
3. Photolysis
4. Radiolysis (γ or x-ray)
5. Atom bombardment

<u>Detection</u>:
1. Visible-ultraviolet spectroscopy
2. Infrared spectroscopy
3. Electron spin resonance
4. Magnetic susceptibility
5. Calorimetry

B. Types of Matrices

The matrix, a glass or crystaline solid, should have the following properties(9): 1- <u>Inertness</u> (to the species studied), 2- <u>Rigidity</u> to prevent diffusion, 3- <u>Transparency</u> in the desired spectral range. It should not absorb or scatter the incident light. Thus, the inert gases, nitrogen, and oxygen, deposited at a slow rate, make a desireable matrix. 4- <u>Volatility</u>. The matrix should be formable from gas phase deposition, yet have a low enough vapor pressure to remain intact at pressures of 10^{-3} - 10^{-4} mm of mercury.

Defining M/A as the ratio of the moles of matrix gas to moles of reactive substances, Becker and Pimentel(9) measured the efficiency of isolation as a function of temperature for various matrix gases.

The well known infrared spectrum of the equilibrium, $2NO_2 \rightleftarrows N_2O_4$, was used as the standard. Xenon, argon, and nitrogen were found to form the most efficient matrices.

C. Experimental Effects

Conditions which have an effect on the yield and results are as follows: 1- Diffusion, understood in crystals but not in glasses. 2- Cage effect. Sowden and Davidson(10) felt that in some cases the quantum yield of photolytic decomposition was negligibly small in the rigid matrix compared with the yield in the gas phase. Even if fragmentation occurs, the fragments are held in close proximity so that recombination is likely. On the other hand, the cage effect can be utilized as in the case of the formation of methyl nitrate from nitromethane in a matrix(11): This reaction cannot be efficiently performed in the gas phase. An extreme effect would be the interaction of a very reactive radical with the matrix itself. 3- Local heating. The generation of free radicals in situ generally occurs in an energy-rich situation. As this excess energy is transformed into heat, the local temperature rises above the ambient temperature, permitting local diffusion which permits more reactions, etc. (i.e. - a chain reaction) (12). Thus, this maximum local temperature reached and its character, are of crucial importence in the maintainence of matrix rigidity. 4- An effect which shifts the frequency of absorption of a trapped species from that of the free species in the gas phase. Becker and Pimentel(9) attribute this to the dielectric constant of the matrix, whereas Ketelaar and van der Elsken(13) feel that it can be treated as a polarization of the environment.

D. Concentration

One of the major reasons for the development of the matrix inclusion method was to isolate and leisurely study detectable concentrations of free radicals. A question naturally arises as to the maximum concentration of free radicals that can be obtained. The immediate interest is that thick but dilute suspensions cannot be conveniently studied spectroscopically. Of a more practical nature is interest in the high latent energy that can be obtained in a solid with a high concentration of free radicals.

Statistical treatments(14,15) based on the various possible packing arrangements showed that trapped radicals could not exceed 10-14%. Later treatments, made for specific lattices(16) and for the nitrogen atom in an N_2 molecular lattice(17,18,12), indicate still smaller attainable concentrations. A further discussion of the packing of radicals in a lattice is contained in a later section.

III. EXPERIMENTAL RESULTS

A. Infrared.

Although the experimental technique varies with the conditions desired, the apparatus and procedure of Becker and Pimentel(9) are fairly generally applicable and well described. Some reactions that have been studied are: Iodine, carbon disulphide, and ClO_2 degradation products(6); tetramethyl-tetrazene and S_2Cl_2-SCl_2 degradation products(10); the photolysis of nitromethane and methyl nitrite(11);

The well known infrared spectrum of the [illegible] [illegible] [illegible] from the most efficient conditions.

C. Photochemical Effects

Conditions [illegible] [illegible]

D. Concentration

One of the major reasons for the development of the matrix isolation method was to [illegible] [illegible]

[illegible]

III. EXPERIMENTAL RESULTS

A. Infrared.

Although the [illegible] [illegible]

and hydrogen bonding and the structures of methanol(19) and water(20).

Much work has been done on the decomposition of hydrazoic acid in order to isolate the imine radical(21,22,5), the first attempts being on the pure solid acid. Pimentel and co-workers obtained reproducible results using the matrix inclusion technique(23). Subsequent work(24) tends to confirm the presence of the imine radical, although diimide and azide amine (NH_2N_3) could possibly be present.

In a study on the photolysis of diazomethane in argon and nitrogen matrices(25), "unstable species" were observed in the infrared. The data suggest the conclusion that methylene is present as well as a tautomeric structure of diazomethane.

Ketelaar and others have worked with the infrared absorption of various ions in salts. In a study of the bifluoride and nitrate ions in alkali metal halide disks, it was shown that the frequency shift increases with decreasing lattice constant, and that mixed crystals were formed(26). Subsequent studies emphasized the effect of polarization on the frequency shifts(13).

A recent study of the spectra of the frozen oxides of nitrogen(27) is quite interesting. Working in several matrices and employing new techniques, Crawford and Co-workers detected the NO monomer, as well as cis and trans dimers; NO_2 monomers, and three dimers thereof. These results were correlated to explain the bands in the two forms of N_2O_3 and covalent N_2O_5.

Infrared methods yield more information than any other method about any process taking place. They thus give a more nearly complete picture of the chemistry involved, and at the same time serve as an aid in identifying unknown species. Light scattering is usually not serious, but low absorption coefficients require higher concentrations for study than do other methods.

B. Electron Spin Resonance

Electron spin resonance (ESR) is most selective for studying free radicals and also for determining their concentration. The main difficulty lies in the superposition of spectra and the difficulty of recording a derivative. Foner and others(28) obtained ESR spectra of hydrogen atoms in argon, krypton, and xenon matrices at 4.2°K. They discovered that there are at least two, and possibly three, trapping sites in the lattice. The nature of these trapping sites is discussed as well as the interaction of the H-$_{1s}$ and Xe-$_{5s}$ orbitals. These data were analyzed and interpreted by Adrian(29), who assumed that the spectral shifts result from van der Waals interactions and or the Pauli exclusion principle. By calculating these two effects separately and combining them for a final result, he accounted for the observed increases and decreases of the hyperfine structure splitting.

C. Other Techniques

The electronic transitions in the NH_2 radical have been observed spectroscopically for the radical trapped in an oxygen matrix(30). This method is selective and only a little less sensitive than ESR.

It is unfortunate that high-scattering crystalline matrices make ultraviolet spectroscopy difficult. Thus most studies have been made in glassy matrices. Peyron and others(31) obtained spectroscopic evidence for triatomic nitrogen from the radiation emitted from solid nitrogen. They claim the presence of N_2-N species, as opposed to the linear molecule proposed earlier(32). Evidence for the analogous N_2-O compound is also presented. A substantial theoretical discussion on the assignment of energy levels is also presented.

Other studies have been performed in which the emission spectra of trapped radicals were examined. The species N_2, O_2, and NO were further studied(33,34), and a large amount of information regarding the identity of atoms and molecular emitting species was accumulated. Chemiluminescence, due possibly to the formation of ethylene from methylene in an inert matrix, of deuterated as well as protonated forms of ethylene, have made feasible an examination of the excited states in an inert matrix(35).

IV. SUMMARY

This seminar has attempted to show the use of matrix inclusion spectroscopy as a means of examination of unstable species. The variety of preparative and detection methods available emphasizes the versatility of the method. The method has already been used in kinetic studies of the <u>cis-trans</u> isomerization of nitrous acid(36).

The possibilities of forming species by mixing reactive gases just before freezing have not yet been investigated(8). The use of molecular beams will enable the study of those inorganic molecules normally only available at high temperatures. Other interesting problems mentioned by Pimentel are the effect of the matrix on hyperfine coupling constants in ESR spectra(29), the effect of matrices on the lifetime of forbidden atomic transitions, radiation induced reactions, kinetics of free radical reactions, too fast to measure at ordinary conditions, and the discovery of new species.

BIBLIOGRAPHY

1. L. Vegard, Nature, <u>113</u>, 716 (1924).
2. B. Smaller, M. S. Matheson, and E. L. Yasaitis, Phys. Rev., <u>94</u>, 202 (1954).
3. R. Livingston, H. Zeldes, and E. H. Taylor, ibid., <u>94</u>, 725 (1954).
4. I. L. Mador, J. Chem. Phys. <u>22</u>, 1617 (1954).
5. I. L. Mador and M. C. Williams, ibid., <u>22</u>, 1627 (1954).
6. I. Norman and G. Porter, Proc. Roy. Soc., <u>A230</u>, 399 (1955).
7. E. Whittle, D. A. Dowes, and G. D. Pimentel, J. Chem. Phys., <u>22</u>, 1943 (1954).
8. A. M. Brass and H. P. Broida, Eds., Formation and Trapping of Free Radicals, Academic Press, N.Y., 1960; Chapter 4, G. C. Pimentel.
9. E. D. Becker and G. C. Pimentel, J. Chem. Phys., <u>25</u>, 224 (1956).
10. R. G. Sowden and N. Davidson, J. Am. Chem. Soc., <u>78</u>, 1291 (1956).
11. H. W. Brown and G. C. Pimentel, J. Chem. Phys., <u>29</u>, 883 (1958).
12. S. G. Reed and C. M. Herzfeld, ibid., <u>32</u>, 1 (1960).
13. J. A. A. Ketelaar and J. van der Elsken, ibid, <u>30</u>, 336 (1959).
14. J. L. Jackson and E. W. Montroll, ibid <u>28</u>, 1101 (1958).

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IV. SUMMARY

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REFERENCES

[illegible]

15. S. Golden, ibid, 29, 61 (1958).
16. P. L. Chussin, ibid, 31, 159 (1959).
17. J. L. Jackson, ibid, 31, 154 (1959).
18. B. J. Fontana, ibid, 31, 148 (1959).
19. M. van Thiel, E. D. Becker, and G. C. Pimentel, ibid,, 27, 95 (1957(,
20. M. van Thiel, E. D. Becker, and G. C. Pimentel, ibid., 77, 486 (1957).
21. F. O. Rice and M. Freamo, J. Am. Chem. Soc., 75, 548 (1953).
22. F. O. Rice and C. Grelecki, ibid., 79, 1880 (1957).
23. E. D. Becker, G. C. Pimentel, and M. van Thiel, J. Chem. Phys., 26, 145 (1957).
24. M. van Thiel and G. C. Pimentel, ibid, 32, 133(1960).
25. D. E. Milligan and G. C. Pimentel, ibid, 29, 1405 (1958).
26. J. A. A. Ketelaar, C. Haas, and J. van der Elsken, ibid, 24, 624 (1956).
27. W. G. Fateley, H. A. Bent, and B. Crawford Jr. ibid., 31, 204 (1959).
28. S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, ibid, 32, 963 (1960).
29. F. J. Adrian, ibid, 32, 972 (1960).
30. G. W. Robinson and M. McCarthy Jr., ibid, 30, 999 (1959).
31. M. Peyron, E. M. Hörl, H. W. Brown, and H. P. Broida, ibid, 30, 1304 (1959).
32. D. E. Milligan, H. W. Brown, and G. C. Pimentel, ibid, 25, 1080 (1956).
33. H. P. Broida and M. Peyron, ibid, 32, 1068 (1960).
34. L. J. Schoen and H. P. Broida, ibid, 32, 1184 (1960).
35. T. D. Goldfarb and G. C. Pimentel, ibid, 33, 105 (1960).
36. G. C. Pimentel, J. Am. Chem. Soc., 80, 62 (1958).

KINETICS OF COMPLEX FORMATION

J. S. Oh November 15, 1960

I. INTRODUCTION.

A great deal of kinetic data for substitution reactions of complex ions has been obtained for inert complexes of cobalt(III), chromium(III), and a few related elements. Because of the great variety and stability of complexes of these elements, it would be expected that much information on the rates and mechanisms of substitution reactions of complex ions could be obtained from their study.

Substitution reactions are divided into three categories:

(1) Acid hydrolysis

$$MA_5X^n + H_2O = MA_5H_2O^{n+1} + X^-$$

(2) Base hydrolysis

$$MA_5X^n + OH^- = MA_5OH^n + X^-$$

(3) Anation

$$MA_5H_2O^n + X^- = MA_5X^{n-1} + H_2O$$

Kinetic studies of the transition metal complexes have recently been reviewed.[1,2]

The resemblance of chromium(III) to cobalt(III) in complex formation is remarkable. These species almost invariably exhibit a coordination number of six, and there is a striking similarity in color and crystalline form of complexes of the two metal ions. The one great difference between chromium(III) and cobalt(III) is their electronic structures, which have perhaps the most important influence on the rates of substitution reactions. Relatively few studies on the kinetics of substitution reactions of chromium(III) have been reported. Study of the behavior of chromium(III) complexes in aqueous solution is complicated by the marked tendency of chromium to form polynuclear complexes containing oxo and hydroxy bridges. Kinetic data for substitution reactions of chromium(III) complex ions are summarized in Table I.

II. EXPERIMENTAL TECHNIQUES.

The rate of a chemical reaction is defined as the time rate of change of the concentration of either a reactant or a product, and any property which is a function of a molecular concentration can be used to evaluate a reaction rate. There are several experimental techniques which have been used to study kinetics of substitution reactions of chromium(III) complex ions.

A. Direct chemical analysis.

The direct analysis of either products or reactants is the most obvious way of studying the rate of reaction involving a complex. Kilpatrick[15], for instance, followed the aquation reaction:

$$[Cr\{OC(NH_2)_2\}_6]^{+3} + 6H_2O \rightarrow [Cr(H_2O)_6]^{+3} + 6OC(NH_2)_2$$

by a gravimetric procedure involving precipitation of the reactant complex by the insoluble cobalticyanide. However, gravimetric techniques are not adapted to repetitive measurement, and titrimetric procedures are usually favored. Yatsimirski[4] studied the above aquation reaction by using the titrimetric procedure.

Many reactions involve the replacement of halides by nucleophilic reagents, as in the reaction:

$$[Cr(H_2O)_5Cl]^{+2} + H_2O \rightarrow [Cr(H_2O)_6]^{+3} + Cl^-$$

In principle, argentometric titration of the liberated chloride would be a sensitive method. Elving and Zemel[11] studied the kinetics of the above aquation reaction by using argentometric titration in acidic medium. They concluded that formation of a chloride bridge between Cr(III) and Ag(I) is followed by the loss of AgCl and the addition of the water to the residual pentacoordinate chromium species.

B. Spectrophotometry.

The spectrophotometric method is suited to kinetic studies of substitution reactions of complex ions. Some rate studies can be made by simple visual observation of color change when the distinct colors of complexes are well known. Kostmas and King[8] studied the reaction:

$$[Cr(H_2O)_6]^{+3} + NCS^- \leftrightarrows [Cr(H_2O)_5NCS]^{+2} + H_2O$$

and Schläfer and Kling[14] studied the aquation reaction of $[Cren_3]^{+3}$, using this method.

C. Electrometry.

E.M.F., conductometric, and pH measurements can all serve as useful techniques. In all cases, the change in the measured electrical property is assumed to be proportional to the extent of reaction.

The aquation of cis-$[Cr(en)_2Cl_2]Cl$ was studied in a chloride concentration cell.[12] A silver-silver chloride reference electrode dipped into a standard chloride solution in one compartment and another silver-silver chloride electrode into the reacting solution in the other compartment. Nitric acid was used both in the salt bridge and the two solutions. The combined concentration cell was immersed in a water thermostat. E.M.F. values were measured with a potentiometer, and the chloride ion concentration produced in a given time was calculated from the relationship:

$$E.M.F. = 2.303 \frac{RT}{F} \log \frac{[Cl^-]\ reactant}{[Cl^-]\ standard}$$

This procedure can be used for a relatively fast reaction.

D. Chromatography.

Maki[16] developed a chromatographic method for analyzing aqueous mixtures of inert complexes. Later, Bjerrum and coworkers[17] studied the separation of cobalt(III) and other complexes on columns of activated alumina, using aqueous salt solutions of proper composition as eluants. Before the analysis, the column was treated with the eluting solution. Then 2-5 ml. of complex solution was added. The eluting solution was added just at the moment when the complex mixture had passed into the column. When an extra pressure (0.5-1 atm.) was applied, an experiment could usually be finished within 15-30 min. The authors found that this method can be used for the separation of cis- and trans- complexes and mixtures of inert complex ions.

E. Other methods

The measurement of the optical rotation of complexes provides additional data concerning reaction mechanisms of dissociative processes which, in addition to causing isomeric change, can precede substitution.

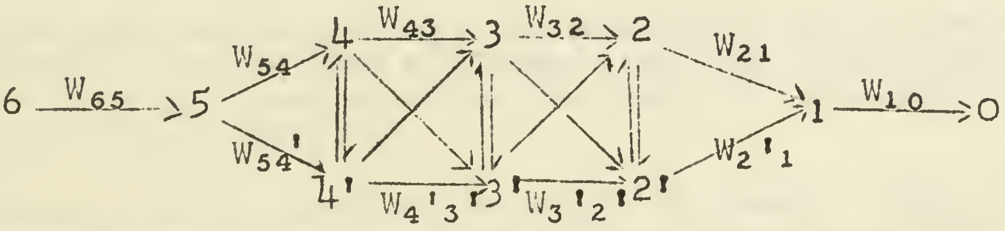
Also isotopic tracer techniques can yield much additional information concerning the finer details of reaction mechanism.

III. RATES OF DECOMPOSITION AND TRANSFORMATION MECHANISM OF REACTIONS OF CHROMIUM(III) AMMINES IN AQUEOUS SOLUTION.

A kinetic study of aquation and base hydrolysis was made by Bjerrum and coworkers.[3] According to the absorption spectrum of acidic hexammine chromium(III) nitrate, the transformation proceeds independently of the hydrogen ion concentration. After 300 hours, the absorption curve reached an appearance which is very similar to that of $[Cr(H_2O)_6]^{+3}$ ion. They found the rate constant:

$$k_{-6} = 10^{12.3} e^{-12600/RT} \quad (\text{in sec}^{-1})$$

The aquation of $[Cr(NH_3)_6]^{+3}$ ion in acidic solution was shown to consist of 20 consecutive and simultaneous exchanges of ammonia with water and cis-, trans-isomerization.



where the numbers in the figure give n in $[Cr(NH_3)_n(H_2O)6-n]^{+3}$; 2,3,4 stand for the cis- and 2', 3', 4' for the trans-complexes, and W_{65} is the probability per unit time of the hexammine reacting to form the pentammine.

A similar scheme can be established for the hydroxylation of hexammine down to trihydroxo-triammine in basic solution.

The complete rate expression for the reaction of every intermediate is rather complicated, but may be readily calculated by matrix algebra. Luteo salt decomposes according to a first order reaction:

$$k_{-6} = \frac{-d\ln[Cr(NH_3)_6]^{+3}}{dt} = W_{65}$$

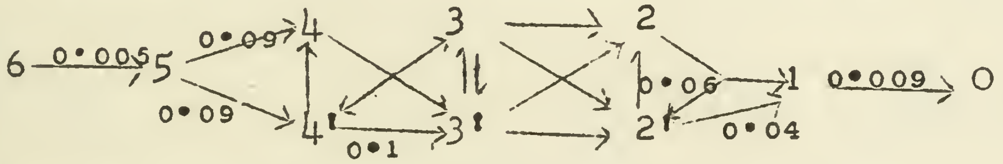
In the same way the rate of the decomposition of pentammine and monoammine can be expressed in a simple manner.

$$k_{-5} = \frac{-d\ln[Cr(NH_3)_5H_2O]^{+3}}{dt} = W_{54} + W_{54}' \; , \; k_{-1} = \frac{-d\ln[Cr(NH_3)(H_2O)_5]^{+3}}{dt} = W_{10}$$

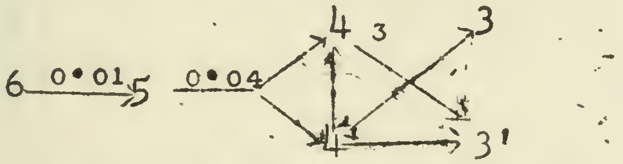
In the case of the decomposition of tetrammine, triammine and diammine, however, the rate expression is very complicated.

The decomposition of the complex ions was studied by chromatogarphic analysis of the reaction mixtures and a pH-titration method, and the existence of a relatively stable monoammine ion was proved.

Bjerrum reported the kinetic data of aquation and base hydrolysis:



rate constant (hr^{-1}) in 0.1 M HNO_3 at 40°C.



rate constant (hr^{-1}) in 0.1 M NaOH at 40°C.

As a whole, the hydroxoammine complexes are much less stable than the corresponding aquo complexes.

IV. SUMMARY.

An appreciable amount of data is available on the rates of aquation. These studies give a linear plot for first order kinetics. This result is to be expected since the rate is dependent only on the concentration of the complex.

From Table I three conclusions might be drawn. One is that increasing chelation slows down the rate of aquation. The second is that divalent monochloro complexes react slower than the univalent dichloro complexes, and the last is that trans-complexes react slower than the corresponding cis-complexes.

The rates of aquation of Cr(III) complexes are usually greater than that of the corresponding complexes of Co(III). This is as expected on the basis of crystal field theory since Co(III) (d^6) will resist changes in the octahedral arrangement of ligand more strongly than Cr(III) (d^3). However, the rate of base hydrolysis is greater for Co(III) complexes than for those of Cr(III).

Table I

Complex ions	Aquation				Base hydrolysis				Ref.
	k Mn^{-1}	temp. °C.	Eact kcal/mole	ΔS^* e.u.	k Mn^{-1}	temp. °C.	Eact kcal/mole	ΔS^* e.u.	
$[Cr(NH_3)_6]^{+3}$	$8.5x10^{-5}$	40	26	-5	$1.7x10^{-4}$	40			3
$[Cr(NH_3)_5(H_2O)]^{+3}$	$1.4x10^{-3}$	40			$6.6x10^{-4}$	40			3
cis-$[Cr(NH_3)_4(H_2O)_2]^{+3}$	$1.6x10^{-3}$	40			$5.0x10^{-2}$	40			3
trans-$[Cr(NH_3)_4(H_2O)_2]^{+3}$	$1.6x10^{-3}$	40							3
cis-$[Cr(NH_3)_2(H_2O)_4]^{+3}$	$5x10^{-5}$	40							3
trans-$[Cr(NH_3)_2(H_2O)_4]$	$7x10^{-4}$	40							3
$[Cr(NH_3)(H_2O)_5]^{+3}$	$1.5x10^{-4}$	40							3
$[Cr(OC(NH_2)_2)_6]^{+3}$	$3.8x10^{-4}$	30	27	4					4
$[Cr(NH_3)_5Cl]^{+2}$	$4.8x10^{-4}$	25	21.8	-8.8					5.6
$[Cr(NH_3)_5Br]^{+2}$	$3x10^{-3}$	25	22	-5					5
$[Cr(NH_3)_5I]^{+2}$	$1x10^{-2}$	0							5
$[Cr(NH_3)_5(NCS)]^{+2}$	$5.6x10^{-6}$	25	24.9	-7.8					7
$[Cr(H_2O)_5(NCS)]^{+2}$	$5.5x10^{-7}$	25	28	-3					8
$[Cr(NH_3)_2(NCS)_4]^{-1}$	$1.5x10^{-2}$	60	27	+3					9
$[Cr(H_2O)_5Cl]^{+2}$	$3.2x10^{-4}$	25							10,11
$[Cr(H_2O)_4Cl_2]^{+1}$	$1 x 10^{-1}$	25							10
cis-$[Cren_2Cl_2]^{+1}$	$2x10^{-2}$	25	22	-3	1.7	25			12,13
trans-$[Cren_2Cl_2]^{+1}$	$2.3x10^{-3}$	25			2.2	25			13
$[Cren_3]^{+3}$	$4.9x10^{-4}$	25	24.6	-1					14

BIBLIOGRAPHY

1. F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", John Wiley and Sons, Inc., New York, 1958, Chapt. 3.

2. J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry", Interscience Pub. Inc., New York, 1960, Chapt. 2.

3. J. Bjerrum and G. G. Lamm, Acta Chem. Scand., 9, 216 (1955); E. Jorgensen and J. Bjerrum, Acta Chem. Scand., 12, 1047 (1958); J. Bjerrum and E. Jorgensen, J. Inorg. and Nuclear Chem., 8, 313 (1958).

4. K. B. Yatsimirski and E. I. Yasinskine, J. Gen. Chem., (USSR) 24, 1361 (1956).

5. H. Freundlich and R. Bartels, Z. Phys. Chem., 101, 177 (1922).

6. M. Ikuta, H. G. and McAdie and MaF. W. Smith, Can. J. Chem., 34, 1361 (1956).

7. A. W. Adamson and R. G. Wilkins, J. Am. Chem. Soc., 76, 3379 (1954).

8. C. Postmus and E. L. King, J. Phys. Chem., 59, 1216 (1955).

9. A. W. Adamson, J. Am. Chem. Soc., 80, 3183 (1958).

10. N. Bjerrum, Z. Phys. Chem., 59, 336, 581 (1907).

11. P. J. Elving and B. Zemel, J. Am. Chem. Soc., 79, 5855 (1957).

12. J. Selvin and J. C. Bailar, Jr., J. Am. Chem. Soc., 79, 4285 (1957).

13. R. G. Pearson, R. A. Munson and F. Basolo, J. Am. Chem. Soc., 80, 504 (1958).

14. H. L. Schlafer and O. Kling, J. Inorg. and Nuclear Chem., 8, 320 (1958).

15. M. Kilpatrick, J. Am. Chem. Soc., 50, 358 (1928).

16. M. Maki, Japan Analyst 4, 512 (1956).

17. A. Jensen, J. Bjerrum and F. Woldbye, Acta Chem. Scand., 12, 1202 (1958).

THE CHEMISTRY OF GALLIUM(I)

Robert J. Niedzielski November 22, 1960

I. INTRODUCTION

Gallium, a group three element, exhibits a characteristic oxidation state of +3 in the majority of its compounds. However, a number of compounds have been isolated, the empirical formulas of which would suggest that gallium is capable of exhibiting oxidation states of +1 and +2. The existence of the latter is now open to serious question. On the other hand, there appears to exist rather conclusive evidence that gallium does indeed exhibit a +1 valency, although it is very unstable with respect to oxidation to the tripositive state.

The major amount of work elucidating the chemistry of gallium(I) has been carried out within the past eight years. As late as 1950, it was pointed out (1) that there was no real evidence for the existence of monovalent gallium. It is this phase of gallium chemistry with which this report will be concerned, both in simple compounds and in a number of coordination compounds which have just recently been prepared (2).

II. BINARY COMPOUNDS OF GALLIUM(I)

A. Halides

The greatest amount of work on the chemistry of gallium(I) has been carried out on the halides. This work resulted from studies of the anomalous divalency of gallium, reported from time to time for the gallium-halogen systems. Thus, gallium "dichloride" was first prepared in 1878 by de Boisbaudran (3), who had discovered and named the element itself. It was subsequently prepared by other workers (4), utilizing the reaction between gallium(III) chloride and hot gallium metal, but in no case were the conditions for the preparation well established, the product purity was in doubt, and the properties were not investigated to any great extent. The divalent condition, arising from the empirical formula $GaCl_2$, was thus not explained. Sidgwick aptly remarks that "This has no parallel elsewhere and no theoretical explanation" (1). The meaning of this statement can be more fully realized by considering the electronic configuration of gallium.

Perhaps the earliest study of consequence on gallium dichloride was that of Klemm and Tilk (5), who reported that solid $GaCl_2$ is diamagnetic, indicating the absence of a simple Ga^{+2} specie. To account for this behavior, two structural formulations were proposed. These were both based on the dimeric unit Ga_2Cl_4. One involved a gallium-gallium bond and the other an ionic unit $Ga(I)[Ga(III)Cl_4]$. The latter formulation was doubted since monovalent gallium had not been shown to exist (1). This belief had earlier received support from a vapor phase study of gallium(III) chloride and the products from its reaction with excess gallium (4). This study indicated that quantities of $GaCl_2$ molecules exist in the vapor phase above 400°C. under the conditions of the experiment. No evidence for the existence of gallium monochloride was obtained.

Watt, et al., (6), studying lower oxidation states of elements, observed a three electron reduction of gallium trihalides with potassium in liquid ammonia. On the other hand, the anodic oxidation of gallium in liquid ammonia produced a mean valence number for gallium of 2.25 (7, 8). The anolyte was found to be strongly reducing in character. Similar results were obtained in glacial acetic acid, gallium(I) appearing to be formed by the anodic oxidation of the metal in that solvent (9). The solution behavior was interpreted as being due to a mixture of singly and triply charged cations.

Phase-diagram studies of halide systems were also carried out, the iodide system being the first studied (3). The authors investigated the phase diagram of the gallium iodides and confirmed the existence of gallium(I), as well as gallium(II). X-ray powder patterns confirmed the isolation of three distinct gallium iodides. Although no distinction could be made as to the exact nature of the gallium(II) iodide structure, it was reasoned that the demonstration of the gallium(I) oxidation state gave weight to the unsymmetrical arrangement Ga(I)[Ga(III)Cl_4]. Somewhat similar results have since been reported for the bromide system, in which a material of limiting composition $GaBr_{1.3}$ was obtained (10). The same study showed that addition of aluminum(III) bromide to the system resulted in a compound Ga($AlBr_4$), which compares structurally with Ga_2Br_4. Molten metal-metal halide combinations have also indicated subhalide formation in these systems (11, 12).

To establish conclusively the structure of the gallium dihalides, physical methods have been extensively utilized. Woodward and coworkers have studied Raman spectra of the fused gallium dihalides (13, 14). The bromide was prepared by heating gallium(III) bromide in a sealed, evacuated tube with slightly less than the theoretical amount of gallium metal. The excess gallium(III) bromide was then sublimed from the mixture. The results of studies on the chloride and bromide indicate that the correct formulation of the species is Ga(I)[Ga(III)X_4] This conclusion is supported by the electrical conductivity of the melts The observed spectra were not consistent with the alternative symmetrical formulation, or any ions derivable from it.

Woodward, et al., have observed similar results for the Raman spectra of the tetrahalogeno-gallate(III) ion in aqueous solution (15, 16, 17). A regular tetrahedral configuration was assigned to the GaX_4^- specie as a result. The species thus formed were isoelectronic with $GeBr_4$.

Conductivity studies of fused gallium dichloride and dibromide have shown them to be typical molten salts (18), completely dissociated into ions. The variations of conductivity and viscosity with temperature have been shown to be typical of compounds in which the cation is smaller than the anion. It is suggested that the dihalides can be considered as addition compounds of the trihalides, $GaCl \cdot GaCl_3$.

Perhaps the best proof of the structure of the gallium dihalides was offered by the x-ray structure study of Ga_2Cl_4 by Garton and Powell (19). It was found that the compound was composed of $GaCl_4^-$ tetrahedra and Ga^+ ions. The unit cell is orthorhombic, containing four Ga_2Cl_4 groups. Each Ga^+ ion was found to be surrounded by eight chlorine atoms, from six different tetrahedra, at the corners of an irregular dodecahedron.

The common method of preparation of the dihalides for the above studies involves reaction between the trihalide and slightly more than the necessary amount of gallium metal (20). This is followed by removal of the more volatile trihalide by distillation. The preparation requires special equipment and can be time-consuming. Recently, it has been found that good yields of the desired product can be more easily obtained in a simple, rapid manner (21). In this procedure gallium metal is heated with stoichiometric quantities of mercury(I) or (II) halides. Reaction is essentially complete in three hours.

Gaseous GaF was formed when the metal was heated with AlF_3 at 1000°C. (22).

B. Oxide, Sulfide, and Selenide

The compounds of gallium(I) with the group six elements are not as well characterized as those with the halogens. Thus, a product of a composition which lies between GaO and Ga_2O has been obtained by sublimation of a mixture of gallium(III) oxide and gallium. However, this product gave no new x-ray lines (23). Gastinger claims that the lower oxide is formed by heating the metal in a carbon dioxide current under a slight vacuum. Gallium(I) oxide was formed at 10 mm. and 850° (24).

The sulfide has been studied by Brukl and Ortner (25), and the results have been substantiated by Johnson and Warren (26). In the former case, gallium(III) sulfide was prepared by passing sulfur vapor over metallic gallium at 1300°C. Reduction of this species by hydrogen produced small crystals of GaS. This compound decomposed at 700°C. in a vacuum, giving an easily oxidizable precipitate on the walls of the tube, corresponding in composition to Ga_2S. Johnson and Warren obtained essentially the same results, except that the original gallium(III) sulfide was formed by passing hydrogen sulfide over gallium at 800°C. X-ray diagrams subsequently showed existence of three different sulfides (27).

The selenides have been prepared similarly from the elements at red heat (28). Gallium(I) selenide was shown to exist by x-ray spectrum.

III. COORDINATION COMPOUNDS OF GALLIUM(I)

This field of gallium(I) chemistry has only recently begun to draw attention. The first addition compounds isolated were those of benzene with gallium dichloride and dibromide (21). Good analyses were obtained for $Ga_2X_4 \cdot C_6H_6$. Rundle and Corbett (29) claim that the Ga^+ ion is strongly solvated by benzene. This was later verified by the work of McMullan and Corbett (30).

Recently, coordination compounds of gallium(I) tetrachloro- and tetrabromogallate(III) have been prepared with a number of oxygen and nitrogen donors (2), the results comprising the bulk of this section of the report. This study was an outgrowth of an investigation of the strong reducing power of the gallium(I) species. The coordination compounds which formed had the empirical formula GaX_2L_2, where L is a monodendate ligand.

Magnetic studies, electrical conductivity measurements, and molecular weight determinations were carried out on the complexes that were isolated. All of these methods demonstrated that the coordination compounds have structures of the type $(GaL_4)^+(GaX_4)^-$, in which the gallium(I) ion has a coordination number of four.

The question of the stereochemistry of these compounds was not as easily resolved, however. The majority of the ligands used were sufficiently small to fit almost any arrangement of four bonds about the gallium(I) ion. Therefore, two ligands were specifically synthesized for the structural investigation. Both of these were quadridendate: 1,2-ethylene morpholine, and 2,2',2"-trimethoxytriethylamine. Both ligands unexpectedly gave addition compounds. However, the products were very insoluble and inert and could not be characterized further at the time. Further work on the stereochemistry of four-coordinated gallium(I) is now in progress. The authors did suggest, however, the possibility of an sp^3d configuration, with one of the positions occupied by the unshared pair of electrons of the gallium(I) ion.

Exception to the above proposal has been taken by Dyatkina (31). The suggestion is made that the bonds are formed by the p^3d orbitals of the central atom, based on calculations of the hybrid bond strengths.

IV. CONCLUSION

The existence of the monovalent state of gallium has been quite well substantiated. As has been seen, however, the structure and chemical behavior of some of the systems merit further attention. The isolation of coordination compounds of this species expands this area still further.

REFERENCES

1. N. V. Sidgwick, The Chemical Elements and Their Compounds, Vol. 1, Oxford, p. 477 (1950).
2. S. M. Ali, F. M. Brewer, J. Chadwick, and G. Garton, J. Inorg. Nucl. Chem., 9, 124 (1959).
3. J. D. Corbett and R. K. McMullan, J. Am. Chem. Soc., 77, 4217 (1955).
4. A. W. Laubengayer and F. B. Schirmer, J. Am. Chem. Soc., 62, 1578 (1940).
5. W. Klemm and W. Tilk, Z. anorg. allgem. Chem., 207, 175 (1932).
6. G. W. Watt, J. L. Hall, and G. R. Choppin, J. Phys. Chem., 57, 567 (1953).
7. A. W. Davidson and J. Kleinberg, J. Phys. Chem., 57, 571 (1953).
8. A. W. Davidson and J. Kleinberg, J. Am. Chem. Soc., 74, 736 (1952).
9. A. W. Davidson and F. Jirik, J. Am. Chem. Soc., 72, 1700 (1950).
10. J. D. Corbett and A. Hershaft, J. Am. Chem. Soc., 80, 1530 (1958).
11. J. D. Corbett and R. K. McMullan, J. Am. Chem. Soc., 78, 2906 (1956).
12. J. D. Corbett and S. v. Winbush, J. Am. Chem. Soc., 77, 3964 (1955)
13. L. A. Woodward, N. N. Greenwood, J. R. Hall, and I. J. Worrall, J. Chem. Soc., 1505 (1958).
14. L. A. Woodward, G. Garton, and H. L. Roberts, J. Chem. Soc., 3723 (1956).

Magnetic studies, [illegible] and molecular weight [illegible] [illegible]

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10. CONCLUSION

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REFERENCES

1. [illegible]
2. [illegible]
3. [illegible] J. Am. Chem. Soc. [illegible]
4. [illegible] J. Am. Chem. Soc. [illegible]
5. [illegible]
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12. [illegible]
13. [illegible]
14. [illegible]
15. [illegible]

15. L. A. Woodward and A. A. Nord, J. Chem. Soc., 3721 (1956).
16. L. A. Woodward and A. A. Nord, J. Chem. Soc., 2655 (1955).
17. L. A. Woodward and G. H. Singer, J. Chem. Soc., 716 (1958).
18. N. N. Greenwood and I. J. Worrall, J. Chem. Soc., 1680 (1958).
19. G. Garton and H. M. Powell, J. Inorg. Nucl. Chem., 4, 84 (1957).
20. L. S. Foster, Inorganic Syntheses, 4, 111 (1953).
21. R. C. Carlston, E. Griswold, and J. Kleinberg, J. Am. Chem. Soc., 80, 1532 (1958).
22. D. Welti and R. F. Barrow, Proc. Phys. Soc., 65A, 629 (1952).
23. W. Klemm and I. Schnick, Z. anorg. allgem. Chem., 226, 353 (1936).
24. E. Gastinger, Naturwissenschaften, 42, 95 (1955).
25. A. Brukl and G. Ortner, Naturwissenschaften, 18, 393 (1930).
26. W. C. Johnson and B. Warren, Naturwissenschaften, 18, 666 (1930).
27. A. Brukl and G. Ortner, Monatsh., 56, 358 (1930).
28. W. Klemm and H. U. v. Vogel, Z. anorg. allgem. Chem., 210, 45 (1934).
29. R. E. Rundle and J. D. Corbett, J. Am. Chem. Soc., 79, 757 (1957).
30. R. K. McMullan and J. D. Corbett, J. Am. Chem. Soc., 80, 4761 (1958).
31. M. E. Dyatkina, Russ. J. Inorg. Chem., 4, 1309 (1959).

LIQUID-LIQUID EXTRACTION OF METAL SALTS FROM AQUEOUS SOLUTION USING ALKYL PHOSPHORUS DERIVATIVES

Nicholas A. Matwiyoff November 29, 1960

I. INTRODUCTION

Liquid-liquid or solvent extraction involves the partitioning, under equilibrium conditions, of a solute between two immiscible liquids. At equilibrium, the chemical potential of the solute must be identical in each of the two liquids, and the ratio of the activity of the solute in one liquid to that in the other liquid must be a constant, which is termed the molal distribution constant K_D. In an ideal system containing two or more solutes, the feasibility ~~of~~ separating or fractionating these solutes is dependent upon the separation factor which, for a pair of solutes is defined as the ratio of their molal distribution coefficients. However, practical separations even of solutes having similar distribution coefficients have been accomplished by the technique of counter-current distribution (1).

A wide variety of systems for the extraction of inorganic salts from aqueous solution have been studied. Typical examples of these are:

(1) the extraction of an ion-association complex of ferric chloride into ether from a hydrochloric acid solution (2), and

(2) the extraction of thenoyl trifluoroacetone chelates of zirconium and hafnium into benzene from an aqueous chloride solution (3).

In recent years much research concerning solvent extraction systems has been devoted to the study of the derivatives of the organic phosphates which, in contrast to most of the other organic extractants, allow favorable distribution coefficients in systems exhibiting a wide range of acidities. It is the purpose of this report to discuss the chemistry involved in the extraction of inorganic salts from aqueous solutions by derivatives of organic phosphates. Those persons interested in the manipulations and practical calculations involved in solvent extraction are referred to the excellent discussions by Laitinen (1) and Morrison and Freiser (4).

II. GENERAL CONSIDERATIONS

For the purposes of discussion, the organo-phosphorus solvent-extraction occurs by: (1) neutral derivatives of the tri-alkyl phosphates (e.g., tri-*n*-butyl phosphate, di-*n*-butyl phosphonate, and tri-*n*-butyl phosphine oxide); and (2) alkyl phosphoric acids which interact with an aqueous phase by cation exchange. In each of the preceding systems, the phosphorus compounds, which are viscous liquids or solids, are usually dissolved in an inert, water-insoluble diluent such as carbon tetrachloride or petroleum ether. The aqueous phase generally contains the solute to be extracted, an acid to prevent irreversible hydrolysis of the solute, and a "salting-out" agent which promotes the extraction of the solute by the organic solvent.

In the systems considered, the behavior of the solute cannot always be described by the molal distribution coefficient K_D since the relevant activities often are unknown. The significant quan~~ti~~ty in the latter cases is the distribution coefficient D which is defined as the ratio of the total concentration of the metal in the organic to that in the aqueous phase. If the state of the metal in each of the phases is known, the distribution coefficient can be related to the equilibrium of the metal ion between the two phases, and the effects of the extraction variables on D can be assessed. For example, in the solvent extraction of metal nitrates from acid aqueous solutions by tri-*n*-butyl phosphate (TBP) in an inert diluent, it has been determined (5,6,7) that the metal nitrates apparently exist in the organic phase as a single molecular complex $M(NO_3)_p \cdot qTBP$. The following equilibrium expression (in which a denotes the aqueous and o the organic phase) describes the overall process of extraction

$$M^{P+}_{(a)} + pNO_3{}^{\ominus}{}_{(a)} + qTBP_{(o)} \rightleftarrows [MNO_{3_p} \cdot qTBP]_{(o)} \qquad (1)$$

since

$$K_{eq} = \frac{[MNO_{3_p} \cdot qTBP]_{(o)}}{[M^{P+}]_{(a)}[NO_3{}^-]^P{}_{(a)}[TBP]^q_o} \qquad (2)$$

and

$$D = \frac{[MNO_{3_p} \cdot qTBP]_{(o)}}{[M^{P+}]_{(a)}} \qquad (3)$$

then

$$\log D = \log K_{eq} + p \log(NO_3{}^-)_{(a)} + q \log (TBP)_{(o)} \qquad (4)$$

Through the study of the dependence of D on $[NO_3{}^-]_a$ and $[TBP]_o$ and by the use of equation 4, the solvation number q can be determined, and the effect of "salting-out" agents can be qualitatively assessed.

Irving, et al, (8) have described a quantitative method for the treatment of partition equilibria by jointly considering step-equilibria (neglected in expressions 1 through 4) and the partition law. The method, which provides complex functions for distribution ratios and solvation numbers and has been applied rigorously only to simple systems, will not be considered here.

III. SOLVENT EXTRACTION WITH NEUTRAL DERIVATIVES OF TRI-ALKYL PHOSPHATES

A. Interactions in the Organic and Aqueous Phases.

Although the neutral phosphate derivatives have been successfully applied as extractants for a large number of metal salts of the transition, rare-earth, and actinide series, the specific interactions that occur during extraction have not been established with certainty. The behavior of solvent extraction systems indicates that the following considerations are significant:

(1) the formation of a neutral, ion-association complex in the aqueous phase;

(2) the nature of the ion-association complex in relation to the coordinating tendency and activity coefficient of the anion;

(3) the interaction of the phosphate derivative with the ion-association complex, probably at the interface, with the formation of a compound soluble in the organic solvent; and

(4) the nature of the compound extracted into the organic phase.

It has been shown by studies of metal chlorides, nitrates, and perchlorates that extraction of the metal salts by organo-phosphate derivatives increases as ion association in the aqueous phase to complexes of the type $[M^{p+}X_pH_2O_n]$ and $[M^{p+}H_2O_{n+p}](ClO_4)_p$ increases (9,10, 11,12,13,14). However, in the metal phosphate and sulfate systems, the opposite trend is observed since stable inextractable anionic complexes are formed, e.g., hydrated $[UO_2(SO_4)_2]^=$ (15). Hence solvent extraction is usually conducted on concentrated perchlorate, nitrate, or chloride solutions.

The organic phosphate derivatives interact by displacing water from the ion-association complexes with the formation of solvates which are soluble in the organic solvent. Although the mechanism of this interaction is unknown, specific solvates in which the phosphate derivative enters the coordination sphere of the metal ion appear to be formed. By studies of the dependence of the distribution ratio D on the concentration of the phosphate derivative in the organic phase, it is possible to determine solvation numbers q (6), for the unhydrated species in the organic phase, for example:

(1) For the lanthanides - $M(NO_3)_3 \cdot qTBP$, $q = 3$;

(2) For zirconium - $Zr(NO_3)_4 \cdot qTBP$, $q = 2$;

(3) For uranium(VI) - $UO_2(NO_3)_2 \cdot qTBP$, $q = 2$.

The application of the method of continuous variations to the system TBP-cobalt(II) chloride definitely indicates the formation of a compound having the stoichiometry $CoCl_2(TBP)_2$, in accordance with the behavior of $CoCl_2$-TBP extraction systems (16). Additional support for the hypothesis of the formation of definite solvates in the organic phase was obtained from: (1) the study of the properties and composition of saturated solutions of uranyl nitrate, cerium(III) nitrate, and thorium(IV) nitrate in TBP (5); (2) the preparation of compounds corresponding to the composition $UO_2(NO_3)_2P_2$ (where P = organo-phosphate derivatives) (17); and (3) the study of the infra-red spectra of TBP solutions of metal salts (12).

The solvating and extracting powers of the phosphate derivatives generally increase with basicity (15,17,18,19) (i.e., tri-alkyl phosphate < dialkyl phosphonate < alkyl phosphinate < tri-alkyl phosphine oxide), but attempts to relate either the solvating or extracting power solely to a heat term in the expression for the free energy of transfer have not been successful (19,20,21). Thus although it is probable that changes in the solvation energy of the species being

distributed between the two phases are of major importance in determining extractability, it is also necessary to consider extra order-disorder transitions which occur in each phase during extraction.

B: Applications

Some of the separations which can be achieved using TBP as an extractant are:

(1) Uranium(VI), protactinium(V), and thorium(IV) in acidic chloride solutions (22);

(2) Scandium, thorium(IV), and zirconium(IV) in acidic chloride and nitrate solutions (23);

(3) Thorium(IV) and the rare earths in acidic nitrate solutions (24);

(4) The trans-curium elements from large quantitites of curium (25); and

(5) Iron(III), cobalt(II), and nickel(II) in acidic chloride solutions (17).

In addition to serving as a basis for practical separations of other metals, extraction data have been used to evaluate hydrolysis and olation reactions of heavy metals, among them zirconium (13) in an aqueous chloride solution and niobium (26) in an aqueous nitrate solution.

In the extraction of the rare earths from acidic chloride and nitrate solutions, it has been shown that extractability (defined here as log *D*) increases with increasing atomic number (decreasing basicity of the rare-earth ion) (27). The extractability is not a linear function of atomic number, however, and a minimum point in the plot of log *D* vs. Z often is observed. In addition, Hesford and co-workers claim that an odd-even effect (the lanthanides of even atomic number lying on one curve and those of odd atomic number lying on another curve of the plot of the property of the lanthanide vs. atomic number), similar to that observed by Surls (28) in the ion-exchange behavior of the lanthanides, is discernible (29,30). Nonetheless, the similarities between the solvent-extraction behavior of the lanthanides and actinides have been demonstrated (31).

IV. SOLVENT EXTRACTION WITH ALKYL-PHOSPHORIC ACIDS

The alkyl phosphoric acids extract metal ions primarily by a process of cation-exchange between the extractable metal ion in the aqueous phase and the acidic hydrogen of the extractant in the organic phase. The dialkyl phosphoric acids, to which the discussion is limited, exist as extremely stable dimers in inert diluents such as carbon tetrachloride and benzene (32,33). Such association directly affects extraction behavior, and the interactions that occur in the dialkyl phosphoric acid solvent extraction systems are complex. However, below are listed examples of reaction types which can be applied to describe the solvent extraction of transition, rare-earth, and

actinide metal salts by dialkyl phosphoric acids (HX):

$$UO_2^{++}{}_{(a)} + 2(HX)_{2(o)} \rightarrow UO_2(XHX)_{2(o)} + 2H^+{}_{(a)} \text{ (low conc. of U(VI)) (32)} \quad (5)$$

$$[UO_{2_n}X_{2_n}(HX)_2]_{(o)} + UO_2^{++}{}_{(a)} + (HX)_{2(o)} \rightarrow [UO_{2_{n+1}}X_{2_{n+1}}(HX)_2]_o + 2H^+_a$$

$$\text{(high conc. of U(VI)} \quad \text{(30)} \quad (6)$$

$$Ln^{+++}_{(a)} + 3(HX)_{2(o)} \rightarrow Ln(XHX)_{3(o)} + 3H^+{}_{(a)} \text{ (}Ln^{+++}\text{ = Lanthanide ion) (34,35)} \quad (7)$$

In view of the strength of the hydrogen bonds in the alkyl phosphoric acids (33), it is probable that the entities $UO_2(XHX)_2$ and $Ln(XHX)_3$ (which have also been isolated from saturated solutions of $Ln(NO_3)_3$ and $UO_2(NO_3)_2$ in dialkyl phosphoric acids (36)) are chelate complexes analogous to those obtained in solvent extraction with acetylacetone and thenoyltrifluoroacetone (41).

In agreement with the proposed "mechanism" for extraction (equations 5, 6 and 7 preceding), the distribution coefficients generally vary inversely with the aqueous acidity and directly with the concentration of the organic extractant. Anions such as $PO_4^{\equiv}$ and $SO_4^{=}$, which form complexes with the cations in the aqueous phase, hinder the extraction by competing with the alkyl phosphate anions (15).

The dialkyl phosphoric acids provide larger distribution ratios and separation factors than the neutral organo-phosphates and have been applied to:

(1) the separation of Y(III), Sc(III), La(III), Ac(III), Pm(III), Tm(III), and Am(III) on a tracer scale (37);

(2) the isolation of trans-uranium elements (38,39,40);

(3) the large-scale preparation of high-purity U(VI) (39).

As with the neutral organo-phosphates, it appears possible to study olation and complexation reactions of the heavy metal ions by solvent extraction.

V. CONCLUSION

A complete understanding of the solvent extraction systems discussed in this report presumes an understanding of the nature of concentrated aqueous solutions and the nature of solutions of metal salts in "organic" solvents. Even though our knowledge of the latter systems is incomplete, the behavior of solvent extraction systems can at least be correlated through the consideration of ion-association and coordination equilibria with the neutral organo-phosphate derivatives and through the consideration of ion-exchange and chelation with the dialkyl phosphoric acids.

Solvent extraction has been applied in the fractionation of micro- and macro-quantities of a variety of metal salts, and it rivals ion-exchange techniques both in the variety of conditions that may be employed and in the degree of fractionation that may be effected.

BIBLIOGRAPHY

1. H. A. Laitinen, Chemical Analysis, McGraw-Hill Book Company, Inc., New York, 1960.
2. G. H. Morrison, Anal. Chem., 22, 1388 (1940).
3. G. Schultz and E. M. Larsen, J. Am. Chem. Soc., 72, 3610 (1950).
4. G. H. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry, Wiley and Sons, New York, 1957.
5. T. V. Healy and H. A. C. McKay, Trans Faraday Soc., 52, 633 (1956).
6. E. Hesford and H. A. C. McKay, ibid, 54, 573 (1958).
7. T. V. Healy, J. Kennedy, and G. M. Waind, J. Inorg. Nucl. Chem., 10, 137 (1959).
8. H. Irving, F. Rossotti, and R. Williams, J. Am. Chem. Soc., 77, 1906 (1955).
9. H. A. C. McKay, Chem. and Ind., 1954, 1549.
10. S. Siekierski, J. Inorg. Nucl. Chem., 12, 129 (1959).
11. E. Hesford and H. A. C. McKay, ibid, 13, 165 (1960).
12. J. R. Ferraro, ibid, 10, 319 (1959).
13. K. Alcock, F. C. Bedford, W. H. Hardwick, and H. A. C. McKay, ibid, 4, 100 (1957).
14. A. E. Levitt and H. Freund, J. Am. Chem. Soc., 78, 1545 (1956).
15. C. Blake, C. Baes, K. Brown, C. Coleman, and J. White, Geneva Conf. on Peaceful Uses of Atomic Energy, P/1550.
16. H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem., 10, 306 (1959).
17. L. Burger, J. Phys. Chem., 62, 590 (1958).
18. T. V. Healy and J. Kennedy, J. Inorg. Nucl. Chem., 10, 128 (1959).
19. T. H. Siddall, Jr., J. Am. Chem. Soc., 81, 4176 (1959).
20. L. I. Katzin, D. M. Simon, and J. R. Ferraro, ibid, 74, 1191 (1952).
21. L. I. Katzin and J. R. Ferraro, ibid, 6040 (1952).
22. D. F. Peppard, G. W. Mason, and M. V. Gergel, J. Inorg. Nucl. Chem., 3, 370 (1957).
23. D. F. Peppard, G. W. Mason, and J. L. Maier, ibid, 3, 215 (1956).
24. E. Hesford, H. A. C. McKay, and D. Scargill, ibid, 4, 321 (1957).
25. N. M. Isaac, J. W. Wilkins, and P. R. Field, ibid, 15, 151 (1960).
26. J. Hardy and D. Scargill, ibid, 13, 174 (1960).
27. D. F. Peppard, W. J. Driscoll, R. J. Sironen, and S. McCarty, ibid, 4, 326 (1957).
28. J. P. Surls, UCRL-3209 (1956).
29. D. Scargill, K. Alcock, J. M. Fletcher, E. Hesford, and H. A. C. McKay, J. Inorg. Nucl. Chem., 4, 304 (1957).
30. E. Hesford, E. E. Jackson, and H. A. C. McKay, ibid, 9, 279 (1959).
31. G. F. Best, E. Hesford, and H. A. C. McKay, ibid, 12, 136 (1959).
32. C. F. Baes, R. A. Zingaro, and C. F. Coleman, J. Phys. Chem., 62, 129 (1958).
33. D. F. Peppard, J. R. Ferraro, and J. W. Mason, J. Inorg. Nucl. Chem., 7, 231 (1958).
34. D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, ibid, 4, 344 (1957).
35. G. Duyckaerts, Ph. Dréze, and A. Simon, ibid, 13, 332 (1960).

36. D. F. Peppard and J. R. Ferraro, ibid, 10, 275 (1959).
37. D. F. Peppard, G. W. Mason, W. J. Driscoll, and R. J. Sironen, ibid, 7, 276 (1958).
38. D. F. Peppard, S. W. Moline, and G. W. Mason, ibid, 4, 344 (1957).
39. C. A. Blake, C. F. Baes, and K. B. Brown, Ind. Eng. Chem., 50, 176 (1958).
40. D. F. Peppard, G. W. Mason, W. J. Driscoll, and S. M. McCarty, J. Inorg. Nucl. Chem., 12, 141 (1959).

NITROSYL DERIVATIVES OF METALS

Raymond Longhi December 6, 1960

I. INTRODUCTION

The existence of metal nitrosyl derivatives was suggested as early as 1891, when Berthelot(1) reported the formation at a blue complex resulting from the vapor phase reaction of nickel carbonyl and nitric oxide. The familiar "brown ring" test for nitrate and nitrite ions attributes its color to the species $[Fe(NO)]^{+2}$, which arises from the absorption of nitric oxide by acidic (H_2SO_4) solutions at iron(II) salts(2).

Nitric oxide is classified as an "odd molecule" and is essentially a "free radical". The unexpected stability of this paramagnetic species may be accounted for by the molecular orbital treatment which places the unpaired electron in an antibonding orbital distributed over the entire molecule(3). The dimer $(NO)_2$ does exist at low temperatures and infrared studies have been made on this species(4). The ionization at the nitric oxide molecule occurs easily (I.P. is 9.5ev.)(5)

II. BOND TYPES

It is generally agreed that the nitrogen serves as the donor atom in the nitrosyl complexes(5,6). Reduction at the nitroprusside ion $[Fe(CN)_5NO]^{-2}$ yields an ammine $[Fe(CN)_5NH_3]^{-3}$, whereas treatment with alkali gives a nitro compound $[Fe(CN)_5NO_2]^{-4}$. Electron diffraction studies(7) have been used to determine bond distances. Nitric oxide might enter into coordination in any of the following manners(5,6,8,9)

A. As NO^+

This involves first the donation at the odd electron to the metal followed by normal electron pair donation by the resulting nitrosonium ion (i.e., $\overset{-}{M} \leftarrow \overset{+}{N} \equiv O$). Most known compounds fall into this category, and because the NO^+ ion is isoelectronic with CO and CN^-, a close analogy is expected between their complexes, e.g.,

$K_2[Fe(CN)_5NO]$ $K_3[Fe(CN)_5CO]$ $K_4[Fe(CN)_5CN]$

At present unresolved differences of opinion concerning this type of bonding exist in the field. Wilkinson and associates(10) believe that the neutral nitric oxide first donates two electrons, and then its unpaired electron couples with an unpaired <u>d</u>-electron on the metal to form a <u>pi</u>-bond.

B. As NO^-

This species results by the gain of an electron from some electropositive material. The resulting NO^- ion then behaves as a normal ligand (i.e., $\overset{+}{M} \leftarrow N = \overset{-}{O}$). Very little evidence exists for compounds possessing this type bonding, although the pink diamagnetic $[Co(NH_3)_5NO]^+$ is believed to contain the NO^- group. On the basis of infrared studies,

Wilkinson(11) has proposed that iron tetranitrosyl has three NO groups coordinated as NO^+ and the other as the NO^- ion. However, Sidgwick(12) suggests the structure $[Fe(NO)_3]^- NO^+$ in order to obtain the inert gas configuration. The NO^- ion is concluded to be present(13) in the monomeric(14) sodium nitrosyl complex, prepared by passing dry nitric oxide into a solution of sodium in liquid ammonia. The diamagnetism of this compound and the fact that its chemical properties and x-ray diffraction pattern differ from sodium hyponitrite $Na_2(NO)_2$ are cited as evidence in support of this proposal.

C. As neutral NO

This arises from donation of two electrons to the metal followed by coordination as an electrically neutral unit (i.e., $M \leftarrow NO$). Although many authors have postulated complexes containing the coordinated neutral NO molecule, there is very little evidence for its existence, and no stable species have been isolated. Perhaps the best evidence for the transient presence of such a complex is given by Kolthoff's(15) polarographic reduction studies of nitroprusside.

D. Miscellaneous

The proposal for nitric oxide double-bonded to the metal has been made(6,7), but considerable doubt has been raised concerning its validity. Nitric oxide serving as a bridging group is considered in the following section.

III. STRUCTURE DETERMINATION

Magnetic susceptibility measurements give an indication of the number of unpaired electrons and often furnish evidence for the bond type. Conductivity studies produce data concerning the nature of these complexes, and the examination of polarographic reduction waves for nitrosyl complexes frequently presents evidence for possible intermediates that can not be isolated from solution. Electron diffraction methods have been used to estimate bond distances, and X-ray diffraction studies have clarified the structures of several nitrosyl complexes, but the use of these two techniques has been rather limited to date. The most widely used and successful technique at the present is infrared analysis. The nitric oxide molecule has its N-O stretch at 1878 $cm.^{-1}$, but removal of an electron to form NO^+ causes a shift to 2220 $cm.^{-1}$ Coordination of this nitrosyl ion to a metal leads to a decreased N-O stretching frequency, the range being 1938 $cm.^{-1}$ to 1626 $cm.^{-1}$. When the NO^- ion coordinates, the observed frequency is 1050 $cm.^{-1}$.to 1200 $cm.^{-1}$. An extensive listing of absorption peaks for various nitric oxide-metal complexes has been prepared.(10) The following example illustrates how experimental data may be correlated to arrive at a proposed structure.

The reaction of dicyclopentadienyl manganese with nitric oxide yields a compound which analyzes as $(C_5H_5)_3Mn_2(NO)_3$(16). The following data were obtained:

(1) I.R. shows cyclopentadienyl rings bonded to metal
(2) Product shows no reactions of $C_5H_5^-$ ion

Wilkinson(11) has proposed that from [illegible] there [illegible] groups [illegible] and [illegible]. Recently, Griffith(12) suggests the structure [illegible] [illegible]. The [illegible] [illegible] compound [illegible] [illegible].

[illegible]

This [illegible] coordination [illegible] electrically neutral unit [illegible] [illegible].

[illegible] Miscellaneous

[illegible] nitric oxide [illegible] [illegible] in the following section.

VII. [illegible]

Magnetic susceptibility measurements give no indication [illegible] [illegible] infrared analysis. [illegible] [illegible].

The reaction of [illegible] with nitric oxide [illegible] compound whose analysis [illegible]. The following data were obtained:

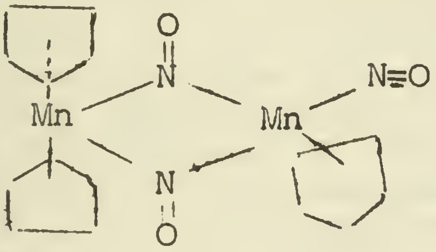
(1) [illegible]

(2) [illegible]

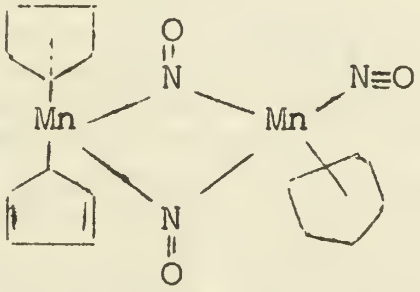
(3) Product reacts with maleic anhydride in CH_2Cl_2
(4) Catalytic hydrogenation gives all nitrogen as ammonia - no amines detected.
(5) Product is monomeric in solution
(6) Product is diamagnetic in solution or crystal phase
(7) Tetrahydrofuran solutions are electrically non conducting
(8) I.R. shows two strong N-O stretching bands at 1732 $cm.^{-1}$ and 1510 $cm.^{-1}$
(9) I.R. spectra are the same in solution or KBr

Some basic assumptions must also be made:
(1) Cyclopentadienyl rings can not act as bridging groups - no suitable orbitals for such bonding
(2) Both bridging and non-bridging NO groups are present
(3) It is unlikely that the NO's are bonded through both the nitrogen and oxygen atoms.
(4) The total number of electrons allocated to the two manganese atoms will be as similar as possible
(5) The Krypton rule applies

The following two structures were proposed with (II) being favored because the product reacts with maleic anhydride.



[I]



[II]

IV. COMPOUND TYPES AND PREPARATIONS

Nitrosyl complexes of varying stability are formed with a variety of transition metals, but no stable species are observed with metals which employ outer d-orbitals in complex formation (e.g.,Zn,Cd,Hg).

A. Metal Nitrosyls M(NO)x

These compounds are prepared by the reaction of nitric oxide (under pressure) on the respective metal carbonyls. Unstable metal nitrosyls are formed with iron, ruthenium, and nickel. The $Fe(NO)_4$ complex is the most stable(17), but it decomposes slowly in air above 0°C.(11). The originally proposed $Ru(NO)_5$(18) was later believed to be $Ru(NO)_4$(5) but Emeléus and Anderson have questioned these postulates(19). With nickel, a variety of reports have indicated such species as polymeric $Ni(NO)_2$ units (5,20), and the ionic species $Ni(NO)^{+}$(21), $Ni(NO)^{+2}$(22), and $Ni(NO)^{+3}$(23).

B. Metal Nitrosyl Carbonyls $M(NO)_x(CO)_y$

These are generally prepared from the higher carbonyls(5),

$$Fe_2(CO)_9 \text{ (or) } Fe_3(CO)_{12} \xrightarrow{NO} Fe(NO)_2(CO)_2$$

$$KCo(CO)_4 + H_2O \xrightarrow{NO} Co(NO)(CO)_3$$

Recently Barraclough and Lewis(24) prepared $Mn(NO)_3Co$ by treating $Mn(CO)_5I$ with NO at 90°C. A group of German workers(33) has confirmed these results using infrared techniques. Substitution for some of the NO groups greatly increases the complex stability, although treatment with pyridine, phenanthroline(8), and amines(12) results only in replacement of the carbonyls.

C. Metal Nitrosyl Halides $M(NO)_yX_z$

These may be prepared by the reaction of nitric oxide with the metal halides or metal carbonyl halides. Observed stabilities go $Fe > Co > Ni$ and $I > Br > Cl$ and no fluorides are known(5).

D. Cationic Metal Nitrosyls $[M(NO)_x]^{+n}$

No generalities concerning methods of preparation can be made. The $Fe(NO)^{+2}$ ion is a well-known example in this category, and no ferric complexes have been prepared. The black $[Co(NH_3)_5NO]Cl_2$ and red $[Co(NH_3)_5NO](NO_3)_2$ have received much attention because of their dissimilar stabilities. The black isomer was originally thought to be paramagnetic(25), but Asmussen(26) has shown both to be diamagnetic. Infrared does not distinguish between NO^- and hyponitrite structures, but chemical evidence(27) points to a black dimeric hyponitrite compound and a monomer containing NO^- for the red isomer. The apparent diamagnetism of the black complex must arise from pairing of odd electrons on the two cobalt atoms(28).

E. Anionic Metal Nitrosyls $[M(NO)Y_x]^{-n}$

This type complex is very common among the transition metals. The most stable forms have Y as the CN^- ion, but complexes containing I^-, Cl^-, NO_2^- or NH_3 have been prepared. The best synthetic approach for compounds of the type $[M(CN)_5NO]^{-n}$, where M may be Fe, Mn, Mo, or Ru is to allow the metal hexacyano complex to react with hydroxylamine or nitric acid. Nitrato ruthenium complexes of this form are successfully extracted from fission reaction products with tri-*n*-butyl phosphate (TBP) in nitric acid(30,34).

F. Six-Coordinate Complexes

Most well-known metal nitrosyl complexes are in this category and stable compounds containing other than cyanide ions are uncommon.

G. Five-Coordinate Complexes

Some nitrosyl complexes are among the few known examples of five-coordinate compounds. These are the dialkyldithiocarbamates, which are obtained as $[M(NO)(R_2NCS_2)_2]$ where M is V(31), Fe, or Co(5).

1. Metal Nitrosyl Carbonyls [illegible]

These are [illegible] prepared from the carbon [illegible](17),

[illegible]

[illegible]

Recently [illegible] and Lewis(?) [illegible] A group of German workers [illegible] has confirmed [illegible] the [illegible] although [illegible] of the carbonyls.

2. Metal Nitrosyl Halides [illegible]

These may be prepared by the reaction of nitric oxide [illegible] metal halides [illegible]

3. Carbonyl metal nitrosyl [illegible]

No generalizations concerning methods of preparation can be made. [illegible] is a well-known example in this category [illegible] have been prepared. The black [illegible] have received much attention because of their [illegible] The black [illegible] but [illegible] does not distinguish between bridged [illegible] evidence(27) points to [illegible] and a [illegible] the two cobalt atoms(29).

4. [illegible] metal nitrosyls [illegible]

[illegible] is very common among the transition [illegible] the most stable [illegible] The best [illegible] of the type [illegible] in which [illegible]

5. [illegible] Complexes

[illegible]

6. [illegible] Complexes

[illegible] complexes are among the first known [illegible] compounds. These are the [illegible]

Calculations by Daudel and Bucher(32) indicate that the dsp^3 hybridization leads to a tetragonal pyramid structure with the metal atom near the center of the base. The stability decreases as Fe > Co >> V.

H. Four-Coordinate Complexes

When nitric oxide is allowed to react with $K_2[Ni(CN)_4]$ in liquid ammonia or in absolute alcohol, the compound $K_2[Ni(NO)(CN)_3]$ is obtained(35). The indication is that the nitric oxide first enters as NO^- and is converted to NO^+ in the complex(36). With platinum, both NO and CO form analogous ions $[PT(NO)Cl_3]^-$ and $[PT(CO)Cl_3]^-$(5). The recently reported neutral, anionic, and cationic species $[(C_6H_5)_3P]_2NiNOBr$(37), $[Fe(CO)_3NO]^-$ (38), and $[Rh(NO)_2(NH_3)_2]^+$(39) are believed to be four-coordinate complexes.

I. General Survey

Nitrosyl derivatives have been prepared for a number of elements. In the following table references are included for complexes not previously mentioned.

Na	Ba(44)	V	Cr(8,40)	Mn	Fe	Co	Ni	Cu(5)	B(43)	P(43)	Se(8)
K(13)			Mo	Re(8)	Ru	Rh	Pd(41,42)			As(43)	
					Os(6)		Pt			Sb(43)	

V. SUMMARY

Although several bond types are possible, the NO^+ ion is most frequently found coordinated in nitrosyl complexes. The most stable compounds are formed with metals containing unpaired d-electrons since coupling with the "odd electron" in nitric oxide may lead to pi-bond formation. Infrared techniques appear to be the most useful at the present time. Inspite of the large quantity of available data, much controversy still exists and a great deal of experimental and theoretical work remains to be done. Several excellent reviews on this topic have been published(5,6,8,9).

REFERENCES

1. M. Berthelot, Compt. rend., 112, 1343 (1891).
2. T. Moeller, Qualitative Analysis, McGraw Hill Book Co., Inc., N.Y., (1958), pp. 391 and 406.
3. E. Cartmell and G.W.A. Fowles, Valency and Molecular Structure, Butterworths Scientific Publications, London, (1956), pp. 101 and 161.
4. W. G. Fateley, H. A. Bent, and B. Crawford, Jr., J. Chem. Phys., 31, 204 (1959).
5. G. Addison and J. Lewis, Quart. Revs., 9, 115 (1955).
6. J. A. Mattern and S. J. Gill in, The Chemistry of the Coordination Compounds, edited by J. C. Bailar, Jr., Reinhold Pub. Corp., N.Y., (1956), pp. 531-540.
7. L. O. Brockway and J. S. Anderson, Trans. Faraday Soc., 33, 1233 (1937).

8. T. Moeller, J. Chem. Educ., 23, 441, 542 (1946).
9. D. J. Morgan, Talanta, 3, 113 (1959).
10. J. Lewis, R. Irving, and G. Wilkinson, J. Inorg. Nucl. Chem., 7, 32 (1958).
11. W. P. Griffith, J. Lewis, and G. Wilkinson, J. Chem. Soc., 3993 (1958).
12. N. V. Sidgwick, The Chemical Elements and Their Compounds, Vol. 1, Oxford, p. 686 (1950).
13. L. F. Audrieth and J. Kleinberg, Non-Aqueous Solvents, John Wiley and Sons, Inc., N.Y., (1953), p. [illegible]
14. E. Zintl and A. Harder, Ber., 66, 760 (1933),
15. I. M. Kolthoff and P. E. Toren, J. Am. Chem. Soc., 75, 1197 (1953).
16. T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 2, 38 (1956).
17. W. Manchot and E. Enk, Ann. 470, 275 (1929).
18. V. W. Manchot and W. J. Manchot, Z. anorg. allgem. Chem., 226, 385 (1936).
19. H. J. Emeleús and J. S. Anderson, Modern Aspects of Inorganic Chemistry, D. Van Nostrand Co., Inc., N.Y., (1938), p. 1[illegible]
20. R. L. Mond and A. E. Wallis, J. Chem. Soc., 121, 32 (1922).
21. J. S. Anderson, Z. anorg. allgem. Chem., 229, 357 (1936).
22. H. Reihlen, Z. anorg. allgem. Chem., 230, 223 (1937).
23. W. P. Griffith, J. Lewis, and G. Wilkinson, J. Chem. Soc., 1775 (1959).
24. G. Barraclough and J. Lewis, Proc. Chem. Soc., 81 (1960).
25. D. Mellor and D. Craig, J. Proc. Roy. Soc., N.S. Wales, 78, 25 (1944).
26. R. Asmussen, O. Bostrup, and J. Jensen, Acta. Chem. Scand., 12, 24 (1958).
27. R. Nast and M. Rohmer, Z. anorg. allgem. Chem., 285, 271 (1956).
28. W. P. Griffith, J. Lewis, and G. Wilkinson, J. Inorg. Nucl. Chem., 7, 38 (1958).
29. R. Nast and E. Proeschel, Z. anorg. allgem. Chem., 256, 159 (1948).
30. G. Rundstam, Acta. Chem. Scand., 13, 1481 (1959).
31. L. Malatesta, Gazz. Chim. Ital. 71, 615 (1941).
32. R. Daudel and A. Bucher, J. Chim. Phys., 42, 6 (1945).
33. V. W. Hieber, W. Beck, and H. Tengler, Z. Naturforsch., 15 b, [illegible] (1960).
34. P. G. M. Brown, J. Inorg. Nucl. Chem., 13, 73 (1960).
35. R. Nast and E. Proeschel, Z. anorg. allgem. Chem., 256, 145 (1948).
36. V. W. Hieber and R. Nast, Z. anorg. allgem. Chem., 244, 23 (1940).
37. R. D. Feltham, J. Inorg. Nucl. Chem., 14, 307 (1960).
38. V. W. Hieber and K. Bentner, Z. Naturforsch., 15b, 323 (1960).
39. V. W. Hieber and K. Heinicke, Z. Naturforsch, 14b, 819 (1959).
40. J. Lewis and R. G. Wilkins, J. Chem. Soc., 56 (1955).
41. W. Manchot and A. Waldmüller, Ber., 59b, 2363 (1926).
42. J. Smidt and R. Jira, Chem. Ber., 93, 162 (1960).
43. T. C. Waddington and F. Hanberg, Z. anorg. allgem. Chem., [illegible], 185 (1960).
44. A. Mentrel, Compt. Rend., 135, 740 (1902).

SELECTED RECENT WORK ON THE USE OF INFRARED SPECTROSCOPY IN THE STUDY OF THE STRUCTURE OF COMPLEXES

Edward Frühauf December 13, 1960

INTRODUCTION

Of the several methods which are available to the coordination chemist for the determination of structure, Infrared Spectroscopy is one of the newer methods, and it is being used more often as time goes on. Taken alone, infrared data often do not lead to a final structural conclusion, but when they are used with other physical methods, they do serve very useful purposes. A recent book(5) summarizes these applications of infrared spectroscopy.

CIS-TRANS ISOMERS

To date, examination of infrared spectra has not provided a general method for distinguishing between cis- and trans- isomers because the spectra do not differ appreciably. Studies are now being carried out in an effort to find generalities which can be applied to all cis- and trans- isomers. Trans- isomers are expected to have fewer bands than cis- isomers because trans-complexes have more symmetry.

The infrared spectra have been reported for cis - and trans- dinitrotetrammine cobalt(III) ion in the rock salt region(2). The spectra are very similar, but distinct differences are observed. The spectrum of the cis-isomer is more complex than that of the trans-isomer.

The infrared spectra of several cis- and trans- isomers of various cobalt(III) tetrammines have been reported in an effort to obtain significant differences(7). In general, it was found that the spectra of these isomers vary slightly in the 6.0 and 12.0 micron regions, and that the trans-isomers absorb at wave lengths 0.04-0.08 microns lower than the corresponding cis-isomers, in the 6.0 micron region.

The cis- and trans- glycine complexes of cobalt(III) and platinum(II) have been chosen for an infrared study in an effort to correlate spectral data to configuration(13). As expected, the cis-isomers give slightly more complex spectra than the trans-isomers. On the basis of comparing spectra, the configuration of bis-(glycino)-palladium(II) has been assigned as trans. All attempts to prepare the cis-isomer yielded a compound which had an infrared spectrum identical to that of the trans-isomer.

By comparing the infrared spectra of bis-(salicylaldimino)-nickel(II) and bis-(sarcosino)-zinc(II) to those of analogous compounds the structures of which have been determined by the X-Ray method and considering in particular the N-H stretching frequencies, evidence has been obtained for certain structures of these compounds(20).

In a more recent paper(8), the infrared spectra have been reported for the cis- and trans-isomers of dinitro- and dichloro-bis-(ethylenediamine)-cobalt(III) salts. The major difference observed between these spectra occurred in the N-H asymmetric deformation frequencies where the cis-isomer always displayed more splitting than the trans-isomer.

In an effort to use a criterion other than color for assigning the structures of two differently colored forms of a triethylenetriamine complex, $[Co(tren)Br_2]Br$, the infrared spectra of these two forms were compared with the spectrum of the corresponding dichloro- complex, the structure of which is known. It was concluded that these colored compounds were cis- and trans- isomers and not crystalline modifications of the same compound(16).

METAL-OLEFIN COMPOUNDS

The infrared spectra of many metal olefin complexes have been reported in the literature(5), but much of this information is not useful for structure study. Generally, the carbon-carbon double bond or triply bond stretching frequencies are lowered when the olefin bonds to a metal atom. Hence, one can determine if a multiple bond is participating in bonding with a metal atom.

Cis- and trans-2-butene react with platinum(II) chloride to form complexes of the formula $[Pt(2\text{-butene})Cl_2]_2$. The infrared spectra of the two resulting platinum complexes are different, but decomposition of either complex gives back the original olefin. This indicates that the geometrical isomerism of the olefins is preserved in the complexes(3).

METAL-SANDWICH COMPOUNDS

Infrared studies have provided a very useful source of structural information for the metal-sandwich compounds, that is the compounds where groups such as the cyclopentadienyl anion (Cp) are bonded to metal atoms through π-bonds. The infrared spectra also furnish a way of distinguishing σ- and π-bonded (cyclopentadienyl) metal compounds.

The spectra of various sandwich compounds represented as $[(\pi\text{-Cp})_2M]^{+n}$ are very similar, and the various assignments have been made(6). Sandwich structures for the compounds Cp_2W^{+2+3}, Cp_2Fe^+, and other were strongly suggested by their close spectral similarity to ferrocene and other compounds of known sandwich structure(5).

The spectrum of $[Fe(C_5H_5)_2(CO)_2]$ suggests that one of the C_5H_5 groups is π-bonded and the other is σ-bonded(12).

BRIDGED COMPLEXES

Infrared spectroscopy has provided a very useful method for the structural investigation of polynuclear carbonyls, nitrosyls, cyanides, and other bridged complexes where donor molecules appear in bridge and/or terminal positions. Information can be obtained as to whether a molecule like carbon monoxide is bonded in a bridge, in a terminal position, or in both.

One of the studies which clearly demonstrates this fact was concerned with the structures of the iron carbonyls, $[Fe(CO)_5]$ and $[Fe_2(CO)_9]$(17). In the spectrum of $[Fe_2(CO)_9]$ are two carbonyl bands which fall in the same region as those for $[Fe(CO)_5]$. In addition to these, there is a strong carbonyl band at lower frequency. The high frequency carbonyl bands have been assigned to terminal carbonyl groups, and the low frequency carbonyl bands have been assigned to bridging carbonyl groups. The spectrum is entirely consistent with the structure as determined by the X-Ray method.

STRUCTURAL ISOMERISM

The structural isomerism of the nitrite anion has been clearly demonstrated by the infrared method in the complex $[Co(NH_3)_5NO_2]Cl_2$(10). By comparing the spectra of nitroalkanes and alkyl nitrites to that of the $[Co(NO_2)_6]^{-3}$, it was concluded that the nitrogen rather than the oxygen atom donates in this anionic complex. It was observed that the spectra of the red and yellow forms of $[Co(NH_3)_5NO_2]Cl_2$ were different, and after comparing these spectra to these spectra to those obtained for $[Co(NO_2)_6]^{-3}$, it was concluded that in the red isomer the nitrite is bonded through oxygen and that in the yellow isomer the nitrite ion is bonded through nitrogen.

Structural isomerism is theoretically possible with urea and thiourea, but structural isomers of these ligands have not yet been isolated. Infrared evidence has shown that some metals bond through one atom of a given ligand whereas others bond through another atom(11)(21).

COMPLEXES WITH ORGANIC LIGANDS

Several structures have been reported for copper(II) tartarate trihydrate. Investigators have based their structure determinations on conductometric, spectrophotometric, potentiometric, pH, polarographic and recently, infrared methods(4). Consideration of the observed C-O stretching and the O-H bending frequencies indicated that one of the previously proposed structures is most probable. This structure has the tartarate anion bonded to the copper atom through two carboxylate and one hydroxyl groups and the three waters complete the coordination sphere of the copper atom.

Infrared evidence strongly suggests that copper(II) monoglutamate has a dimeric structure involving the two copper atoms being joined together by two glutamate anions and a water bridge. Water bridges are uncommon, but the band at 2880 $cm.^{-1}$ indicates the presence of a strongly coordinated water molecule(1).

Pyridinaldazine forms complexes with metal ions where the metal to ligand ratio is 3:1, 2:1 and 3:2. Infrared spectra of these compounds justify certain structures and also suggest that all of the donor sites on pyridinaldazine do not always participate in bonding with a given metal atom(19).

Much is known about the behavior of ethylenediaminetetraacetic acid (EDTA) complexes in solution, but little is known of their properties in the solid state. A recently reported summary should be consulted for a survey of (EDTA) studies(15). The previously unreported spectra for various (EDTA) complexes have been determined(14) and have furnished information about the chelate structure and bonding in these complexes.

REFERENCES

1. Das Sarma, B., J. Am. Chem. Soc., 78, 892 (1956).
2. Faust, J., and Quagliano, J., J. Am. Chem. Soc., 76, 5346 (1954).
3. Jonassen, H., and Kirsch, W., J. Am. Chem. Soc., 79, 1279 (1959).
4. Kirschner, S., and Kiesling, R., J. Am. Chem. Soc., 82, 4174 (1960).
5. Lewis, J., and Wilkins, R., Modern Coordination Chemistry, Interscience Publishers Inc., New York (1960).
6. Lippincott, E., and Nelson, R., J. Am. Chem. Soc., 77, 4990 (1955).
7. Merritt, P., and Wiberley, S., J. Phys. Chem., 59, 55 (1955).
8. Morris, M., and Busch, D., J. Am. Chem. Soc., 82, 1521 (1960).
9. Nakamoto, K., Fujita, J., and Murata, H., J. Am. Chem. Soc., 80, 4817 (1958).
10. Penland, R., Lane, T., and Quagliano, J., J. Am. Chem. Soc., 78, 887 (1956).
11. Penland, R., Mizushima, S., Curran, C., and Quagliano, J., J. Am. Chem. Soc., 79, 1575 (1957).
12. Piper, T.S., and Wilkinson, G., Chem. and Ind., (1955) 1296.
13. Saraceno, A., Nakagawa, I., Mizushima, S., Curran, C., and Quagliano, J., J. Am. Chem. Soc., 80, 5018 (1958).
14. Sawyer, D., and McKinnie, J., J. Am. Chem. Soc., 82, 4191 (1960).
15. Seivers, R., Thesis, University of Illinois (1960).
16. Selbin, J., and Bailar, J. C., Jr., J. Am. Chem. Soc., 82, 1524 (1960).
17. Sheline, R., and Pitzer, K., J. Am. Chem. Soc., 72, 1107 (1950).
18. Stoufer, R., and Busch, D., J. Am. Chem. Soc., 82, 3491 (1960).
19. Stratton, W., and Busch, D., J. Am. Chem. Soc., 82, 4834 (1960).
20. Svatos, G., Curran, Co., and Quagliano, J., J. Am. Chem. Soc., 77, 6159 (1955).
21. Yamaguchi, A., Penland, R., Mizushima, S., Lane, T., Curran, C. Quagliano, J., J. Am. Chem. Soc., 80, 527 (1958).

SOME NEWLY DISCOVERED π-COMPLEXES

Edward L. Safford January 3, 1961

I. INTRODUCTION

Although a few transition metal π-complexes have been known for many years, only in the last ten has this field of chemistry recieved significant attention. The first π-complex, $PtCl_2(C_2H_4)$, was reported in 1827 by Zeis~~s~~e (1) but only since 1951 have its structure and bonding been clearly established.

The opening of this new area of chemistry was heralded by the preparation of bis-cyclopentadienyl-iron (ferrocene) in 1951 (2,3). From this beginning, the field has expanded to include cyclopentadienyls of the majority of metals and metalloids (4) and transition metal complexes of several other unsaturated systems.

π-Complexes are close cousins to the metal carbonyls and are in the majority of cases prepared from them. The unsaturated hydrocarbon often shares the coordination sphere with carbonyl groups. Most of the known π-complexes follow the E.A.N. rule and are diamagnetic. They often involve zero-valent metal atoms and, in a few cases, even formally negative metal ions (5). Air sensitivity, but thermal stability, is common. Many have been purified by vacuum sublimation.

Within the last two years, several reviews of work in this field have been published. An annotated list of these and other pertinent reviews is given in the bibliography. This report is limited, for the most part, to papers published in the last two years and to consideration of ligands other than cyclopentadienyl anion.

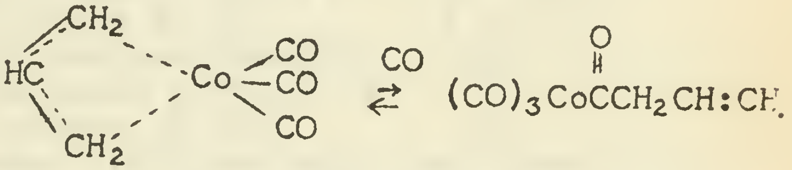
II. COMPLEXES OF NON-CONJUGATED π-BONDING LIGANDS

A. Complexes of ethylenes

Bonding in π-complexes is accepted to be a combination of σ-donation to the metal and π-donation back to the π-system by overlap of d-orbitals with π-antibonding orbitals (6). The double bond remains essentially unchanged and there is little charge separation (7). Structures involving metal-carbon σ-bonds (8,9) have been shown to be incorrect (10). The ability of electron-withdrawing substituents to stabilize ethylene complexes indicates that with ethylene, back-donation is the more important factor. It has been postualted that such substituents operate by lowering the antibonding orbital of the ethylene (11). Existence of supposed fluoro-olefin-complexes (12, 13) was, and the existence of an iron-acrylonitrile complex (14), is thus explained. No other iron-olefin complexes have been reported.

The most stable ethylene complexes are those of Ni, Pd, and Pt (15), which are reported to form with ethylene itself (16), allyl anion (17), acrylonitrile (11, 18), and several other substituted ethylenic hydrocarbons (19, 20). In a study of relative stabilities of olefin complexes with platinum, it was found that cis-disubstituted ethylenes complex more strongly than their trans isomers, a mono-substituted ligand is more effective than a symmetrically disubstituted ethylene, and branching aids complex stability (20), whereas a phenyl-substituent lowers it (19).

Little work has been done recently on other metals. A cobalt-allyl anion-carbonyl complex (I) has been prepared, which reacts as shown with CO (21). Formation constants have been determined for a number of silver-olefin complexes (22) and a kinetic study has indicated the intermediate formation of an ethylene-mercuric complex (23).

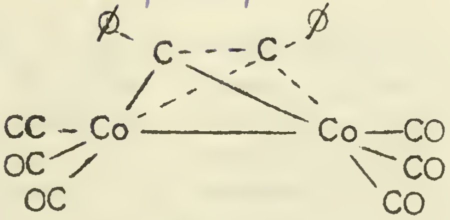


I

B. Complexes of acetylenes

The first acetylene complex reported was a platinum derivative of $[Me_2C(OH)C\equiv]_2$ prepared in 1945 (24). Several others have since been observed (25). The greatest variety is found in the compounds of tungsten although manganese yields an extensive series also (26). In very few cases, however, are these complexes of the acetylene itself. Upon complexing with a transition metal, acetylenes often undergo reaction within the coordination sphere to produce a variety of products. Thus are obtained complexes of quinones (27, 73), tropolones (29), substituted benzenes (30, 31), cyclopentadienes (32), and others, which will be noted later in the report. Iron carbonyl will even bring about trimerization of benzonitrile (33). The monovalent ions of group IB metals form polymeric acetylide-π-complexes (34).

Bonding in acetylene complexes is similar to that in olefin complexes (25), but there are two pairs of π-orbitals which can accommodate two metal atoms (6). Such a case is seen in the cobalt-diphenyl-acetylene complex, II (35). A similar nickel acetylene, complex is reported in which the carbonyls are replaced by two π-bonded cyclopentadienyl rings (36). Here, again, electron withdrawing goups aid stability as shown by perfluoroacetylene complexes (37).



II

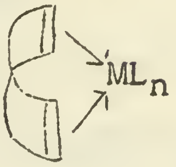
C. Diolefin complexes

It has been contended that the greater stability of diolefin complexes as compared to those of ethylenes is due to conjugation (38). This may be true in some cases (39), but in most diene complexes conjugation is impossible and the added stability comes from

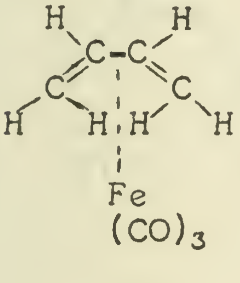
proper positioning of the π-bonds in the diene molecule (40-44). Norbornadiene (III) reportedly forms complexes with molybdenum (44), iron, ruthenium, copper (41), cobalt (45), palladium, platinum (46) and silver (22,41,46). Another common ligand is 1,5-cyclooctadiene, which forms complexes with molybdenum, ruthenium (42), tungsten (43), and palladium (47). Molybdenum (48), iron (38), and palladium (49), form diolefin complexes with 1,3-cyclo-hexadiene. These all have the general structure IV.

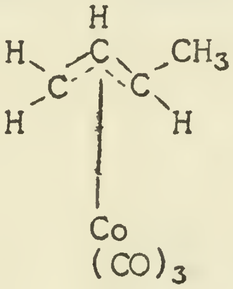

III

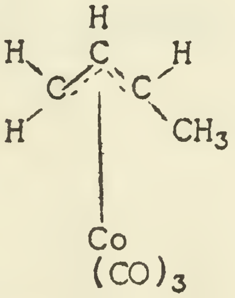
1,3-Butadiene complexes are reported with iron (38) and cobalt (50, 51). The former, $C_4H_6\ Fe(CO)_3$, shows no typical diene reactions and gives an IR-spectrum similar to that of the 1,3-hexadiene complex (38). The structure V is assumed in which bonding is similar to that in ferrocene. Two isomers of the complex formed from butadiene and cobalt hydrocarbonyl have been observed. To these are assigned, on the basis of IR and NMR spectra, structures VI and VII (51).



IV


V


VI


VII

III. COMPLEXES WITH CYCLIC CONJUGATED HYDROCARBONS

A. Bonding considerations

In 1956, Longuet-Higgins and Orgel (52,53) predicted on the basis of molecular orbital calculations that a nickel complex of cyclobutadiene should remove the diradical character of the free diene and stabilize it with respect to acetylene. Therefore, such a complex should be preparable.

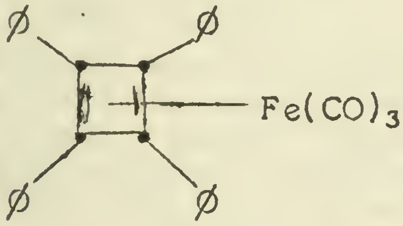
More recently, D. A. Brown (54) has treated complexes of the series $C_nH_nMY_m$ and $Y_mMC_nH_nMY_m$, in which $4 \leq n \leq 8$. Three types of bonding are distinguished: 1) σ-donation of electrons from the ring to the metal, 2) non-transfer π-interaction, and 3) δ-donation of electrons from filled d-orbitals of the metal to empty anti-bonding ring orbitals. The second is the major contribution, and calculations on it indicate that iron cyclobutadiene complexes may be as stable as cyclopentadienyls. Larger rings should form less stable complexes, and the relative stability of cyclobutadiene complexes decreases with transition metals to the right of iron. The frequent presence of carbonyl and similar ligands, Y, is shown to be expected.

In the binuclear complexes, metal orbitals overlap on each side of the ring, creating three-center molecular orbitals. Stabilization energy calculations predict these to be less stable than mononuclear complexes. Heterocyclic and polycyclic ring systems have also been treated (55).

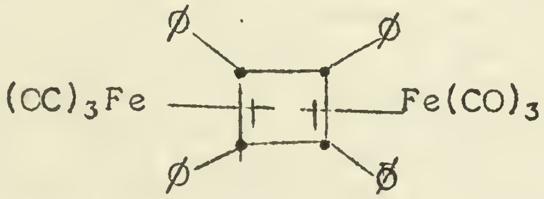
It is found that bis-cyclopentadienyl complexes are well handled by a strong ligand-field model in the majority of cases. This probably holds for benzene complexes as well (56,57).

B. Complexes of four-membered rings - cyclobutadiene

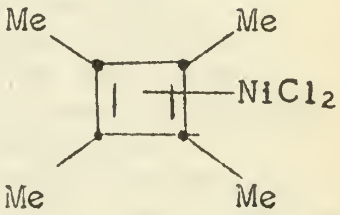
On the basis of his calculations, Brown has suggested structures VIII and IX for $(\emptyset_2C_2)_2Fe(CO)_3$ and $(\emptyset_2C_2)_2Fe_2(CO)_6$ (31,54). A palladium analog of VIII is reported (30). Complexes of cyclobutadiene and its derivatives have recently been prepared with nickel (X) (58) and silver (XI) (59).



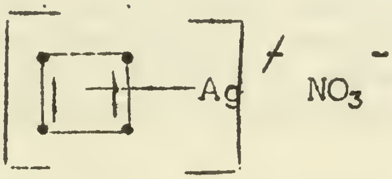
VIII



IX



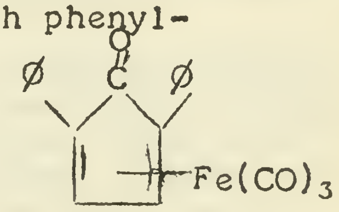
X



XI

C. Complexes of five-membered rings - cyclopentadienyl derivatives

When an acetylene reacts with an iron carbonyl, one of the products is of the form $(C_2R_2)_2Fe(CO)_4$. The first compound of this sort to be identified was that from the reaction with phenylacetylene (XII) (60-63). Diphenylacetylene yields tetracyclone (31, 64, 65) as has been confirmed by direct synthesis (66). The latter authors (66) report preparation of similar complexes of chromium, molybdenum, manganese, and cobalt, and present a discussion of the bonding involved. Reactions of acetylenes with cobalt, ~~rhodium~~, and manganese carbonyls yield products similar to those described for iron (67,68).



XII

Methylcyclopentadiene complexes have been prepared (69, 70) which ~~and~~ show anomalous magnetic properties (69). Triphenyl phosphonium and pyridinium derivatives have been combined with Group VIA metals (71), and molybdenum is reported to form a dinuclear indene complex held together by a metal-metal bond (72).

D. Complexes with six-membered rings - benzene and derivatives.

The study of the chemistry of metal-arene complexes began in 1954 when Zeiss (73) established the structures of the polyphenyl chromium complexes first observed by Hein in 1919 (74). In 1955, Fischer reported that chromium trichloride and benzene react when heated under CO pressure to yield $(C_6H_6)_2Cr^+$, which may be easily reduced to dibenzene chromium (O) (75). A better preparation has since been worked out (76). Fischer reported the brown-black product to be analogous to ferrocene, which is to be expected as $C_5H_5^-$ and C_6H_6 are isoelectronic (77, 78). This similarity has been confirmed by crystal structure determination (79), but unlike ferrocene, dibenzene chromium shows no aromatic character (81). The gas phase heat of formation is reported as -58.3 kacl/mole (80).

Hein (74) (and Zeiss (73)) treated $CrCl_3$ with ØMgBr and hydrolyzed the black reaction mixture in air. The product was, as shown by Zeiss, *bis*-biphenyl-chromium (I). More recently, Zeiss has reported (82) that if the reaction is run in tetrahydrofuran, an intermediate, $Ø_3Cr \cdot 3THF$, may be isolated as red crystals. If the solvent is removed, Hein's black reaction mixture results, which, upon air-free hydrolysis, yields dibenzene chromium(O), biphenyl-benzene-chromium(O), and *bis*-biphenyl-chromium(O). The latter has been synthesized directly (87). In ether, $CrCl_3$ and ØMgBrform π-complexes directly, and no intermediate is observed. Several mechanisms have been proposed for this reaction (82-84). It appears that triphenyl chromium rearranges to π-complexes when not stabilized by coordinated THF. If the THF is replaced with an acetylene, the latter will be cyclized within the coordination sphere to yield a variety of substituted benzenes and complexes (85, 86). Sandwich chromium complexes have been prepared from toluene, p-xylene, mesitylene, and hexamethyl benzene (76).

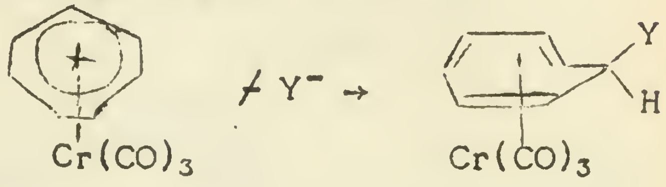
In 1957, Fischer (89, 90), Nichols and Whiting (91), and Natta and co-workers (92) independently discovered preparations of the "half-sandwich," arene-chromium-tricarbonyl complexes. An extensive series of benzene derivatives, including several condensed aromatic systems, has been shown to form such complexes (72, 93). A mesitylene-manganese (I) analog is reported (88).

In reactions completely analogous to those of chromium, molybdenum (94), tungsten (95), and vanadium (96) have been shown to form dibenzene complexes. Ruthenium (97) and iron (98) form dipositive sandwich complex ions with mesitylene. No other valence states have yet been attained. A benzene complex of ruthenium has also been prepared (97). Iron and manganese form *cyclo*pentadienylarene "sandwich" complexes (88). An acenaphthene-iron-carbonyl, $C_{12}H_8[Fe(CO)_3]_2$, is reported, in which all of the π-electrons are involved in the bonding (72). An interesting cobalt-benzene complex $(C_6H_6)_3Co_3(CO)_2$, has been prepared (99).

E. Complexes with seven-membered rings - cycloheptatriene

*Cyclo*heptatriene can yield complexes either as a tropylium ion, isoelectronic with benzene, or as a pseudo benzene structure (XIII) which bypasses the methylene group (100). Complexes of the first type

have been reported with molybdenum (101), chromium (102), and vanadium (103). The second type is obtained when tropylium-chromium-tricarbonyl (XIV) reacts with a variety of bases (102). Iron and molybdenum carbonyls form this type of complex directly (100,103). With palladium(II), platinum(II), and rhodium(I), *cyclo*heptatriene forms complexes apparently analogous to those of *cyclo*octa-1,5-diene (41).



XIV XIII

F. Complexes with eight-membered rings - cyclooctatetraene

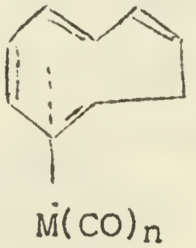
The well known tub configuration of *cyclo*octatetraene suggests the possibility of diene-like complexing. This is indeed the manner of bonding in its complexes with rhodium and platinum (105). However, there is strong evidence that in the mononuclear iron complex, $C_8H_8Fe(CO)_3$ the ring is flat (104-106) and may even possess some aromatic character (104). Such a possibility has been predicted by Brown (107) on the basis of molecular orbital calculations. The binuclear complex, $C_8H_8Fe_2(CO)_6$, is probably a symmetrical, flat-ring complex (104), although the possibility of diene bonding exists (105).

G. Complexes with nine-membered rings - cyclononatetraene

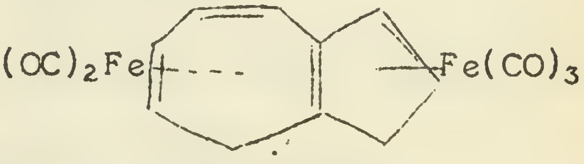
Although this hydrocarbon is not known, its bicyclic tautomer, 8,9-dihydroindene, forms tricarbonyl complexes with iron, tungsten (72), molybdenum (72, 108), and, perhaps, chromium (72). There is evidence that these complexes are of the form XV.

H. Complexes with azulene

The complexes $C_{10}H_8Fe_2(CO)_5$ (109) and $C_{10}H_8Mo_2(CO)_6$ (110) have been prepared. The assigned structure for the iron complex (XVI) has been treated by molecular orbital theory by Brown (107) and found reasonable. The molybdenum complex is similar.



XV



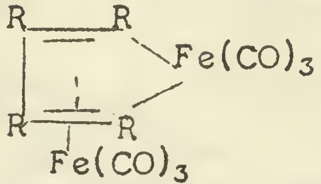
XVI

I. Complexes of heterocyclic systems

When the hetero-atom is a nonmetal, its donor properties may interfere with π-bond formation unless the atom is blocked or is a poor donor to the metal involved (111). The latter explanation is invoked in the case of the reported thiophene-chromium-tricarbonyl (112), whereas the former is applied in thiophenedioxide-iron-tricarbonyl (66). A thiophene-iron-tricarbonyl is reported, also (109). *N*-methylpyridinium iodide has been complexed to Cr, Mo, and W (5, ~~113~~ 111, 114).

The only complexes so far prepared in which the hetero-atom is a metal are of the form $(R_2C_2)_2Fe_2(CO)_6$. These are prepared from iron carbonyls and thiophene (115) or acetylenes (31, 64, 116, 117). The structure (XVII) has been determined by X-ray examination (118).

Reaction of this with ϕPCl_2 produces the pentaphenyl phosphole complex with the loss of an $Fe(CO)_3$ group (117). The complex $(C_2R_2)_2Fe(CO)_3$, previously referred to as a possible cyclobutadiene derivative, could also be formulated in the manner of XVII.



XVII

Brown has made molecular orbital calculations on complexes of this form by considering them as analogous to symmetrical binuclear complexes with the exception that the three-center orbitals are bent 90°. As a result, these complexes should be slightly less stable than those with symmetrical structures (119).

IV. CONCLUSION

Although this branch of chemistry is, for practical purposes, only ten years old, much elucidation has been achieved, and many interesting and potentially useful reactions have been observed. Its growth and development will bear watching.

BIBLIOGRAPHY

1. Zeise, Pogg. Annalen, 9, 632(1827); see review # 10.
2. T. J. Kealy and P. L. Pauson, Nature, 168, 1039(1951).
3. S. A. Miller, J. A. Tebboth, and J. F. Tremain, J. Chem. Soc., 1952, 632.
4. See review 7.
5. E. O. Fischer and K. Öfele, Z. Naturforsch., 14b, 736(1959).
6. See review 8, p. 93-4.
7. D. B. Powell and N. Sheppard, Spectrochim. Acta, 13, 69(1958).
8. A. A. Babushkin, L. A. Gribov, and A. D. Hellman, Doklady Acad. Sci. URSS, 123, 46(1958).
9. A. D. Hellman, A. A. Babushkin, and L. A. Gribov, Chem. Soc. Spec. Publ. No. 13, 116 (1959).
10. D. B. Powell and N. Sheppard, J. Chem. Soc., 1960, 2519.
11. G. N. Schrauser, J. Am. Chem. Soc., 82, 1008(1960).
12. K. F. Watterson and G. Wilkinson, Chem. and Ind. 1959, 991
13. K. F. Watterson and G. Wilkinson, ibid., 1960, 1358.
14. S. F. A. Kettle and L. E. Orgel, ibid., 1960, 49.
15. See review 1 p. 487.
16. W. M. MacNevin and S. A. Giddings, Chem. and Ind., 1960, 1191.
17. B. L. Shaw, Proc. Chem. Soc., 1960, 247.
18. G. N. Schrauzer, J. Am. Chem. Soc., 81, 5310 (1959).
19. J. R. Joy and M. Orchin, J. Am. Chem. Soc., 81, 305 (1959).
20. J. R. Joy and M. Orchin, ibid., 310 (1959).
21. R. F. Heck and D. S. Breslow, ibid., 82, 750 (1960).
22. J. G. Traynham and J. R. Olechowski, ibid., 81, 571 (1959).
23. K. Ichikawa, H. ouchi, and S. Araki, ibid., 82, 3880(1960).
24. A. Gelman, S. V. Bukhovets and E. Meilakh, Compt. Rend. Acad. Sci. URSS, 46, 105(1945); S. V. Bukhovets, Izvest. Sekt. Platiny drug. blagorod Metal., Inst. obshchei neorg. Khim., 29, 55(1955); S. V. Bukhovets and K. A. Molodova, Zhur. neorg. Khim., 2, 776(1957) ibid. 3, 1540 (1958).
25. J. Chatt, L. A. Duncanson, and R. G. Guy, Chem. and Ind., 1959, 430.

Reaction of this with HCl produces the pentaphenyl [illegible], together with the loss of an Fe(CO)$_3$ group (147).
The complex $(C_6H_5C_2)_2Fe_2(CO)_6$, previously referred to as a possible cyclobutadiene derivative, could also be formulated in the manner of XVII.


XVII

Brown has made molecular orbital calculations on complexes of this form by considering them as [illegible] symmetrical binuclear complexes with the exception that the bridge-center orbitals are bent 90°. As a result, these complexes would be slightly less stable than those with symmetrical structures (117).

IV. CONCLUSION

Although this branch of chemistry is, for practical purposes, only ten years old, much elucidation has been achieved, and many interesting and potentially useful reactions have been observed. Its growth and development will bear watching.

BIBLIOGRAPHY

1. Zeiss, [illegible], 9, 432(1957); see review # 10.
2. T. J. Kealy and P. L. Pauson, Nature, 168, 1039(1951).
3. S. A. Miller, J. A. Tebboth, and J. F. Tremaine, J. Chem. Soc., 1952, 632.
4. See review 7.
5. E. O. Fischer and R. Jira, Z. Naturforsch., 10b, 354(1955).
6. See review 8, p. 41-43.
7. D. R. Powell and N. Sheppard, Spectrochim. Acta, 13, 69(1958).
8. A. N. Nesmeyanov, [illegible], and [illegible], Doklady Akad. Nauk SSSR, 125, 96(1959).
9. A. N. Nesmeyanov, [illegible], and [illegible], [illegible] No. 11, 1[illegible] (1959).
. D. R. Powell and N. Sheppard, J. Chem. Soc., 1960, 2519.
. G. N. Schrauzer, J. Am. Chem. Soc., 81, 5310(1959).
. R. L. Patterson and G. Wilkinson, Chem. and Ind., 1959, 991.
. R. [illegible] and G. Wilkinson, ibid., 1960, 1558.
. J. [illegible] and [illegible], ibid., 1960, 84.
. See review 1, p. 457.
. R. [illegible] and [illegible], Chem. and Ind., 1960, 1191.
. R. [illegible], Proc. Chem. Soc., 1960, 357.
. G. N. Schrauzer, J. Am. Chem. Soc., 81, 5310 (1959).
. [illegible] and [illegible], J. Am. Chem. Soc., 81, [illegible] (1959).
. [illegible] and [illegible], ibid., 137(1959).
. R. F. Heck and D. S. Breslow, ibid., 82, 750 (1960).
. [illegible] and [illegible], ibid., 81, 571 (1959).
. [illegible], [illegible], and [illegible], ibid., 82, [illegible] (1960).
. [illegible], [illegible], and [illegible], [illegible] SSSR, 124, [illegible] (1959); [illegible]
[illegible]
[illegible], ibid., 2, 1562 (1959).
. J. Chatt, L. M. [illegible], and L. M. Venanzi, Chem. and Ind., 1958, 120.

26. W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. S. D. King, and C. Hoogzand, J. Inorg. Nucl. Chem., 9, 204(1959).
27. H. W. Stenberg, R. Markby, and I. Wender, J. Am. Chem. Soc., 80, 1009 (1958).
28. H. W. Sternberg, J. G. Shukys, D. C. Donne, R. Markby, R. A. Friedel, and I. Wender, ibid., 81, 2339 (1959).
29. W. Hübel and E. Weiss, Chem. amd Ind., 1959, 703.
30. L. Malatesta, G. Santarella, L. Vallarino, and F. Zingales, Angew. Chem., 72, 34(1960).
31. W. Hübel and E.H. Braye, J. Inorg. Nucl. Chem., 10, 250 (1959).
32. T. H. Coffield, K. G. Ihrman, and W. Burns, J. Am. Chem. Soc., 82, 4209 (1960).
33. S. F. A. Kettle and L. E. Orgel, Proc. Chem. Soc., 1959, 307.
34. D. Blake, G. Calvin, and G. E. Coates, ibid., 1959, 396.
35. W. G. Sly, J. Am. Chem. Soc., 81, 18 (1959).
36. M. Dubeck, ibid., 82, 502 (1960).
37. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, Chem. and Ind., 1960, 1137.
38. B. F. Hallam and P. L. Pauson, J. Chem. Soc., 1958, 642.
39. G. Winkhaus and G. Wilkinson, Proc. Chem. Soc., 1960, 311.
40. T. A. Manuel and F. G. A. Stone, Chem. and Ind., 1960, 231.
41. E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 1959, 3178.
42. M. A. Bennett and G. Wilkinson, Chem. and Ind., 1959, 1516.
43. T. A. Manuel and F. G. A. Stone, ibid., 1959, 1349.
44. R. Petit, J. Am. Chem. Soc., 81, 1266 (1959).
45. G. Winkhaus and G. Wilkinson, Chem. and Ind., 1960, 1083.
46. R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, J. Am. Chem. Soc., 82, 535(1960).
47. G. Calvin and G. E. Coates, J. Chem. Soc., 1960, 2008.
48. E. O. Fischer and W. Fröhlich, Z. Naturforsch, 15b, 266(1960).
49. E. O. Fischer and W. Helmut, Chem. Ber. 93, 2075 (1960).
50. C. L. Aldridge, H. B. Jonassen, and E. Pulkkinen, Chem. and Ind., 1960, 374.
51. D. W. Moore, H. B. Jonassen, J. B. Joyner, and A. J. Bertrand, ibid., 1960, 1304.
52. L. E. Orgel, ibid, 1956, 153.
53. H. C. Longuet-Higgins and L. E. Orgel, J. Chem. Soc., 1956, 1969.
54. D. A. Brown, J. Inorg. Nucl. Chem., 10, 39(1959).
55. D. A. Brown, ibid., 10, 49(1959).
56. J. Chatt and B. L. Shaw, J. Chem. Soc., 1959, 705.
57. F. A. Matsen, J. Am. Chem. Soc., 81, 2023 (1959).
58. R. Criegee and G. Schröder, Angew. Chem., 71, 70 (1959); Review 8, p. 96.
59. M. Avram, E. Marica, and C. D. Nenitzescu, Chem. Ber., 92, 1088 (1959).
60. E. R. H. Jones, P. C. Wailes, and M. C. Whiting, J. Chem. Soc., 1955, 4021.
61. F. A. Cotton and J. R. Leto, Chem. and Ind., 1958, 1593.
62. G. N. Schrauzer, Chem. and Ind., 1958, 1404.
63. J. R. Leto and F. A. Cotton, J. Am. Chem. Soc., 81, 2970 (1959).
64. G. N. Schrauzer, ibid., 81, 5307 (1959).
65. G. N. Schrauzer, Chem. and Ind., 1958, 1403.

66. E. Weiss and W. Hübel, J. Inorg. Nucl. Chem., 11, 42(1959).
67. R. Markby, H. W. Sternberg, and I. Wender, Chem. and Ind., 1959, 1381.
68. T. H. Coffield, K. G. Ihrman, and W. Burns, J. Am. Chem. Soc., 82, 1251 (1960).
69. L. T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 9, 86(1959).
70. R. Riemschneider and H. G. Kassahn, Z. Naturforsch., 14b, 348(1959).
71. E. W. Abel, A. Singh, and G. Wilkinson, Chem. and Ind., 1959, 1067.
72. R. B. King and F. G. A. Stone, J. Am. Chem. Soc., 82, 4557(1960).
73. H. H. Zeiss and M. Tsutsui, Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York, N.Y., September, 1954, p. 29-O:, H. H. Zeiss and W. Herwig, J. Am. Chem. Soc., 78, 5959(1956).
74. F. Hein, Ber., 52, 195(1919); ibid., 54, 1905 (1921).
75. E. O Fischer and W. Hafner, Z. Naturforsch., 10b, 665(1955).
76. E. O. Fischer and W. Hafner, Z. anorg. Chem., 286, 146(1956).
77. T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3, 104 (1956).
78. E. O Fischer, Chem. and Ind., 1956, 153.
79. E. Weiss and E. O. Fischer, Z. anorg. u. allgem. Chem., 286, 142 (1956).
80. E. O. Fischer and S. Schreiner, Chem. Ber., 91, 2213 (1958).
81. H. P. Fritz and E. O. Fischer, Z. Naturforsch, 12b, 67(1957).
82. M. Tsutsui and H. Zeiss, J. Am. Chem. Soc., 81, 1367 (1959).
83. M.S. Kharasch et O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y. (1954), p. 117.
84. F. Hein, Chem. Ber., 89, 1816 (1956).
85. W. Herwig, W. Metlesics, and H. Zeiss, J. Am. Chem. Soc., 81, 6203 (1959).
86. W. Herwig and H. Zeiss, ibid., 81, 4798 (1959).
87. E. O. Fischer and D. Seus, Chem. Ber., 89, 1809 (1956).
88. T. H. Coffield, V. Sandel, and R. D. Closson, J. Am. Chem. Soc., 79, 5826 (1957).
89. E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, Z. Naturforsch., 13b, 458 (1958).
90. E. O. Fischer and K. Öfele, Chem. Ber., 90, 2532 (1957).
91. B. Nichols and M. C. Whiting, Proc. Chem. Soc., 1958, 152.
92. G. Natta, R. Ercoli, and F. Calderazzo, Chimiae Industria, 40, 287 (1958); G. Natta, R. Ercoli, F. Calderazzo, and E. Santambrogio, ibid., p. 1003.
93. E. O. Fischer and N. Kriebitzsch, Z. Naturforsch., 15b, 465 (1960).
94. E. O. Fischer and H. O. Stahl, Chem. Ber., 89, 1805 (1956).
95. E. O. Fischer, F. Scherer, and H. O. Stahl, Chem. Ber., 93, 2065 (1960).
96. E. O. Fischer and H. P. Kögler, Chem. Ber., 90, 250 (1957).
97. E. O. Fischer and R. Böttcher, Z. anorg. u. allgem. Chem. 291, 305 (1957)..
98. E. O. Fischer and R. Böttcher, Chem. Ber., 89, 2397 (1956).
99. E. O. Fischer and O. Beckart, Angew. Chem. 70, 744(1958).
100. E. W. Abel, M. A. Bennett, and G. Wilkinson, Proc. Chem. Soc., 1958, 152
101. H. J. Dauben and L. P. Honnen, J. Am. Chem. Soc., 80, 5570(1958)
102. J. D. Munro and P. L. Pauson, Proc. Chem. Soc., 1959, 267.

103. R. B. King and F. G. A. Stone, J. Am. Chem. Soc., 81, 5263(1959).
104. T. A. Manuel and F. G. A. Stone, Ibid., 82, 366(1960).
105. F. A. Cotton, J. Chem. Soc., 1960, 400.
106. M. D. Rausch and G. N. Schrauzer, Chem. and Ind., 1959, 957.
107. D. A. Brown, Chem. and Ind., 1959, 126.
108. R. B. King and F. G. A. Stone, ibid., 1960, 232.
109. R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, ibid., 1958, 1592.
110. R. Burton and G. Wilkinson, ibid., 1958, 1205.
111. B. Moore and G. Wilkinson, Proc. Chem. Soc., 1959, 61.
112. E. O. Fischer and K. Öfele, Chem. Ber., 91, 2395(1958).
113. E. O. Fischer and S. Schreiner, Angew. Chem., 69, 205(1957).
114. E. O. Fischer and K. Öfele, Chem. Ber., 93, 1156 (1960).
115. H. D. Kaez, R. B. King, T. A. Manuel, L. D. Nichols and F. G. A. Stone, J. Am. Chem. Soc., 82, 4749(1960)
116. J. R. Case, R. Clarkson, E. R. H. Jones, and M. C. Whiting, Proc. Chem. Soc., 1959, 150.
117. E. H. Braye and W. Hübel, Chem. and Ind., 1959, 1250.
118. A. A. Hock and O. S. Mills, Proc. Chem. Soc., 233(1958).
119. D. A. Brown, J. Inorg. Nucl. Chem., 11, 9(1959).

REVIEWS

Olefin complexes

1. B. E. Douglas, "Coordination Compounds of Metal Ions with Olefins and Olefin-Like Substances," Chemistry of the Coordination Compounds, J. C. Bailar, Jr., ed. Reinhold Publishing Corporation, New York (1956), p. 487. Complexes reported are discussed for each metal in turn and a consideration of structures is given in some detail. 110 references.

Cyclopentadienyl complexes

2. F. A. Cotton and G. Wilkinson, "On the Question of Octahedral Binding in Bis-Cyclopentadienyl Compounds," Z. Naturforsch., 9b, 453 (1954). Theories of electronic structure are critically discussed. 25 references.
3. E. O. Fischer, "Metallverbindungen des Cyclopentadiens und Indens," Angew Chem., 67, 475(1955). Mono- and di-cyclopentadienyl and di-indenyl complexes of metals are reviewed. 59 references.
4. P. L. Pauson, "Ferrocene and Related Compound," Quart. Revs., , 9, 391 (1955). Review of substituted and unsubstituted metallocenes. 88 references.
5. M. D. Rausch, M. Vogel, and H. Rosenberg, "Ferrocene: A Novel Organometallic Compound," J. Chem. Educ., 34, 268(1957). Reactions of ferrocene are reviewed. 51 references.
6. M. L. H. Green, "Hydrido-Komplexe der Übergangsmetalle", Angew. Chem., 72, 719(1960). Transition metal hydrides, including those of cyclopentadienyl complexes are considered. 94 references.
7. M. D. Rausch, "Cyclopentadienyl Compounds of Metals and Metalloids," J. Chem. Educ., 37, 568 (1960). All known cyclopentadienyl complexes are documented. 118 references.

Bonding and structure

8. L. E. Orgel, "Metal-Ligand Bonds," Chem. Soc. (London) Spec. Publ. No. 13, 93(1959). Discussion of bonding in transition metal carbonyls and π-complexes and mechanisms of reactions between acetylenes and iron carbonyls. 23 references.

General

9. F. A. Cotton, "Alkyls and Aryls of Transition Metals," Chem. Revs., 55, 551 (1955). Review of all compounds with transition metal-carbon bonds including a thorough review of work by Hein and Zeiss on polyphenyl chromium compounds. 168 references.
10. E. O. Fischer, "Coordination Compounds of Unsaturated Hydrocarbons with Metals," Chem. Soc. (London) Spec. Publ. No. 13, 73(1959). General review of all classes of -complexes. 78 references.
11. E. O. Fischer and H. P. Fritz, "Compounds of Aromatic Ring Systems and Metals," Advances in Inorganic Chemistry and Radio-Chemistry, H. J. Emeleus and A. G Sharpe, eds., 1, 55 (1959). Comprehensive survey of work on 5-, 6-, and 7-

membered ring aromatic complexes of metals. 232 references.

12. G. Wilkinson and F. A. Cotton, "Cyclopentadienyl and Arene Metal Compounds," *Progress in Inorganic Chemistry,* F. A. Cotton, ed., *1*, 1(1959). Extensive survey of the title subject. 398 references.

Miscellaneous

13. R. Nast, "Complex Acetylides of Transition Metals," *Chem. Soc. (London) Spec. Publ. No. 13*, 103(1959). 23 references.
14. H. W. Sternberg and I. Wender, "Metal Carbonyls and Related Compounds as Catalytic Intermediates in Organic Synthesis," *Chem. Soc. (London) Spec. Publ. No. 13,* 35(1959). Role of π-complexing discussed briefly. 61 references.

SOME PERFLUOROALKYL DERIVATIVES OF CERTAIN METALS AND NON-METALS

Thomas A. Donovan

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I. INTRODUCTION

A perfluoroalkyl group is an alkyl group in which each of the hydrogen atoms has been replaced by a fluorine atom. The compounds discussed in this seminar may be classified according to the general formulae $(R_f)_aM$(I) and $(R_f)_aMX_b$(II) in which R_f represents a perfluoroalkyl group, X represents a halogen atom, and M may represent Li, Mg, Zn, Hg, Si, Ge, P, As, Sb, S, or Se(1).

II. ALKALI METAL DERIVATIVES

C_3F_7Li(III) is the only well-characterized perfluoroalkyl derivative of the alkali metals(2). Compound III is unstable with respect to heat and moisture and has only been investigated in ethereal solution. Reaction of III with Et_2SiCl_2 yields $Et_2(C_3F_7)SiCl$ and $Et_2Si(C_3F_7)_2$.

III. ALKALINE EARTH DERIVATIVES

Among the possible alkaline earth derivatives, only the perfluoroalkyl Grignard reagents have been prepared and investigated(3-6). The conditions necessary for a successful synthesis are far more rigorous than those employed in the preparation of an analogous hydrocarbon Grignard reagent. The products are quite unstable, and, as with III, are never isolated from solution.

IV. DERIVATIVES OF THE IIB ELEMENTS

A. Derivatives of Zinc

The perfluoroalkyl derivatives of zinc are similar to those of magnesium. However, the zinc compounds may be prepared under milder conditions and exhibit a higher degree of stability(7). Thus, the perfluoroalkyl zinc compounds may be isolated in the form of solvated species(7,8).

B. Derivatives of Mercury

The perfluoroalkyl derivatives of mercury are far more stable than their magnesium and zinc analogues, and a number of interesting and useful techniques are available for the preparation of these compounds(9-12). The enhanced stability of the mercury derivatives renders feasible the determination of physical constants, and values which have been reported are listed in section X. Some interesting complex species of the types $Hg(R_f)X_3^-$, $Hg(R_f)_2X_2^-$, $Hg(R_f)_2X^-$, etc., are formed in aqueous mixtures of $(Rf)_2Hg$ or R_fHgX and KX(10).

V. DERIVATIVES OF THE IVB ELEMENTS

A. Derivatives of Silicon

Silicon forms a number of perfluoroalkyl derivatives of the general type $(R_f)_{4-y}SiX_y$. However, only a few of these compounds have been well-characterized, and a large portion of the available information is in the form of patent reports(13,14). It has been reported(13) that certain of these silanes may be polymerized to heat resistant, flexible resins with high dielectric constants.

B. Derivatives of Germanium

CF_3GeI_3 is the only perfluoroalkyl derivative of germanium which has been prepared and characterized(15). The compound is a fairly stable, low-boiling liquid which is decomposed in the presence of aqueous alkali.

VI. DERIVATIVES OF THE VB ELEMENTS

Phosphorus, arsenic, and antimony have been shown to form a wide variety of perfluoroalkly derivatives ranging from $(R_f)_3M$ to R_fMX_4(16-24 The chemistry of these compounds is quite extensive with respect to the comparative youth of this area of research. Only selected methods of preparation and certain novel reactions will be considered during this seminar.

A. Reactions with Ammonia and Amines

$(CF_3)_2MCl$ (M = P,As) will condense with ammonia and a number of amines to give products of the general type $(CF_3)_2MNR_2$(25,26). There appears to be little tendency for these compounds to undergo further condensation, although $[(CF_3)_2As]_2NH$ is known(26).

B. Reactions with Diborane

Phosphinoborine low polymers of the type $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ result from the condensation of $(CF_3)_2PF$ and diborane(22).

C. Reactions with Nickel Tetracarbonyl

$(CF_3)_3P$ reacts with $Ni(CO)_4$ to yield a mixture of $(CF_3)_3PNi(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$(27,28). The isolation of such adducts is somewhat unusual in view of recent unsuccessful attempts to obtain similar complexes with $PtCl_2$(29).

D. Condensed Compounds

Dimers of the form $(CF_3)_2MM(CF_3)_2$ (M = P, As, Sb) have been obtained by prolonged shaking of $(CF_3)_2MI$ with mercury(16,18,30). Similarly, the tetramer, $(CF_3P)_4$, and the pentamer, $(CF_3P)_5$, result when CF_3PI_2 is shaken with mercury for an extended period(24).

E. As(I) and As(II)

$(CF_3)_2As$ is prepared by the reduction of $(CF_3)_2AsI$ with $LiAlH_4$ or a ZnCu alloy in 5N HCl(17). CF_3As is prepared from CF_3AsI_2 in a similar manner.

F. Complexes of Antimony

$(CF_3)_3SbCl_2$ is the parent compound of a number of complex species of the general form $[Sb(CF_3)_3X_3]^-$ (X = OH,F,Cl,Br) (31). Crystalline pyridinium and nitrosylium salts of these anions have been isolated.

VII. DERIVATIVES OF THE VI ELEMENTS

A. Derivatives of Sulfur

The known perfluoroalkyl derivatives of sulfur are limited to the species $(CF_3)_2S$(32), CF_3SCl(32), CF_3SF_3(33), $(CF_3)_2SF_4$(34,35), CF_3SF_5(34,35), and $(C_3F_7)_2S$(36). CF_3SCl may be condensed with amines and phosphines to yield compounds of the type CF_3SNR_2 and CF_3SPR_2(37).

B. Derivatives of Selenium

$(CF_3)_2Se$, CF_3SeCl, CF_3SeBr, and CF_3SeCl_3 are the only perfluoroalkyl derivatives of selenium which have been prepared and characterize (38). The selenium compounds are, in general, more stable than their sulfur analogues.

VIII. CHARACTERIZATION OF PERFLUOROALKYL COMPOUNDS

The more stable perfluoroalkyl compounds discussed in this seminar were characterized by microanalysis, molecular weight determinations, and a qualitative examination of infra-red spectra. The less stable derivatives of lithium and magnesium were characterized by their reactions with various organic functions. The application of modern physical methods to these compounds has been quite limited although some data concerning bond angles and bond distances are available from electron diffraction studies(39).

IX. CONCLUSION

The field of perfluoroalkyl compounds is a young and rapidly expanding field of research. The recent review by Lagowski(1) is recommended as a primary source for references to the original literature.

X. PHYSICAL CONSTANTS OF SOME PERFLUOROALKYL COMPOUNDS

Compound	M.P.	B.P.	Reference
CF_3HgCl	76°		9
CF_3HgI	80°(sub.)		11
C_2F_5HgF	99-100°(S.T.)		12
C_2F_5HgCl	103-4°(S.T.)		12
C_2F_5HgBr	78-9°(S.T.)		12
C_2F_5HgI	98°(S.T.)		12
C_3F_7HgI	77°(S.T.)		10
$(CF_3)_2Hg$	163°(S.T.)		11
$(C_2F_5)_2Hg$	106-7°(S.T.)		12
CF_3SiF_3		-42°	14
CF_3SiBrF_2		12-3°	14

Compound	M.P.	B.P.	Reference
CF_3GeI_3		40-2°(10^{-3} mm)	15
$(CF_3)_3P$		17.3°	16
$(CF_3)_2PF$	-150°	-11.9°	22
$(CF_3)_2PI$		73°	16
CF_3PCl_2		37°	16
CF_3PI_2		133°/413 mm	16
$(CF_3)_3PCl_2$	20.5°	71°/368 mm	16
$(CF_3)_2PCl_3$		107°	23
CF_3PCl_4	-52°	104°	24
$(C_3F_7)_2PCl$	-75°	118-9°	19
$(C_3F_7)_2PI$	-108°	135°	19
$C_3F_7PCl_2$	-90°	86.4°	19
$C_3F_7PI_2$	-18°	190°	19
$(C_3F_7)_2PCl_3$		184°	19
CF_3As		-12.5°/753 mm	17
$(CF_3)_2As$		19°	17
$(CF_3)_3As$		33.3°	30
$(CF_3)_2AsF$		25°	17
$(CF_3)_2AsCl$		46°	17
$(CF_3)_2AsBr$		59.5°/745 mm	17
$(CF_3)_2AsI$		92°	30
CF_3AsCl_2		71°	17
CF_3AsBr_2		118°/745 mm	17
CF_3AsI_2		183°d	17
$(CF_3)_3AsF_2$		57-8°	17
$(CF_3)_3AsCl_2$		98.5°	17
$(CF_3)_2AsCl_3$		93.5°/722 mm	17
$(C_2F_5)_3As$		120°	20
$(CF_3)_3Sb$	-58°	71.7°	18
$(CF_3)_2SbCl$		88°	18
$(CF_3)_2SbBr$		113°	18
$(CF_3)_2SbI$		129°	18
CF_3SbBr_2		155°	18
CF_3SbI_2		200°	18
$(CF_3)_3SbCl_2$	-34°	101°	18
$(CF_3)_3SbBr_2$	-16°		18
$(CF_3)_2SbCl_3$	27°	13°/5mm	18
CF_3SCl		-0.7°	32
CF_3SF_3	-110°	-7°	33
$(CF_3)_2SF_4$		20.5°	34
CF_3SF_5	-86.9°	-20.4°	34
$(C_3F_7)_2S$		90°	36
$(CF_3)_2Se$		-2°	38
CF_3SeCl		31°	38
CF_3SeBr		53.5°	38
CF_3SeCl_3	88-9°		38

XI. BIBLIOGRAPHY

1. J. J. Lagowski: Quart. Revs., 13, 323(1959).
2. O. R. Pierce, E. T. McBee, and G. F. Judd: J. Am. Chem. Soc., 76, 474(1954).
3. R. N. Hazeldine: J. Chem. Soc., 1273(1954).
4. E. T. McBee, C. W. Roberts, and A. F. Meiners: J. Am. Chem. Soc., 79, 335(1957).
5. R. N. Hazeldine: J. Chem. Soc., 3423(1952).
6. O. R. Pierce, A. F. Meiners, and E. T. McBee: J. Am. Chem. Soc., 75, 2516(1953).
7. R. N. Hazeldine and E. G. Walaschewski: J. Chem. Soc., 3607(1953).
8. W. T. Miller and E. Bergmann: ACS Abstracts 126, 35M(1954).
9. H. J. Emeléus and R. N. Hazeldine: J. Chem. Soc., 2948(1949).
10. H. J. Emeléus and J. J. Lagowski: J. Chem. Soc., 1497(1959).
11. H. J. Emeléus and R. N. Hazeldine: J. Chem. Soc., 2953(1949).
12. J. Banus, H. J. Emeléus, and R. N. Hazeldine: J. Chem. Soc., 3041(1950).
13. H. J. Passino and L. C. Rubin: U. S. Pat. 2,686,194 - Aug. 10, 1954; C.A. 49, 1363h(1955).
14. J. H. Simons and R. D. Dunlap: U. S. Pat. 2,651,651 - Sept. 8, 1953; C.A. 48, 10056a(1954).
15. H. C. Clark and C. J. Willis: Proc. Chem. Soc., 282(1960).
16. F. W. Bennett, H. J. Emeléus, and R. N. Hazeldine: J. Chem. Soc., 1565(1953).
17. H. J. Emeléus, R. N. Hazeldine, and E. G. Walaschewski: J. Chem. Soc., 1552(1953).
18. J. W. Dale, H. J. Emeléus, R. N. Hazeldine, and J. H. Moss: J. Chem. Soc., 3708(1957).
19. H. J. Emeléus and J. D. Smith: J. Chem. Soc., 375(1959).
20. P. B. Ayscough and H. J. Emeléus: J. Chem. Soc., 3381(1954).
21. A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber, and D. L. Herring: J. Am. Chem. Soc., 79, 249(1957).
22. A. B. Burg and G. Brendel: J. Am. Chem. Soc., 80, 6161(1958).
23. H. J. Emeléus, R. N. Hazeldine, and R. C. Paul: J. Chem. Soc., 563(1955).
24. W. Mahler and A. B. Burg: J. Am. Chem. Soc., 80, 6161(1958).
25. G. S. Harris: J. Chem. Soc., 512(1958).
26. W. R. Cullen and H. J. Emeléus: J. Chem. Soc., 372(1959).
27. H. J. Emeléus and J. D. Smith: J. Chem. Soc., 527(1958).
28. A. B. Burg and W. Mahler: J. Am. Chem. Soc., 80, 2334(1958).
29. M. A. A. Beg and H. C. Clark: Can. J. Chem., 38, 119(1960).
30. G. R. A. Brandt, H. J. Emeléus, and R. N. Hazeldine: J. Chem. Soc., 2552(1952).
31. H. J. Emeléus and J. H. Moss: Z. anorg. allgem. Chem., 282, 24(1955).
32. R. N. Hazeldine and J. M. Kidd: J. Chem. Soc., 3219(1953).
33. E. A. Tyczkowski and L. A. Bigelow: J. Am. Chem. Soc., 75, 3523(1953).
34. E. A. Clifford, H. K. El-Shamy, H. J. Emeléus, and R. N. Hazeldine: J. Chem. Soc., 2372(1953).
35. G. A. Silvey and G. H. Cady: J. Am. Chem. Soc., 72, 3624(1950).
36. M. Hauptschein and A. V. Grosse: J. Am. Chem. Soc., 73, 5461(1951).
37. H. J. Emeléus and S. N. Nabi: J. Chem. Soc., 1103(1960).
38. J. W. Dale, H. J. Emeléus, and R. N. Hazeldine: J. Chem. Soc., 2939(1958).
39. H. J. M. Bowen: Trans. Far. Soc., 50, 463(1954).

XIX. BIBLIOGRAPHY

1. J. J. Lorenzini: [illegible], 1., 123(1953).
2. [illegible], [illegible], and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
3. R. J. [illegible]: J. Chem. Soc., [illegible](1953).
4. [illegible], C. R. [illegible], and [illegible]: J. Am. Chem. Soc., 79, [illegible](1957).
5. R. [illegible]: J. Chem. Soc., [illegible](1953).
6. [illegible], [illegible], and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
7. [illegible] and [illegible]: J. Chem. Soc., [illegible](1953).
8. [illegible] and [illegible]: [illegible], 174, [illegible](1954).
9. [illegible] and [illegible]: J. Chem. Soc., [illegible](1954).
10. [illegible] and [illegible]: J. Chem. Soc., [illegible](1951).
11. [illegible] and [illegible]: J. Chem. Soc., [illegible](1951).
12. J. [illegible], [illegible], and [illegible]: J. Chem. Soc., 3031(1953).
13. [illegible] and [illegible]: [illegible] - Sept. 12, 1952; Can. 49, [illegible](1955).
14. [illegible] and [illegible]: [illegible] - Sept. 8, 1953; Can. 49, [illegible](1955).
15. [illegible] and [illegible]: [illegible] Chem. Soc., [illegible](1953).
16. [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1951).
17. [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1953).
18. [illegible], [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1951).
19. [illegible] and [illegible]: J. Chem. Soc., [illegible](1950).
20. [illegible] and [illegible]: J. Chem. Soc., [illegible](1951).
21. [illegible], [illegible], [illegible], [illegible], and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
22. [illegible] and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
23. [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1953).
24. [illegible] and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
25. [illegible]: J. Chem. Soc., [illegible](1950).
26. [illegible] and [illegible]: J. Chem. Soc., [illegible](1953).
27. [illegible] and [illegible]: J. Chem. Soc., [illegible](1953).
28. [illegible] and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
29. [illegible] and [illegible]: [illegible] J. Chem., 31, [illegible](1953).
30. [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1953).
31. [illegible] and [illegible]: [illegible] Chem., [illegible](1953).
32. [illegible] and [illegible]: J. Chem. Soc., [illegible](1951).
33. [illegible] and [illegible]: J. Am. Chem. Soc., 75, [illegible](1953).
34. [illegible], [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1951).
35. [illegible] and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
36. [illegible] and [illegible]: J. Am. Chem. Soc., 73, [illegible](1951).
37. [illegible] and [illegible]: J. Chem. Soc., [illegible](1953).
38. [illegible], [illegible], and [illegible]: J. Chem. Soc., [illegible](1951).
39. [illegible]: Trans. Faraday Soc., 49, [illegible](1953).

SYNTHESIS AND SELECTED REACTIONS OF CYANOGEN

Kenneth W. Whitten January 17, 1961

I. INTRODUCTION

Cyanogen, which is also known as dycyan and oxalonitrile, is a colorless, flamable, extremely poisonous gas. Gay-Lussac prepared cyanogen by the thermal decomposition of silver cyanide in 1815 (26). For many years cyanogen was primarily a chemical of academic interest because it could not be prepared economically, and the products of its reactions could be obtained by other more feasible or economical methods.

At the present time cyanogen is of interest to the chemical industry as a high-energy fuel (heat of formation = 73.8 kcal./mole)(34) A stoichiometric mixture of cyanogen and oxygen produces the hottest flame of any known chemical reaction (ca. 4640°±150°K.) (13,14). The cyanogen flame is useful for welding and cutting new heat-resistant metals. Due to its high latent energy cyanogen could be employed as a rocket and missile propellant when mixed with an oxidizing agent such as fluorine. Vallee and coworkers (67,68) have utilized the oxygen-cyanogen flame in flame photometry to obtain much higher temperatures than other fuels, with the exception of cyanogen and ozone (60a), are capable of producing. Because of these and other potential uses of cyanogen, several commercially attractive syntheses have been developed.

II. STRUCTURAL DATA AND PHYSICAL CONSTANTS

The structural data and physical constants of cyanogen are summarized in Table I and Table II.

Table I

Structural Data

		Reference
Carbon-carbon bond length	1.37±0.02 Å	46
Carbon-nitrogen bond length	1.16±0.02 Å	46
Carbon-carbon-nitrogen bond angle	180°	8
Carbon-carbon double bond character	40-65%*	46,72

* Different workers have reported different values in this range.

Structure: :N:::C:C:::N: is the most likely structure with other resonance forms making some contribution

Table II

Physical Constants

Constant	Value	Reference
Boiling point	-21.17° C.	15, 49
Melting point	-27.9° C.	15, 49
Critical temperature	128.3° C.	11

Constant	Value	Reference
Critical pressure	59.6 atm.	11
Dipole moment	0.38 Debye	6
Heat of combustion	261.8 kcal./mole	34,53
Heat of dissociation	120-130 kcal./mole	52
Soly. in ethanol	26 gm./100 gm.	34
Soly. in water (30°C.)	0.73 gm./100 gm./2 hrs.*	34
Soly. in water (30°C.)	2.03 gm./100 gm./97 hrs.*	34

* On standing in contact with water, cyanogen undergoes chemical reaction to form a variety of products.

III. STABILITY OF CYANOGEN

The heat of formation of cyanogen is of the same order as that of acetylene, and energy is released explosively when cyanogen reacts with oxidizing agents such as fluorine (39), chlorine monoxide (2), and ozone (62). Cyanogen reacts explosively with the oxygen in air when subjected to an electric spark (20).

Pure cyanogen is relatively stable and can be shipped in stainless steel tanks with no special hazards. In the pure form it shows no appreicable decomposition even at 65°C. Most inorganic compounds accelerate the decomposition of cyanogen.

IV. PREPARATION OF CYANOGEN

In the period 1815-1915, cyanogen was prepared by the thermal decomposition of heavy metal cyanides. Recently various other methods have developed. Cyanogen has been found in varying quantities in the effluent gases from the destructive distillation of coal and in natural gas, but neither of these sources is utilized commercially.

A. From Metal Cyanides

1. Noble metal cyanides (26,50,60,63) and copper(II) cyanide (36) undergo thermal decomposition to produce cyanogen. An inert gas such as nitrogen or carbon dioxide is employed as a carrier. An oxidizing agent such as iron(III) chloride, phosphorus(V) chloride, or mercury(II) chloride enhances the yield of cyanogen, and lower temperatures are required. This procedure is not efficient, and the possibility of an explosion due to the presence of small amounts of silver fulminate or mercury fulminate renders the method undesirable(22). In addition, paracyanogen is usually formed during the thermal decomposition of heavy metal cyanides.

2. In the laboratory cyanogen is usually prepared by the reaction of copper(II) sulfate with potassium cyanide in alkaline solution (42). Some carbon dioxide and hydrogen cyanide are also produced in this reaction, but these impurities are easily removed by passing the mixture of gases through a drying train which consists of a tower of dry sodium hydroxide, an aqueous solution of silver nitrate, and a tower of anhydrous calcium chloride. Janz produced cyanogen from sodium cyanide and copper(II) sulfate (32a).

3. Cyanogen and hydrogen cyanide are produced by the action of various oxidizing agents on acidic solutions of potassium hexacyanoferrate(II), hexacyanoferrate(III) and cyanides (50a). Ultraviolet irradiation of potassium hexacyanoferrate(III) in aqueous solution produces cyanogen (57).

4. Electrolysis of molten cyanides produces cyanogen and the free metal. The electrolysis of molten potassium and sodium cyanides (8, 66) and barium cyanide (37) between carbon electrodes has been investigated.

B. From Hydrogen Cyanide and Cyanogen Halides

1. Deville and Troost prepared cyanogen in 1863 by passing hydrogen cyanide through a porcelain tube heated to redness (54). The by-products were carbon, hydrogen, and nitrogen.

2. Hydrogen cyanide is oxidized by air when a mixture of air and hydrogen cyanide is passed over a silver catalyst at 300-600°C. (40). The yield is rather low, and polymeric by-products are produced.

3. Hydrogen cyanide reacts with an aqueous suspension of copper(II) oxide to produce cyanogen and a complex cyanide, $Cu[Cu(CN)_3]$, which yields additional cyanogen on heating (24).

4. Hydrogen cyanide reacts with chlorine in the vapor phase (30-200°C.) to produce cyanogen chloride, which reacts with additional hydrogen cyanide to form cyanogen in quantitative yields at 400-700°C.(35). No polymers are formed in this process, and pure cyanogen is obtained by passing the reaction mixture through a water-scrubbing tower. Hydrogen reacts with cyanogen chloride when passed thoough a hot quartz tube at 850°C. to produce cyanogen in 95% yield(21).

5. Lower alkenes react with cyanogen chloride in the vapor phase over a metal halide catalyst to produce cyanogen in 70% yield and a halide derivative of the alkene (29).

6. Electrolysis of hydrogen cyanide in aqueous or liquid sulfur dioxide medium yields cyanogen (30, 54a).

C. From Oxalic Acid and Glyoxal Derivatives

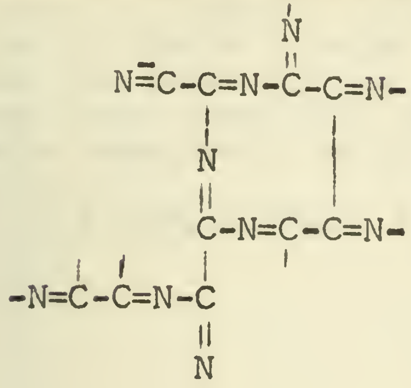
The dehydration of ammonium oxalate or oxamide with phosphorus(V) oxide or phosphorus(V) sulfide under reduced pressure at temperatures of 100-290°C. produces cyanogen (28, 45).

Various other methods for producing cyanogen have been investigated (9).

V. PARACYANOGEN

At elevated temperatures paracyanogen, the solid polymeric form of cyanogen, is produced. The structure of paracyanogen is not known, but its chemical inertness and insolubility suggest that it is either

a three-dimensional system (I) or a fused ring system (II) (59).



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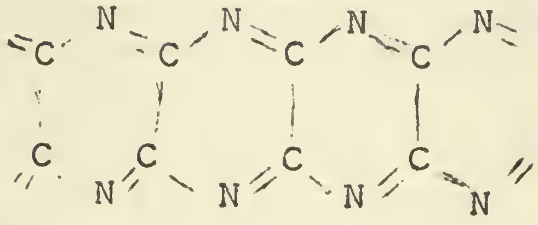


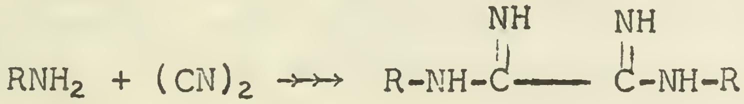
II

When cyanogen is heated to 300-400°C. at atmospheric pressure, paracyanogen is produced (7, 65). At 860° in the presence of an inert carrier gas, paracyanogen depolymerizes to monomeric cyanogen (45, 56, 61, 65), and there is little decomposition to elemental carbon and nitrogen until the temperature reaches 1200°C. (38). Ultraviolet irradiation (4, 5) and high-voltage electric discharges(58) convert cyanogen to paracyanogen.

Paracyanogen is insoluble in water, liquid cyanogen, and alcohol, partially soluble in strong bases, and soluble in concentrated sulfuric and hydrochloric acids. Dilution of the concentrated sulfuric acid solution precipitates the polymer (19, 33, 47).

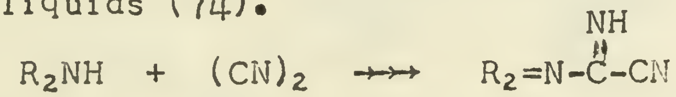
VI. SELECTED REACTIONS OF CYANOGEN

A. Cyanogen reacts with aliphatic primary amines at 0°C. in aqueous solutions to form dialkyloxamidines (75), which are white crystalline solids or colorless liquids that form hydrochlorides easily.



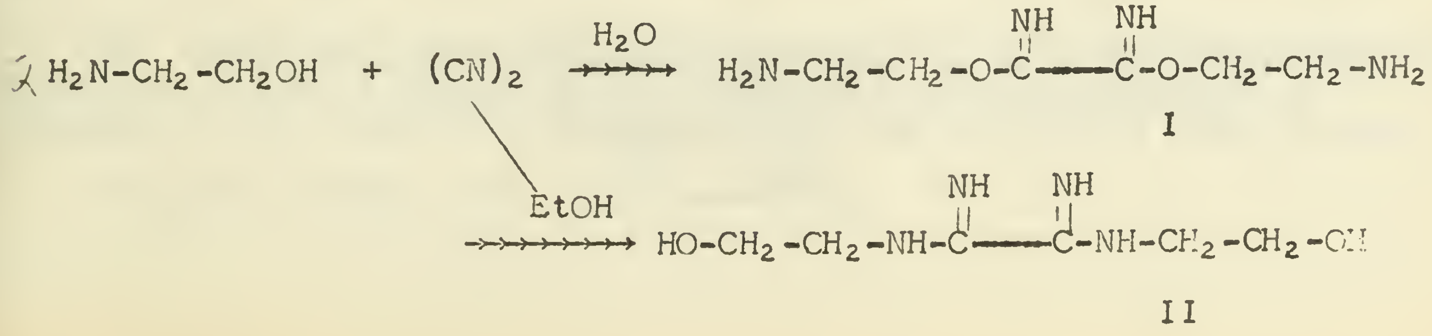
$$RNH_2 + (CN)_2 \longrightarrow R\text{-}NH\text{-}\overset{NH}{\overset{\|}{C}}\text{——}\overset{NH}{\overset{\|}{C}}\text{-}NH\text{-}R$$

B. Cyanogen reacts with secondary aliphatic amines at 0°C. in organic solvents to produce N,N-dialkylcyanoformamidines, which are colorless liquids (74).



$$R_2NH + (CN)_2 \longrightarrow R_2{=}N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}CN$$

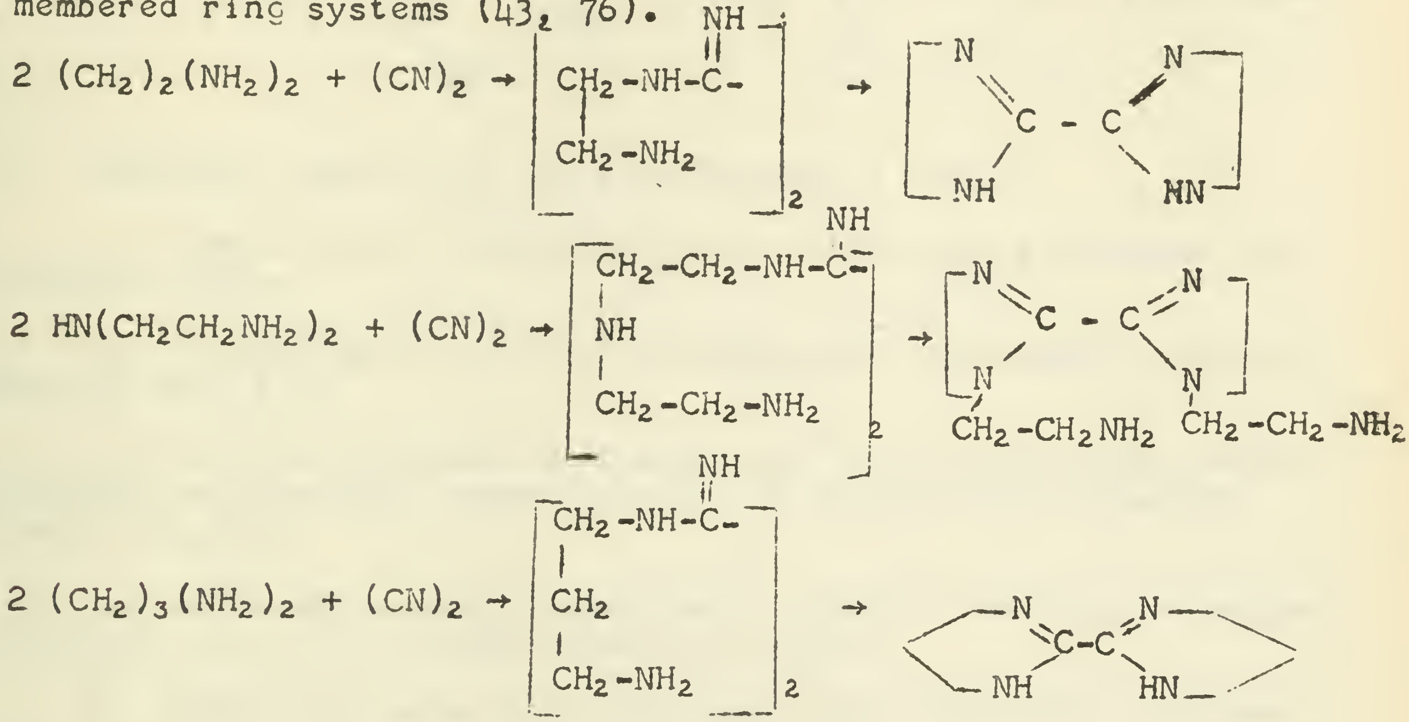
C. Cyanogen reacts with alkanolamines in aqueous solutions to produce bis(2-aminoalkyl)oxalidiimidates(I), whereas in alcoholic solutions the products are bis(2-hydroxyalkyl)oxamidines(II) (27,73).



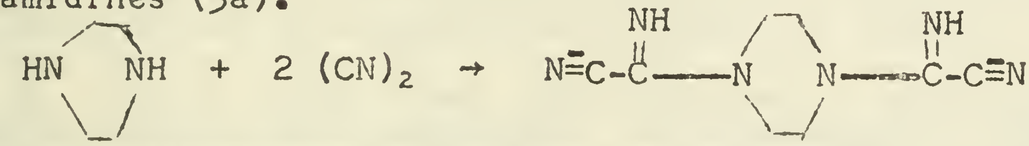
$$H_2N\text{-}CH_2\text{-}CH_2OH + (CN)_2 \xrightarrow{H_2O} H_2N\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{NH}{\overset{\|}{C}}\text{——}\overset{NH}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad \text{I}$$

$$\xrightarrow{EtOH} HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\overset{NH}{\overset{\|}{C}}\text{——}\overset{NH}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH \quad \text{II}$$

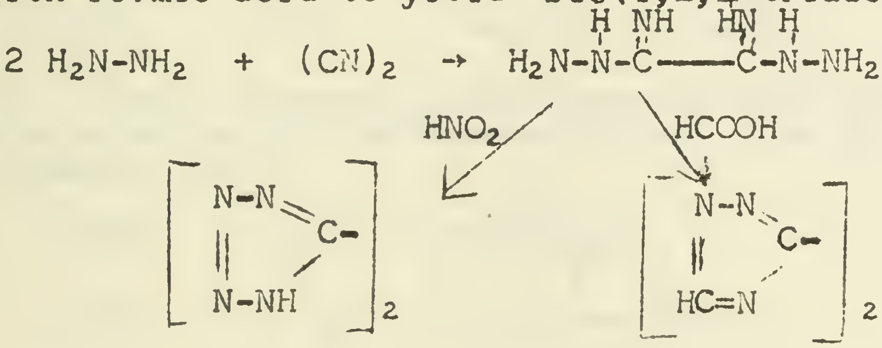
D. Cyanogen reacts with aliphatic diamines to produce various types of compounds depending on the number of methylene groups between the two amino groups. When two or three methylene groups separate the two amino groups, aminoalkyloxamidines form at low temperatures, but these compounds decompose at room temperature to form five- and six- membered ring systems (43, 76).



E. Cyanogen reacts with heterocyclic diamines to form biscyanoformamidines (5a).

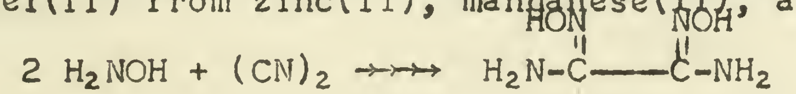


F. Cyanogen reacts with hydrazine in cold aqueous solution to form oxaldiimidic acid dihydrazide (8, 17, 18), which undergoes reaction with nitrous acid to form bis(1,2,3,4-tetrazol-5-yl) (I) and with formic acid to yield bis(1,2,4-triazol-3-yl) (II) (51).



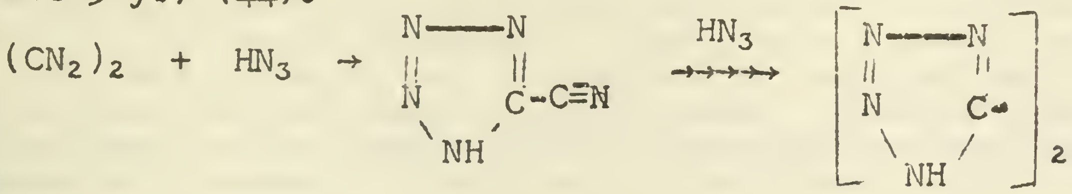
I

G. Cyanogen reacts with hydroxylamine to form oxaldihydroxamide, a product which is useful in the separation of small amounts of nickel(II) from zinc(II), manganese(II), and cobalt(II) (12, 25, 64).



$$2\ H_2NOH + (CN)_2 \longrightarrow H_2N-\overset{\overset{HON}{\|}}{C}-\overset{\overset{NOH}{\|}}{C}-NH_2$$

H. Cyanogen reacts with hydrazoic acid to form 5-cyanotetrazole, which will react with excess hydrazoic acid to form bis (1,2,3,4-tetrazol-5-yl) (44).



I. Cyanogen reacts with various inorganic acids:

1. Concentrated hydrochloric acid hydrolyzes cyanogen to form oxamide (55).

2. Concentrated acetic acid hydrolyzes cyanogen to yield oxamide and urea (3).

3. Phosphorus-containing acids and carboxylic acids react with cyanogen at 50-90°C. under pressure to yield cyanoformamide, $N\equiv C\text{-}CO\text{-}NH_2$ (70,71).

4. Sulfurous acid is oxidized to sulfuric acid by cyanogen in the absence of air at room temperature (69).

5. Cyanogen reacts with refluxing hydriodic acid to form glycine, ammonium iodide, and free iodine (23).

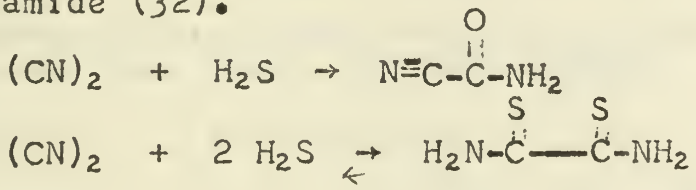
J. Cyanogen is hydrolyzed by aqueous solutions of strong bases, forming cyanides and cyanates with traces of oxalates (41).

K. Alkali amides react with cyanogen in liquid ammonia to produce cyanides and cyanamides. It is noteworthy that sodium amide (48) and potassium amide (16) react differently.

$$3\,KNH_2 + (CN)_2 \rightarrow KCN + K_2NCN + 2\,NH_3$$

$$2\,NaNH_2 + (CN)_2 \rightarrow Na_2NCN + NH_4CN$$

L. Liquid hydrogen sulfide reacts with cyanogen in a 1:1 molar ratio to produce thiocyanoformamide and in a 2:1 molar ratio to form dithiooxamide (32).



$$(CN)_2 + H_2S \rightarrow N\equiv C\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2$$

$$(CN)_2 + 2\,H_2S \rightleftarrows H_2N\text{-}\overset{S}{\overset{\|}{C}}\text{—}\overset{S}{\overset{\|}{C}}\text{-}NH_2$$

M. Sodium hydrogen sulfide reacts with cyanogen in alcoholic solution to form the sodium salt of dithiooxamide (1, 42). Sodium sulfide reacts with cyanogen to form sodium cyanide and sodium cyanamide.

VII. SUMMARY

Various preparations of cyanogen have been discussed together with selected reactions of cyanogen with organic nitrogen compounds and certain inorganic compounds. Cyanogen is a promising high temperature fuel, and cyanogen can be employed in the synthesis of compounds which contain several basic nitrogen atoms. Some of these compounds might be used in the preparation of coordination compounds, and new compounds with several primary amine functional groups could be prepared from cyanogen.

REFERENCES

1. Angeli, A., Gazz. Chim. Ital., 23, II, 103 (1893).

2. Balard, A. J., Ann. Chim. Phys. [2] 57, 257, 277 (1843); Ann. 14, 174 (1835).

3. Beketoff, N., Ber., 3, 872 (1870).

4. Berthelot, D., and Gaudechon, H., Compt. rend., 155, 207 (1912).

5. Bladin, J. A., Ber., 18, 1546 (1885).

5a. Boillot, A., Compt. Rend., 76, 1132 (1873).

6. Braune, H., and Asche, T., Z. physik. Chem., B14, 18 (1931).

7. Briner, E., and Wroczynski, A., Compt. rend., 151, 314 (1910).

8. Brockway, L. O., Proc. Natl. Acad. Sci. (U.S.), 19, 868 (1933).

9. Brotherton, T. K., and Lynn, J. W., Chem. Revs., 59, 841 (1959).

10. Bucher, J. E. J., Ind. Eng. Chem., 9, 251 (1917).

11. Cardoso, E., and Baume, G., Compt. rend., 151, 141 (1910).

12. Chatterjee, R., J. Indian Chem. Soc., 15, 608 (1938).

13. Conway, J. B., and Grosse, A. V., J. Am. Chem. Soc., 80, 2972 (1958

14. Conway, J. B., Smith, W. F. R., Liddell, W. M., and Grosse, A. V., J. Am. Chem. Soc., 77, 2026 (1955).

15. Cook, R. P., and Robinson, P. L., J. Chem. Soc., 1935, 1001.

16. Cornell, E. F., J. Am. Chem. Soc., 50, 3312, 3316 (1928).

17. Curtis, T., and Dedichen, G. M., J. prakt. Chem., [2] 50, 245 (1894

18. Dedichen, G.M., Chem. Zentr., 1937, I, 86.

19. Delbruck, H., J. prakt. Chem., 41, 161 (1847).

20. Dixon, H. B., J. Chem. Soc., 49, 385 (1886); Dixon, H. B., Strange E. H., and Graham. E., J. Chem. Soc., 69, 761 (1896).

21. Dixon, J. K., and Longfield, J. E., U. S. Patent 2,730,430; C. A. 50, 6001g (1956).

22. Ellis, H. R., Chem. News, 100, 155 (1909).

23. Emmerling, A., Ber., 6, 1351 (1873).

24. Fierce, W. L., and Millikan, A. F., U. S. Patent 2,841,472; C. A., 52, 16710b (1958).

25. Fischer, E., Ber., 22, 1931 (1889).

26. Gay-Lussac, L. J., Ann. Chim. et. Phys. [1] 95, 175 (1815).

27. Graminski. E. L., "The Reaction of Cyanogen with Aminoalcohols," Publication No. 18,752, Uni. Microfilms, Ann Arbor, Mich. (1958).

28. Henry, L., Ber., 2, 307 (1869)

29. Heumer, H., U. S. Patent 2,723,185 C. A. 50, 2660b (1956); British Patent 751, 402.

30. Hutchings, Le Roi E., U. S. Patent 2,793,991; C. A., 51, 12712b (1957).

31. Jacquemin, G. Ann. Chim. et Phys. [6] 6, 140 (1885).

32. Jander, G., and Schmidt, H., Wien. Chem.-Ztg., 46, 49 (1943).
Gay-Lussac, J. J. Ann. Chim., [1] 95, 195 (1815).
Anschutz, R., Ann., 254, 262 (1889)
Liebig, J., and Wohler, F., Ann. Physik, 24, 167 (1832).

32a. Janz, G. J., *Inorganic Syntheses*, 5 43 (1957)

33. Johnston, J. J., Ann., 22, 280 (1837).

34. Knowlton, J. W., and Prose, E. J., J. Research Natl. Bur. Standards, 46, 489 (1951).

35. Lacy, B. S., Bond, H.A., and Hinegardner, W. W., U. S. Patent 2,399,361 C.A., 40, 4744 (1946); British Patent 579,785.

36. Lallemand, A., Compt. rend., 58, 750 (1863).

37. Mehner, H., German Patent 91,814.

38. Meyer, V., and Goldschmidt, H., Ber., 15, 1164 (1882).

39. Moissan, H., *Traite de Chimie Minerale*, Vol. II, p. 324, Masson et Cie., Paris (1905).

40. Moje, W., U. S. Patent 2,712,493: C. A. 49, 1519i (1955).

41. Naumann, R., Z. Elektrochem., 16, 773 (1910).

42. Noir, Cecile, and Tcheng-Datchange, M., Compt. rend., 187, 126 (1928).

43. O'Gee, R. C., "The reaction of Cyanogen with Ethylenediamine and its Alkyl Derivatives," Publication No. 3426, University Microfilms, Ann Arbor, Michigan (1951).

44. Oliveri-Mandala, E., and Passlacqua, T., Gazz. Chim. Ital., 41, II, 430 (1911).

45. Ott, E., Ber., 52, 657 (1919).

46. Pauling, L. Springall, H. D., and Palmer, K. G., J. Am. Chem. Soc., 61, 927, (1939).

47. Pauly, H., and Waltzinger, E., Ber., 46, 3132 (1913).

48. Perret, A. and Perrot, R., Compt. rend., 199, 955 (1934).

49. Perry, J.H., and Bardwell, D.C., J. Am. Chem. Soc., 47, 2629 (1925).

50. Rammelsberg, K. F., Mem. Proc. Chem. Soc., 3, 458 (1847-48).

50a. Ricca, B., and Pirrone, F., Ann. Chim. Appl., 18, 550 (1928).

51. Rinman, E. L., Ber., 30, 1193 (1897).

52. Robertson, N. C., and Pease, R. N., J. Chem. Phys., 10, 490 (1942)

53. Rossini. F. D., et. al., Selected Values of Chemical Thermodynamic Properties. Government Printing Office, Washington, D.C. (1952).

54. Sainte Claire-Deville, H., and Troost, L., Compt., rend., 56, 897 (1863).

54a. Schmidt, H., and Meinert, H., Z. anorg. u allgem. Chem., 293, 214 (1957).

55. Schmitt, R., and Glutz, L., Ber., 1, 66 (1868).

56. Schutzenberger, P., and Schutzenberger, L., Compt., rend., 111, 774 (1890).

57. Schwarz, R., and Tede, K., Ber., 60B, 70, (1927).

58. Shekhter, A., and Syrkina, K., Compt. rend. Acad. Sci. U.R.S.S., 26, 446 (1940).

59. Sidgwick. N.V., The Organic Chemistry of Nitrogen, p. 299, Clarendon Press, Oxford (1937).

60. Strakosch, J., Ber., 5, 693 (1872).

60a. Streng, A. G., and Grosse, A. V., J. Am. Chem. Soc., 79, 5583 (1957).

61. Terwen, J. W., Z. physik. Chem., 91, 494 (1916).

62. "Theories Fuel Researchers Bear in Mind," Chem. Eng. News, 35, p.22 (May 27, 1957).

63. Thomsen, J., Thermochemische Untersuchungen, Bd. IV, p. 390, J. A. Barth, Leipzig (1886).

64. Tiemann, F., Ber., 22, 1936 (1889).

65. Troost, L., and Hautefeuille, P., Compt. rend. 66,736, 798 (1868).

66. Tzentnershver, M., and Szper, J., Congr. Inter. Elec., Paris, Sect. u, Rapport No. 4, (1932); Chem. Abstracts 27, 2635 (1933).

67. Vallee, B. L., and Baker, M. R., J. Opt. Soc. Am., 45, 773 (1955).

68. Vallee, B. L., and Baker, M. R., Anal. Chem., 27, 320(A) (1955).

69. Vorlander, D., Ber., 44, 2475 (1911).

70. Welcher, R. P., U. S. Patent 2,804,470; C.A., 52, 2894a (1958).

71. Welcher, R. P., U. S. Patent 2,804,471; C.A., 52, 2894c (1958).

72. Wheland, G. W., Resonance in Organic Chemistry, p. 85. John Wiley and Sons, Inc., New York (1955).

73. Woodburn, H. M., and Graminski, E. L., J. Org. Chem., 23, 819(1958).

74. Woodburn, H. M., Morhead, B. A., and Bonner, W. H., J. Org. Chem., 14, 555 (1949).

75. Woodburn, H. M., Morehead, B. A., and Chih, C. M., J. Org. Chem., 15, 535 (1950).

76. Woodburn, H. M., and O'gee, R. C., J. Org. Chem., 17, 1235 (1952).

77. Zehrun, W. S., III, "The Reaction of Cyanogen with Some Nitrogen Heterocycles. Note on the Reaction of Heterocyclic Cyanoformamidines with Some Primary Amines," Publication No. 23,479, University Microfilms, Ann Arbor, Michigan (1957).

RECENT STUDIES OF BORON-NITROGEN COMPOUNDS AND AN OVERWORKED ANALOGY

Professor Riley Schaeffer, Indiana University February 14, 1961

Since the discovery of borazole ($B_3N_3H_6$) in 1926, many investigators have studied this molecule and numerous derivatives have been prepared. The fact that borazole is isoelectronic with benzene has attracted much attention, and it is perhaps not unfair to say that the analogy between the two compounds has been somewhat overworked and from a chemical point of view differences between the two are at least as important as similarities.

In the last few years, synthetic advances have substantially simplified work with borazole itself. The simplest route at present appears to be

$$3NH_4Cl + 3BCl_3 \rightarrow B_3Cl_3N_3H_3 + 9HCl$$

$$B_3Cl_3N_3H_3 + 3NaBH_4 + 3NR_3 \rightarrow 3NaCl + 3NR_3BH_3 + B_3N_3H_6$$

Recent studies in our laboratories have followed two lines which are discussed. Study of exchange of hydrogens between borazole and deuterium containing substances leads to three classes of behavior:

1) B_2D_6, $NaBD_4$ and D_2 exchange with BH bonds of borazole
2) ND_3, DCl and DCN exchange with NH bonds of borazole
3) D_2S, D_2C_2 and PD_3 neither exchange nor react.

The mechanism of exchange reactions is considered briefly as well as some aspects of addition of HX compounds (the general reaction being

$$3HX + B_3N_3H_6 \rightarrow B_3H_3X_3N_3H_6$$

which are related to the exchange studies. The mass spectra of isotopic borazoles are discussed briefly.

In a second line, a general technique has recently been devised for the synthesis of saturated borazoles (isoelectronic with cyclohexanes). For the parent substance the synthesis is

$$B_3N_3H_6 + 3HCl \rightarrow B_3H_3Cl_3N_3H_6$$

$$2N_3H_3Cl_3N_3H_6 + 6NaBH_4 \rightarrow 3B_2H_6 + B_3N_3H_{12} + 6NaCl$$

The physical and chemical properties of these substances shed further light on the analogy between carbon and boron-nitrogen compounds. In particular, isotope exchange studies and isomer problems are discussed.

THE CHEMISTRY OF ASTATINE

Kenneth W. Whitten February 21, 1961

I. INTRODUCTION AND HISTORICAL BACKGROUND

In 1940, Corson and MacKenzie(8) reported that substances which decayed by α-particle emission were obtained by bombarding bismuth targets with 32-Mev α-particles. From the bismuth target, they observed two α-particle periods: one of half-life 7.5 hours and one of the order of months. Later the same year Corson, MacKenzie, and Segre(9) reported that the ranges of the two groups of α-particles associated with the 7.5 hr. activity were 6.1 cm. (60%) and 4.2 cm. (40%). By chemical tests these workers eliminated Tl, Bi, Pb, and Po as sources of the 7.5-hour activity and noted that the chemical properties of the source element were similar to those of polonium.

The following experiments were performed on the dissolved bismuth targets to establish differences between the properties of known elements and the unknown source of the 7.5-hour activity(9);

A. From 0.25 M HNO_3, Po was deposited on metallic Bi, but the unknown activity was not deposited.

B. From 6 M HCl solutions of Bi, Po, and unknown activity fractional sulfide precipitation showed different ratios of Po and unknown activity in each sample. Similar results were obtained for the fractional hydrolysis of Bi.

C. Potassium iodide was added to a sample containing Po and unknown activity in 0.25 M HNO_3, and the liberated I_2 was extracted into CCl_4. Extraction of the unknown activity into CCl_4 was incomplete. The extracted I_2 was reduced with SO_2 and precipitated with Ag^+. The precipiated AgI contained the unknown activity but no Po.

D. Potassium iodide was added to a solution of Po and unknown activity in 0.25 M HNO_3, and the liberated I_2 was distilled off. Some of the unknown activity was found in the distilled I_2, but no Po had distilled out of the reaction mixture.

E. It was observed that the unknown activity was precipitated (reduced) by Zn in acidic solution, and that the unknown activity precipitated as a sulfide from acidic solution.

F. Under conditions by which the halogens (Cl, Br, I) are precipitated quantitatively by Ag^+, the unknown activity was only partially precipitated.

G. Samples of unknown activity were injected into hyperthyroid guinea pigs, and after 4.5 hours the unknown activity was found to be 100 times as great in the thyroid as in equal masses of other portions of the body.

On the basis of the above data, Corson, MacKenzie, and Segre(9) concluded that the source of the unknown activity was element number 85, astatine (later shown to be At^{211}).

Astatine occurs in nature only as short-lived, rare, branch product in the decay of the uranium and thorium radioactive series(20). Only one chemical isolation of astatine from a natural source has been reported, and this was the 0.9-minute α-emitting At^{219}(20). Numerous isotopes of astatine have been reported [see reference (33) for references to the original literature], but of these isotopes only At^{211} is really useful in an investigation of the chemical properties of astatine(4, 8, 9, 22, 25).

The chemical properties of astatine are rather different from those of iodine since At is decidedly more metallic, and caution must be exercised in planning experiments and interpreting experimental data.

II. PREPARATION OF ASTATINE

Bombardment of Bi^{209} with α-particles in the 21-29 Mev energy range produces At^{211} free from other radio-active species(22). Above 28 Mev, At^{210} is produced, but At^{210} rapidly decays by electron capture to undesirable Po^{210}. If the energy of the bombarding α-particle beam is very high Po^{210} is produced along with At^{210} and At^{211}(22). Astatine is volatile and can be purified by vacuum distillation techniques(9, 22). Astatine may be dissolved in concentrated HNO_3, H_2SO_4, or $HClO_4$(3, 9, 15, 22) for chemical investigations. Various modifications of this preparatory procedure have been employed(3, 9, 15, 22). All of the procedures for the production of astatine yield solutions which are 10^{-10}-10^{-12} molar in astatine.

Various constants of astatine are tabulated in Table I.

Table I

Constants for Astatine

Constant	Value	Reference
Standard Electrode Potential	-0.4 v, -0.7 v.	21, 19
First Ionization Potential	9.2 ev, 10.4 ev	13, 34
Second Ionization Potential	20.1 ev	13
Ground State Vib. Freq. (At_2^{211})	172.9 ± 4.3 cm.$^{-1}$	26
Dissociation Energy (At_2^{211})	0.8 ev	11
Nuclear Spin (At^{211})	9/2	12
D_{I^-}/D_{At^-}*	1.41	12

* Ratio of diffusion coefficients in 1% NaCl containing 1.2×10^{-3} M and KI and 4×10^{-3} M Na_2SO_3.

III. ANALYTICAL PROCEDURES

Astatine is quite volatile from glass surfaces and counting is usually done on samples which have been evaporated on platinum(22). Astatine (At^{211}) is determined most easily by its α-activity(9) since 60% of the atoms decay to Bi^{207} by emission of an α-particle of 5.94 Mev while 40% of the decay occurs by electron capture to yield Po^{211}. However, Po^{211} emits 7.43 Mev α-particles with a half-life of 0.005 second, and one α-particle per decay of an At^{211} nucleus is obtained.

Aten(3) and Johnson(22) have employed similar procedures for the determination of astatine. To HNO_3 or $HClO_4$ solutions containing astatine and carrier iddide, sufficient $AgNO_3$ and sulfite are added to precipitate both astatine and iodine quantitatively. Astatine is carried completely on the precipitate with less than 0.5% remaining in the filtrate.

Garrison and co-workers(15) have developed two methods for the determination of At^{211} in biological materials. In both methods the sample is digested in $HClO_4$ and HNO_3 and then evaporated to concentrated $HClO_4$ which is diluted to 3 $\underline{M}$ $HClO_4$.

A. Tellurous acid and HCl are added to the sample, and SO_2 is passed through the solution to reduce the tellurous acid to metallic tellurium, which carries astatine quantitatively.

B. A silver foil is immersed in the 3 $\underline{M}$ $HClO_4$ solution of astatine, and astatine precipitates on the foil quantitatively. The silver foil procedure is simpler, requires less time, and is easily adapted to routine procedures.

Barton(4) has shown that astatine can be extracted into diisopropyl ether and separated from many impurities, e.g., Po, Bi, Pb, Tl, etc.

IV. IDENTIFICATION OF OXIDATION STATES OF ASTATINE.

Four oxidation states of astatine have been reasonably well characterized: a (-1) state, which coprecipitates with AgI; a zero state, which is extracted into organic solvents; a (+5) state, which carries on insoluble iodates; and an intermediate (+1 or +3 or both) state, which neither carries on insoluble iodates nor extracts into organic solvents.

The chemistry of astatine has been studied largely through solvent extraction techniques on solutions which are 10^{-10} -10^{-16} molar in astatine. Investigations have shown that the behavior of iodine on a micro scale is different from its behavior on a macro scale, and behavior should be expected for astatine.

Kahn and Wahl(23) studied the distribution of iodine between water and benzene and found that for very low concentrations of iodine the partition coefficient was lower than for higher concentrations. Good and Edwards(18) have reported similar results for the distribution of iodine between water and carbon disulfide.

Katzin(24) has shown that traces of impurities can react with iodine to produce water-soluble I_3^- which leads to decreased solubility of iodine in organic solvents. In the light of these investigations (18, 23, 24), caution is indicated in the interpretation of experimental data from solvent extraction studies.

A. Solvent Extraction Studies:

Johnson and co-workers(22) performed a series of extractions to elucidate the chemical behavior of astatine. These workers reported the partition coefficients shown in Table II.

Table II

Partition Coefficients for At_2 and I_2

Solvent System	At_2	I_2(macro)	I_2(tracer)
C_6H_6-0.01 M HNO_3	242	400	------
CCl_4-0.01 M HNO_3	91	85	31

The difference between the partition coefficients for I_2 on a macro scale and a tracer scale is noteworthy.

Extraction of CCl_4 and C_6H_6 solutions of astatine with 0.1 M NaOH gave very small partition coefficients(22), which indicates that in basic solution astatine disproportionates into At^- and a positive oxidation state. When AgI was precipitated from the 0.1 M NaOH solution (to which excess NH_3 had been added), all of the α-activity was carried by AgI. After the NaOH solution was acidified with HNO_3, only a part of the α-activity was carried by AgI. When the NaOH solution of astatine was acidified and re-extracted with the original organic phases, small partition coefficients were obtained.

Johnson and co-workers(22) employed solvent extraction to study possible oxidation and reduction of At(O) by a series of reagents. At(O) was dissolved in organic solvents and extracted with 0.01 M HNO_3 to give the partition coefficients listed in Table III (column 3). The organic phase was then extracted with the final aqueous phase (column 2) to give new partition coefficients (column 4).

Table III

Redox Studies on At(O) by Solvent Extraction

Solvent	Final Aq. Phase	Part. Coeff. with 0.01 M HNO_3	Part. Coeff. with final Aq. phase	Interpretation
1. C_6H_6	0.25 M $FeSO_4$ 0.01 M HNO_3	91	89	At^0 is not reduced
2. CCl_4	Sat'd. H_3AsO_3	90	49	At^0 is slowly reduced
3. CCl_4	1.1 M KI 0.01 M HNO_3	50	0.4	Formation of interhalogen compd.

4.	C_6H_6	Sat'd. I_2 0.01 $\underline{M}$ HNO_3	200	64	Slight effect
5a.	C_6H_6	Sat'd. SO_2 0.01 $\underline{M}$ HNO_3	200	3	At^0 reduced. AgI carried all activity
5b.	CCl_4	same as 5a	85	0.8	same as 5a
6.	CCl_4	0.25 $\underline{M}$ $Fe(NO_3)_3$ 0.01 $\underline{M}$ HNO_3	85	2	At^0 is partially oxidized
7.	C_6H_6	0.05 $\underline{M}$ $Hg(NO_3)_2$ 0.01 $\underline{M}$ HNO_3	200	0.01	Possible complexing
8.	CCl_4	Br_2 0.1 M 0.01 $\underline{M}$ HNO_3	85	0.05	At^0 is rapidly oxidized
9a.	C_6H_6	0.01 $\underline{M}$ $K_2S_2O_8$*	200	5	Slow oxidation of At^0
9b.	C_6H_6	0.1 $\underline{M}$ $K_2S_2O_8$**	200	0.1	Rapid oxidation of At^0
10.	C_6H_6	3 $\underline{M}$ HCl	50	0.66	Interhalogen(?)
11.	C_6H_6	0.1 $\underline{M}$ KIO_3 0.1 $\underline{M}$ HNO_3	200	16	Slight Oxidation of At^0

* cold

** 50°C.

Two chloro-complexes of iodine, ICl_2^- and ICl_4^-, are known, and ICl_2^- can be extracted into ethers from HCl solutions(17). Neumann(29) prepared solutions of astatine in HCl and found that astatine was extracted into diisopropyl ether. The extractability approached a maximum at 8-9 $\underline{M}$ HCl as expected(6). Neumann's data suggest that at HCl concentrations greater than 3 $\underline{M}$ a single complex anion (probably $AtCl_2^-$) exists. Appelman has also studied the interhalogen compounds of astatine(2).

The reactions of HIO with phenols and HBrO with benzene have been investigated(7, 32). Neumann(29) obtained evidence for similar reactions of HAtO.

B. Carrying Experiments

Carrying experiments have been performed to obtain information about the solubility of astatine compounds and possible oxidation states.

1. Hydroxides carry astatine as indicated in Table IV.

Table IV

Carrying of Astatine by Hydroxides

	HNO_3 Stock Soln.		HNO_3 Stock Soln. oxidized by hot $K_2S_2O_8$	
Precipitant	NaOH	NH_4OH	NaOH	NH_4OH
Aluminum hydroxide	----	7-15%	----	7-15%
Bismuth hydroxide	40-60%	----	50-60%	----
Ferric hydroxide	40-50%	30-40%	97-99%	85-90%
Lanthanum hydroxide	5-8%	----	97-99%	----

2\. Precipitation of HgS in HCl carries astatine, as a function of the acidity of the solution(22)

3\. When $AgIO_3$ is precipitated from HNO_3 solutions of astatine, carrying depends on the order of reagent addition. If Ag^+ is added first, poor carrying (5-20%) results, whereas addition of IO_3^- before Ag^+ gives much better carrying (40-80%).

4\. Oxidation of astatine with $NaBiO_3$, IO_4^-, Cl_2, Ce(IV), and $S_2O_8^=$ gives no astatine-containing compound which is carried by KIO_4(1), but in view of the great variety of periodate anions(31) no conclusions should be drawn about the existence of astatine in the +7 oxidation state.

5\. See carrying experiments under Introduction and Historical Background.

C. Electrochemistry and Migration Experiments

Johnson and co-workers(22) deposited astatine electrolytically at both the anode and the cathode employing gold electrodes. The interpretation of the data is not obvious.

Solutions of astatine dissolved in cold concentrated HNO_3 were treated so that solutions of pH 1-pH=13 were obtained, whereas other samples were subjected to the action of various oxidizing and reducing agents. In all cases, the astatine migrated as a negative ion under the influence of an electric field.

V. SUMMARY

The preparation and identification of astatine have been discussec together with procedures for its quantitative determination. The reactions of astatine have been studied by solvent extraction and carrying procedures. Astatine is much more metallic than iodine, and its chemical properties are more similar to those of polonium than of iodine.

The behavior of iodine on a micro scale differs from its properties on a macro scale, and trace impurities may influence its

reactions on a macro scale. It is probable that similar discrepances would be observed for astatine if astatine could be studied on a macro scale. The activity of astatine is so high that it can never be investigated on even a milligram scale, and so the properites of element number 85 on a macro scale may remain forever unknown.

Referecnes (1, 3a, 21) are recent reviews on the chemistry of astatine.

Reference(27) is a comprehensive treatment of solvent extraction as applied to inorganic analysis, and reference(28) is a review of recent developments in solvent extraction techniques.

BIBLIOGRAPHY

1. Anders, E., Ann. Rev. Nuclear Sci., 9, 203 (1959).
2. Appelman, E. H., J. Inorg. and Nuclear Chem., 14, 308 (1960).
3. Aten, A. H. W., Doorgeest, T., Hollstein, U., and Moeken, H. P., Analyst, 77, 774 (1952).

3a. Bagnall, K. W., Chemistry of the Rare Radioelements, pp. 97-114, Butterworths Scientific Publications, London, England (1957).

4. Barton, G. W., Ghiorso, A., and Perlman, I., Phys. Rev., 82, 13 (1951).
5. Basson, J. K., Anal. Chem., 28, 1472 (1956).
6. Campbell, D. E., Laurene, A. H., and Clark, H.M., J. Am. Chem. Soc., 74, 6193 (1952).
7. Cofman, V., J. Chem. Soc., 1040 (1919).
8. Corson, D. R., and MacKenzie, K. R., Phys.,Rev., 57, 250 (1940).
9. Corson, D. R., MacKenzie, K. R., and Segre, E. Phys. Rev., 57, 459 (1940).
10. Derbyshire, D. H., and Waters, W. A., J. Chem. Soc., 573 (1950).
11. Drowart, J., and Hornig, R. E., J. Phys. Chem., 61, 980 (1957).
12. Durbin, P. W., U. S. Atomic Energy Commission Document, UCRL-3013 (1955).
13. Finkelnburg, W., Phys. Rev., 77, 303 (1950).
14. Freiser, H., and Morrison, G. H., J. Inorg. and Nuclear Chem., 9, 221 (1959).
15. Garrison, W. M., Gile, J. D., Maxwell, R. D., and Hamilton, J. G., Anal. Chem., 23, 204 (1951).
16. Garvin, H. L., Green, T. M., Lipworth, E., and Nierenberg, W. A., Phys. Rev. Letters, 1, 74 (1958).
17. Gillam, A. E., and Morton, R. A., Proc. Roy. Soc., A132, 152 (1931).
18. Good, M. L., and Edwards, R. R., J. Inorg. and Nuclear Chem., 2, 196 (1956).
19. Haissinsky, M., Comite interm. thermodynam. et cinet. electrochim. Compt. rend. reunion 1951, 218 (1952); C.A. 46, 1857a (1952).
20. Hyde, E. K., and Ghiorso, A., Phys. Rev., 90, 267 (1953).
21. Hyde, E. K., J. Chem. Educ., 36, 15 (1959).
22. Johnson, G. L., Leininger, R. F. and Segre, E., J. Chem. Phys., 17, 1 (1949).
23. Kahn, M., and Wahl, A. C., J. Chem. Phys., 21, 490 (1953).
24. Katzin, L. I., J. Chem. Phys., 21, 490 (1953).
25. Kelly E. L., and Segre, E., Phys. Rev., 75, 999 (1949).
26. Majumdar, K., and Varshni, T. P., Indian. J. Phys., 28, 103 (1954).
27. Morrison, G. H., and Freiser, H., Solvent Extraction In Analytical Chemistry, John Wiley and Sons, Inc., New York, N.Y. (1957).
28. Morrison, G. H., and Freiser, H., Anal. Chem., 30, 632 (1958).

29. Neumann, H. M., J. Inorg. and Nuclear Chem., 4, 349 (1957).
30. Perrier, C., and Segre, E., J. Chem. Phys., 5, 712 (1937).
31. Sidgwick, H. V., The Chemical Elements and Their Compounds, 1237-39 Oxford University Press, Oxford, England (1950).
32. Soper, F. G., and Smith, G. F., J. Chem. Soc., 2757 (1927).
33. Strominger, D., Hollander, J. M., and Seaborg, G. T., Rev. Modern Phys., 30, 585 (1958).
34. Varshni, T. P., Z. Physik., 135, 512 (1953).

RECENT PROGRESS IN THE CHEMISTRY OF THE PHOSPHONITRILIC COMPOUNDS

F. Y. Tsang

February 28, 1961

I. INTRODUCTION

Phosphonitrilic compounds have been known and characterized for over seventy years. Although compounds of this class could be of some commerical use, e.g., as oil additives or plasticizers they are at present still almost exclusively of theoretical interest.

This seminar is devoted to two branches of the chemistry of the phosphonitrilics: preparations and structural considerations. In both of these sections, the trimeric and tetrameric cyclic compounds are of main interest. A table of physical constants of a variety of phosphonitrilic compounds is included on page 108.

II. PREPARATIONS

A. Halides

1. Phosphonitrilic chlorides

The usual method of preparation is by the partial ammonolysis of PCl_5 using ammonium chloride in sym-$C_2H_2Cl_4$ as solvent. The original separation of the various polyhomologs by Stokes has recently been reinvestigated by Paddock et.al.(14) The ammonolysis mixture has been shown to contain cyclic phosphonitrilics with ring systems containing as many as 17 PN units.

2. Phosphonitrilic fluorides and mixed chloro-fluoro derivative

These derivatives are obtainable from the phosphonitrilic chlorides by a variety of methods. Fluorination reactions using PbF_2(19), KSO_2F(21,15), or NaF(13,26), either dry or in solvents, have been reported. (See table for compounds obtained)

3. Phosphonitrilic bromides and mixed chloro-bromo derivatives

The trimeric bromide was first prepared in 1892 by heating the initial product of ammonolysis of PBr_5 with excess PBr_5 in a sealed tube(2). The yield was much improved when PBr_5 and NH_4Br were allowed to react in sym-$C_2H_2Cl_4$(3). Furthermore, some hitherto-unknown tetramer was also isolated.

In seeking an improved yield, K. John and T. Moeller(12) have carried out modifications of the above reaction under a wide variety of conditions. The best yield (50-60% overall), as reported, can be obtained by slowly heating a mixture of PBr_3 and NH_4Br in sym-$C_2H_2Cl_4$ with slow additio of excess bromine (3 days from room temperature to 130°C), and continued heating for eleven days at 140-145°C.

If the reaction temperature is raised,* overall yields are decreased (to 33% at 175°C), but the tetramer to trimer ratio is increased ($\frac{8}{92}$ at 140-145°C. to $\frac{45}{55}$ at 175°C).

*sym $C_2H_2Br_4$ is used for medium.

The compounds $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$ and $P_3N_3Cl_2Br_4$ have been prepared by similar reactions(18).

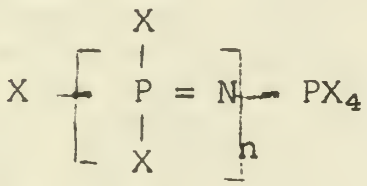
4. Linear phosphonitrilic halides

This homolog series, i.e., $(PNX_2)nPX_5$ is neither well defined nor understood. In fact, only two members had been prepared and purified, viz., R_2NCl_7(8,9), and P_2NCl_7(12).

The compound P_2NBr_7 can absorb Br_2 reversibly as follows

$$\underset{\text{yellow}}{P_2NBr_7} \xrightarrow[80^{\circ}-100^{\circ}C]{Br_2} \underset{\text{red}}{P_2NBr_9} \xrightarrow[\text{stand at room}]{Br_2} \underset{\text{red}}{P_2NBr_{9+x}}$$

Presumably the homologs, $(PNX_2)nPX_5$, exist as



$$X-\left[\underset{X}{\overset{X}{P}}=N\right]_n-PX_4$$

B. Oxygen compounds

Hydrolysis(23) and alcoholysis(17) reactions have been carried out using the trimeric and tetrameric chlorides,

$$(PNCl_2)n + nH_2O \rightarrow Pn(NH)nOn(OH)n$$
$$n=3,4$$

$$(PNCl_2)n + \left\{\begin{array}{l}NaOR\\ \text{or } ROH\end{array}\right. \rightarrow [PN(OR)_2]n$$

$$R=Me,\ Et$$

C. Nitrogen compounds

The azide, $[PN(N_3)_2]_3$, has been prepared(10). It has a surprisingly high thermal stability and low melting point.

The hydrazide, $[PN(N_2H_3)_2]_3$, can be obtained(13), by reaction of the trimeric chloride nitric anhydrous N_2H_4 in anhydrous ether. It forms crystalline derivatives with aldehydes.

The preparation of the completely ammonated derivatives presented a challenge. deFiequelmont found(6) that exhaustive ammonation of $(PNCl_2)_3$ will lead to the formation not of the completely ammonated phosphonitrilic ring, but to (PN-NH)n - a phospham. It has recently been shown(1) that $(PNCl_2)_{3,4}$ with liquid ammonia under pressure will yield completely ammonated phosphonitrilics. Under the influence of heat, these compounds lose ammonia, giving phospham.

The isocyanates have also been prepared and investigated(24).

D. Carbon compounds

The reaction between $\text{Ø}PCl_4$ and NH_4Cl gives(22) a mixture of two different compounds, both analyzing as $[PN\text{Ø}Cl]_4$ (melting points, 148° and 248°C). Both can be hydrolyzed to give exclusively phenylphosphinic acid, indicating that the phosphorus atoms are symmetrically substituted by phenyl groups. This information leads to the suggestion that these compounds are stereoisomers.

Searle, (20) in allowing $(CH_3)_2PCl_3$ to react with NH_4Cl, obtained in small yields some trimeric and tetrameric methyl phosphonitriles, which are soluble in H_2O, and do not polymerize upon heating.

III. TRIMERIC AND TETRAMERIC PHOSPHONITRILIC RING STRUCTURE

A. Structural data

X-ray data (27) indicate that to within experimental accuracy, all the P-N bonds in $(PNCl_2)_3$ are equal (1.61±0.04Å). This low value (compared to 1.78Å in $NaHPO_3NH_2$) suggests the bond order to be somewhat higher than unity.

Thermodynamic calculations made by Hartley(11) also showed a high bond order, as indicated by his calculated bond energy of 75-80 Kcal/mole for the P-N bond in both the trimer and tetramer.

A two-dimensional Fourier and difference synthesis followed by three-dimensional least-square refinement(27) showed that $(PNCl_2)_3$ molecules actually exist as puckered rings in crystals, even though in vapor phase and solution they are most probably planar as indicated by infrared and Raman studies(5). The infrared frequency stretching of the P-N bond in the ring is virtually independent of the mass of the groups attached to the ring, but it does increase(decrease) considerably when the electronegativity of the substituents decreases(increases)(11,14).

Tetrameric phosphonitrilic chloride molecules have a puckered ring structure in crystals. This has recently(25) been shown to be of the boat form, whereas the corresponding fluoride has the chair form. In solution and in the vapor phase, there are indications that the boat, planar, and chair forms are all energetically comparable(14).

Infrared data are given in the Table of Physical Constants.

B. Interpretation and discussions

All evidence requires that there be some π-bonding between the phosphorus and nitrogen atoms. Since the phosphorus atoms have already used sp^3 hydridization to form four σ-bonds, they evidently must use d orbitals for π bonding. Thus most recently all authorities in this field agree on the fact that the π-bonding in the ring is of the type $p\pi$-$d\pi$, in contrast to the $p\pi$-$p\pi$ system in the carbocyclic or B-N rings.

From here there are two different theories to account for the rest of the experimental data. The first is that by Craig and Paddock(4), suggesting aromaticity in the ring, i.e. the electrons are delocalized around the ring, or in other words the six atomic orbitals combine to give six molecular orbitals. Paddock stated (16), "....$(PNCl_2)_3$ is like benzene in having resonance of a Kekule type structure and also aromaticity..." and "... Not only, therefore, do the phosphonitrilics exhibit aromatic character, but they do so under conditions which allow much more freedom to the shape and size of the molecule than is possible in the carbocyclic series..."! The second theory is that of Dewar, Lucken, and Whitehead(7), who suggested that actually a localized P-N-P 3-centered type π-bond is energetically favored, this in effect will allow distortion of the ring from planarity without involving loss of resonance energy.

III. TRIMERIC AND TETRAMERIC PHOSPHONITRILIC RING STRUCTURE.

A. Structural Data

[illegible] (57) reports, that to within experimental accuracy, all the P-N bonds in (PNCl$_2$)$_3$ are equal (1.60±0.01Å). This low value (compared to 1.78Å for a single bond) suggests the bond order to be somewhat higher than unity.

Thermodynamic calculations made by Hartley(71) also showed a high bond energy, in comparison to his calculated bond energy of [illegible] kcal/mole for the P-N bonds in [illegible] and [illegible].

A two-dimensional Fourier and difference synthesis followed by three-dimensional least-squares refinement(43) showed that (PNCl$_2$)$_4$ molecules actually exist as puckered rings in crystals, even though in vapor phase and solution they are most probably planar as [illegible] studies(?). The infrared frequency corresponding of the P-N bond in the ring is virtually independent of the nature of the groups attached to the ring, and it does increase considerably when the electronegativity of the substituents increases(3)(13)(14).

Tetrameric phosphonitrilic chlorides are known to have a puckered ring structure in crystals. This has recently(85) been shown to be of the bath form, whereas the corresponding fluoride has the chair form. In solution and in the vapor phase, there are indications that the boat, planar, and chair forms are all conformationally interconvertible.

Infrared data are given in the Table of Physical Constants.

B. Delocalization and Distortion

All evidence indicates that there is some π-bonding between the phosphorus and nitrogen atoms. Since the phosphorus atoms have already used sp^3 hybridization to form σ-bonds, they evidently must use d orbitals for π bonding. Thus most reports find substantiation in this light by the fact that the π-bonding in the ring would not be planar, in contrast to the π-system in the carbocyclic or B-N rings.

From here there are two different theories to account for the rest of the experimental data. The first in time is by Craig and Paddock(?), suggesting delocalization in the ring, i.e., the electrons are delocalized around the ring, which, with the six atomic orbitals, [illegible] the molecular orbitals. Paddock stated (101), "...(PNCl$_2$)$_3$ is thus unique in having resonance of a Kekulé type structure and also aromaticity..." and "... not only, therefore, do the phosphonitriles exhibit aromatic character, but they do so under conditions which allow much more freedom to the shape and size of the molecule than is possible in the carbocyclic series..." The second theory is that of Dewar, Lucken, and Whitehead(?), who suggests that actually a localized P-N-P 3-centered type π-bond is energetically favored, and the effect is the distortion of the ring into a nonplanar form without involving loss of resonance energy.

We must bear in mind, however, that the 3d orbitals of the phosphorus atom are ordinarily too diffused to bond effectively with the 2p orbitals of the nitrogen atom. Indeed, unless we have extremely electronegative groups like fluorine or chlorine on the phosphorus atom, the stabilization energy is not very large. (This is indicated by the difference between the P-N stretching frequency in the ring compound and that of a single P-N bond (ie., of about 750 cm^{-1} as in $NaHPO_3NH_2$).

IV. CONCLUSION

From the above suggestion of π-stabilization, together with the presumed fact that substitution reactions on the ring are of SN2 type, we can quite safely conclude that the original goal of this line of research, i. e. - the formation of an inert and thermally-stable high polymer, can be abandoned. In its place will grow a fascinating field of theoretical research on this new pπ-dπ type ring system.

TABLE OF PHYSICAL CONSTANTS

Section	Compound	Melting Point, $^{\circ}$C.	Boiling Point, $^{\circ}$C.	$\bar{\nu}$ P-N, Cm^{-1}
II-A-1	$P_3N_3Cl_6$	114	256.5	1218
	$P_4N_4Cl_8$	123.5	188	1305
	$P_5N_5Cl_{10}$	41	223-224/13mmHg	1325
	$P_6N_6Cl_{12}$	91	261-263/13mmHg	1324
	$P_7N_7Cl_{14}$	237.5	289-294/13mmHg	
	rubber	-	-	1365-1380
II-A-2	$P_3N_3F_6$	27.1	51.8	1287
	$P_3N_3F_4Cl_2$	-	115-117	1322
	$P_3N_3F_2Cl_4$	-	140-142	
	$P_4N_4F_8$	30.4	80.7	
	$P_4N_4F_6Cl_2$	-12.1	105.8	
	$P_4N_4F_4Cl_4$	-24.9	130.5	
	$P_5N_5F_{10}$	-	122/751mm.Hg	
	$P_6N_6F_{12}$	-	147	
II-A-3	$P_3N_3Cl_5Br$	123.5	-	
	$P_3N_3Cl_4Br_2$	136.5	-	
	$P_3N_3Cl_2Br_4$	167	-	
	$P_3N_3Br_6$	191	-	1186
	$P_4N_4Br_8$	202	-	1277
II-B	$P_3N_3(OMe)_6$	-	-	1275,1235
	$P_4N_4(OMe)_8$	-	-	1337
II-C	$P_3N_3(N_3)_6$	$<$-20	$\sim$ 250	
	$P_3N_3(N_2H_3)_6$	-	-	1218
	$P_3N_3(NH_2)_6$	-	-	1175
	$P_4N_4(NH_2)_8$	-	-	1240
	$P_3N_3(NCS)_8$	41-42	-	
	$P_4N_4(NCS)_8$	90	-	
	$P_4N_4\text{Ø}_4Cl_4$	148	-	1292
		248	-	1313,1294,1282
	$P_3N_3(CH_3)_6$	-	-	820

REFERENCES

1. Audrieth, L. F., Steinman, R., and Toy, A.D.F., Chem. Revs. 32, 109 (1943).
2. Besson, A., Compt. rend., 114, 1179 (1892).
3. Bode, H., Z. anorg. u. allgem. Chem., 252, 113 (1943).
4. Craig, D.P., and Paddock, N.L., Nature, 181, 1052 (1958).
5. Daasch, L.W., J. Am. Chem. Soc., 76, 3403 (1954).
6. deFiequelmont, A.M., Compt. rend., 200, 1045 (1935).
7. Dewar, M.T.S., Lucken, E.A.C., and Whitehead, M.A., J. Chem. Soc., 1960, 2423.
8. Goehring, M., and Heinke, J., Z. anorg. u. allgem. Chem., 278, 53(1955).
9. Groeneveld, W.L., Visser, J. H., and Senter, A.M.J.H., J. Inorg. Nucl. Chem., 8, 245(1958).
10. Grundman, C., and Ratz, R., Z. Naturforsch., 10b, 116-7(1955).
11. Hartley, S.B., Bulletin, Albright and Wilson Mfg. Ltd., Research Dept.
12. John, K., and Moeller, T.,J. Am. Chem. Soc., 82, 2647(1960).
13. John, K., Tsang, F., and Moeller, T., Chem. and Ind. (To be published).
14. Paddock, N.L., The Phosphonitrilic Fluoride (presented at the International Symposium on Fluorine Chemistry, July 1959), Albright and Wilson Mfg. Ltd. Research Dept.
15. Paddock, N. L., J. Chem. Soc., 1960, 3608.
16. Paddock, N.L., Research, 13, 94(1960).
17. Ratz, R., and Hess, M., Ber., 84, 849(1951).
18. Rice, R.G., Daasch, L.W., Holden, J.R., and Kohn, E.L., J. Inorg. Nucl. Chem., 5, 190(1958).
19. Schmitz-Dumont, O., and Malter, M., Z. anorg. u. allgem. Chem; 298, 193(1959).
20. Searle, H.T., Proc. Chem. Soc., 1959, 7.
21. Seel, F., Z. anorg. u. allgem. Chem., 295, 316(1958),
22. Shaw, R.A., and Stratton, C., Chem. and Ind., 1959, 52.
23. Stokes, H.N., Am. Chem. J., 18, 78(1896).
24. Tesi, G., Otto, R.J.A., Sherif, F.G. and Audrieth, L.F., J. Am. Chem. Soc., 82, 528(1960).
25. Tromans, F.R., Bulletin, Albright and Wilson Mfg. Ltd. Research Department.
26. Tullock, C.W., and Coffman, D.D., J. Org. Chem. 25, 2016(1960).
27. Wilson, A., and Corroll, D.F., J. Chem. Soc., 1960, 2548.

GENERAL REFERENCE:

Emeleus, H.J., and Sharpe, A.G.(editors), Advances in Inorganic Chemistry and Radiochemistry, Academic Press, New York and London, 1959.

INTERNAL ROTATION IN INORGANIC CHEMISTRY

Donald A. Bafus March 7, 1961

I. THE ORIGIN OF THE BARRIER TO INTERNAL ROTATION.

Restricted rotation about a single bond was found to occur in a molecule nearly 30 years ago. The first measurements were made in 1932 on ethane, and a barrier of 0.36 kcal./mole was found to exist in the molecule.

In an attempt to explain theoretically the origin of the barrier, Eyring(1) applied quantum mechanics to the problem, assuming a simple type of interaction between the hydrogen atoms. The value obtained agreed very well with the experimentally determined value, and thus the fundamental problem of the barrier to internal rotation seemed to be solved. Some six years later, a more nearly accurate determination of the specific heat required that the height of the potential barrier be about 3 kcal./mole which is about ten times as large as that obtained originally. This instigated further theoretical considerations of the origin of the barrier to internal rotation about a single bond.

In 1939, Gorin, Walter, and Eyring(2) attempted to treat the barrier to internal rotation by refined quantum mechanical calculations, but met with no appreciable success.

In the years between 1939 and 1948, no significant theoretical contributions were made in this area.

In 1948, Lassettre and Dean(3) proposed a qualitative explanation for the barrier to rotation, which was based on dipole and quadrupole interactions in the molecule. They followed this in 1949 with a quantitative treatment along this line. However, the quadrupole moments obtained have been criticized as overly large and probably an artifact of the type of multipole expansion used in this treatment.

In 1951, Oosterhoff(5) proposed what appeared to be a better explanation for the barrier to internal rotation. He calculated the coulbmb interactions of protons and spherical electronic clouds and also included octapole moments. He adjusted the quadrapole moments to fit the barrier of rotation and proceeded to calculate the barriers to rotation of some molecules. He found that the barrier to rotation in ethane could be explained only if the C-H bond were surprisingly ionic in character.

In 1952, van Dranen(6) and, later in 1955, Mason and Kreevoy(7) attempted to calculate the importance of van der Waal's repulsion to the barrier and found that it could account for only a small fraction of the barrier which is observed.

Direct simple Coulomb calculations of electrostatic interactions based on spherical charge distributions permit a rough representation of the actual situation and give the maximum possible value for a purely electrostatic barrier.

If direct repulsions between atoms were important, the atoms would be pushed back as the internal torsion brings them opposite to one another. This has been treated in a very general way by Kivelson(8), and his formulas can be applied to many molecules

Derivatives of the hindering potential with respect to the various molecular coordinates can be obtained. This type of analysis can show that moving the atoms near the bond about which the internal rotation is occuring has less effect on the barrier than changing the length of the axial bond.

The conclusion that Wilson(9) came to in considering the above arguments is that the barrier to rotation must be an inherent property of the axial bond and not due to the direct forces between attached atoms or to those parts of the electron distribution which are out on the attached bond at any considerable distance.

In 1958, Pauling(10) suggested that the barrier to internal rotation was due to the contribution of higher orbitals, such as the *d*- and *f*-orbitals, to the bond about which the rotation is occuring. One serious criticism of this postulate is that these orbitals are at too high an energy above the others to make any significant contribution. However, rough calculations made on some molecules give reasonable agreement with the experimental values and give indication that there might be some contribution from these high orbitals.

It can be concluded from the above arguments that there is at present no satisfactory theoretical explanation for the barrier to internal rotation about a single bond.

II. METHODS AVAILABLE TO STUDY THE BARRIER TO INTERNAL ROTATION.

There are several methods available to determine the energy differences between rotational isomers and which of these isomers is the most stable of the species. Such methods include infrared, Raman, and nuclear magnetic resonance spectroscopy in the gas and liquid phases; x-ray diffraction in the solid state; and electron diffraction in the gas phase. However, there are only a few which lend themselves to the determination of the *height* of the barrier to internal rotation.

The classical method, which has been used until recently developed instrumental methods, and by far the most generally applicable, is that of determining the entropy of the material and comparing it to the calculated third law entropy. The third law entropy assumes free rotation about the bonds, whereas the measured entropy measures the actual entropy of the material. Thus the difference between these values should be the entropy due to restricted rotation. From this the barrier to rotation can be calculated.

Microwave spectroscopy was discovered in 1934, but very little use was made of this method until after World War II. This has become a very important tool in the determination of the barrier to internal rotation. The major drawbacks to this method are that the material must have a permanent dipole moment and must be in the gas phase. An excellent review article on the application of microwave spectroscopy to determine the barrier to rotation is given by Lin and Swalen(11).

If direct repulsions between atoms were important, the atoms would be pushed back as the internal rotation brings them nearer to one another. This has been treated in a more general way by Eliason(10), and his treatment can be applied to many molecules.

Derivatives of the hindering potential with respect to the various molecular coordinates can be obtained. This type of analysis has shown that moving the atoms near the bond about which the internal rotation is occurring has less effect on the barrier than changing the length of the axial bond.

The conclusion that Eliason(10) came to in considering the above arguments is that the barrier to rotation must be an inherent property of the axial bond and may not be due to the direct forces between attached atoms or to those parts of the electron distribution which are out on the attached atoms if an investigation are made.

In 1950, Pauling(11) suggested that the barrier to internal rotation was due to the contribution of [illegible] character, such as the d- and f-orbitals, to the bond about which the rotation is occurring. Further refinement of this approach [illegible] [illegible] [illegible] it is found [illegible] [illegible] contribution from these high orbitals.

It can be concluded from the above arguments that there is at present no satisfactory theoretical explanation for the barrier to internal rotation about a single bond.

II. Methods Available for the Study of Internal Rotation.

There are several methods available to determine the energy differences between rotational isomers and which of these isomers is the most stable of the species. Such methods include infrared, Raman and nuclear magnetic resonance spectroscopy in the liquid state, electron diffraction in the solid state and electron diffraction in the gas phase. However, these methods, of course, give little information in the determination of the height of the barrier to internal rotation.

The classical method, which has been most widely used [illegible] for the most generally applicable, is that of determining the entropy of the material and comparing it to the calculated third law entropy. The third law entropy assumes free rotation about the bonds, whereas the measured entropy comprises the actual motions of the molecule. Thus the difference between these entropies should be the entropy due to restricted rotation. From this the barrier to rotation can be calculated.

Microwave spectroscopy was established in 1934, but very little use was made of this method until after World War II. This has proven a very important tool in the determination of the barrier to internal rotation. The major drawback to this method has been its restriction to molecules with a permanent dipole moment and to the gas phase. An excellent review article on the application of microwave spectroscopy to determine the barrier to rotation is given by Lin and Swalen(12).

Nuclear magnetic resonance also has been used recently to give a measure of the magnitude of barriers in liquids. Barrier heights in the range of 5 to 20 kcal./mole may be determined by measuring the widths of the resonance lines as a function of temperature. The time-scale factor of nuclear magnetic resonance is such that if the barrier height is less than about 5 kcal./mole, the internal rotation appears to be free. A treatise on the application of nuclear magnetic resonance to the determination of the barrier height is given by Pople, Schnieder, and Bernstein(12).

A recent development based upon the dispersion and the absorption of sounds waves in liquids and gases has been applied by Tabauchi(13). This method allows a rapid equilibrium which cannot be followed by the usual chemical methods to be followed. From the measurement of this equilibrium and the measurement of the relaxation time of the compound, an Arrhenius plot can be obtained, and from this the barrier to internal rotation can be determined.

III. PROPERTIES RELATED TO INTERNAL ROTATION IN INORGANIC CHEMISTRY.

There are many compounds which show the property of restricted rotation in inorganic chemistry. Among these are H_2O_2, N_2H_4, S_2Cl_2, and N_2F_4. There are other compounds the properties of which suggest such as the trans-$[Pt(SR_2)_2X_2]$ where R is some alkyl radical and X equals Cl, Br, I, and NO_2.

Giguere, et al.(14) have determined the calorimetric barrier to internal rotation and in hydrogen peroxide and found that it is approximately 3.5 kcal./mole. Giguere and Bain(15) have used the infrared spectrum of hydrogen peroxide to determine the value of the barrier to be 4.7 kcal./mole. In contrast to these two values, Massey and Bianco(16) determined the barrier to rotation to be 0.32 kcal./mole by the method of microwave spectroscopy, which is probably the more nearly correct value for this barrier. Inaddition to determining the height of the barrier, Massey and Bianco determined the value for the dihedral angle and found the value to be 95±10 degrees.

Hirota(17), using electron diffraction, infrared, and Raman Spectroscopy, has investigated by S_2Cl_2 and S_2Br_2. He found the values of the dihedral angles to be 82.5° and 83.5° for sulfur monochloride and sulfur monobromide respectively. The barrier to internal rotation which he observed for S_2Cl_2 is on the order of 17 kcal./mole. This value seems to be quite high if it is compared with the value for H_2O_2.

Linde and Mann(18) have investigated the microwave spectrum of N_2F_4 and have tenatively identified the peak due to the torsional vibration. They feel that this peak is not for the molecule in the ground state, but rather in some higher vibrational state, and thus conclude that the barrier to internal rotation must be at least 3 kcal./mole. They also determine the dihedral angle for this molecule to be 65±2°.

Several other inorganic molecules have been investigated and barriers to internal rotation have been determined, as well as the dihedral angle, these are HNO_3(19), CH_3BF_2(20), B_2Cl_4(21), H_2S_4(22), and Si_2Cl_6(23).

Another [illegible] technique that has been used recently to give a measure of the [illegible] of [illegible] in [illegible] is the [illegible] of the [illegible] as a function of temperature. [illegible] factor of [illegible] (31).

A recent development [illegible] the dispersion and the absorption of [illegible] in [illegible] and [illegible] has been applied by [illegible]. From the measurement of the [illegible] and the measurement of the [illegible] time of the [illegible] and from this the [illegible] can be determined.

(ii). [illegible]

There [illegible] very few [illegible] about the presence of [illegible] There [illegible] Cl, Br, I, [illegible]

[illegible] et al. [illegible] have [illegible] the calculated [illegible] and found that it is approximately [illegible] kcals./mole. [illegible] the infrared spectrum of [illegible] the value of the [illegible] to be [illegible] kcals./mole. [illegible]

[illegible](17), [illegible] Raman spectroscopy, has investigated [illegible] he found the values of the [illegible] respectively. [illegible] This [illegible]

[illegible] have [illegible] the [illegible] vibrations. They [illegible] kcals./mole. They also [illegible]

Several other [illegible] have been given [illegible] these are [illegible] (21), [illegible] (22).

Another interesting application of internal rotation to inorganic molecules is to the Pt(II) complexes mentioned above. All the trans-complexes of the compound with thioethers have dipole moments between 2.2 and 2.5 D., which is in contrast to the phosphine complexes which have zero dipole moment. The possibility of restricted rotation about the axial S-Pt-S bond, with a favored orientation of the thioether groups with respect to one another, could very easily account for the rather large dipole moments of these molecules.

REFERENCES

1. H. Eyring, J. Am. Chem. Soc., 54, 3191 (1932).
2. E. Gorin, J. Walter, and H. Eyring, J. Am. Chem. Soc., 61, 1876 (1939).
3. E. N. Lassettre and L. B. Dean, J. Chem. Phys., 16, 151(1948).
4. E. N. Lassettre and L. B. Dean, ibid., 17, 317 (1949).
5. L. Oosterhoff, Discussions Faraday Soc., 10, 79 (1951).
6. J. van Dranen, J. Chem. Phys., 20, 1982 (1952).
7. E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc., 77,5808 (1955).
8. D. Kivelson, J. Chem. Phys., 22, 1733 (1954); 23, 2230, 2236 (1955).
9. E. B. Wilson, Jr., Proc. Nat. Acad. Science, 43, 816 (1957).
10. L. Pauling, Proc. Nat. Acad. Sciences, 44, 211 (1958).
11. C. C. Lin and J. D. Swalen, Rev. Mod. Phys., 31, 841 (1959).
12. J. A. Pople, W. G. Schnieder, and H. J. Berstein, High-resolution Nuclear Magnetic Resonance. McGraw-Hill Book Co., Inc. New York 1959.
13. D. Tabauchi, J. Chem. Phys., 28, 1014 (1958).
14. P. A. Giguere, I. D. Lin, J. S. Dugsdale, and J. A. Morrison, Can. J. Chem., 32, 117 (1954).
15. O. Bain and P. A. Giguere, Can. J. Chem., 33, 527 (1955).
16. J. T. Massey and D. R. Bianco, J. Chem. Phys., 22, 442 (1954).
17. E. Hirota, Bull. Chem. Soc. Japan, 31, 130 (1958).
18. D. R. Linde, Jr., and D. E. Mann, J. Chem. Phys., 31, 1129 (1959).
19. A. Palm and M. Kirkpatrick, J. Chem. Phys., 23, 1562 (1955).
20. R. E. Naylor, Jr., and E. B. Wilson, Jr., J. Chem. Phys., 26, 1057 (1957).
21. D. E. Mann and L. Fano, J. Chem. Phys., 26, 1665 (1957).
22. F. Feher and R. Schulze-Rettmer, Z. anorg. allgem. Chem., 295, 262 (1958).
23. Y. Morino and E. Hirota, J. Chem. Phys., 28, 185 (1958).

Another interesting [illegible] molecule [illegible]

REFERENCES

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THE CHEMISTRY OF POLONIUM

Raymond Longhi

March 14, 1961

I. INTRODUCTION

In 1898, while attempting to account for an unknown source of "excess activity" present in pitchblende ores, Mme. Curie discovered polonium (1). Processing extremely large quantities of uranium ore enabled her to concentrate this very active material by precipitation with bismuth, after which a rough separation was achieved by fractional precipitation of bismuth hydroxide followed by a vacuum fractional sublimation of the sulfides. This work was an amazing chemical achievement since pitchblende ores contain only approximately 0.1 mg. of polonium per ton. The new element was named for her native Poland (2), but the term "radioactivated bismuth" persisted for some time (3).

II. METALLIC POLONIUM

Twenty-two isomers of element number 84 (mass numbers ranging from 196 to 218) are known, but the most common is the α-emitter of half-life 138.4 days and mass number 210, which is found in radioactive equilibrium with Ra^{226} in all uranium minerals (4). The atomic weight of this species has been calculated to be 209.990±0.002 (5), and is most frequently used in chemical studies since it may be prepared in milligram quantities by the bombardment of $^{209}_{83}Bi$,

$$^{209}_{83}Bi \xrightarrow{(n,\gamma)} {}^{210}_{83}Bi \xrightarrow[5\ \text{days}]{B^-} {}^{210}_{84}Po$$

The longer-lived isotopes of mass number 208 and 209 would be better for chemical work because their respective half-lives of 3 years and 100 years result in lower activity, but unfortunately they can only be prepared in very small quantities (6). The other isotopes are short-lived, and no evidence for an inactive species exists (7).

The metal may be prepared by vacuum sublimation of electrodeposited material (usually on Au or Pt). When pure, it has a silvery appearance. X-ray diffraction studies indicate two allotropic forms: The α-form is simple cubic and the β-form is rhombohedral (8). The temperature limits for phase coexistence have been established (9), but these appear to be a function of the sample size and its history. The metal can also be prepared from the hydroxide or tetrachloride (10).

$$\text{o}(OH)_4^+ \left\{ \begin{array}{ll} 1. & NH_2OH \\ 2. & Aq.NH_3 \\ 3. & \text{Anhyd. } NH_3 \\ 4. & N_2H_4 \\ 5. & \text{Sodium Dithionate} \end{array} \right] \longrightarrow Po \longleftarrow \left[\begin{array}{ll} 1. & Alk.SnCl_2 \\ 2. & TiCl_3 \\ 3. & \text{Sodium} \\ & \text{Dithionate} \\ & \text{in } HCl \end{array} \right\} + Po(Cl)_4$$

In the metallic state polonium resembles bismuth, lead, and thallium as closely as it does tellurium. It is easily mistaken for lead, being easily scratched, rather soft, and of the same color.

By analogy with tellurium, one would expect a Po(VI) valence state, but evidence for its existence is inconclusive and subject to question. Polonium forms a disulfate whereas tellurium does not, and the "extremely unstable hydride" of the former remains a subject for debate in the literature. With the exception of the dioxide, most polonium compounds exhibit high vapor pressures and many can be sublimed at atmospheric pressure below 100°C (14). However, a number of analogies can be made with respect to the periodic position of the element in Group VI (4,12,13).

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Density	1.27	2.06	4.82	6.75	9.20±0.17
M.P., °C.	-218.9	119.0	217.4	449.8	262±5
B.P., °C.	-187.96	444.6	684.8	1390	962±2
Covalent Radius, Å	0.74	1.04	1.17	1.37	1.53
First I.P., v.	13.614	10.357	9.750	9.01	8.43
Crystal Radius for X^{+6} in XO_4^{-2}, Å.	0.09	0.29	0.42	0.56	0.67
$E^0(H_2X \rightarrow X+2H^+ +2e^-)$	-0.815	-0.14	+0.42	+0.56	+0.67
$E^0(X+2e^- \rightarrow X^{-2})$	-----	-0.48	-0.92	-1.14	-1.1±0.3

Polonium can be separated from sulfur, selenium, and tellurium by anion-exchange chromatography of the chloride complexes (15). The sample is oxidized with fuming nitric acid, evaporated to dryness, and after being dissolved in 12$\underline{N}$HCl, is passed over a strongly basic Dowex resin.

Elution Order	Element	Eluent	Determined As
First	Sulfur	12$\underline{N}$HCl	Sulfate with barium
Second	Selenium	6$\underline{N}$HCl	Free selenium after SO_2 reduction
Third	Tellurium	2$\underline{N}$HCl	Free tellurium after SO_2 reduction
Fourth	Polonium	1$\underline{N}$$HClO_4$ or 1$\underline{N}$$HNO_3$	By electroscope methods

III. BIOLOGICAL CONSIDERATIONS

Since polonium is essentially a pure α-emitter, normal radiation shielding is not required. However, due to the high volatility of its compounds, very stringent laboratory controls are necessary. By international agreement, the maximum permissible body burden for ingested Po^{210} is 4.5×10^{-12} gram (0.02 μc)(3,16). Most chemical studies are done with quantities representing 5×10^7 this tolerance. All work is performed in sealed low-pressure dry-boxes, but additional gloves and special clothing must be worn since polonium is capable of penetrating natural rubber or neoprene (3). Eating and smoking are strictly prohibited in the laboratory, and daily radiation checks

are essential. The high specific α-activity of 10^{13} disintegrations per minute per milligram of polonium (4) also creates numerous problems. Within a few days glassware becomes etched and very fragile. Closed-system work (x-ray tubes) is extremely dangerous since sealed capillaries may develop pressures up to six atmospheres in the course of a week. Hydrated compounds explode within a matter of hours (3), and most compounds are capable of oxidizing nitrogen in the air to form basic nitrates (17).

With the exception of accidental human exposure, biological studies are limited to animal observations. Polonium is absorbed to a considerable extent through the skin, but oral or blood stream ingestions are the most critical (18). Upon ingestion one observes destruction of white blood cells (13) and a reduction of blood sugar and glycogen content (19), combined with severe epithelial tissue damage in the spleen, kidney, and intestinal areas (20). The lowest polonium contents are found in the brain. Daily ingestions of two micro curies (4.5×10^{-10} gram) result in death within 170 to 290 days (21) with massive tissue damage and severe hemorrhaging being characteristic of the late stages. Most ingested polonium concentrates in the red cells of the blood with 90-97% of it associated with the hemogloben (13,22). It is reported that polonium compounds are not passed on to offspring since they are unable to penetrate the fetal membrane during pregnancy (13). The possible role of this element as a source of leukemia, bone, and lung cancer has been reviewed (23) as well as treatment procedures following human exposure at the critical level (24).

IV. COMPOUNDS

Because of its position in Group VI, one would expect polonium to exhibit valence states of -2,+2,+4, and +6. The +4 state is the most frequently observed, and the +6 state is somewhat questionable. Recently this species was proposed on the basis of electrochemical studies, and an E^0 for Po(IV)/PoVI of 1.5 v.was reported (25). However, the interpretation of electrochemical data must be treated with caution. Paneth(26) has pointed out that polonium behaves as a "zwitter-element" since it may be electrolytically deposited on, or dissolved off, both the anode and cathode.

A. Polonides

Compounds of the type MPo (where M=Be,Hg,Ni,Pb,Pt,Zn, or 2Na)(16) are generally prepared directly from the elements at elevated temperatures (300-350°C)(3).

B. Hydride

Evidence for the existence of a simple hydride is questionable. It is claimed (27) that the addition of magnesium powder to hydrochloric acid solutions of polonium produces the volatile Po[illegible]. However, Sidgwick (28) points out that if produced, this compound had a maximum yield of 0.1%, was unstable at -180°C, and had a maximum decomposition half-life of five minutes.

C. Oxides and Hydroxides

Black solid polonium monoxide is reported to be the product of decomposition of polonium sulphotrioxide or selenotrioxide (29).

Air oxidation of the pure metal produces PoO_2 (17,30), which is stable up to 900°C at 1 atm. pressure, does not have an observable vapor pressure at room temperature, and exists in two phases (tetragonal and face-centered cubic). Its chemistry resembles that of TeO_2, and treatment with acids produces quadrivalent salts (i.e., H_2SO_4 gives $2PoO_2 \cdot SO_3$, and H_2SeO_4 gives $2PoO_2 \cdot SeO_3$). These compounds may also be prepared from the tetrachlorides (31). No evidence for a trioxide has been reported, although its existence has been suggested by trace electrodeposition studies (29). The compound $PoO(OH)_2$ has been described. Although it is much less acidic than tellurous acid, reaction with potassium hydroxide yields K_2PoO_3 (16,32). A yellow compound of the formula $Po(OH)_4$ is obtained by treating acidic $PoCl_4$ solutions with ammonium hydroxide (6).

D. Halides

Polonium does not form a volatile hexafluoride, as might be expected, and numerous reports (3,4,13,16,33,34,35,36) contain no evidence for the formation of a fluoride compound of any type.

The bright yellow solid tetrachloride is prepared either by evaporation of PoO_2 in HCl (17) or direct combination of the elements at 125-200°C (37). The ruby-red dichloride is prepared from the tetrachloride by thermal degradation in vacuum at 200°C. (35,38), hydrogen reduction at 200°C. (35), or hydrogen sulfide or carbon monoxide reduction at 150°C. (38). Continued heating produces the free metal (35,38). Both $PoCl_2$ and $PoCl_4$ give $PoCl_2 \cdot 2NH_3$ when treated with ammonia gas (4). A number of hexachloropolonites of the form M_2PoCl_6 (where M=Cs, NH_4, $(CH_3)_4N$, Rb, and K) are produced by evaporation of hydrochloric acid solutions of $PoCl_4$ and MCl_2. All are yellow solids which are isomorphous with the corresponding tellurium complexes (4,16).

The known polonium-bromine compounds are $PoBr_4$ (4,13,17,39,40), $PoBr_2$(3,4,39), $PoBr_4 \cdot XNH_3$(16), Cs_2PoBr_6, and $(NH_4)_2PoBr_6$ (39). The latter two are structurally like the corresponding tellurium compounds.

A number of preparations for PoI_4 (41) and the hexaiodopolonites of potassium and cesium (16) have been described. There is no evidence for the formation of a diiodide compound.

The solid salmon-pink $PoCl_2Br_2$ is produced by treating the dichloride with dry bromine gas (39). Neither the dichloride nor the dibromide reacts with iodine vapor, but unstable mixed halogen compounds are believed to form when they are treated with iodine in carbon tetrachloride solution (41).

E. Other Compounds

A number of other polonium compounds such as nitrates (42), sulfides (43), and organic derivatives (16) have been investigated. Lecoin (44) found that polonium metal is more volatile in carbon monoxide than in argon or nitrogen. This observation suggests the formation of a volatile carbonyl compound.

Air oxidation of the [illegible]

4\. Halides

[illegible] for the formation of a [illegible] complex of the type.

The bright yellow [illegible]

The known [illegible]

A number of [illegible]

The [illegible]

5\. Other Compounds

A number of [illegible] compounds.

Halogen Compounds of S,Se,Te, and Po (4,11,12,13)*

Type	F	Cl	Br	I
E_2X_2	S_2F_2 M=-120.5 B=-38.4	S_2Cl_2 M=-80 B=138	S_2Br_2 M=? B=90(d)	
		M=-85 Sc_2Cl_2 B=127(d)	M=? Se_2Br_2 B=(d)	
EX_2		Scl_2 M=-78 B=59(d)		
		$SeCl_2$ vapor only	$SeCr_2$ vapor only	
		M=208 $TeCl_2$ B=324	M=? $TeBr_2$ B=339	
		M=355 $PoCl_2$ B=190(s)	M=275 $PoBr_2$ B=110/30mm	
EX_4	M=-124 SF_4 B=-40	M=-31 SCl_4 B=solid only		
	M=4.5 SeF_4 B=93	M=? $SeCl_4$ B=solid only	M=(d) $SeBr_4$ B=solid only	
	M=129.6 TeF_4 B=solid only	M=224 $TeCl_4$ B=390	M=363.5 $TeBr_4$ B=414(d)	M=280(d) TeI_4 B=solid only
		M=300 $PoCl_4$ B=390	M=330 $PoBr_4$ B=360/200	M=200 (s) PoI_4 B=dec.
EX_6	SF_6 M=-50.8 B=-63.8(s)			
	M=-34.6 SeF_6 B=-46.6(s)			
	M=-37.8 TeF_6 B=-38.9(s)			
E_2X_{10}	S_2F_{10} M=-92 B= 24			
	M=-34 Te_2F_{10} B=54			

* Temperatures in °C.; M=Melting point; B=Boiling point; d=Decomposes
s=Sublimes

V. USES AND APPLICATIONS

The expense involved in the production of pure polonium has prevented its use on an industrial scale. However, it is employed in specialized cases where cost is of no concern. The metal mixed with beryllium forms an excellent neutron source virtually free from γ-radiation (3). Its action on trace quantities of fluorine allows the evaluation of this element in reference to the sodium produced (3). The use of Po^{210} in nuclear batteries (45) and specialized spark plugs has also been reported (3). Because of its high α-activity, polonium is easily followed and determined, and for these reasons it is most useful for investigations of metal transfer between electrodes in high vacuum systems (46). More uses will no doubt evolve when the element is available to academic institutions at a less prohibitive price.

VI. SUMMARY

The development of polonium chemistry is by no means complete, and much research and explaination are still necessary. It is interesting to note that our knowledge of this element noticeably exceeds that of radium in spite of the fact that both were discovered simultaneously and gram quantities of the latter have been available for the past fifty years. The stereochemistry of polonium compounds has been discussed with respect to other Group VI elements (47), and several reviews of the element, its properties, and compounds are available (3,4,13,16).

BIBLIOGRAPHY

1. M. Curie, Compt. rend., 126, 1101 (1898).
2. P. Curie and M. Curie, ibid., 127, 175 (1898).
3. K. W. Bagnall, Quart. Revs., 11, 30-48 (1957).
4. K. W. Bagnall, Chemistry of the Rare Radioelements, pp. 3-94, Butterworths Scientific Publications, London, England (1957).
5. A. H. Wapstra, J. Inorg. and Nuclear Chem., 3, 329-32 (1957).
6. H. J. Emeleus and J. S. Anderson, Modern Aspects of Inorganic Chemistry, pp. 409-10, 3rd. ed'n., Routledge and Kegan Paul Ltd., London, England (1960).
7. G. Hevesy and A. Guenther, Nature, 125, 744 (1930).
8. C. R. Maxwell, J. Chem. Phys., 17, 1288-92 (1949).
9. J. M. Goode, J. Chem. Phys., 26, 1269-71 (1957).
10. K. W. Bagnall, P.S. Robinson, and M.A.A. Stewart, J. Chem. Soc., 3426-8 (1958).
11. T. Moeller, Inorganic Chemistry, p. 482, 519, John Wiley and Sons, Inc., N.Y. (1952).
12. J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, Inorganic Chemistry, pp. 326, 346, 379, 423, 439, and 455, D. C. Heath and Company, Boston (1960).
13. H. V. Moger, Polonium, 392 pp., Office of Technical Services Department of Commerce, Washington 25, D.C. (1956). TID-5221.
14. H. Mabuchi, Bull. Chem. Soc. Japan, 31, 245-6 (1958).
15. Y. Sasaki, Bull. Chem. Soc. Japan, 28, 89 (1955).
16. R. Spence, Proc. Roy. Soc., A243, 1-14 (1957).
17. K. W. Bagnall and R. W. M. D'Eye, J. Chem. Soc., 4295-9 (1954).
18. R. J. Della Rosa and J. N. Stannard, U. S. Atomic Energy Comm., UR-519, 11 pp. (1957).

19. A. Y. Shulyatikova, Trudy Vsesoyuz. Konf. Med. Radiol., Eksptl. Med. Radiol (Moscow), 111-17 (1957), C.A., 52, 8366f (1958).
20. G. W. Casarett, U.S. Atomic Energy Comm., UR-477, 26 pp. (1956).
21. R. K. Davis, W. T. Rockhold, and D. S. Anthony, U. S. Atomic Energy Comm., MLM-961, 31 pp. (1954).
22. J. E. Campbell and L. H. Talby, Proc. Soc. Exptl. Biol. Med., 87, 221-3 (1954).
23. J. Furth and J. L. Tullis, Cancer Research, 16, 5-21 (1956).
24. D. Callihan and D. Ross, U.S. Atomic Energy Comm., ORNL-1381 (Rev.), 15 pp. (1952).
25. N. Matsuura and M. Haissinsky, J. chim. phys., 55, 475-82 (1958).
26. F. Paneth, Z. Elektrochem., 31, 572 (1925).
27. F. Paneth, and A. Johannsen, Ber., 55, 2622 (1922).
28. N. V. Sidgwick, The Chemical Elements and Their Compounds, pp. 995-7, Vol. II, Clarendon Press, Oxford, England (1951).
29. G. Hevesy and F. Paneth, Monatsh. 36, 45 (1915).
30. A. W. Martin, J. Phys. Chem., 58, 911-13 (1954).
31. K. W. Bagnall and J. H. Freeman, J. Chem. Soc., 4579-82 (1956).
32. K. W. Bagnall and J. H. Freeman, J. Chem. Soc., 2161-3 (1957).
33. F. Weigel, Angew. Chem., 71, 289 (1959).
34. H. Emeleus, A. G. Maddock, G. L. Miles, and A. Sharpe, J. Chem. Soc., 1991 (1948).
35. J. J. Burbage, Rec. Chem. Prog., 14, 157 (1953).
36. M. Haissinsky, J. chim. phys., 34, 94 (1937).
37. E. F. Joy in Polonium, Ed. by H. V. Noyer, pp. 35, 36, and 93, Office of Technical Services, Department of Commerce, Washington 25, D. C. (1956). TID-522 .
38. K. W. Bagnall, R.W.M. D'Eye, and J. H. Freeman, J. Chem. Soc., 2320 (1955).
39. K. W. Bagnall, R. W. M. D'Eye, and J. H. Freeman, J. Chem. Soc., 3959-63 (1955).
40. E. F. Joy, Chem. Eng. News. 32, 3848 (1954).
41. K. W. Bagnall, R.W.M. D'Eye, and J. H. Freeman, J. Chem. Soc., 3385-9 (1956).
42. K. W. Bagnall, D. S. Robertson, and M.A.A. Stewart, J. Chem. Soc., 3633-6 (1958).
43. K. W.Bagnall and D. S. Robertson, J. Chem. Soc., 1044-6 (1957).
44. M. Lecoin, J. chim. phys., 28, 411 (1931).
45. W. Schorr, Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, 15, 310-16 (1956).
46. P. F. Browne, Proc. Phys. Soc., 68B , 564-6 (1955).
47. S. C. Abrahams, Quart. Revs., 10, 407-36 (1956).

CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS IN INORGANIC MEDIA

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I. INTRODUCTION

The chemistry of the atoms produced in nuclear reactions is a field of radiochemistry that is not too well understood. The beginning of such studies can be traced back to 1934 when L. Szilard and T. A. Chalmers (1) irradiated ethyl iodide with neutrons and found that most of the iodine activity could be extracted with water. The conclusion they arrived at was that the iodine-carbon bond was broken when an I^{127} nucleus captured a neutron and was converted to I^{128}. The chemical effects of nuclear transformations in which the parent atom is isotopic with the product atom are referred to as Szilard-Chalmers reactions, after the discoverers. A number of general reviews are available on work that has been done in this field of radiochemistry (2,3,4,5).

II. RECOIL ENERGETICS

The chemical effects accompanying a nuclear process are the result of recoil by the atom undergoing the reaction. The (n,γ) reaction in which the product atom is isotopic with the target atom has been studied most extensively. In this process, a nucleus captures a neutron which has been slowed to thermal energies. The resultant "compound nucleus" (6) contains an excitation energy comparable to the binding energy of the neutron captured. The nucleus is then de-excited by the emission of gamma radiation. Conservation of momentum requires that when a gamma-ray leaves a nucleus it must impart an equal amount of momentum to the product nucleus. Since bond energies lie in the range of 2 to 5ev and nuclear binding energies are of the order of several Mev, bond breakage seems inevitable. A relationship between the recoil energy of an atom and the photon emitted is given by

$$E_M = \frac{536\ E\gamma^2}{M}$$

where M is the mass of the recoiling atom.

III. NEUTRON CAPTURE BY POTASSIUM PERMANGANATE

A classical example of a "hot-atom" inorganic reaction is the bombardment of potasssium permanganate with neutrons. As far back as 1940, Libby (7) performed an experiment in which Mn^{56} was produced and the products examined to determine the chemical fate of the radioactive manganese. The radioactive distribution of products was determined by counting the Mn^{56} after converting it to either MnO_2 or $KMnO_4$ and analyzing the relative activities.

Some of the conclusions that he reached are as follows:

1) In solution, nearly all of the permanganate ions bombarded are disrupted.

2) The major recoil species formed are MnO_3^{+}, MnO_2^{+3}, MnO^{+5}, and Mn^{+7}.

3) The distribution of products can be explained by a competition between hydration and oxidation in solution. The intermediates in acid or neutral solution oxidize water and are reduced to a lower oxidation state and appear as MnO_2. In alkaline solutions reactions of the types

$$MnO_3^{+} + 2OH^{-} = MnO_4^{-} + H_2O$$

or

$$MnO_3^{+} + H_2O = MnO_4^{-} + 2H^{+}$$

apparently predominate.

4) Retention (percentage of radioactivity ending up as starting material) increases in strongly acidic solution. This is explained by the ability of the exchange reaction

$$\overset{*}{Mn}O_3^{+} + MnO_4^{-} = \overset{*}{Mn}O_4^{-} + MnO_3^{+}$$

to compete with the oxidation process.

IV. THE APPLICATION OF ELECTROPHORESIS TO THE SEPARATION OF PRODUCTS

For any Szilard-Chalmers reaction, the separation of the radioactive products is of major importance. There are many advantages of electrophoresis over wet-chemical methods for analyzing products(8). By summing up the counting rates under the different peaks, a quantitative estimate of the various radioactive products is obtained. There is no loss due to experimental technique. The signs of the charges on the various product ions are apparent. The identity of the products can be ascertained by comparing their migration rates with those of known species. The parent can be readily identified by chemical tests since it is present in macro quantities.

V. THE (n,γ) REACTION IN OXYANIONS

Among the oxyanions which have been irradiated with neutrons, there is a large variation in retention (9). Also for a given anion, the retention changes as the cation is varied. Experiments using mixed crystals (10) suggest that oxygenated recoil species are formed in reactions between recoil atoms and surrounding oxyanions or dislodged oxygens.

Table I

Effect of Environment of K_2CrO_4 Crystals on Retention

Recoil Source	Diluent	Source Molecule(mole %)	%Retention
K_2CrO_4	K_2SO_4	2.77	69
K_2CrO_4	K_2BeF_4	1.56	25
K_2CrO_4	none	100	61

Although the recoil atom can find an oxygen as easily in a sulfate medium as in a chromate medium, the same thing is not possible in a $BeF_4^=$ medium. The 25% retention in the $BeF_4^=$ medium can be explained by assuming that the recoiling atom does not move far enough out of the hot zone to escape annealing effects.

When a crystalline alkali bromate is irradiated and wet-chemical methods of analysis are employed, radioactive bromine is found in both the bromide and bromate forms (11,12). Various investigators report the bromate percentage over the range of 10-20% (13). Irradiated cesium bromate analyzed by electrophoresis yielded an additional unknown species present in amounts exceeding the bromate fraction. Two recent publications (14,15) have speculated on the chemical state of this material. In contrast, neutron irradiation of crystalline potassium iodate results in the bulk of the activity appearing in the iodate phase. Wet-chemical methods of analysis and electrophoresis both indicate that the activity is distributed between IO_3^- and I^- only (16). Irradiation of alkali chlorates gives results similar to those found with bromates (17). An experiment was performed to determine whether the behavior is due to the chemical properties of the halogen or those of the crystal lattice (18). Potassium iodate was bombarded with fast neutrons to form $Cl^{38}[K^{41}(n,\gamma)Cl^{38}]$, which recoiled through an iodate medium. The results indicated that radiochlorine in an iodate lattice behaves in a manner very similar to that of radiochlorine in a chlorate lattice.

Neutron irradiations of phosphorous have been investigated by numerous workers. For the reaction $n + {}^{31}PO_4 = {}^{32}PO_4 + \gamma$ the neutron binding energy is released in the form of 20 gamma-rays of energies 3 to 9 Mev (19). Energy considerations predict that the nuclear recoil energy should produce bond rupture and chemical changes in the phosphate group. Sellers (20,21) found that the compounds tetrasodium pyrophosphate, trisodium trimetaphosphate, and disodium phosphate underwent essentially no change upon irradiation. The incompletely oxidized oxyanions such as phosphite and hypophosphite were moderately stable when exposed to neutron irradiation, and furthermore phosphate did not show any appreciable amounts of hypophosphite or phosphite in its products. Sellers thus concluded that only a small amlunt of P-O bond breakage occurs during irradiation. In contrast to the above results, Lindner and Harbottle (22) recently reported the following distribution of products upon neutron irradiation of anhydrous disodium hydrogen phosphate.

1 tripolyphosphate	12.2%
2 pyrophosphate	11.7%
3 unknown	12%
4 isohypophosphate	27.1%
5 hypophosphate	2.8%
6 orthophosphate	9.3%
7 diphosphite	7.7%
8 phosphite	8.2%
9 hypophosphite	6.2%

Both of the above workers used electrophoresis to identify their products. The only significant experimental difference was in the length of bombardment. The large variation in results can be attributed to radiation damage.

VI. THE SZILARD-CHALMERS REACTION IN COORDINATION COMPOUNDS

A limited numberof coordination compounds have been studied(23,24). One such study was the $[Co^{59}(n,\gamma)Co^{60}]$ and $[Cl^{37}(n,\gamma)Cl^{38}]$ reaction in cis- and trans-$[Co(en)_2Cl_2]NO_3$. The following table summarized the results obtained.

Table II

Product Distribution of Co^{60} Following Complex Irrodiation

Target Compound	Post Irrodiation Treatment	% as Parent	% as other Isomer	% as Co^{++}
cis-$[Co(en)_2Cl_2]NO_3$	none	3.1	0.1	88.9
trans-$[Co(en)_2Cl_2]NO_3$	none	7.3	0.1	82.3
cis-$[Co(en)_2Cl_2]NO_3$	annealed at 100° for 1 hr.	42.9	0.2	
trans-$[Co(en)_2Cl_2]NO_3$	"	48.0	0.1	

The data obtained upon analysis of the Cl^{38} activity were very similar except that 12.5% and 15% appeared in the form of the cis- and trans- parent isomers respectively. Since bond rupture should be more favorable for Cl^{38} recoil then for Co^{60} recoil, this suggests that retention is due to secondary processes rather than to a failure of the target molecule to rupture. A number of other effects are evident from examination of Table II.

When d- and l-$[Co(en)_3]NO_3$ were irradiated, the results were in agreement with those given in Table II concerning the conversion of the parent to the other isomer.

VII. CHEMISTRY OF ATOMS FORMED BY OTHER HOT-ATOM PROCESSES

A variety of nuclear reactions other than the (n,γ) reaction have been investigated. Some of these are the following:

a) Isomeric transitions involve the emission of a gamma-ray when the nucleus goes from a metastable state to the ground state with a measurable half-life. Internal conversion can be of importance in this process because of the difference in recoil energy that the product atom received. Experiments have been carried out to illustrate the fact (26).

b) Beta decay has been used to study covalent bond rupture in cerium acetylacetonate when cerium decays to praseodymium(4). Other investigators have studied the decay of $Se^{83}O_3^=$ and $Te^{132}O_3^=$ in order to determine the chemical state of the halogen produced.

c) Fission product recoil has been examined with the radioactive iodine produced in fission of U^{235}(27). Although the results are interesting, radiation damage appears to be quite large.

REFERENCES

1. L. Szilard and T. A. Chalmers, Nature, 134, 462 (1934).
2. J. E. Willard, Ann. Rev. Phys., Chem., 6, 141 (1955).
3. D. L. Baulch and J. F. Duncan, Quart. Revs., 12, 133 (1958).
4. A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, 1951, Chapter 8.
5. J. E. Willard, Ann. Rev. Nuclear Sci. 3, 193 (1953).
6. G. Friedlander and J. W. Kennedy, Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, 1960. Chapter 11.
7. W. Libby, J. Am. Chem. Soc., 62, 1930 (1940).
8. J. Jach, H. Kawahara and G. Harbottle, J. Chromatography, 1,501(1958).
9. G. Harbottle and N. Sutin, "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeléus and A. G. Sharpe, Eds., Academic Press Inc. New York, 1959, p. 271.
10. G. Harbottle, J. Chem. Phys., 22, 1083 (1954).
11. G. E. Boyd, J. W. Cobble, and S. Wexler, J. Am. Chem. Soc., 74, 4675 (1952).
12. J. W. Cobble and G. E. Boyd, J. Am. Chem. Soc., 74, 1282 (1952).
13. J. Jach and G. Harbottle, Trans. Faraday Soc., 54, 520 (1958).
14. I. G. Campbell, J. Inorg. Nuclear Chem., 15, 46 (1960).
15. G. Harbottle, J. Am. Chem. Soc., 82, 805 (1960).
16. R. E. Cleary, W. A. Hamill, and R. R. Williams, J. Am. Chem. Soc., 74, 4675 (1952).
17. K. J. McCallumaand O. G. Holmes, Canad. J. Chem., 29, 691 (1951).
18. M. Vlatkovie and A. H. W. Gten, J. Inorg. Nuclear Chem., 13, 331 (1960).
19. B. B. Kinsey, G. A. Bartholomew, and W. H. Walker, Phys. Rev., 85, 1012 (1952).

20. P. A. Sellers, T. R. Sato, and H. H. Strain, J. Inorg. Nuclear Chem., 5, 31 (1957).
21. T. R. Sato, P. G. Sellers, and H. H. Strain, J. Inorg. Nuclear Chem., 11, 84 (1959).
22. L. Lindner and G. Harbottle, J. Inorg. Nuclear Chem., 15, 386 (1960).
23. R. F. Mitchell and D. S. Martin, J. Inorg. Nuclear Chem., 2, 286 (1956).
24. H. Rauscher and G. Harbottle, J. Inorg. Nuclear Chem., 4, 155 (1957).
25. H. E. Rauscher, N. Sutin, and J. M. Miller, J. Inorg. Nuclear Chem., 12, 378 (1960).
26. G. Seaborg, G. Friedlander, and J. Kennedy, J. Am. Chem. Soc., 62, 1309 (1940).
27. D. Hall and G. N. Walton, J. Inorg. Nuclear Chem., 6, 288 (1958).

ELECTRON TRANSFER AND HETEROGENEOUS CATALYSIS

Robert L. Gerteis April 4, 1961

I. INTRODUCTION

Inasmuch most heterogeneous catalysis involves chemisorption of adsorbate on a catalytic surface, which from the observed heats of adsorption implies chemical bonding, there must be some degree of electron transfer (1). Thus, in order to understand the nature of the bond formed on chemisorption, the electron donor and acceptor properties of both the catalytic surface and the adsorbate must be known. Once something is known about the bond holding the chemisorbed species, the kinetics of the heterogeneous process may be considered. These kinetics are presumed to involve three steps: (1) the adsorptio of the reactants on the surface of the catalyst; (2) the surface rearrangement of the reactants; and (3) the desorption of the products (2). Two mechanisms have been proposed for the surface reaction or rearrangement. The Langmiur mechanism considers all the reactants and the products to be in the primary chemisorbed layer (3), whereas the Rideal mechanism considers the reaction as occurring between one of the reactants in a primary layer and the second reactant in a secondary layer which is held by van der Waals' forces and possibly by weak valence forces (4).

Since this broad subject has been covered in a seminar which was given two years ago (5), the theory will be reviewed only very briefly, and experimental methods and recent work will be emphasized.

II. THEORY OF GAS ADSORPTION

Physical adsorption, in which the adsorbate is held to the surface of the solid by van der Waals' forces, and chemisorption, in which either ionic or covalent bonds are formed, are the two general types of gas adsorption. Experimentally the difference between these two is not well defined; however, physical adsorption is believed to involve energies of the order of less than 10 kcal. per mole whereas chemisorption is believed to involve energies greater than 20 kcal. per mole (6). In the light of the two main theories which deal with bonding between metallic atoms in the solid state, the nature of the bonding of the adsorbate to a solid surface becomes clearer. The energy band theory (Bloch and Brillouin) considers the valency electrons of the metal as all moving freely through a lattice of positively charged cores which provides a periodic potential field rising abruptly at the surface of the metal (7). Pauling's valence bond theory considers the metal lattice in terms of sp hybrid bonds which possess a varying amount of p character (8). In band theory, the (n+1)s and nd levels broaden into overlapping bands, so that the party empty d-levels of the metal atom give rise to holes in the d-band, which can be measured from magnetic data. The valence bond theory permits a

maximum of six electron pairs in the d^2sp^3 or d^3sp^2 orbitals. Pauling has calculated empirically the percent d character of transition metals from bond lengths (8). An inverse relationship between the percent d character and the bond energies of chemisorbed hydrogen has been observed for a series of transition metals (9).

III. EXPERIMENTAL METHODS

In order to study the electronic interaction between the adsorbate and the surface under the simplest of conditions, it is necessary to carry out experimental work with rigorously cleaned metal surfaces, preferably at liquid nitrogen temperatures. These conditions most nearly meet the requirements fro ideal adsorption, i.e., monolayer of adsorbate, isolated reaction sites, and absence of foreign species which can modify the electronic interaction between the metal surface and the adsorbate. Rigorously cleaned metal surfaces are prepared by flashing metal filaments (10), depositing metal films from the vapor phase (11), and bombarding solid surfaces with positive ions (12). By measuring changes which oocur on adsorption in the dipole moment (13), work function (14), resistance (15), and magnetic properties (16) of the metal, one can gain some insight as to the nature of the electronic interaction. The great differences observed in the work function for emission from different planes by field emission studies (17), the different growth rate observed for different bands in the infrared spectrum of CO chemisorbed on Pd (18), and the mass spectra data from the exchange of one to four hydrogen atoms of ethane with deuterium (19) indicate that the assumption that all reaction sites at the surface are equivalent is fallacious. Also the techniques of electron paramagnetic resonance (20, 21) and nuclear magnetic resonance (22) have been used. Recently a relationship between the number of valence electrons associated with CO chemisorbed on different metal surfaces and the infrared wave number of the CO band has been observed (23). The investigation at liquid helium temperatures of the electron paramagnetic resonance of silicon shows a line associated with the silicon surface which appears when the surface of the sample is mechanically damaged (21). Finally, diffraction patterns of low energy electrons, produced by a crystal surface, indicate the structure of monolayers of adsorbed gases (24).

IV. RECENT ADVANCES IN THE CATALYSIS OF HYDROGENATION REACTIONS

In a series of papers, Burwell and his coworkers have reported on the study of the change in catalytic activity of alkanes with deuterium (25), the isotopic exchange of alkanes with deuterium (26), the ring cleavage resulting from the hydrogenolysis of cyclopropane(27) and the addition of deuterium or hydrogen to olefins (28). The following observations were made: For isotopic catalytic activity of chromia increases to a maximum at 470°C. whereas the surface area remains constant and the number of moles of attached water decreases. After the maximum, the activity declines as sintering destroys the surface. From mass spectra fragmentation patterns of [illegible] of the reaction going to the first or second coupling, finding that deuterium exchanged exclusively the position 4 [illegible] of [illegible] which from each [illegible] (7), [illegible] between the product 4 [illegible] and the [illegible] of [illegible] has been observed for a series of [illegible] (9).

III. EXPERIMENTAL STUDIES

In order to study the electronic interaction between the adsorbate and the surface under the idealized conditions, it is necessary to carry out experimental work with atomically clean metal surfaces, preferably at liquid nitrogen temperatures. Under these conditions [illegible] the measurements involve [illegible] adsorption, i.e., migration of adsorbate, possible reaction sites, the absence of foreign species which can modify the electronic interaction between the metal surface and the adsorbate. Atomically clean metal surfaces are prepared by flashing metal filaments (10), depositing metal films from the vapor phase (11), and bombarding metal surfaces with positive ions (12). By measuring changes which occur on adsorption in the [illegible] (13), work function (14), resistance (15), and magnetic properties (16) of the metals, one can gain some insight as to the nature of the electronic interaction. The [illegible] observed in the work function for [illegible] by field emission studies (17), the different [illegible] observed [illegible] in the infrared spectra of [illegible] (18), and the [illegible] data from the [illegible] of [illegible] (19) indicate that the assumption that all adsorption sites on the surface are equivalent is [illegible]. Also the techniques of electron spin resonance (ESR) (20, 21) and nuclear magnetic resonance (22) have been used. Recently a relationship between the number of unpaired electrons associated with CO chemisorbed on different metal surfaces and the infrared wave number of the CO band has been observed (23). The investigation at liquid helium temperatures by the [illegible] of [illegible] with the silicon surfaces which appears when the [illegible] is [illegible] (24). Finally, [illegible] produced by a [illegible] of [illegible] (25).

IV. RECENT ADVANCES IN THE CATALYSIS OF [illegible]

In a series of papers, Burwell and his coworkers have reported on the study of the changes in catalytic activity of [illegible] with deactivation (26), the [illegible] of [illegible] the rate of [illegible] resulting from the [illegible] and the addition of [illegible] (27). [illegible] increases to a maximum at [illegible] (28), [illegible] the [illegible] of [illegible]. After [illegible], the activity [illegible] the surface. [illegible] deuterium-exchanged hexanes, it is found that primary hydrogen atoms exchange about five times as readily as secondary hydrogen atoms. Addition of deuterium to olefins involves simple cis addition of two deuterium atoms to the double bond.

Frye, Pickering, and Eckstrom, in studying the reaction kinetics of the hydrogenation of CO catalyzed by iron, found that changes in total pressure, in H_2/CO ratio at constant total pressure, and in temperature reversibly changed the surface quality of the catalyst.(29) Consequently, a change in the reaction rate occurred. Since the immediate change in the rate of CO conversion is followed by a continuing change in rate over an extended period of time, the observed kinetics must be a combination of the ordinary reaction kinetics and the kinetics associated with the change in the surface quality of the catalyst. Also since the changes are reversible, the steady state reaction is a function of temperature, pressure, and gas composition only and thus is essentially not dependent on the immediate previous history of the catalyst. Recently the kinetics of the reaction have been fully worked out (30).

V. CONCLUSION

In order to understand the nature of the bond formed on chemisorption, it is well to keep in mind the donor and acceptor properties of both the catalyst and the adsorbate. Also it is wise to be aware of the danger involved in assuming that the bulk and surface properties of metals are the same. Differences between electronic states of bulk and surface metal atoms are to be expected. Finally, rigorously purified metal surfaces and high vacuum techniques are required in order that electronic interactions may be studied under the simplest of conditions.

VI. REFERENCES

1. R. V. Culver and F. C. Tompkins, Advances in Catalysis, 11, 68 (1959).
2. D. D. Eley, Z. Elektrochem., 60, 797 (1956).
3. I. Langmuir, Trans. Faraday Soc., 17, 607 (1921).
4. E. K. Rideal, Proc. Cambridge Philos. Soc., 35, 130 (1938).
5. C. H. Travaglini, Inorganic Seminars, January 13, 1959, p. 43.
6. P. M. Gundry and F. O. Tompkins, Quart. Revs., 14, 257 (1960).
7. H. M. Hulburt, Catalysis, 2, 167 (1954).
8. L. Pauling, Proc. Roy. Soc. (London), A196, 343 (1949).
9. O. Beck, Discuss. Faraday Soc., 8, 118 (1950).
10. J. K. Roberts, Proc. Roy. Soc., (London), A152, 445 (1935).
11. O. Beeck, A. E. Smith, and A. Wheeler, Proc. Roy. Soc. (London), A177, 63 (1940).
12. H. E. Farnsworth, R. E. Schlier, T. H. George, and R. M. Burger, J. Appl. Phys. 26, 252 (1955).
13. J. C. P. Mignolet, Rec. trav. chim., 74, 685 (1955).
14. R. V. Culver and F. C. Tompkins, Advances in Catalysis, 11, 82(1959)
15. R. Suhrmann and K. Schultz, Z. physik. Chem., 1, 69 (1954).
16. R. W. Selwood, Advances in Catalysis, 9, 93 (1957).

17. H. M. Hulburt, Catalysis, 2, 200 (1954).
18. V. A. Crawford, Quart. Revs., 14, 385 (1960).
19. C. Kemball, Proc. Chem. Soc., 1960, 264.
20. D. E. O'Reilly, Advances in Catalysis, 12, 76 (1960).
21. G. K. Walters, J. Phys. Chem. Solids, 14, 43 (1960).
22. D. E. O'Reilly, Advances in Catalysis, 12, 34 (1960).
23. R. A. Gardner and R. H. Petrucci, J. Am. Chem. Soc., 82, 5051 (1960).
24. L. H. Germer and C. D. Hartman, J. Phys. Chem. Solids, 14, 75 (1960).
25. R. L. Burwell, Jr., A. B. Littlewood, M. Cardew. G. Pass, and C. T. H. Stoddart, J. Am. Chem. Soc., 82, 6272 (1960).
26. G. Pass, A. B. Littlewood, and R. L. Burwell, Jr., J. Am. Chem. Soc., 82, 6281 (1960).
27. C. T. H. Stoddart, G. Pass, and R. L. Burwell, Jr., J. Am. Chem. Soc., 82, 6284 (1960).
28. A. B. Littlewood and R. L. Burwell, Jr., J. Am. Chem. Soc., 82, 6287 (1960).
29. C. G. Frye, H. L. Pickering, and H. C. Eckstrom, J. Phys. Chem., 62, 1509 (1958).
30. J. E. Powers, J. Phys. Chem., 63, 1219 (1959).

STRUCTURE AND BONDING IN TRANSITION METAL PNICTIDES[+] AND CHALCOGENIDES

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Binary compounds formed by the transition metals and the pnigogens (P, As, Sb, Bi) and chalcogens (S, Se, Te) are receiving increasing attention primarily as a result of the search for systems with unique electrical and magnetic properties. Notable contributions are being made by Kullerud and his associates (1) (phase relations); Rundquist (2), Grønvold (3), Westrum (4), Kjekshus (5), and Lafitte (6) (structure and thermodynamics); Chiba (7), Yuzuri (8), Hirahara (9), Schmid (10), and Lotgering (11)(electrical and magnetic properties); and by Kuz'min and Zhuravlev (12)(structure, superconductivity).

Some attempts have been made to describe the electronic arrangement in particular isostructural compounds (eg., Cornish (13), Jellinek (14), and Pearson (15) on the NiAs $B8_1$ compounds), and a more general approach to the higher chalcogenides and pnictides has been proposed by Dudkin, et. al. (16). This approach merits some attention since it promises to predict electrical and magnetic properties of all metalloid rich transition metal pnictides and chalcogenides.

Dudkin suggests that semi-conducting bonds are involved in these compounds. As defined by Mooser and Pearson (17), these bonds require that (a) the compounds contain an element from the non-metal side of the Zintl border; (b) all s and p orbitals in this element be occupied; and (c) if a metal atom with unoccupied bonding orbitals (Pauling metallic orbitals) exists, there must be no direct interaction between it and other metal atoms with similar unoccupied orbitals. Dudkin has applied this concept to MX_3 (DO_2) and MX_2 (C2, C18) compounds with considerable success. The model will be discussed with reference to these compounds, and in addition, the MX_2 (C6) compounds. Distributions of these compounds in the group VIII transition metal families are given in the tables at the end of the abstract.

In the skutterudite DO_2 structure, each metal atom is octahedrally coordinated with six pnictide atoms, and each pnictide atom in turn is surrounded tetrahedrally by two metal atoms and two pnictide atoms. Each octahedron shares each corner with one other octahedron. Occupancy of all pnictide s and p orbitals requires three electrons in the hybridized d^2sp^3 metal orbitals. In the cobalt family, all non-bonding d orbitals will be occupied; these compounds should be semiconductors and diamagnetic. This appears to be true. Substitution of Fe for Co should not alter the electrical behavior but should introduce the paramagnetic contribution of one unpaired electron. The substitution leads to paramagnetism, but the conduction is metallic.

In the pyrite C2 structure, the coordination of metal and metalloid is essentially the same as in the skutterudites, with each metalloid tetrahedrally bonded to three metal atoms and one metalloid atom. Corners of the octahedron are shared with two other octahedra. In the marcasite structure an edge is shared as well, and the metalloid/metalloid distance is greater than in the pyrite structure. More significant is the appearance of chains of metal atoms along the c axis, and the apparent interaction of metal atoms in the pnictides with the subsequent distortion of the metal/pnictide octahedra.

[+] The terms pnigogen and pnictide were coined by Prof. A. E. van Arkel for Group VA elements and compounds. The root: πνίγω, I choke; the allusion: Stickstoff.

While Dudkin's model describes very accurately conduction characteristics in these compounds, it does not differentiate between C2 and C18 structures. Extension of the model to the C6 (CdI_2) structure in which layers of metal/chalcogen octahedra sharing six of their twelve edges are formed, introduces additional complications. In this instance a satisfactory model must describe the C6/$B8_1$ transition regions found in some of these sytems.

DISTRIBUTION OF STRUCTURE TYPES, GROUP VIII TRANSITION METALS

MX_3 Pnictides	Cubic DO_2		MX_2 Chalcogenides	Trigonal C6
	Co/P,As,Sb	Ni/P		Ni/Te
	Rh/P,As,Sb	Pd/P	Rh/Te	Pd/Te
	Ir/P,As,Sb			Pt/S,Se,Te

MX_2 Pnictides and Chalcogenides

Orthorhombic C18			Cubic C2		
Fe/P,As,Sb	Co/Sb (?)	Ni/As,Sb			
Ru/P,As,Sb					Pd/As,Sb
Os/P,As,Sb					Pt/P,As,Sb,Bi
Fe/Se,Te (S)	Co/Te		Fe/S –	Co/S,Se	Ni/S,Se
			Ru/S,Se,Te	Rh/S,Se,Te	
			Os/S,Se,Te	Ir/Te	

REFERENCES

1. G. Kullerud and H. S. Yoder, Econ. Geol., 54, 533-71 (1959).
   G. Kullerud, et. al., Carnegie Inst. Wash. Yearbook, 59, 110 ff. (1960).
2. S. Rundqvist and A. Hede, Acta Chem. Scand., 14, 893-902 (1960).
3. A. Kjekshus and F. Grøvold, Ibid., 13, 1767-74 (1959).
4. F. Grønold and E. F. Westrum, Ibid., 13, 241-8 (1959).
5. F. Grønold, T. Thurmann, E. F. Westrum, and N. E. Levatin, Ibid., 14, 634-40 (1960).

[illegible] A. Kjekshus, Ibid. 14, 1623-6 (1960).

6. M. Lafitte, Bull. Soc. Chim. France, 1959 1223-33.
7. I. Tsubokawa and S. Chiba, J. Phys. Soc. Japan, 14, 1120-5 (1960).
8. M. Yuzuri, Ibid., 15, 2007-12 (1960).
9. S. Fujime, M. Murakami, and E. Hirahara, Ibid., 16, 183-6 (1961).
10. H. Schmid, Cobalt, No. 7, 26-32 (June 1960).
11. F. K. Lotgering, Philips Research Reports, 11, 337-50 (1956).
12. R. N. Kuz'min, N. N. Zhuravlev, and S. A. Losievskaya, Soviet Phys., Crystallography 5, 202-6 (1960).
13. A. J. Cornish, Acta Met., 6, 371-4 (1958).
14. F. Jellinek, Ost. Chem. Zeitung, 60, 311-21 (1959).
15. W. B. Pearson, Can. J. Phys., 35, 886-92 (1957).
16. L. D. Dudkin, Soviet Phys. Technical Phys., 3, 216-20 (1958).
    L. D. Dudkin and V. I. Vaidanich, Soviet Phys. Solid State, 2, 1384-9 (1961).
    L. D. Dudkin, Soviet Phys. Doklady, 4, 903-6 (1960).
17. E. Mooser and W. B. Pearson, J. Electronics, 1, 629-43 (1956).
18. C. M.Pleass and R. D. Heyding, Unpublished data.

CLATHRATE COMPOUNDS

Edward L. Safford April 18, 1961

I. INTRODUCTION

A. Inclusion compounds

The clathrate compounds are among several types classified as inclusion compounds. In these, one molecular species is physically included in cavities in the crystal lattice or even within the molecule of another. Thermodynamically they may be treated as a solution of a liquid or gas in a solid (1,2). On the basis of their cavities, inclusion compounds may be divided into three classes. First is the type in which the included or "guest" species is contained between layers of atomic or molecular thickness of the including or "host" species. The cavity is bounded in only one dimension. Examples of this are the lamellar graphite compounds(3) and certain clays which have absorptive properties (4).

In the second class are those with channels running through their crystals. These are of two sub-classes. Urea, for example, can crystallize in the presence of a guest in a hexagonal form which has long, narrow, cylindrical tubes running parallel to each other for the length of the crystal. It can, as a result, include straight chain hydrocarbons and separate them from mixtures with branched compounds (5). Certain zeolitic crystals, $K_2O.Al_2O_3.nSiO_2$ (n is an integer from 1 to 6) have large three-dimensional cavities, separated by wide "windows". The effect is that of a network of intersecting channels of variable diameter (6). This structure accounts for the usefulness of these minerals as ion exchange agents and "molecular sieves."

The compounds in class three are similar to the zeolites, with the exception that the windows are small and a molecule trapped in the cavity cannot escape. These are known as clathrates.

B. Historical

The gas hydrates have been known since 1810, when Davy prepared chlorine hydrate (28). Only since 1949, however, has their true nature been understood (10). Another early contribution was that of Dianin who, in 1914, reported an organic compound with inclusion properties (7). It was observed by Caspari in 1927, that p-hydroquinone when crystallized from methanol included solvent and crystallized in a form different from that usually observed. He designated the new form β-quinol (8). In 1945, H. M. Powell opened the field of clathrate chemistry by determining the structure of the β-quinol-SO_2 adduct, using X-rays (9). He called it a "clathrate" (= "a lock") which he defined as "[a compound] in which two or more components are associated without ordinary chemical union but through complete enclosure of one set of molecules in a suitable structure formed by another (10)."

CLATHRATE COMPOUNDS

Edward L. [illegible]　　　　April [illegible], 19[illegible]

I. INTRODUCTION

A. Inclusion Compounds

The clathrate compounds are among several types generally known as inclusion compounds. In these, one molecular species is physically included in cavities in the crystal lattice or even within the molecule of another. Thermodynamically they may be treated as a solution of a liquid or gas in a solid (1,2). On the basis of their cavities, inclusion compounds may be divided into three classes. First is the type in which the included or "guest" species is contained between layers of a single or particular arrangement of the including or "host" species. The cavity is bounded in only two dimensions. Examples of this are the [illegible] and certain clays which have absorptive properties (3).

In the second class are those with channels running through their crystals. [illegible] of the [illegible]. Urea, for example, can crystallize in the presence of [illegible] in a hexagonal form which has long, narrow, cylindrical tubes running parallel to each other for the length of the crystal. [illegible] straight chain [illegible] and [illegible] with [illegible] compounds (4). [illegible] in [illegible] to [illegible], generally [illegible]. The [illegible] intersecting [illegible] (5). This [illegible] accounts for the [illegible] and "molecular sieves."

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II. GENERAL CONSIDERATIONS

A. Characteristics

Clathrate hosts are often found to have molecular shapes which do not lend themselves to compact packing and therefore leave cavities in the crystal (11). At first, it was considered that the guest was merely physically held in these cavities (12). However, the structures of many clathrate hosts are metastable in the absence of guest, indicating some type of interaction, probably of a van der Waals nature. In some cases, covalency may be involved, and the dividing line between clathrate and complex formation can be exceedingly fine [cf. (13)].

The primary factor affecting clathrate formation, however, is the relationship between the sizes of guest and cavity. If the guest is larger than the cavity, the host may distort so as to accommodate it. Most host lattices, however, are held together by hydrogen- or partially covalent bonds and can be only slightly distorted. An alternative is to go to a different crystalline form (14).

The theoretical composition of a clathrate is governed only by the number of available cavities in the lattice. There is no guarantee that these will all be filled. The actual composition usually has less than the maximum amount of guest component.

B. Preparation

In most cases, preparation is a relatively simple matter of dissolving the host material in the guest, if it is a liquid, or dissolving host and guest in a solvent which cannot form a clathrate, and crystallizing. If the guest is a gas, it usually must be put under pressure (11).

III. CLASSES OF CLATHRATES

A. Hydrogen bonded structures

1. Hydrates

Bonding of water molecules in clathrates is similar to that in normal ice and as such is quite rigid. To accommodate guests of various sizes, water must employ several crystalline forms. In all of these each oxygen is surrounded tetrahedrally by hydrogens. These tetrahedra, joined at corners, build up an array of pentagonal dodecahedra, each composed of 20 water molecules. This unit has been proposed as the basic structure of liquid water(15). Table I summarizes the commonly reported water-clathrate structures and associated maximum-composition formulas, together with the guest molecules which have been included.

In a recently reported study of the hydrates of tetraalkylammonium and -phosphonium salts, five crystal structure types have been identified by single-crystal X-ray studies. Three of these have been observed in gas hydrates as well. All are composed

of $H_{40}O_{20}$ dodecahedra, packed, in the hydrates, so as to leave larger cavities having 12 pentagonal and 2, 3, or 4 hexagonal faces (15). The latter structure probably corresponds to the structure commonly called II. Another recent paper reports the preparation of several new double hydrates of Ar, Kr, and Xe with several organic solvents (16).

Thermodynamic calculations of the dissociation pressures of several gas hydrates using a hard-sphere model and a Lennard-Jones potential function have been very successful (1). These also predict heats of formation quite closely and indicate little thermodynamic difference between ice and lattice structure I. There has been some question as to the validity of determined heats of formation, however, (2,17).

2. Quinol clathrates

Quinol (p-hydroquinone) crystallizes in hexagonal rings of hydrogen-bonded oxygens with the phenyl rings projecting alternately above and below. Since each quinol takes part in two such rings, a macromolecular three dimensional network results. In β-quinol, two of these networks interpenetrate so that the hexagonal rings of the two networks alternate vertically. The phenyl rings enclose a cage between two hexagons in which a guest may be included. The pertinent data for these cages are given in Table II. The structure is somewhat flexible, for it can expand to an estimated free diameter of 5.2 Å in the SO_2 clathrate (18). The more compact α-quinol can include guests also, but only half as many (19). Its structure is more complex and not well understood(2

If each β-quinol cage is filled, the composition is G.3 quinol, and almost any guest will fill the cavities.unless, like He or H_2O, it is too small or, like CCl_4, it is too large. With little or no guest componenet, the lattice is metastable with respect to the α-form, although "empty" β-quinol may be prepared by crystallization from ethanol (21).

TABLE II: β-QUINOL STRUCTURE

Average cavity diameter		7.9Å (5
Free diameter***		4.2Å* (5
		4.6Å** (5
Number of peripheral atoms		24 (18)
Radii (18)	12 C @ 3.9 Å	
	6 C @ 4.2 Å	
	6 C @ 3.8 Å	
Free Volume***		0.05cm³/cm³ (5)

* Using covalent radius of C

** Using collision radius of C

*** Value for Ar clathrate

By thermodynamic calculations, van der Waals has predicted heats of clathrate formation rather well and derived that the dissociation pressure of the guest should obey the expression $p_G = C\,[y\,/\,(1 - y)]$, in which C is a characteristic temperature constant, and y is the fraction of the cavities which are filled(18). This has been verified for the clathrates of Ar (22), CH_4, and N_2 (19). That CO_2 and N_2O do not obey this expression is expected, for they violate several of the assumptions made in its derivation (19). At high pressures carbon dioxide is found to yield a 6:1 (quinol:CO_2) clathrate which has the α-quinol structure (19).

TABLE I: GAS HYDRATES

Cavity	#*	z*	a*	d*	V*
Structure I:	Unit cell 46 H_2O, Free volume 0.46 cm^3/cm^3 (5)				
Small (pentagonal dodecahedra)	2	20(10)	3.95 Å (10) 3.94 Å (5)	5.1Å(10) 5.2Å(5)	169 Å^3 (15)
Large (tetrakaidecahedra - 12 pentagonal, 2 hexagonal faces)	6	24(10)	4.30 Å (10) (8 @ 4.04 Å, 8 @ 4.42 Å, 4 @ 4.65 Å 4 @ 4.24 Å (1))	ca.5.8Å(10) 5.9 Å (5)	216 Å^3 (15)
Structure II.	Unit cell 136 H_2O (10), Free volume cm^3/cm^3 (5)				
Small (distorted pentagonal dodecahedra)	16	20(10)	3.91 Å (10) (3.77-3.95Å)(10)	5.0 Å(10) 4.8 Å(5)	169 Å^3(15)
Large (hexakaidecahedra - 12 pentagonal, 4 hexagonal faces)	8	28(10)	4.73 Å (10)	6.7 Å(10) 6.9 Å (5)	250 Å^3(15)

Intermediate Structure

Small (as in structure II)

Large (pentakaidecahedra - 12 pentagonal, 3 hexagonal faces (15))
238 Å^3 (15)

* # = cavities per unit cell:, z = atoms on the periphery of the cavity; a = mean radius of the cavity (to atomic centers); d= free diameter of the cavity; V = free volume of the cavity.

Maximum Composition Formulas (11)

Structure I (Unit cell dimension = 12 Å)

$G_1 \cdot 5\ 3/4\ H_2O$	where G_1 is a small molecule, viz. CH_4, H_2S, Ar, Kr, Xe, CF_4, C_2H_6, C_2H_4, O_2, N_2, CO_2.
$G_2 \cdot 7\ 2/3\ H_2O$	where G_2 is a larger molecule, viz., Br_2, SO_2, Cl_2, CH_3Br, CH_3SH.
$2G_1 \cdot 6G_2 \cdot 46H_2O$	(the structure I double hydrate).

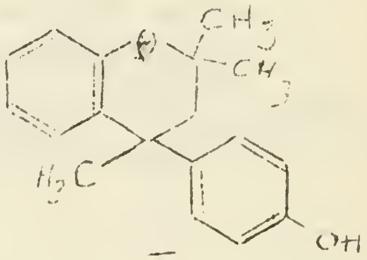
Structure II (Unit cell dimension - 17 Å)

$G_3 \cdot 17\ H_2O$	where G_3 is a still larger molecule, viz., C_3H_8, CH_3I, C_2H_5Cl, CH_3COCH_3, CH_2Cl_2, $CHCl_3$, CCl_4, n-C_4H_9OH, $CH_3COC_2H_5$, $(CH_3)_2NH$, $C_2H_5NH_2$.
$2G_1 \cdot G_3 \cdot 17H_2O$	(the structure II double hydrate)

3. Phenol clathrates

The phenol and β-quinol clathrate structures are similar but phenol cannot be macromolecular since there is only one oxygen per molecule. The unit cell is a rhombohedron with one cage (composed of 12 phenol molecules) at each corner. These enclose a larger cage in the center (23). Clathration of CH_3OH, C_2H_5OH, n-C_3H_7OH, and $(CH_2OH)_2$ by 7 di- and 3 tri-methyl phenols has been reported (24). Structures are the same as for phenol, and the cavity can hold 3 CH_3OH, 2 C_2H_5OH, or one larger molecule. Higher alcohols are included in a channel structure.

4. Dianin's compound (I) clathrates



I

Dianin prepared this compound by condensation of phenol with mesityl oxide and found that it included fixed amount of several solvents (7). Recent work (25 - 27) has shown it to be a clathrate host, retaining some 50 organic solvents as well as Ar, CO_2, NH_3, SO_2, and I_2. Crystal structure determination has shown it, also, to have planar hexagons of hydrogen bonded oxygens (27). The cavity formed is about twice the size of that in β-quinol (25) and is slightly egg-shaped (27). It represents one of the few cases in which both the "empty" and "filled" clathrates are stable and have the same lattice dimensions (25).

B. Cyclodextrins

Three cyclodextrins are known, designated as α-, β-, and γ-. They were first prepared in 1903 by F. Schardinger using enzyme decomposition of amylose (28). All are composed of glucose units bonded as in starch (28) in the shape of a ring (28, 29). It has been well established that these form inclusion compounds (30) and do so even in solution (30-33). Binding in this case must be of an acid-base nature, for it is found that more nucleophilic molecules are more tightly held (32). It is reasonable to expect strong interactions with the inside of such a ring (32), and it is observed that cyclodextrin inclusion alters properties which depend on the electronic environment (30, 32, 34).

The exact form of the solid inclusion compounds has been unknown until recently. Alpha-dextrin forms stable crystalline compounds with Cl_2, I_2, Kr, Xe, O_2, CO_2, C_2H_4, CH_4, C_3H_8, and C_4H_{10} (35-37). and apparently must have a closed structure. Mandelcorn has suggested that the rings might pack in a staggered fashion so as to isolate cavities (11), and this has been confirmed by an X-ray analysis of the α-dextrin-iodine adduct (29). Models predicted α-dextrin to have an outer diameter of 13 Å and a thickness of 7.0 Å. The determined cavity length was 6.7 Å, indicating some interpenetration in closing the holes (29).

The behavior of the three cyclodextrins differs due to the differences in cavity size (cf. Table III). The guest must be neither too large nor too small, and its shape may affect its inclusion by affecting its ability to interact (36). A separation scheme has recently been developed, based on the ability of one dextrin to form a clathrate with a species which will not react with another dextrin (38).

TABLE III: CYCLODEXTRINS*

Dextrin	Glucose units	Cavity diameter
α-	6	6 Å
β-	7	4.5 Å (29) 8 Å
γ-	8	10-11 Å

*Taken from (28) unless indicated.

It has been found that the cyclodextrins tend to include preferentially, one enantiomorph or isomer over another (13,30,39). This property is of interest because of its implication about enzymes.

D. Coordination-compound clathrates

The first clathrate of this type $Ni(CN)_2.NH_3.C_6H_6$, was prepared in 1897 by adding benzene to a solution of nickel cyanide in aqueous ammonia. The structure of this compound was determined in 1952 by Rayner and Powell (40). The nickel atoms are arranged in square layers, each atom joined to four others by cyanide groups. The ammonia molecules are located above and below every other nickel atom so that alternate nickels have four carbons and six nitrogens around them. Succeeding layers are in identical positions leaving a space in the center of each square in which the aromatic ring fits.

The benzene may be removed from this clathrate in vacuo. However, the "empty" clathrate is metastable and slowly reverts to a compact form (41). Formation of this complex may be used to remove small amounts of benzene from hydrocarbon mixtures. Decomposition of the clathrate produced benzene of better than reagent grade (42).

Biphenyls form adducts with this coordination compound in which the two rings may occupy adjacent cavities although the structure is unknown (43).

The crystal structure of a hydrate, $Ni(CN)_2.NH_3.1/4H_2O$, has recently been determined. The layers in this are the same but are so arranged that ammonia molecules project toward the square holes in the succeeding layers. Although the layers are closer, there is more free space than in the benzene clathrate, and van der Waals forces are strong enough to caus puckering of the layers. The position of the water molecules is not clear (44).

A series of clathrates of the form, M^{II} (nitrogen base)$_4$(bidentate anion)$_2$, have recently recieved considerable attention because by choosing the proper combination of metal, nitrogen base, and anion, the complex may be designed to include selectively, a given compound. Most separations of this kind have been done with xylene mixtures (46-54), but other and larger hydrocarbons may be treated also (45, 46). The majofity of these clathrates involve

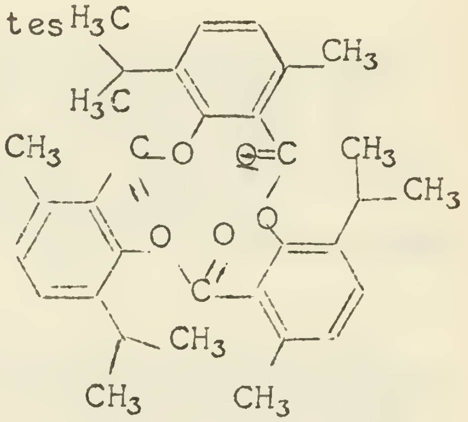
nickel(II) coordination compounds although manganese (II), iron(II) cobalt(II), copper(II), and zinc(II) complexes have been tried (45,46,51-54). The nitrogen bases are variously substituted pyridines.

Good separations of aromatic nitro compounds have been achieved with a chromatographic column packed with a nickel complex of the above type. Aliphatic nitro compounds did not separate as well(55).

Double-salt clathrates of benzene have been prepared, in which the nitrogen-bonded nickel of $Ni(CN)_2.NH_3$ has been replaced by Cu, Cd, or Zn (56).

D. Tri-ortho-tyhmotide (II) clathrates

This is a representative of those clathrates in which the host lattice is held together by van der Waals forces and can, therefore, adapt quite easily to various sized guests. Variations up to nearly 1 Å in all cell dimensions are observed with various guests, and a widely varied series of compounds can be included, viz., alcohols, ethers, alkyl halides, esters, and iodine (14).



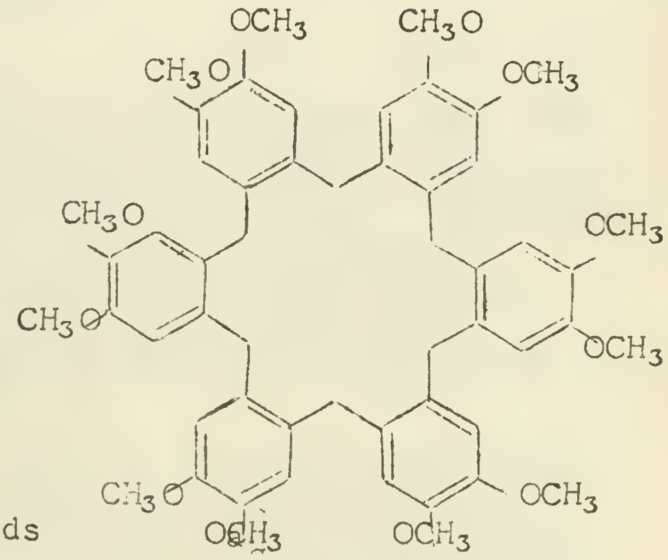
II

If a molecule is larger than the cavity can accomodate, a channel structure results. In both structures, the molecule must be restricted in width but not be too short. Neither host structure is stable when "empty". The cavity is thought to be cigar-shaped and is not parallel to the c-axis. The unit cell contains six molecules and three cavities(14).

Tri-ortho-thymotide is observed to exist as only one enantiomorph in clathrate crystals (14) and, as a result, includes preferentially one of two enantiomorphic guest molecules. It may be used as a resolving agent for alkyl halides (57).

E. Miscellaneous

Cyclohexaveratil (III) (58) has been found to include benzene and several derivatives as well as CS_2 and aliphatic acids and esters (58, 59). The structures of the clathrates are unknown, but infrared spectra indicate two forms.



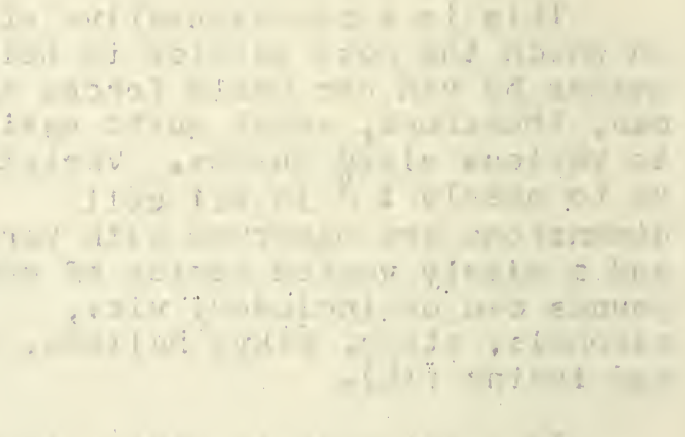
In the study of enzymes, various model compounds have been synthesized and tested for inclusion properties. Certain cyclic disulfides composed of amino acid units have been found to form crystalline inclusion compounds with quinones (60, 61). These are probably clathrates.

nickel(II) coordination compounds of [illegible] (14), [illegible] cobalt(II), copper(II), and rhodium(I) complexes have been found (56,58,61-63). The nitrogen bases are usually substituted pyridines.

Good resolutions of several [illegible] compounds have been achieved with a stereospecific polymer coated with a nickel complex of dimethylglyoxime. Aliphatic nitro compounds are resolved on nickel(II).

Clathrate-type structures of numerous [illegible] are formed, in which the nitrogen-bonded planes of $Ni(CN)_2NH_3$ have been replaced by Cu, Cd, or Zn (65).

3a. Tri-ortho-thymotide (II) clathrates

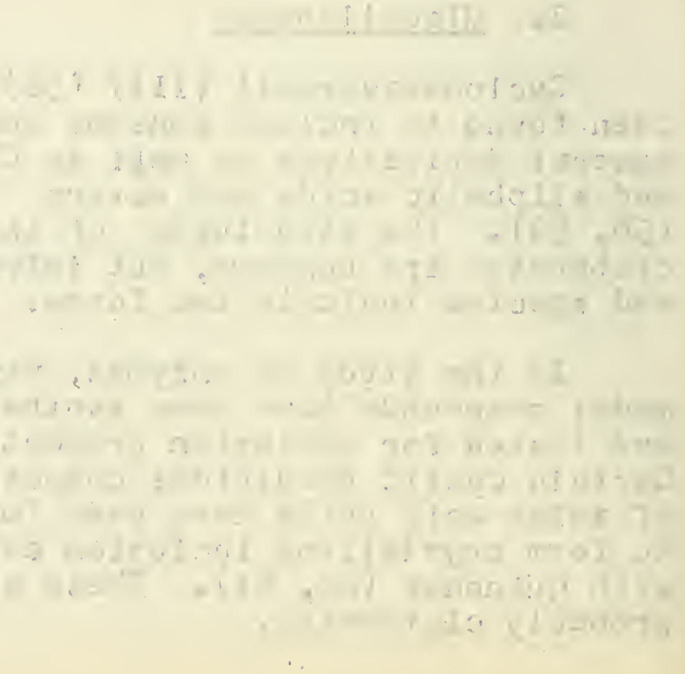

II

This is a [illegible] of [illegible] in which the host molecule is held together by van der Waals forces and can, therefore, occur quite easily in various chiral forms. Variations in [illegible] dimensions are observed with various guests, and a widely varied series of compounds can be included, e.g., alcohols, aldehydes, esters, alkyl halides, ethers, and ketones (61).

If a molecule is [illegible] the crystal and [illegible], a chiral crystal is obtained. In both structures, the molecule must be of similar length but not too [illegible]. [illegible] structure is [illegible]. The cavity is [illegible] and the [illegible] unit cell contains six molecules and three [illegible].

Tri-ortho-thymotide is [illegible] to [illegible] and [illegible], including [illegible], and the [illegible] molecules. It may be used as a [illegible].

3b. Miscellaneous



Cyclotriveratrylene (III) (66) has been found to include benzene and [illegible] as well as CS_2 and aliphatic acids and esters (66, 67). The structures of the clathrates are unknown, but infrared spectra indicate the former.

In the field of polymers, [illegible] model compounds have been synthesized and tested for inclusion properties. Certain cyclic [illegible] compounds of [illegible] have been found to form crystalline inclusion compounds with [illegible]. These are probably clathrates.

It has been found that xylenes and similar hydrocarbons may be separated by complexing with various p-amino triphenyl methanes (62). Clathrate formation appears to be the only reasonable explanation for these complexes.

The inclusion compounds of potassium benzenesulfonate are rather unusual. With small molecules such as C_2H_5OH, C_5H_5N, or $C_2H_5NH_2$, it forms zeolitic adducts. With larger molecules, e.g., naphthalene or benzene, it forms nonstoichiometric but reproducible adducts the composition of which is a function of temperature only. The difference lies in the mechanism of formation in the two cases. The compounds are formed by bathing $KO_3SC_6H_5$ crystals in the hydrocarbon vapors under pressure (63).

IV. USES OF CLATHRATES

Some uses - separations employing coordination compounds and tri-ortho-thymotide- have been indicated. The dextrins may, in the future, find use as asymmetric catalysts and as protective compounds. It has been found that auto-oxidizable substances such as vitamins are protected by dextrin inclusion (34, 64). A process for use of an α-dextrin clathrate of CO_2 as a baking powder has been patented (64).

Until recently, the gas hydrates have been only curiosities and nuisances (65), but it has been discovered that propane hydrate can be used in the conversion of saline water. The two are mixed at ca. 35°F. and 57 p.s.i. to crystallize the hydrate, $C_3H_8 \cdot 17H_2O$, which is separated and decomposed to potable water (66).

Beta-quinol finds use because of its ability to trap, hold, and separate gaseous molecules. Oxygen (67) and nitric oxide (68) have been included in β-quinol for magnetic measurements at low temperatures to prevent magnetic coupling and dimerization, respectively. Recently, a radioactive krypton clathrate has been prepared for study (69). The quinol clathrates are granular materials which may contain up to 10% by weight of gas. They may well find use as a convenient means of storing and handling gases, particularly the inert ones (11).

V. CONCLUSION

It seems plausible that clathrates are more common than the small amount of attention given to them would indicate. Unfortunately, there is no way to establish, definitely, a compound as a clathrate except by single crystal X-ray analysis. From the variety of those so far discovered, however, it appears reasonable that there should be many more as yet undiscovered. It is also evident that preparative possibilities are almost limitless, particularly in such fields as coordination-compound clathrates.

The unusual properties and abilities of clathrate compounds have already prompted a number of interesting and potentially useful applications. It is expected that use of these will become more wide-spread as they are further investigated and developed, and that new applications will be forthcoming.

It has been found that [illegible] (1957). [illegible]

The interesting occurrence of [illegible] rather unusual [illegible] with [illegible] The components [illegible]

IV. USES OF CLAYS

[illegible]

[illegible]

[illegible]

V. Conclusions

[illegible]

[illegible]

REFERENCES

1. J. C. Platteeuw and J. H. van der Waals, Mol. Phys., 1, 91(1958).
2. J. H. van der Waals and J. C. Platteeuw, Nature, 183, 462 (1959).
3. R. C. Croft, Quart. Revs., 24, 1 (1960).
4. R. M. Barrer and J. S. S. Reay, J. Chem. Soc., 1958, 3824.
5. A. E. Smith, Am. Chem. Soc., Div. Petrol. Chem., Symposium No.33, 5(1955); H. Schlenk, ibid., p. 35.
6. R. M. Barrer, Nature, 178, 1410(1956); R. M. Barrer and D. A. Langley, J. Chem. Soc., 1958, 3804, 3811, 3817.
7. A. P. Dianin, J. Russ. Phys. Chem. Soc., 46, 1310(1914); Chem. Zentr. 1915, I, 1063.
8. W. A. Caspari, J. Chem. Soc., 1927, 1093.
9. D. E. Palin and H. M. Powell, Nature, 156, 334 (1945).
10. J. H. van der Waals and J. C. Platteeuw, Advances in Chemical Physics (I. Prigogine, editor. Interscience Publishers, Inc.) 2, 1 (1959).
11. L. Mandelcorn, Chem. Revs., 59, 827(1959).
12. F. D. Cramer and H. Windel, Chem. Ber., 89, 354 (1956).
13. H. M. Powell, J. Inorg. and Nuclear Chem., 8, 546 (1958).
14. D. Lawton and H. M. Powell, J. Chem. Soc., 1958, 2339; A.C.D. Newman and H. M. Powell, ibid., 1952, 3747.
15. Anonymous, Chem. Eng. News, Feb. 13, 1961, p. 40.
16. J. G. Waller, Nature, 186, 429 (1960).
17. R. M. Barrer, Nature, 183, 463 (1959).
18. J. H. van der Waals, Trans. Faraday Soc. 52, 184 (1956).
19. G. Peyronel and G. Barbieri, J. Inorg. and Nuclear Chem., 8, 582, (1958).
20. H. M. Powell, J. Chem. Soc., 1948, 61.
21. D. F. Evans and R. E. Richards, J. Chem. Soc., 1952, 3932.
22. J. C. Platteeuw, Rec. trav. chim., 77, 403 (1958).
23. M. von Stackelberg, A. Hoverath, and C. Scheringer, Z. Elektrochem., 62, 129(1958).
24. E. Terres and K. Thewalt, Brennstoff-Chem., 38, 257 (1957).
25. H. M. Powell and B. D. P. Wetters, Chem. and Ind. (London), 1955 256.
26. W. Baker and J. F. W. McOmie, Chem. and Ind. (London), 1955, 256.
27. W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wild, J. Chem. Soc., 1956, 2010:, ibid., 2018.
28. F. D. Cramer, Revs. Pure Appl. Chem. (Australia), 5, 143(1955).
29. W. J. James, D. French, and R. E. Rundle, Acta Cryst., 12, 385 (1959).
30. W. Lautsch, W. Broser, W. Biedermann and H. Gnichtel, J. Polymer Sci., 17, 479(1955); Angew. Chem., 66, 123(1954).
31. W. Lautsch, W. Bandel, and W. Broser, Z. Naturforsch., 11b, 282 (1956).
32. W. Broser and C. Bahr, Z. Naturforsch, 10b, 121 (1955).
33. W. Lautsch, H. Rauhut, W. Grimm, and W. Broser, Z. Naturforsch., 12b, 307(1957).
34. H. Schlenk, D. M. Sand, and J. A. Tillotson, J. Am. Chem. Soc. 77, 3587 (1955).
35. F. Cramer and F. M. Henglein, Angew. Chem., 68, 649, (1956).
36. F. Cramer and F. M. Henglein, Chem.Ber., 90, 2561(1957).
37. E. Cramer and F. M. Henglein, ibid., 2572.
38. F. Cramer and F. M. Henglein, ibid., 91, 308 (1958).
39. F. Cramer and W. Dietsche, Chem., and Ind. (London), 1958, 892.
40. J. H. Rayner and H. M. Powell, J. Chem. Soc., 1952, 319.

41. J. R. Dacey, J. F. Smelko, and D. M. Young, J. Phys. Chem., 59, 1058 (1955).
42. A. L. Jones and P. S. Fay, U. S. Patent 2,732,413, June 24, 1956.
43. J. Leicester and J. K. Bradley, Chem. and Ind. (London), 1955, 1449.
44. J. H. Rayner and H. M. Powell, J. Chem. Soc., 1958, 3412.
45. F. V. Williams, J. Am. Chem. Soc., 79, 5876 (1957).
46. W. D. Schaeffer, W. S. Dorsey, D. A. Skinner, and C. G. Christian, J. Am. Chem. Soc., 79, 5870 (1957).
47. C. G. Christian, U. S. Patent 2,774,802, Dec. 18, 1956; C.A., 51:7410a (1957).
48. W. D. Schaeffer, U. S. Patent 2,798,069, July 2, 1957: C.A., 52:2088e(1958).
49. W. D. Schaeffer and J. D. Wordie, U, S. Patent 2,798,103, July 2, 1957; C.A., 52:2086g (1958).
50. W. D. Schaeffer, U. S. Patent 2,798.891, July 9, 1957; C.A. 52:2086i(1958).
51. W. D. Schaeffer, A. C. McKinnis, and W. S. Dorsey, U. S. Patent 2,849,511, Aug. 26, 1958; C.A., 53:3145i(1959).
52. W. D. Schaeffer, U. S. Patent 2,849,513, Aug. 26, 1958; C.A. 53:4310g (1959).
53. W. D. Schaeffer, ibid., 2,876,226, March 3, 1959; ibid., 16164.
54. W. D. Schaeffer, ibid., 2,876,227; ibid.
55. W. Kemula and D. Sybilska, Nature, 185, 237 (1960).
56. R. Baur and G. Schwarzenbach Helv. Chim. Acta, 43, 842 (1960).
57. H. M. Powell, Nature, 170, 155 (1952).
58. V. Caglioti, A. M. Liquori, N. Gallo, E. Giglio, and M. Scrocco, J. Inorg. and Nuclear Chem., 8, 572 (1958).
59. N. Gallo, E. Giglio, and A. M. Liquori, Ricerca Sci., 28, 173(1958); C.A., 52:19984c (1958).
60. W. Lautsch and D. Gunther, Naturwissenshaften, 44, 492 (1957).
61. W. Lautsch, et. al., Kolloid-Z., 161, 36 (1958).
62. W. D. Schaeffer, U. S. Patent 2,769,851, Nov. 6, 1956; C.A., 51:9686a (1957).
63. R. M. Barrer, Nature, 176, 745(1955).
64. H. Schlenk, D. M. Sand, and J. A. Tillotson, U. S. Patent 2,827,452, Mar. 18, 1958; C.A., 52:12901e (1958).
65. F. D. Otto and D. B. Robinson, A. I. Ch. E. Journal, 6, 602(1960).
66. Anonymous, Chem. Eng. News, Jan. 2, 1961, p. 37.
67. H. Meyer, M. C. M. O'Brien, and J. H. VanVleck, Proc. Roy. Soc. A243, 414(1958).
68. A. H. Cooke and H. J. Duffus, Proc. Phys. Soc. (London) 67A, 525(1954).
69. D. J. Chleck and C. A. Ziegler, Intern. J. Appl. Radiation and Isotopes, 7, 141(1959).

ANHYDROUS METAL NITRATES

Willard B. Howe April 25, 1961

I. INTRODUCTION

Until recently, the metals of Groups IA and IIA were virtually the only elements reported to form anhydrous nitrates readily. Referral to a handbook provides the few commonly used exceptions. This report is concerned with the preparation and properties of a few rather extensively studied compounds of the heavy metals.

II. PREPARATION

Early unsuccessful attempts to prepare anhydrous nitrates of cations which are usually strongly hydrated invariably employed thermal degradation of the hydrates. However, this always leads to the formation of basic nitrates or oxides.

In 1909 (1), freshly prepared N_2O_5, dissolved in anhydrous HNO_3, was reported to produce anhydrous nitrates of Mn(II), Cu(II), Ni(II), and Co(II) from the corresponding hydrated salts. More recently the preparation of $Th(NO_3)_4$ has been effected similarly (2). Chretien and Boh (3) treated the oxides of calcium, magnesium, and lead (II) with acetyl nitrate, producing the metal nitrates in good yield. $Ti(NO_3)_2$ and $Sn(NO_3)_4$ are reported to form in this reaction:

$$ClNO_3 + MCl_4^{-} \xrightarrow{-78^{o}C.} M(NO_3)_4 + 4Cl_2 \quad (4)$$

$$M = Ti, Sn$$

By far the most extensively studied preparatory method employs the reaction of N_2O_4 liquid or N_2O_4-NO_2 vapors with metals or metal oxides (5-18). Addison (15) has clearly demonstrated that these reactions yield nitrates uncontaminated by nitrites according to the equations:

$$M + 2N_2O_4 \rightarrow M(NO_3)_2 + 2NO \quad (a)$$

$$MO + N_2O_4 \rightarrow M(NO_3)_2 + N_2O_3 \quad (b)$$

Zinc has been shown to react by two mechanisms (5-7). One mechanism is operable below 14°C. and leads to the direct isolation of $Zn(NO_3)_2$. Above 14°C., the reaction yields $Zn(NO_3)_2 \cdot 2N_2O_4$. Addison and coworkers have shown that NO_2 cannot be the rate-determining species by comparison of its equilibrium concentration with the overall reaction rate. By careful study of the effect of N_2O_3 on the reaction rate, he concluded that the reactive species is the $[NO][NO_3]$ complex (6) produced as indicated by the equations.

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows [NO][NO_3] \rightleftarrows [NO]^{+} + [NO_3]^{-} \quad (c)$$

The addition of N_2O_3 would be expected to affect the concentration of NO^+, in two ways:

According to equation (d), NO_2 would increase in concentration,

$$N_2O_3 \rightleftarrows NO + NO_2 \quad (d)$$

which would favor recombination of NO_2 in the ionic complex. Secondly, the lack of symmetry of N_2O_3 would increase the dielectric constant of the medium and favor the ionic complex. Indeed it has been shown that N_2O_3 in a 40 mole % solution increases the conductivity by a factor of 10^5 (6).

At the higher temperature, the concentration of the active species is independent of temperature. Hence, Addison (6) proposed this scheme:

$$N_2O_4 \xrightarrow{Zn} 2NO_2 \quad (e)$$

$$NO_2 + Zn \rightarrow NO + ZnO \quad (f)$$

$$2NO + 4N_2O_4 \rightarrow Zn(NO_3)_2 . 2N_2O_4 + N_2O_3 \quad (g)$$

Inasmuch as reaction (g) is much more rapid than the overall reaction with Zn, reactions (e) or (f) are rate-controlling. This scheme also explains the known existence of green N_2O_3 in the reaction mixture (6).

Further study of reactions in N_2O_4 has shown that the addition of a basic solvent greatly increases the rate of reaction with metals which react with pure N_2O_4, Table A, and such addition makes possible the reaction of N_2O_4 with certain other metals, Table B, (15).

A	B
Alkali Metals	Uranium
Calcium	Manganese
Silver	Cobalt
Mercury	Copper
Zinc	Cadmium
	Indium

Thus the synthesis of nitrates of the metals in Table B is most commonly carried out in a solution containing 20% by weight of ethyl acetate. Addison (11, 15) has proposed that the basic solvent stabilizes nitrosyl ion by forming a complex with it, (equation (h)).

$$N_2O_4 \rightleftarrows 2NO_2 \underset{\leftarrow}{\overset{n \ \text{solvent}}{\rightarrow}} [(\text{solvent})_{\underline{n}} NO][NO_3] \rightleftarrows [(\text{solvent})_{\underline{n}} NO]^+ + NO_3^-$$

He has isolated many such complexes. These, in general, are stable below 0°C. (15). Furthermore, N_2O_4 complexes with tertiary amines have been shown to be ionic (21).

Anhydrous iron(III) nitrate is synthesized from $FeCl_3$ and N_2O_4 because the metal itself, is unreactive toward N_2O_4, even upon addition of a basic solvent (15, 16). This reaction (i) produces a highly stable N_2O_4 adduct from which the unsolvated nitrate is obtained with some difficulty by fractional vacuum sublimation above 120°C.

$$FeCl_3 + 4N_2O_4 \rightarrow Fe(NO_3)_3 . N_2O_4 + 3NOCl \quad (i)$$

III. BONDING IN N_2O_4 ADDUCTS

The compounds $CO(NO_3)_2 . 2N_2O_4$, $Zn(NO_3)_2 . 2N_2O_4$, $In(NO_3)_3 . N_2O_4$ and $Cu(NO_3)_2 . N_2O_4$ appear to be weak molecular association complexes since all four possess distinct vapor pressures of N_2O_4 at room temperature (5,12,15). In the case of $Cu(NO_3)_2 . N_2O_4$, there is some indication of ionic character of the complex, for there is a sharp infrared absorption peak at 2294 cm.$^{-1}$ (20), attributable to NO^+. A peak at 2252 cm.$^{-1}$ is similarly attributed to the nitrosyl ion in solid $Fe(NO_3)_3 . N_2O_4$ (20). However, Addison has proposed that in the vapor state $Fe(NO_3)_3 . N_2O_4$ is $NOFe(NO_3)_4$, with pentacovalence of iron similar to that in $Fe(CO)_5$. From this $Fe(NO_3)_3 . N_2O_4$ can be prepared (15).

No absorption due to nitrosyl ion is reported for $UO_2(NO_3)_2 . N_2O_4$, although the ionic representation, $NO^+[UO_2(NO_3)_3]^-$, is quite plausible considering the well established existence of $[UO_2(NO_3)_3]^-$ in both the solid state and solution (15,22).

IV. METAL-NITRATE BOND TYPE

The compounds $Cu(NO_3)_2$, $Hg(NO_3)_2$, and $Fe(NO_3)_3$ can be sublimed without thermal decomposition of the vapor (23). Thus one would expect that the metal-nitrate bonds might be covalent or at least involve ion pairs.

Infrared studies indicate that some anhydrous nitrates are covalent or contain nitrate ions distinctly distorted from D_3h symmetry. others, apparently, are essentially ionic in the solid state, possessing three infrared- active vibrational frequencies((24).

Ionic Nitrates

Compound	Symmetric Stretch	Out-of-plane Bend	Assymmetric stretch	Rock	Reference
	ν_1	ν_2	ν_3	ν_4	
$NaNO_3$	----	836 m,sp.	1358 v.s.	not reported	(25)
$AqNO_3$	----	801 v.s.sp.	1348 vs.b.	733s.sp	(25)
$Pb(NO_3)_2$	----	836 w. sp. 801 v.w.	1373 v.b.	726	(19)
$Cd(NO_3)_2$	* 1028 w	805 w.sp. 802 w.sp.	1381 v.s.	751 m	(19)
$Co(NO_3)_2$	----	799 v.s.	1366 s.	762w	(19)
$Co(NO_3)_2 . 6H_2O$	----	807 w.v.b. 836 w.sp.	1372	not reported	(19)

Covalent nitrates possess C2v symmetry. With these compounds there should be associated 6 infrared active fundamental vibrations(24) These are compared to known metal nitrate complexes (26).

Covalent Nitrates

Compound	ν_3 or ν_5	ν_6	ν_2	ν_1	ν_4	Reference
$Mn(NO_3)_2$	759	805 795	1019	1294	1553	(19)
$Cu(NO_3)_2$	770	795 787	1038 1016	1289 1264	1565 1546	(19)
$Zn(NO_3)_2$	746	800 793	1050 1040	1300	1546	(19)
$Hg(NO_3)_2$	----	788	1027	1376	1495	(19)
$R[UO_2(NO_3)_3]$	736		1023	1276	1536	(22)
$K_2(Co(NO_3)_6]$	----	804 799	1034	1287	1531	(26)

These latter spectra may be compared with that of $[Co(NH_3)_5NO_3](NO_3)$ which compound contains both ionic and covalent nitrate.

	ν_3 or ν_5	ν_6	ν_2	ν_1	ν_4
ONO_2	----	803w	1011s	1269s	1495s (26)
	ν_1	ν_2	ν_3	ν_4	
NO_3^-	1052* 1032	828s	1377 1330	----	

* Quagliano(27) has shown that small lattice distortions in ionic nitrates permit the symmetric stretch of nitrate ion.

From the above data it can readily be seen that there are two distinct classes of anhydrous nitrates.

Ultraviolet spectra have also been employed to differentiate between these classes of compounds (28). For this study, $LiNO_3$ was used as a standard, for its spectra in both n-BuOH, and water are identical. Lithium nitrate exhibits a maximum absorption ($\underline{E} = 6$) near 300 mμ, with a minimum absorption at about 280 mμ. Anhydrous $Th(NO_3)_4$ and HNO_3, more covalent materials, possess maxima near 280 mμ, with extinction coefficients 15 and 10, respectively. On the other hand, $Cu(NO_3)_2$ and $Co(NO_3)_2$ have maximum extinction coefficients in this region of about 1000 and 100, respectively.

V. CRYSTAL STRUCTURE

With the exception of that of $Cu(NO_3)_2$ the crystal structure of no transition-metal nitrate has been studied. This compound is orthorhombic, space group Pmn2, and $\underline{a}$=11.12Å., $\underline{b}$=5.05 Å., $\underline{c}$= 8.28 Å. There are 4 molecules per unit cell (29). Each copper ion holds two nitrate ions by Cu-O bonds in a linear chain, with a Cu-O bond distance of 1.9 A°. Roughly perpendicular to this chain are stacks of nitrate ions the oxygen atoms of each of which lie at a distance of 2.5 A°. from the two nearest copper ions.

VI. THE STRUCTURE OF $Cu(NO_3)_2$ VAPOR

Anhydrous $Cu(NO_3)_2$ has been clearly shown to bemonometic in the vapor state. It possess a vapor pressure of 3 mm. Hg at 214°C. (18,30). On the basis of electron diffraction data, Bauer and Addison (31) have concluded that the copper ion is bonded to the nitrate ions in a unique fashion. One nitrate ion is so located that its nitrogen atom is nearest to the copper ion, whereas the other nitrate ion possesses an oxygen atom nearest to the cupric ion and congruent with the Cu-N axis of the first nitrate ion. The nitrate ions are each bent out of a planar configuration.

Pertinent data are:

Bond Distances

$Cu-Oa^1$, Cu-N	1.98 ± 0.03 A°
Cu-Oa, Cu-Ob	2.24 ± 0.04 A°
Cu-Oc	2.64 ± 0.05 A°
$Cu-N_2$	2.72 ± 0.03 A°
$Cu-Ob^1$, CuOc.	3.53 ± 0.04 A°

Bond Angles

$\angle N_2\ O_{a^1}\ Cu = 110^\circ \pm 5^\circ$

$\angle Oa\ N_1\ Ob = 118 \pm 8^\circ$

$\angle Ob^1\ N_2\ Oc^1 = 115 \pm 6^\circ$

Thus the two nitrate ions are different. This structure is in accord with the observation that $Cu(NO_3)_2$ when dissolved in ethyl acetate or acetonitrile produces a conducting solution suggesting reaction in terms of the equation

$$Cu(NO_3)_2 \rightarrow Cu(NO_3)^+ + NO_3^-$$

Furthermore, when $Cu(NO_3)_2$ is dissolved at room temperature in anhydrous ether, a vigorous reaction occurs from which copper is isolated as

$Cu(NO_3)(OCH_3)$ and $Cu(NO_3)(O_2CH)$ (29).

VII. CONCLUSION

The preparation of anhydrous nitrates, heretofore, achieved only with difficulty, has been greatly simplified by employing N_2O_4. The structures of the N_2O_4 solvates are as yet ill defined. In the main, the chemical properties of anhydrous nitrates have not been studied. The physical properties of only a few nitrates have been determined. Thus, there is a wide range of useful information left to be determined.

REFERENCES

1. A. Guntz, F. Martin, Bull. soc. chim. France, 5, 1004 (1909).
2. J. R. Ferraro, L. I. Katzin, and G. Gibson, J. Am. Chem. Soc., 77, 327 (1955).
3. A. Chretien and G. Boh, Compt. rend., 220, 822 (1945).
4. M. Schmeisser, W. Fink, and K. Brandle, Angew. Chem., 69, 780, 781 (1957).
5. C. C. Addison, J. Lewis and R. Thompson, J. Chem. Soc., 1951, 2829.
6. C. C. Addison and J. Lewis, ibid., 2833.
7. C. C. Addison, J. Lewis and R. Thompson, ibid., 2839.
8. J. Gibson, and J. J. Katz, J. Am. Chem. Soc., 73, 5436 (1951).
9. J. R. Ferrard and G. Gibson, J. Am. Chem. Soc., 75, 5747 (1953).
10. C. C. Addison and N. Hodge, Nature, 171, 569 (1953).
11. C. C. Addison and B. J. Hathaway, Chemical Society (London), Special Publication No. 10, 1957, 33-43.
12. C. C. Addison and B. J. Hathaway, Proc. Chem. Soc., 1957, 19.
13. V. Tranbakla and I. Oza, J. Indian Chem. Soc., 33, 911 (1956).
14. C. C. Addison and B. J. Hathaway, J. Chem. Soc., 1958, 3099.
15. C. C. Addison, Angew. Chem. 72, 193 (1960).
16. C. C. Addison and B. J. Hathaway, Proc. Chem. Soc. 1958, 51.
17. T. Moeller and V. D. Aftandilian, J. Am. Chem. Soc., 76, 5249 (1954).
18. T. Moeller, Inorg. Syn., 5, 37 (1957).
19. C. C. Addison and B. M. Gatehouse, J. Chem. Soc., 1960, 613.
20. C. C. Addison and B. J. Hathaway J. Chem. Soc. 1960, 1469.
21. D. Davenport, H. Burkhardt, and H. H. Sisler, J. Am. Chem. Soc. 75, 4175 (1953).
22. B. M. Gatehouse and A. E. Comyns, J. Chem. Soc., 1958, 3965.
23. C. C. Addison and B. M. Gatehouse, Chem. and Ind., 1958, 464.
24. H. Cohn, C. K. Ingold and H. G. Poole, J. Chem. Soc., 1952, 4274.
25. F. A. Miller and C. H. Wilkins, Anal. Chem., 24, 1253 (1952).
26. B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, J. Chem. Soc. 1957, 4222.
27. S. I. Mizushima and J. V. Quagliano, J. Am. Chem. Soc., 75, 4870 (1953).
28. L. I. Katzin, J. Chem. Phys., 18, 789 (1950).
29. G. C. Wallwork, Proc. Chem. Soc., 1959, 311.
30. R. F. Porter, R. C. Schoonmaker, and C. C. Addison, Proc. Chem. Soc., 1959, 11.
31. S. H. Bauer and C. C. Addison, Proc. Chem. Soc., 1960, 251.

Table of Decomposition Temperatures of Anhydrous Nitrates

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	VIII	VIII	IB	IIB
$LiNO_3$ d 225											
$NaNO_3$ n 306.8 d 380	$Mg(NO_3)_2$										
KNO_3 m 334 d 400	$Ca(NO_3)_2$ d 561		$Ti(NO_3)_4$			$Ma(NO_3)_2$ 105-110	$Fe(NO_3)_3$	$Co(NO_3)_2$ 100-105	$Ni(NO_3)_2$	$Cu(NO_3)_2$ [illegible]	$Zn(NO_3)_2$ d 240
$RbNO_3$ d 310	$Sr(NO_3)_2$ d 572	$Y(NO_3)_3$					IB $AgNO_3$ m212 d. 404	IIB $Cd(NO_3)_2$		IIIA $In(NO_3)_3$	IV $Sn(NO_3)_4$ 50
$CsNO_3$ d 414	$Ba(NO_3)_2$ d 592	$La(NO_3)_3$						$Hg(NO_3)_2$		$TlNO_3$ d 206 $Tl(NO_3)_3$	$Pb(NO_3)_2$ d 470

Lanthanons	$Pr(NO_3)_3$	$Nd(NO_3)_3$	$Sm(NO_3)_3$	$Gd(NO_3)_3$
Actinides	$Th(NO_3)_4$ d 500	$UO_2(NO_3)_2$		

THE MECHANISM OF REACTIONS INVOLVING THE TRANS EFFECT

Yorke E. Rhodes April 25, 1961

I. INTRODUCTION

Geometricl isomerism of platinum(II) complexes was first proposed by Werner (1) to account for the observation that there are two monomeric forms of $Pt(NH_3)_2Cl_2$. This fact could not be reconciled with the tetrahedral structure which had been previously assumed. Thus it was possible to assign the structure of the isomers on the basis of the products obtained on substitution of the complex if it was assumed that addition is not accompanied by isomerization and that the final step involves a *trans* elimination. That these assumptions are correct has been shown by x-ray analysis of the isomeric complexes.

In 1926, Chernyaev (2) reported that certain negative ligands have greater directive effects than others, namely that they have a greater labilizing influence on groups which are in *trans* positions than those which are in a *cis* orientation. It was also observed that neutral ligands derived from first-row elements have a much weaker *trans effect* than others, indicative of some interaction of higher orbitals of the ligands in substitution reactions.

As a result of studies involving a large number of substituted platinum(II) complexes, it has been possible to assign an order of directive effects for different ligands. Thus it is found that the order of increasing trans effect is

$$H_2O < OH^- < NH_3 \sim RNH_2 < pyr < Cl^- < Br^- < NCS^- \sim I^- \sim NO_2^- \sim SO_3H^- \sim PR_3$$
$$\sim R_2S \sim SC(NH_2)_2 < NO \sim CO \sim C_2H_4 \sim CN^- \quad (3).$$

This empirical rule and the order of directive effects have found great use in the synthesis of differently substituted square-planar complexes and their *cis* and *trans* isomers. This seminar is concerned with the possible causes of the trans effect in substitution reactions and the probable mechanisms of these reactions. There are several good reviews of the subject currently available (3,4).

II. THEORETICAL CONSIDERATIONS

In general, there have been two approaches to the nature of the causes of the trans effect, the thermodynamic and the kinetic. In the former the relative stabilities of the *cis* and *trans* isomers in terms of bond strengths are considered, whereas the latter and more recent view considers the effect of mechanism and thus the energy of activation of the different types of reaction.

It was early recognized that electrostatic repulsion of negative ligands could not be the cause of the trans effect, for this would have a greater influence on *cis* ligands than on *trans* ligands. Grinberg (5) proposed that the effect was due to the interaction of induced dipoles on the ligands and the central metal atom. Thus a highly polarizable group would have a tendency to weaken the metal-ligand bond in a *trans* orientation to it. However, this theory is

THE MECHANISM OF SUBSTITUTION REACTIONS IN PLANAR [illegible]

[illegible] L. [illegible] April 25, 195[illegible]

I. INTRODUCTION

Geometrical isomerism in platinum(II) complexes was first proposed by Werner (1) to account for the observation that there are two isomeric forms of $Pt(NH_3)_2Cl_2$. This fact would not be consistent with the tetrahedral arrangement which had been previously proposed. Thus it was possible to assign the structures of the isomers on the basis of the products obtained on substitution of the complex if it was assumed that substitution is not accompanied by rearrangement and that the [illegible] involves a [illegible] stereochemistry. That these assumptions are correct has been shown by X-ray analysis of the isomeric complexes.

In 1926 Chernyaev (2) reported that certain negative ligands have greater directive influence than others, namely that they cause a greater labilizing influence on groups which are in trans position than those which are in cis position. It was also observed that neutral ligands derived from fifth-row elements were stronger trans directors than others, indicating a more important role of higher orbitals of the element in substitution reactions.

From a study of reactions involving a large number of substitution platinum(II) complexes, it has been possible to set up an order of directive effects for all common ligands. Thus it is found that the order of increasing trans effect is

$$[illegible]$$

$$[illegible] \ (3).$$

This empirical rule and the order of directive effects have found great use in the synthesis of platinum(II) complexes [illegible] and their cis and trans isomers. This [illegible] is concerned with the possible [illegible] of the trans effect on substitution reactions and the possible mechanisms of these substitutions. There are several good reviews on the subject according to Basolo (4,5).

II. THEORETICAL CONSIDERATIONS

In general, there have been two approaches to the problem of explanation of the trans effect. The thermodynamic [illegible] considers the relative stabilities of the cis and trans products in terms of [illegible], while the kinetic approach considers the effect on activation and [illegible] the rates of replacement of the different groups in complexes.

It was early recognized that a [illegible] of negative ligands could not be the cause of the trans effect, for this would [illegible]. However, [illegible] proposed that the effect was due to the polarization of [illegible] and the central metal atom. Thus, a highly polarizable group would [illegible] the positive charge [illegible] in a [illegible] bond [illegible] rather weak in that many of the known facts are in opposition to it. More recently, it has been suggested that a bimolecular substitution reaction on the central metal atom, proceeding through a trigonal bipyramidal intermediate, is a possible mechanism for the trans effect. This mechanism predicts the observed products on the basis of electrostatic repulsions of the ligands in the five-coordinated intermediate. This mechanism, however, fails to explain the greater trans effect of ethylene, phosphines, and thioethers and also predicts a very high energy of activation since there is a considerable loss of crystal-field stabilization energy in going from a square-planar to a trigonal-bipyramid structure.

Chatt(6), and later Orgel (7), independently proposed that the trans effect may be due to overlap of filled *d*-orbitals of platinum(II) and vacant orbitals on the ligands, thus forming a π bond. A π-bonding ligand causes the electron density of the d_{xz} orbital to be shifted toward it and thus away from the group trans to the ligand. Thus the approach of a nucleophile is enhanced in the trans position. Ligands in the cis position are perpendicular to this *d* orbital and are affected only slightly due to electrostatic effects as a result of the shift in electron distribution. The bond to the trans group, however, will be weakened only if both ligands have a strong trans effect. Thus if all groups in a particular complex are of low trans effect, the electron density of the *d* orbitals of the metal atom will be high, discouraging nucleophilic attack, and the rate of substitution will be slow by either an S_N1 or an S_N2 type of process. If one ligand is replaced by a ligand of high trans effect, S_N2 reactions in the region trans to this group will be enhanced, and S_N1 reactions will be discouraged. Thus the π-bonding theory attributes the relative rates of reaction of *cis* and *trans* complexes to a lowering of the activation energy for the *trans* complex rather than to a weakening of the *trans* metal-ligand bond. On the basis of this theory, it is predicted that where π-bonding is important in the transition state of the reaction of the rate of reaction will be first-order in the concentration of the complex and first-order in the concentration of the nucleophile.

Basolo and Pearson and their group (3,8) have recently considered the effect of solvent on these substitution reactions. It is known that square planar complexes are associated with two molecules of solvent above and below the plane of the complex (9). These solvent molecules are weakly bonded to the central metal atom by long bonds but may enter into the reactions of the complexes as five- or six-coordinated systems. Thus a substitution reaction may involve in the first step a displacement of a solvent molecule by the nucleophile, a dissociation of a molecule of solvent from the complex or a displacment of a trans group by one of the solvating molecules. Thus the rate of substitution may be either first-order or zero-order in concentration of the entering group. This mechanism would be expected to be most important in the absence of π-bonding ligands.

III. KINETIC STUDIES

As a test of these different possible mechanisms for the involvement of the trans effect in substitution reactions of square planar complexes, the relative rates of radiohalogen exchange and hydrolysis of the *cis* and *trans* isomers of many differently substituted complexes have been studied (8,10,11,12,13).

Generally it has been found that displacement reactions of halides in some platinum(II) complexes are second-order reactions; that the rates of substitution decrease in the order of decreasing trans effect and decreasing order to form π-bonds; and that the rates for trans complexes are greater than the rates for cis complexes (13). Basolo (8) has observed that some reactions are zero-order in nucleophile concentration and have nearly identical reaction rates for several different reagents regardless of the charge of the complex. Thus the reaction may be a slow replacement of a trans ligand by a water molecule, followed by a rapid displacement of the molecule of water by an entering group. An alternative to this mechanism is an S_N1 dissociative process followed by a rapid reaction with the nucleophile. It was found that the aquo complexes reacted very rapidly with chloride ion and it is not possible to distinguish between these two mechanisms. Similar effects have been observed by Martin and coworkers (13). It has also been shown that chloro complexes of platinum(II) react more rapidly with solvent (H_2O) than with chloride ion and that the rate-determining step is independent of chloride-ion concentration, thus lending further support to the Basolo mechanism of solvent involvement. The best mechanism consistent with these facts is given below:

$$PtX_4^{2-} + H_2O \rightleftarrows PtX_3H_2O^{1-} + X^{-1}$$

$$PtX_3H_2O^{1-} \overset{slow}{\rightleftarrows} PtX_2H_2O + X^{-1}$$

$$PtX_2H_2O + {}^{*}X^{-1} \rightleftarrows PtX_2{}^{*}XH_2O^{1-}$$

Basolo (14) has recently studied the extent to which solvent participates in the substitution reactions of trans-Pt py_2 Cl_2 by measuring the rate of radiohalogen exchange in different solvents. It was found that the solvents were divided into two groups, those in which the reaction was either first-order in added chloride ion or zero-order in added chloride-ion concentration.

Table I

Rate = k_2(complex)(Cl^-)

Solvent	k_2(l $mole^{-1}min^{-1}$)
CCl_4	10^6
C_6H_6	10^4
m-cresol, t-BuOH	10^1
EtOAc, $(CH_3)_2CO$	1
DMF	10^{-1}
CH_3CN	7.6×10^{-1}

Rate = k_1(complex)

Solvent	k_1(min^{-1})	Dielectric Constant
$(CH_3)_2SO$	2.3×10^{-2}	45
CH_3NO_2	1.92×10^{-3}	39
C_2H_5OH	8.5×10^{-4}	24
n-C_3H_7OH	2.5×10^{-4}	20

glacial HOAc and H_3BO_3 too fast to measure.

Thus the rate of exchange parallels the dielectric constant of the solvent for the latter case, and the solvents in which the rates of reaction are fastest are just those which would be expected to form π bonds. Acetic acid and boric acid enhance the rate of exchange, but acetate and borate anions are poor reagents. As a result it is not possible to determine from this work whether the acids enhance the rate due to π-bonding or to hydrogen bonding. These workers also compared the rates of two similar complexes one of which had the positions above and below the plane blocked by bulky substituents to measure the effect of solvent participation on the rate. Thus the rate of the picoline complex is decreased by a factor of 25 compared to the pyridine complex, undoubtedly due to blocking of the access of solvent to the metal atom by the methyl groups in the picoline molecule.

Complex	k_1(min^{-1})
cis- Pt(4-am-py)$_2$Cl$_2$	6.55x10^{-4}
cis-Pt(-pic)$_2$Cl$_2$	2.88x10^{-5}

This discussion has been limited thus far to the study of only platinum(II) complexes, for these are much more stable, and the isomers are not rapidly isomerized. However, these same effects are expected to apply to palladium(II), nickel(II), and gold(III), which also form square-planar complexes. The trans effect is not as predominant in these complexes and is thus more difficult to observe. Recently (15) the rates of substitution of some Pt(II), Pd(II), and Ni(II) complexes have been compared, and it has been found that they lie in the order 1: 10^5: 5x10^5, respectively. This adds further support to the dissociation theory, for it is known that palladium and nickel have greater tendencies to coordinate fifth- and sixth-groups elements.

In conclusion, it may be said that for reactions involving π-bonding ligands the trans effect is a kinetic process in which multiple bonding stabilizes the transition state of the reaction rather than weakening the trans bond in a thermodynamic sense. For cases in which there can be no π-bonding, it is likely that a dissociation mechanism involving active participation of solvent is occurring rather than a rearrangement to a trigonal bipyramidal intermediate. A direct second-order displacement may occur in some cases, but the hydrolysis mechanism is predominant in most cases.

IV. REFERENCES

1. A. Werner, Z. anorg. Chem., 3, 267 (1893).
2. I. I. Chernyaev, Ann. inst. platine U.S.S.R., 4, 261 (1926).
3. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley and Sons, Inc., New York, N.Y., 1958.
4. J. V. Quagliano and L. Schubert, Chem. Revs., 50, 201 (1952).
5. A. A. Grinberg, Ann. inst. platine U.S.S.R., 10, 58 (1932).
6. J. Chatt, L. A. Duncanson, and L. M. Venanzi, J. Chem. Soc., 4456 (1955).
7. L. E. Orgel, J. Inorg. Nuclear Chem. 2, 137 (1956).
8. D. Banerjea, F. Basolo and R. G. Pearson, J. Amer. Chem. Soc., 79, 4055 (1957).
9. C. M. Harris and R. S. Nyholm, J. Chem. Soc., 4375 (1956).
10. D. Banerjea and K. K. Tripathi, J. Inorg. Nuclear Chem., 7, 78 (1958).
11. L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., J. Amer. Chem. Soc., 79, 2965 (1955).
12. T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., J. Amer. Chem. Soc., 80, 536 (1958).
13. T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., J. Amer. Chem. Soc., 81, 10 (1959).
14. R. G. Pearson, H. B. Gray, and F. Basolo, J. Amer. Chem. Soc., 82, 787 (1960).
15. F. Basolo, H. B. Gray, and R. G. Pearson, J. Amer. Chem. Soc., 82, 4200 (1960).

COORDINATION PHENOMENA IN ELECTROLYTIC SOLUTIONS OF HALIDES AND OXYHALIDES

Devon W. Meek May 2, 1961

I. INTRODUCTION

Reactions in non-aqueous ionizing solvents have attracted much interest during recent years.

The solvent-system formulation of acids and bases envisages for each solvent a self-ionization process. An "acid" is defined as a solute capable of increasing the conentration of the cation characteristic of the pure solvent, whereas a "base" increases the concentration of the corresponding anion of this self-ionization.

The major classification of solvents has been into protonic and non-protonic systems. Gutmann and Lindqvist (1) have suggested a further subdivision of the non-protonic systems. In extending the Bronsted acid-base definition to non-protonic solvents, an anion acceptor is designated as an acid and an anion donor as a base in these systems. Thus, a major emphasis is placed upon the nature of the exchanging ions between solute and solvent.

II. HALIDE SOLVENT SYSTEMS

The limited electrical conductivity of pure polyvalent halides suggests a dissociation mechanism of these substances in the liquid state according to (2,3,4,5,6).

$$AsF_3 + AsF_3 \rightleftarrows AsF_2^+ + AsF_4^-$$

$$BrF_3 + BrF_3 \rightleftarrows BrF_2^+ + BrF_4^-$$

$$IF_5 + IF_5 \rightleftarrows IF_4^+ + IF_6^-$$

$$VF_5 + VF_5 \rightleftarrows VF_4^+ + VF_6^-$$

$$NbF_5 + NbF_5 \rightleftarrows NbF_4^+ + NbF_6^-$$

$$ICl + ICl \rightleftarrows I^+ + ICl_2^-$$

$$AsCl_3 + AsCl_3 \rightleftarrows AsCl_2^+ + AsCl_4^-$$

$$AsBr_3 + AsBr_3 \rightleftarrows AsBr_2^+ + AsBr_4^-$$

$$B_2 + A_1 \rightleftarrows A_2 + B_1$$

Potassium fluoride functions as a good fluoride-ion donor in AsF_3, where SbF_5 forms the SbF_6^- ion in this solvent. (2),

$$\overbrace{KF \quad + \quad AsF_3}^{F^-} \rightleftarrows K^+ + AsF_4^-$$

$$AsF_3 + SbF_5 \rightleftarrows AsF_2^+ + SbF_6^-$$

Dissolution of polyvalent fluorides in BrF_3 results in the formation of compounds which have been formulated as, BrF_2AuF_4, $(BrF_2)_2SnF_6$, BrF_2SbF_6,BrF_2NbF_6, $(BrF_2)_2PTF_6$, and BrF_2RuF_6. (2) Reactions with bases (fluoride ion donors) in BrF_3 produced the fluoride complexes of $VF_6^=$ and $RuF_6^=$, for the first time (7,8). Higher coordination numbers than six are not observed for BrF_3 solutions, e.g.,MoF_6 does not react with bases.

Arsenic trichloride is an ampholytic solvent and can react as an acid as well as a base (6):

$$AsCl_3 + Cl^- \rightleftarrows AsCl_4^=$$

$$AsCl_3 \rightleftarrows AsCl_2^+ + Cl^-$$

The $[AsCl_4]^-$ ion is probably present in many salts that are isolated from this solvent. On the contrary, no compounds are known which contain the $AsCl_2^+$ ion. However conductimetric and potentiometric determinations indicate that this ion probably exists in the solvated form in certain acid chloride solutions,

$$AsCl_3 + SbCl_5 \rightleftarrows AsCl_2^+ + SbCl_6^-$$

$$AsCl_3 + FeCl_3 \rightleftarrows AsCl_2^+ + FeCl_4^-$$

Complex compounds of the unknown arsenic (V) chloride are obtained from the reaction of chlorine with $AsCl_3$-solution of $SbCl_5$ and PCl_5. (9),

$$AsCl_3 + Cl_2 + SbCl_5 \rightleftarrows [AsCl_4][SbCl_6]$$
$$AsCl_3 + Cl_2 + PCl_5 \rightleftarrows [AsCl_4][PCl_6]$$

Fused $AsBr_3$ (3,4,5), $SbCl_3$ (10), and $HgCl_2$ (11) have been investigated by conductimetric and potentiometric titrations as ionizing solvents.

III. OXYCHLORIDE SOLVENT SYSTEMS

A. Complex Formation Possibilities

Numerous coordination compounds seem to be formed by a halogen ion transfer in the polyvalent halide solvents above, but the additional possibility of oxygen coordination must be considered for the oxychloride solvents. (12)

In recent years, a series of crystalline addition compounds of the phosphoryl halides with anhydrous metal halides has been reported. Some of the compounds that have been isolated are $TiCl_4.2POCl_3$ (13), $TiCl_4.SbCl_5.(POCl_3)_3$ (14), $FeCl_3.POCl_3$, $2FeCl_3.3POCl_3.SbCl_5.POCl_3$ (15,18,31) $GaCl_3.POCl_3$ (16,17),$AlCl_3.POCl_3$,$AlCl_3.6POCl_3$, $SnCl_4.2POCl_3$(18), $NbCl_5.POCl_3$,$TaCl_5.POCl_3$(19), $UCl_4.4POCl_3$ (20), and $BCl_3.POCl_3$ (21). In contrast to the compounds which can be isolated from the polyvalent chloride solvents and which may be formulated as having a solvated chloride ion (e.g., $AsCl_4^-$), there are no compounds known which might contain the $POCl_4^-$ ion. Indication of the existence of $POCl_4^-$ ions in solution was obtained from an exchange study with radio chlorine (22,23), but the lack of a known solvate suggests its non existence in the crystalline state. The postulated

[illegible]

$AsCl_3 + Cl^- \rightleftharpoons AsCl_4^-$

$AsCl_3 \rightleftharpoons AsCl_2^+ + Cl^-$

[illegible]

$AsCl_3 + SbCl_5 \rightleftharpoons AsCl_2^+ + SbCl_6^-$

$AsCl_3 + FeCl_3 \rightleftharpoons AsCl_2^+ + FeCl_4^-$

[illegible]

$AsCl_3 + Cl_2 + SbCl_5 \rightarrow (AsCl_4)(SbCl_6)$
$AsCl_3 + Cl_2 + PCl_5 \rightarrow (AsCl_4)(PCl_6)$

[illegible]

iii. DISCUSSION [illegible]

a. [illegible]

[illegible]

[illegible]

ionization schemes are listed below for a number of non-aqueous solvents of this type.

$$NOCl \rightleftarrows NO^+ + Cl^-$$

$$2POCl_3 \rightleftarrows POCl_2^+ + POCl_4^-$$

$$2SeOCl_2 \rightleftarrows SeOCl^+ + SeOCl_3^-$$

$$2COCl_2 \rightleftarrows COCl^+ + COCl_3^-$$

$$SOCl_2 \rightleftarrows SOCl^+ + Cl^-$$

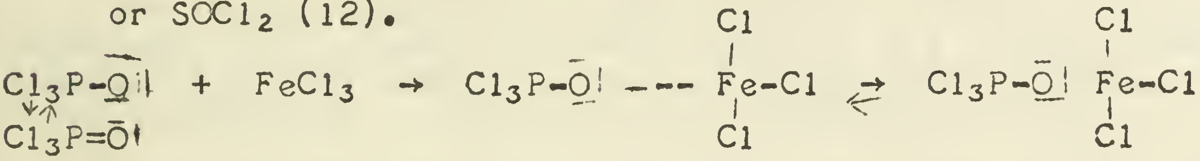
A radiochlorine exchange study (23) indicates that the transfer of activity from $(C_2H_5)_4NCl$ to $POCl_3$ does not proceed through a self-ionization of the solvent. Thus, the above ionization scheme is insignificant in the exchange mechanism.

The mechanism of complex formation is still unsolved. Currently, two theories are being used to explain the data.

1. The complex formation is caused by a chloride ion transfer between the solute and solvent (1,24).

$$POCl_3 + FeCl_3 \rightarrow POCl_2^+ + FeCl_4^-$$

2. The complex formation is caused by a Lewis acid-base interaction to form a coordinate bond through the oxygen atom of the $POCl_3$ or $SOCl_2$ (12).



$$\begin{array}{l} Cl_3P-\overline{\underline{O}}| \\ \updownarrow \\ Cl_3P=\bar{O}| \end{array} + FeCl_3 \rightarrow Cl_3P-\overline{\underline{O}}|\ ---\ \overset{Cl}{\underset{Cl}{Fe}}-Cl \rightleftarrows Cl_3P-\overline{\underline{O}}|\ \overset{Cl}{\underset{Cl}{Fe}}-Cl$$

Mechanism #1 has been used to explain the fact that red ferric chloride solutions in $POCl_3$ become yellow and exhibit absorption spectra characteristic of $FeCl_4^-$ ions upon dilution to about 10^{-4}<u>M</u> (e.g. (25,26,27),

$$FeCl_3 + POCl_3 \rightleftarrows FeCl_3ClPOCl_2 \rightleftarrows POCl_2^+ + FeCl_4^-$$

The Lewis explanation (mechanism #2) for this behavior would suggest an intermediate coordinate bond formation, with a resulting liberation of a chloride ion to form a cationic iron(III) species and $FeCl_4^-$, <u>i.e.</u>,

$$Cl_3PO + FeCl_3 \rightleftarrows [FeCl_3OPCl_3] \rightleftarrows [FeCl_{3-x}(OPCl_3)_{1+x}]^{+x} + XCl^-$$

$$FeCl_3(solv) + Cl^- \rightarrow FeCl_4^-$$

The important point to note is the origin of the chloride used for formation of the $FeCl_4^-$ for each mechanism. The formation of the compound $AlCl_3 \cdot 6POCl_3$ can occur only <u>via</u> mechanism #2. (Compare the composition to that of the complexes $AlCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6NH_3$, and $AlCl_3 \cdot 6(CH_3)_2SO$.)

Recent tracer investigations(22,23,28,29,30), x-ray diffraction studies (14,31), Raman (17) and infrared investigations (32) on solid addition compounds indicate that ionic mechanisms probably have been overemphasized for oxychloride solvents.

B. Phosphorus Oxychloride

1. Solvates

Gutmann, et.al., (33) concluded from a Raman spectral study on the solid $POCl_3 . SbCl_5$ that $SbCl_6^-$ ions exist in the solid. However, Lindqvist (31) recently studied single crystals of $POCl_3 . SbCl_6$ by x-ray analysis and concluded that the antimony is octahedrally coordinated with 5 chlorine atoms and 1 oxygen atom. Lindqvist has also shown that $POCl_3$ is coordinated through the oxygen atom in the $TiCl_4$ complex, i.e. $TiCl_4(OPCl_3)$ (14).

The Raman shifts for the compounds $AlCl_3 . POCl_3$ and $GaCl_3 . POCl_3$ indicate that compound formation occur by coordination of the oxygen atom from the $POCl_3$ with the metal atom to form Cl_3POMCl_3 (17). The P-O frequency in the infrared spectra of solid addition compounds between phosphoryl halides and polyvalent metal halides was shown to shift 50-95 $cm.^{-1}$ to a lower frequency with respect to the pure phosphoryl halide. This shift is interpreted to suggest M-O-P coordination in the solid addition compound of $TiCl_4$, $SnCl_4$, $TiBr_4$, and $FeBr_2$.

2. Conductivity and Potentiometric Studies

The conductimetric and potentiometric titrations of $FeCl_3$ with $(C_2H_5)_4NCl$ give breaks at a mole ratio of 1:1 (27). Conductivity studies show that $SbCl_5$ reacts with $(C_2H_5)_4NCl$ in $POCl_3$ to form $[(C_2H_5)_4N][SbCl_6]$, a strong binary electrolyte (34).

Conductivity and potentiometric titrations of $TiCl_4$ with $(C_2H_5)_4NCl$, $FeCl_3$, and $SbCl_5$ in $POCl_3$ show that $TiCl_4$ can take up 1 or 2 chloride ions or give up 1 chloride ion. The former case indicates the formation of the complexes $[TiCl_5 \text{ solv.}]^-$ and $[TiCl_6]^=$, whereas the latter suggests formation of $[TiCl_3(OPCl_3)_3]^+$ complexes of $[FeCl_4]^-$ and $[SbCl_6]^-$. The $TiCl_4$ is acting as an acid in one case and as a base in the others, thus showing its amphoteric character in $POCl_3$(13). Aluminum chloride also exhibits amphoteric character in $POCl_3$(2).

The necessity for oxygen coordination is compelling in order to explain the behavior of basic metal chlorides. Here the liberation of the chloride is possible in general under the influence of the solvent (2),

$$ZnCl_2 + 1\text{-}3POCl_3 \rightleftarrows [ZnCl(OPCl_3)_{1-3}]^+ + Cl^-$$

B. Thionyl Chloride

Corresponding investigations have been carried out on solutions in $SOCl_2$ and SO_2Cl_2. These ionic solvents are similar in many respects to phosphorus oxychloride. Many of the corresponding solvates with acid chlorides are known. Neutralization leads to chlorocomplexes and can be followed by preparative, conductiometric, and potentiometric studies (2).

The ionization of thionyl chloride has been investigated by conductiometric, potentiometric, and radiochlorine exchange studies (35,36,37,38). The ionization is expressed as:

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^-$$

Spandau and Brunneck (36,37) concluded from conductimetric titrations that $SbCl_5$, $AlCl_3$, and $SnCl_4$ are solvo-acids and that $TiCl_4$ and PCl_5 are amphoteric compounds, e.g.,

$$SbCl_5 + SOCl_2 \rightleftharpoons SOCl[SbCl_6] \rightleftharpoons SOCl^+ + [SbCl_6]^-$$

$$AlCl_3 + SOCl_2 \rightleftharpoons SOCl[AlCl_4] \rightleftharpoons SOCl^+ + [AlCl_4]^-$$

The titration of $AlCl_3$ by $(C_2H_5]_4NCl$ in $SOCl_2$ gives a break at a molar ratio of 1:1. Thus the equation is written as,

$$(C_2H_5)_4NCl + (SOCl)[AlCl_4] \rightleftharpoons [(C_2H_5)_4N][AlCl_4] + SOCl_2$$

The behavior of PCl_5 is described as an example of that of an amphoteric electrolyte in $SOCl_2$. Phosphorus pentachloride reacts with both $(C_2H_5)_4NCl$ and $SbCl_5$ to give conductivity breaks at 1:1 molar ratios. However, the amphoteric PCl_5 probably reacts as a mono-valent solvo-acid and as a monovalent solvo-base according to equations (a) and (b), respectively.

$$PCl_5 + SOCl_2 \rightleftharpoons SOCl[PCl_5] \rightleftharpoons SOCl^+ + [PCl_6]^- \qquad (a)$$

$$PCl_5 \rightleftharpoons PCl_4^+ + Cl^- \qquad (b)$$

IV. CONCLUSION

In spite of the tremendous amount of data that has been given in support of an ionization process for the oxychloride solvents, we may conclude that complex formation of the oxychlorides might be better explained in terms of a polar oxygen bond. This is to be contrasted with the bonding mechanism for complexes of polyvalent chlorides, which behave like Cl^- ion donors.

REFERENCES

1. V. Gutmann and I. Lindqvist, Z. phys. Chem., 203, 250 (1953).
2. V. Gutmann and M. Baaz, Angew. Chem., 71, 57 (1959).
3. G. Jander and K. Günter, Z. anorg. allgem. Chem., 302, 155 (1959).
4. G. Jander and K. Günter, ibid., 297, 81 (1959).
5. G. Jander and K. Günther, ibid., 298, 241 (1959).
6. I. Lindqvist, Acta Chem. Scand., 9, 73 (1955).
7. A. Hepworth, R. D. Peacock, and P. L. Robinson, J. Chem. Soc., 1197 (1954).
8. H. J. Emeleus and V. Gutmann, ibid., 2979 (1949).
9. V. Gutmann, Monatsh. 82, 473 (1951).
10. G. Jander and K. H. Swart, Z. anorg. allgem. Chem., 301, 80(1959).
11. G. Jander and K. Brodersen, Z. anorg. allgem. Chem., 265, 117(1951).
12. W. L. Groeneveld, Rec. trav. chim., 75, 594 (1956).
13. M. Baaz, V. Gutmann, and M. Y. A. Talaat, Monatsh. 91, 548(1960).
14. I. Lindqvist, Private communication to V. Gutmann, ibid., 91, 548 (1960).
15. R. Weber, Pogg. Ann. 208, 132, 452 (1867).
16. N. N. Greenwood and K. Wade, J. Chem. Soc., 1516(1957).

17. H. Gerding, J. A. Koningstein, and E. R. vander Worm, Spectrochim. Acta, 16, 881 (1960).
18. M. Agerman, L. H. Andersson, I. Lindqvist, and M. Zackrisson, Acta Chem. Scand., 12, 477 (1958).
19. I. A. Sheka, B. A. Voitowick, and L. A. Niselson, Russian J. Inorg. Chem., 4, 813 (1959).
20. R. E. Panzer and J. F. Suttle, J. Inorg. Nucl. Chem., 15, 67 (1960).
21. A. B. Burg and M. K. Pross, J. Am. Chem. Soc., 65, 1637 (1943).
22. J. Lewis and D. B. Sowerby, Chem. Soc. Spec. Publications #10, 123 (1957).
23. J. Lewis and D. B. Sowerby, J. Chem. Soc., 336 (1957).
24. V. Gutmann, Rec. trav. Chim., 75, 603 (1956).
25. M. Baaz, V. Gutmann, and L. Hübner, Monatsh. Chem., 91, 537 (1960).
26. V. Gutmann and M. Baaz, ibid., 90, 271 (1959).
27. V. Gutmann and M. Baaz, ibid., 90, 729 (1959).
28. J. L. Houston and C. E. Lang, J. Inorg. Nucl. Chem., 4, 30 (1957).
29. J. L. Houston, ibid., 2, 128 (1956).
30. L. F. Johnson, Jr., and T. H. Norris, J. Am. Chem. Soc., 79, 1584 (1957).
31. I. Lindqvist and C. I. Branden, Acta Chem. Scand., 12, 134 (1958).
32. J. C. Sheldon and S. Y. Tyree, Jr., J. Am. Chem. Soc., 80, 4775 (1958).
33. H. Maschka, V. Gutmann, and R. Sponer, Monatsh. 86, 52 (1955).
34. M. Baaz and V. Gutmann, ibid., 90, 426 (1959).
35. S. S. Sandhu, B. S. Chakkal, and G. S. Sandhu, J. Indian Chem. Soc., 37, 329 (1960).
36. H. Spandau and E. Brunneck, Z. anorg. allgem. Chem., 270, 201 (1952).
37. H. Spandau and E. Brunneck, ibid., 278, 197 (1955).
38. B. J. Masters, N. D. Potter, D. R. Asher, and T. H. Norris, J. Am. Chem. Soc., 78, 4252 (1956).

CORRELATION OF INFRARED SPECTRAL SHIFTS WITH BASICITY

Melvin D. Joesten May 9, 1961

I. INTRODUCTION

The increasing importance of nonaqueous solvents has resulted in many attempts at finding relationships between basicity and some easily measured experimental quantity. More than twenty years ago, infrared stretching frequency shifts, $\Delta\nu$, of a characteristic group, X-H, were found to be related to the strength of the hydrogen bond formed. A linear relationship between stretching frequency shifts of O-H acids on hydrogen bonding and the logarithm of the association constants, log K_{assn}, has been observed. The frequency shift has also been linearly related to the pK_a of the proton donor or acceptor in aqueous solution. Pimentel and McClellan (1) have made a survey of this work in their book on the hydrogen bond.

Recently, the concept has been extended to the measurement of other characteristic groups, such as C=O and I-Cl, in an attempt to measure the basicity of a series of Lewis bases. The same trends were noted here as in the hydrogen-bonded series. Therefore, acids and bases will be defined in the general terms of proton donors or electron pair acceptors and proton acceptors or electron pair donors, respectively.

II. HYDROGEN BONDING METHODS

Badger and Bauer (2) found a linear relation between frequency shift and the interaction energy for hydrogen bond associations in measuring vapor-liquid frequency shifts for HCl, H_2O, HCN, and C_2H_5OH. Later, Badger (3) and Herman (4) found that carboxylic acids did not follow this linear relationship. However, enthalpy values for these interactions were fairly inaccurate. Gordy and Stanford (5,6) measured the frequency shift of the O-D group of CH_3OD in over seventy different solvents. They found a linear relation between pK_a of the solvents as measured in water and the frequency shifts they produced in the O-D band. They obtained basicity constant values for other bases, such as acetophenone, by extrapolation. Hammett (7) noted that their extrapolated value for acetophenone agreed very well with the value he obtained by a different method.

Gordy and Stanford also found a correlation between heats of mixing and frequency shifts, using ΔH_{soln} for $CHCl_3$ in the same bases that they measured the frequency shift of the O-D band. This is indirect evidence for the proposal that $\Delta\nu$ is related to ΔH of hydrogen-bond formation.

Gordy (8) found evidence that the bases he studied showed the same order of basicity with two different acids. He found a linear relationship between $\Delta\nu$ of the O-D band in D_2O and CH_3OD with the same bases.

Tamres and coworkers improved and extended Gordy's work. They measured the electron donor ability of a number of pyridine bases (9), aliphatic amines (9), cyclic ethers (10,11), and benzene derivatives (12). They found that the linear relationship between the O-D stretching frequency shift and pK_a held only for bases similar in structure.

Grunwald and Coburn (13) have derived equations relating the free energy and the frequency shift for reactions involving hydrogen bonding of compounds similar in structure. The equation for structures involving a carbonyl group, $\Delta F^\circ = 0.2 - .005\,\Delta\nu$, and the equation for structures involving the proton acceptor electrons in sp^3 orbitals, $\Delta F^\circ = 1.35 - .005\,\Delta\nu$, are both fitted with the same slope. This suggests that either the Badger rule applies to both sets of data, the greater stability of the carbonyl complexes resulting from their greater entropy; or that ΔH is a linear function of $\Delta\nu$, rather than proportional to it.

Gordon (14) has recently proposed two equations for converting equilibrium constants in aqueous solutions to association constants in nonaqueous solutions.

$$\Delta \log K_{assn.} = -a\,\Delta pK_a^{HA}$$

$$\Delta \log K_{assn.} = b\,\Delta pK_a^{BH^+}$$

He tests these equations by combining the observation of a linear relation between $\Delta\nu$ of O-H acids and $\log K_{assn.}$ when hydrogen bonding takes place with the observation that $\Delta\nu$ has been found to be linearly related to the pK_a of the proton donor or acceptor in aqueous solutions. He finds that a single $\Delta\nu$ $-\log K_{assn.}$ slope does not hold for all O-H association equilibria. Within a given structural series, however, the equations are of value in calculating equilibrium constants in nonaqueous solvents.

Recently, the basicity of eighteen organophosphorus compounds was measured, using phenol as the acid. Changes in free energy, enthalpy, and entropy for the equilibrium reactions were found to vary linearly with the frequency shift of the O-H group (15).

III. EXPERIMENTAL CONSIDERATIONS

A. Temperature

Most of the work done since Badger's correlation of ΔH and $\Delta\nu$ has sought other correlations, such as $\Delta\nu$ and $\log K_{assn.}$, because of the difficulty in obtaining ΔH values experimentally.

Finch and Lippincott (16,17) have found that the bonded O-H frequency for a series of alcohols decreases in frequency and increases in intensity as the temperature decreases. Hughes and coworkers (18) made the same observation on a phenol series. If the absorption coefficients of the free acid or complex are not constant with

Ferric and [illegible] Thus [illegible] (14), [illegible] (15), [illegible] (16, 17), and [illegible] (17). [illegible]

[illegible] (13) [illegible]

[illegible]

$$\log K_{assoc.} = a + b \log [illegible]$$

$$\log K_{assoc.} = a + b/[illegible]$$

[illegible]

[illegible]

III. [illegible]

A. [illegible]

[illegible]

[illegible]

temperature, serious errors would be obtained in the determination of ΔH by infrared methods.

B. Species Present

Another factor to consider is the uncertainty of the reactant or product species present. If dilute solutions in an inert solvent are used, the free acid or base is essentially present in the monomeric form. The nature of the reaction product depends on the relative strengths of the acid and base. The use of the O-H stretching frequency shift as a measure of base strength is applicable only when the acid and base are present as a 1:1 hydrogen-bonded complex (19).

C. Solvent Effects

Bellamy and coworkers (20,21,22) have made a series of studies which effectively demonstrate that the dielectric constant of the solvent has little effect on the infrared frequency shift of a characteristic group.

IV. USE OF FREQUENCY SHIFTS TO ESTABLISH ORDER OF BASICITIES

In addition to the studies on the correlation of $\Delta \nu$ with ΔH and log $K_{assn.}$ as discussed in section II, workers have used measurements of $\Delta \nu$ to establish a relative order of basicity for series of compounds. Recent publications by West and coworkers provide a good example.

West (23) found that the basicity of olefins toward phenol increases with increasing alkyl substitution at the double bond. The opposite effect had been observed earlier using silver ion as the acid.

West and Baney (24) compared the acidity and basicity of a series of silanols and carbinols. They found the silanols to be much more acidic than the carbinols but nearly as basic. They attribute the increased acidity of the silanols to pi-bonding involving one unshared pair of electrons of oxygen and an unfilled *d*-orbital of silicon, which increases the positive character of the proton. They also measured the acidity and basicity of the compounds Ph_3MOH, where M is C, Si, Ge, Sn, or Pb, to see if pi-bonding is important in cases other than silicon (25). They concluded that pi-bonding from oxygen to metal decreases in going from silicon to lead. West has also examined the ether-alkoxysilane-siloxane series (26), and the acetylene series (27).

V. LEWIS ACID-BASE METHODS

Person and coworkers (28,29,30) found a quantitative similarity between the hydrogen bond, B...H-X, and the bond, B...X-Y, where X-Y represents an interhalogen, such as ICl. They found a linear relationship between the added effective charge of the complex, ε_a, and the change in the force constant, Δk, which holds for both Lewis complexes and hydrogen-bonded complexes. The added effective charge is calculated from intensity values, and Δk is calculated from frequency

shifts. This correlation can be explained by the "charge-transfer" model, given in section VI.

Schmulbach (31) proposed the correlation of $\Delta\nu$ with ΔH for Lewis bases, using iodine as the standard Lewis acid. Wenz (32) found this correlation to be linear with respect to the amide series and for certain other Lewis acids, such as SO_2. He found, however, that data for the Lewis acids, phenol and ICl, did not fall on the same line. This indicates again the limitation of using this correlation. Data on other Lewis acids is needed before definite conclusions can be drawn.

VI. THEORETICAL MODEL

The work of Person and coworkers is important because of its experimental support for using the "charge-transfer" model to explain both Lewis acid-base interactions and hydrogen-bond interactions. Mulliken (33) first proposed this model to explain the molecular addition compounds of iodine. Tsubomura (34,35) suggested that the charge-transfer energy was an important factor in causing the increase in intensity that accompanies the frequency shift in hydrogen bonding.

$$\text{B...H-X} \longleftrightarrow (\text{B-H..})^{+}\text{..X}^{-}$$

$$\text{B...X-Y} \longleftrightarrow (\text{B-X..})^{+}\text{..Y}^{-}$$

$$\underline{a} \qquad\qquad\qquad \underline{b}$$

For weak bases the no-bond structure, a, is the most important. As the H-X or X-Y force constant decreases, the ionic structure, b, becomes more important.

VII. SUMMARY

The use of infrared stretching frequency shifts for making qualitative predictions is shown to be of value. In bases of similar structure, log $K_{assn.}$ is linearly related to the infrared frequency shift of a reference group. Progress is being made in the quantitative extension of these relationships.

More emphasis on enthalpy measurements is needed, as enthalpy gives a clearer picture of the strength of interaction in acid-base complexes. It is fairly evident that no simple relationship between enthalpy and frequency shift exists, but with the study of more acid-base systems a correlation of any one system with another may be found.

BIBLIOGRAPHY

1. G. C. Pimentel, A. L. McClellan, The Hydrogen Bond, W. H. Freeman, San Francisco (1960).
2. R. M. Badger, S. H. Bauer, J. Chem. Phys., 5, 839 (1937).
3. R. M. Badger, J. Chem. Phys., 8, 288 (1940).
4. R. C. Herman, J. Chem. Phys., 8, 252 (1940).
5. W. Gordy, S. C. Stanford, J. Chem. Phys., 8, 170 (1940).
6. W. Gordy, S. C. Stanford, J. Chem. Phys., 9, 204 (1941).
7. L. P. Hammett, J. Chem. Phys., 8, 644 (1940).
8. W. Gordy, J. Chem. Phys., 9, 215 (1941).
9. M. Tamres, S. Searles, E. M. Leighly, D. W. Mohrman, J. Am. Chem. Soc., 76, 3983 (1954).
10. S. Searles, M. Tamres, G. M. Barrow, J. Am. Chem. Soc., 75, 71 (1953).
11. S. Searles, M. Tamres, J. Am. Chem. Soc., 73, 3704 (1951).
12. M. Tamres, J. Am. Chem. Soc., 74, 3375 (1952).
13. E. Grunwald, W. C. Coburn, Jr., J. Am. Chem. Soc., 80, 1322 (1958).
14. J. E. Gordon, J. Org. Chem., 26, 738 (1961).
15. G. Aksnes, T. Gramstad, Acta. Chem. Scand., 14, 1485 (1960).
16. J. N. Finch, E. R. Lippincott, J. Chem. Phys., 24, 908 (1956).
17. J. N. Finch, E. R. Lippincott, J. Phys. Chem., 61, 894 (1957).
18. R. H. Hughes, R. J. Martin, N. D. Coggeshall, J. Chem. Phys., 24, 489 (1956).
19. G. M. Barrow, J. Am. Chem. Soc., 78, 5802 (1956).
20. L. J. Bellamy, R. L. Williams, Proc. Roy. Soc., 255A, 22 (1960).
21. L. J. Bellamy, H. E. Hallam, R. L. Williams, Trans. Far. Soc., 54, 1120 (1958).
22. L. J. Bellamy, H. E. Hallam, Trans. Far. Soc., 55, 222 (1959).
23. R. West, J. Am. Chem. Soc., 81, 1614 (1959).
24. R. West, R. H. Baney, J. Am. Chem. Soc., 81, 6145 (1959).
25. R. West, R. H. Baney, D. L. Powell, J. Am. Chem. Soc., 82, 6269 (1960).
26. R. West, L. S. Whatley, K. J. Lake, J. Am. Chem. Soc., 83, 761 (1961).
27. R. West, C. S. Kraihanzel, J. Am. Chem. Soc., 83, 765 (1961).
28. W. B. Person, R. E. Humphrey, W. A. Deskin, A. I. Popov, J. Am. Chem. Soc., 80, 2049 (1958).
29. W. B. Person, R. E. Humphrey, A. I. Popov, J. Am. Chem. Soc., 81, 273 (1959).
30. W. B. Person, R. E. Erickson, R. E. Buckles, J. Am. Chem. Soc., 82, 29 (1960).
31. C. D. Schmulbach, Ph.D. Thesis, University of Illinois, 1958.
32. D. A. Wenz, Ph.D. Thesis, University of Illinois, 1961.
33. R. S. Mulliken, J. Am. Chem. Soc., 74, 811 (1952).
34. H. Tsubomura, J. Chem. Phys., 23, 2130 (1955).
35. H. Tsubomura, J. Chem. Phys., 24, 927 (1956).

SELECTED USES OF NUCLEAR MAGNETIC RESONANCE IN INORGANIC CHEMISTRY

Richard M. Klein May 16, 1961

I. INTRODUCTION

Since the discovery of the nuclear resonance phenomenon independently by Purcell(1) and Bloch(2) in 1946, this technique has grown extremely rapidly in scope and importance and has been used extensively to solve a wide variety of inorganic, as well as organic, chemical problems. The development of commercial NMR spectrometers in 1955 was largely responsible for accelerating the growth in this field.

II. THEORY OF NUCLEAR RESONANCE

A. Magnetic Properties of Nucleii

If a given nucleus has a spin quantum number of I(equals 0, 1/2, 1, 3/2 etc.) then it has 2I + 1 distinct states in which the components of angular momentum along any selected direction will have values I, (I-1)...0...(-I+1), -I. These magnetic quantum numbers (m) all have the same energy in the absence of external fields.

If a uniform magnetic field is now introduced to a nucleus with a magnetic moment (I+0), then <u>m</u> levels may line up with or oppose the field in various ways, giving rise to 2I+1 different equally spaced energy levels. Application of an external frequency can then cause the nucleus to shift from a given energy level to the next higher one, hence causing resonance to occur. The frequency necessary to accomplish this, sometimes referred to as the Larmour or precession frequency, since this latter term describes the process by which the energy is actually transferred in the nucleus, is direcly proportional to the applied field, Ho. In practice, the spectrum is most usually measured by use of a constant applied frequency and Ho is varied until resonance occurs.

B. Chemical Shifts

If any given nucleus, for instance hydrogen, were exposed alone to a magnetic field, resonance would always occur at the same place for each hydrogen nucleus. However, varying magnetic environments, caused by the atoms surrounding this nucleus, cause the same nucleus to experience a different field for each chemically distinct position. This displaement of signals for different chemical environments is called the "chemical shift."

C. Spin-Spin Splitting

In addition to the chemical shift caused by the electronic environment of the nucleus, neighboring nucleii with magnetic moments can interact with the nucleus under study and cause a splitting in the peak, proportional to the scalar product $J_{12}I(_{1})I_{2}$ (J_{12}=coupling constant), and independent of Ho. This can also be pictured as being due to the effect of the neighboring nucleus

interfering with or reinforcing Ho, hence "splitting" the field into higher and lower components. In general, a nucleus B will split the peak from a neighboring nucleus A into as many parts as it (B) has spin states: i.e., into 2I+1 peaks. More theory is given in the reference books devoted to NMR (3,4,5).

III. STRUCTURAL STUDIES

A. Boron Hydrides

Boron exists in two naturally occuring isotopes, of which the B^{11} species (81% abundance) is most used in NMR work due to its high abundance and relatively low spin quantum number (I=3/2).

Proton resonance of B_2H_6 (6,7) shows that the bridge protons precess at a higher field than do the terminal protons. Confirmation of the bridge-like structure was made by Ogg(8) who detected two different hydrogen peaks in the spectra, hence eliminating the ethane-type structure. Further confirmation was provided by the B^{11} spectra, which showed a triplet as a result of splitting by the bridge protons.

The compound B_5H_9, known from crystal structure analysis to have a tetragonal configuration of the boron nucleii, was studied by NMR techniques (7,9). Proton resonance indicates three different types of protons, corresponding to the hydrogen atoms directly bonded to the basal boron atoms (four peaks); four slightly shifted peaks of much lower intensity, corresponding to the apical hydrogen; and a superimposed "bump", due to the bridge hydrogens. B^{11} resonance further confirms the tetrahedral configuration, showing two doublets with an intensity ratio of 4:1.

B. Fluorine Compounds

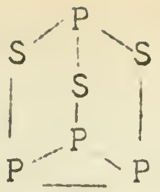
The fluorine nucleus is ideally suited to NMR study, since it gives a very strong signal and high chemical shifts, and has a spin quantum number of 1/2. Much of the theory concerning causes of chemical shifts has been advanced as a result of studies on fluorine-containing compounds (10).

For BrF_5 and IF_5, two fluorine signals were detected with intensities in the ratio of 4:1, supporting the tetragonal pyramid type structure. In SF_4, two equally intense triplets are found at -100 (11), indicating two pairs of structurally non-equivalent fluorine atoms in the molecule, and a trigonal-bipyramid structure.

Similarly, peaks for SO_3F_2 and SF_5.OF (12) indicate that the former has an SO_2F.OF structure whereas the latter has all the fluorine atoms bonded to sulfur in chemically equivalent positions.

C. Phosphorus Compounds

The nuclide P^{31} is the only stable isotope of phosphorus, with I=1/2 It has a smaller magnetic moment than hydrogen or fluorine, and hence its NMR sensitivity is about 7% of that for the latter nucleii. However sharp resonance peaks are obtained.

The structure  for P_4S_3 has been confirmed by NMR(13), which shows a very intense doublet corresponding to the bottom three phosphorus atoms, and a weak quadruplet for the top phosphorus atom.

Five diphosphorus oxyacids, i.e. the pyrophosphite, hypophosphate, pyrophosphite, isohypophosphate, and diphosphite anions (the latter two hitherto only postulated) were detected and their structures elucidated using NMR data (13). This study is significant in that, for the hypophosphate ion, evidence had been cited for and against a symmetrical structure. This study proved that the symmetrical structure is correct.

IV. STUDIES OF COORDINATION COMPOUNDS

A. BF_3 Complexes

Diehl and Ogg (14,15,16,17) have studied the F^{19} resonance in systems containing H_2O, $CH_3OH.BF_3$, and ROH as starting materials. They measured the NMR spectra at 50°C., 20°C., and -80°C. and found, at 50° a sharp peak, which was broadened at 20°, and finally resolved into three separate peaks at -80°. The latter three peaks are due to three complexes, $CH_3OH.BF_3$, $ROH.BF_3$, and $HOH.BF_3$, which coalesce and finally merge into one peak at higher temperatures due to rapid exchange of the BF_3. Furthermore, the area of an individual resonance peak is a measure of the concentration of that particular complex, and hence gives a rough measure of the stability of the complex. Stabilities follow the order $H_2O > CH_3OH > C_2H_5OH >$ *n*PrOH > *n*-BuOH.

These studies also resulted in the suggestion of a possible mechanism for the exchange of BF_3 between the different ligands.

B. Hydrated Cations

Preliminary results from studies of the O^{17} resonance of metal ions in aqueous solutions by Jackson, Taube, and Lemons (18) indicate the possible use of NMR in determining the hydration number of cations. Two O^{17} peaks should be observed, one for the free water and one due to interaction of hydrated water with the cation. The area under the cation curve is then a relative indication of the amount of water of hydration. In this way, $[Co(NH_3)_5H_2O]^{3+}$ was shown to have one water of hydration.

Other cations which gave only one O^{17} peak, such as Al^{3+}, Be^{2+}, and Ga^{3+}, split into free and hydrated water peaks when a paramagnetic ion was added to the solution. Hence, these were also determined to be hydrated, with fairly slow water exchange taking place. This method is not yet refined enough to give exact hydration numbers, but order of magnitude results agree with a coordination number of four for Be^{2+} and six for Al^{3+}.

Axtmann(33) has related the acidity of hydrated cations to the chemical shifts observed. For Ca^{+2}, Cd^{+2}, La^{+3}, Mg^{+2}, Sr^{+2}, Th^{+4}, Zn^{+2}, and ZnO^{+2} hydrates, a plot of pKa vs. Molar proton shifts showed a fairly linear relationship, the most acidic cations giving the largest shifts, due to greater polarization of the H_2O molecule. These ions are all believed to be hexahydrated and electrostatically bonded to water. Those cations which deviate greatly from this linear relationship, UO_2^{+2}, Pb^{+2}, and Al^{+3} are thought to be covalently bonded and hence less polarizing.

C. Correlations With Crystal Field Theory

Shifts in the cobalt NMR spectrum to lower field strength as ligands are substituted for CN in $K_3[Co(CN)_6]$ are believed due to second order paramagnetic susceptibility contributions, and hence would be inversely proportional to Dq in the cobalt crystal field (34,35). Hence, stronger ligands, increasing Dq, decrease the paramagnetic contribution from the d^6 electrons and decrease this downward shift. An order of decreasing paramagnetic contributions with various ligands, and hence a measure of the increasing coordinating power of the ligand, was established as follows; acac $CO_3^{=} > Cl^{-} > CO_3^{-} > H_2O > NH_3 > en > dipy > NO_2 > CN^{-}$. This series is in excellent agreement with spectral data giving the energy difference between the $t_{2}g$ and eg levels in the various cobalt complexes.

V. EXCHANGE STUDIES

The use of NMR to determine rates of exchange was developed by Gutowsky and Saika (19), who showed that a rapid exchange of atoms between molecules which originally possessed two distinct peaks will tend to broaden the peaks and finally result in a single sharp peak. This transition depends on the frequency separation of the components in the complex line, the lifetimes of the chemical states, and, indirectly, upon the lifetime of the nuclear spin states.

Muetterties and Phillips have based several exchange studies on this discovery(20). Their measurements at various temperatures for ClF_3 showed two widely separated doublets at -40°, broadening into two singlets at -15°; two much broader singlets at 0°; and finally one peak at 60°.

Gutowsky's equation for the average lifetime, τ, in a given chemical environment, of a nucleus under going exchange is $\tau = 1/4\pi\delta w$, where δw is the chemical shift between the exchanging environments. Hence, the average lifetime of a given fluorine atom in ClF_3 at -15° and 60° was determined, and from these values an average value of the activation energy of exchange, over this range, of 4.8 kcal. was calculated.

Similar studies were carried out using BrF_3, IF_5, and BrF_5. For studies on SF_4, Muetterties and Phillips took advantage of a more advanced theory by Gutowsky and Holm (21) for finding the average lifetime and activation energy of fluorine exchange. They detected the same spectral features as were present in the other

exchange studies and were able to make the following qualitative estimate about the mechanism of exchange in SF_4.

1) Since the addition of broken glass did not affect the transition temperature between "slow" and "fast" exchange, a wall mechanism was excluded.

2) If a second or higher order process was correct, then the exchange rate should be proportional to the SF_4 concentration. This was borne out by studies of SF_4 in various solvents, in which the transition temperature was increased by 25 to 60^0 by diluting the SF_4.

A mechanism involving a dimeric intermediate using fluorine bridges was proposed and is supported in part by studies on SeF_4 and TeF_4, which associate more readily and also exchange more rapidly than SF_4.

These workers have also postulated on acid-catalyzed exchange mechanism for SiF_6 due to NMR data.

Meiboom (22) has studied the proton transfer in H_2O by means of NMR and determined k_1 and k_2 for the reactions

a) $H_2O + H_3O^+ \xrightarrow{k_1} H_2OH^+ + H_2O$

b) $OH_2 + OH^- \xrightarrow{k_2} OH^- + HOH$

VI. STUDIES IN SOLUTIONS OF AQUEOUS ELECTROLYTES

Hoppe and Whittaker (23) have noted that addition of KNO_3 to HNO_3 results in a large negative proton chemical shift. This is presumed to be due to hydrogen bond formation between the nitrate ion and nitric acid, lowering the electron shielding on the proton. Further interpretation of the data shows that at low nitrate concentrations a 1:2 complex is formed, whereas at a higher ratio of NO_3^-/HNO_3 a 1:1 species results. A similar study also indicates the 1:1 compound H_3NO_4 is formed between water and nitric acid.

Shoolery and Adler (24) made some qualitative studies on electrolytic aqueous solutions and showed that uni-univalent electrolytes tend to break the hydrogen bonds in water and shift the resonance to higher fields. The smaller and more solvated multi-valent electrolytes, however, have a more pronounced effect on the polarization of the proton decreasing the shielding and shifting the resonance to lower frequencies.

VII. CHEMICAL ANALYSIS

NMR is also quite useful both in qualitative and quantitative chemical analysis. Van Wazer et. al.(25) using the system $H_2O-HF-P_2O_5$, studied the P^{31} and F^{19} spectra of equilibrium mixtures from various concentrations of starting materials. They were able to assign peaks to nine different species in the mixture. By measuring the areas under each peak they were able to assign relative molar values for each species and hence calculate several equilibrium constants for the mixture.

Of additional interest are the studies which have detected the presence of hitherto postulated but unknown mixed halides. Coyle and Stone (26) measured the NMR spectra of equilibrium mixtures of BF_3 and BCl_3, BF_3 and BBr_3, and a ternary mixture of BF_3, BCl_3, and BBr_3. In the first two mixtures three quartets typical of the BF_3, BF_2X, and BFX_2 compounds were noted. In the ternary system, the strong BF_3 peak is accompanied by four quartets at the same position as they appeared in the binary mixtures, representing the various possible BF_xX_{3-x} compounds. Another quartet, appearing between the $BFBr_2$ and $BFCl_2$, is attributed unequivocally to BFBrCl. The order of chemical shifts also indicates decreasing π electron donation in the sequence $F > Cl > Br$, and this probably accounts for a Lewis acidity order $BBr_3 > BCl_3 > BF_3$, postulated by Cotton and Leto.

The Sn^{119} NMR spectra of $SnCl_4$, $SnBr_4$, and SnI_4 mixtures (27) gave peaks in the position, and with the relative intensities, that would be expected for a random mixture of all possible mixed halides at equilibrium. In addition, three new peaks corresponding to the hitherto unknown $SnClBrI_2$, $SnClBr_2I$, and $SnCl_2BrI$ were found.

A group from Monsanto has worked on the identity of various mixed halides of phosphrous. NMR data of Groenweghe and Payne(28) showed, for a mixture of $POCl_3$ and $POBr_3$, or the corresponding $PSCl_3$-$PSBR_3$ mixtures, peaks for all the possible mixed halides. The amount of phosphorus present in any given compound was determined to ± 1 mole per cent. Here again random distribution takes place, but in the triply connected phosphorus halides, analysis by NMR detected all the mixed halides of PCl_3-PBr_3. The mixture was not a random one.however (29).

VIII. CONCLUSION

This review touches only on some of the many uses of nuclear magnetic resonance in inorganic chemistry. Not mentioned are studies of compounds in the solid state, many theoretical applications, and more specific uses under the topics mentioned here. Other nucleii adaptable to the technique include Cl, Br, I, Na, Rb, Cs, Pb, Cu, Tl and Sn.

In general, the disadvantages arising from NMR studies are that the interactions disturbing the resonance lines are numerous and often complex, the applications are limitted to certain nucleii, and it is not suitable for analysis of trace concentrations.

On the other hand, it is a non destructive method and hence permits the use of small samples (5-10 mg. for hydrogen and fluorine resonance), and is relatively insensitive to impurities. It takes little time to run, usually can be interpreted simply and unambiguously, and applies to situations where other methods (x-ray infra-red, Raman or ultra-violet) are difficult to apply or are inconclusive(30).

Excellent summaries of references to the work done in this field can be found in chapters 12,18 and 19 of reference (3), and in the review articles of Bersohn (31) and Fraenkel and Segal (32).

Of additional interest are the alkaline earth [illegible] detecting the [illegible]

Thomson's [illegible]

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VIII. CONCLUSIONS

This review [illegible] nuclear magnetic resonance in inorganic chemistry. [illegible]

In summary, [illegible]

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IX. REFERENCES

1. E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev., 69, 37 (1946).
2. F. Bloch, W. W. Hansen, and M. E. Packard, ibid, 69, 127 (1946).
3. J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, New York, McGraw Hill Book Co., Inc., 1959.
4. J. D. Roberts, *Nuclear Magnetic Resonance*, New York, McGraw Hill Book Co., Inc., 1959.
5. L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, New York, Pergamon Press, 1959.
6. J. Kelly, J. Ray, and R. A. Ogg, Phys. Rev., 94, 767 (1954).
7. J. N. Shoolery, Disc. Faraday Soc., 19, 215 (1955).
8. R. A. Ogg, J. Chem. Phys., 22, 1933 (1954).
9. R. Shaeffer, J. N. Shoolery, and R. Jones, J. Am. Chem. Soc., 79, 4606 (1957).
10. A. Saika and C. P. Slichter, J. Chem. Phys., 22, 26 (1954).
11. F. A. Cotton, J. W. George, and J. S. Waugh, ibid, 28, 994 (1958).
12. F. B. Dudley, J. N. Shoolery, and G. H. Cady, J. Am. Chem. Soc., 78, 568 (1956).
13. C. F. Callis, J. R. van Wazer, J. N. Shoolery, and W. A. Anderson, ibid, 79, 2719 (1957).
14. P. Diehl and R. A. Ogg, J. Inorg. Nucl. Chem., 8, 468 (1958).
15. P. Diehl and R. A. Ogg, Nature, 180, 1114 (1957).
16. P. Diehl and R. A. Ogg, Helv. Phys. Acta., 31, 43 (1958).
17. P. Diehl and R. A. Ogg, ibid, 31, 685 (1958).
18. J. A. Jackson, J. F. Lemons, and H. Taube, J. Chem. Phys., 32, 553 (1960).
19. H. S. Gutowsky and A. Saika, ibid, 21, 1688 (1953).
20. E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc., 79, 322 (1957); 81, 1084 (1959).
21. H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228 (1956).
22. S. Meiboom, ibid, 34, 375 (1961).
23. J. A. Hoppe and A. G. Whittaker, ibid, 30, 417 (1959).

D. [illegible]

1. [illegible] (19[illegible]).

2. [illegible] (19[illegible]).

3. [illegible]

4. [illegible]

5. [illegible]

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20. [illegible] (19[illegible]).

21. [illegible] (19[illegible]).

22. [illegible] (19[illegible]).

23. [illegible] (19[illegible]).

24. J. N. Shoolery and B. J. Adler, ibid, 23, 805 (1955).

25. D. P. Ames, S. Onashi, C. F. Callis, and J. R. van Wazer, J. Am. Chem. Soc., 81, 6350 (1959).

26. T. D. Coyle and F. G. A. Stone, J. Chem. Phys, 32, 1892 (1960).

27. T. C. Burke and P. C. Lauterbur, J. Am. Chem. Soc., 83, 326 (1961).

28. L. C. D. Groenweghe and J. H. Payne, Jr., ibid, 81, 6357 (1959).

29. E. Fluck, J. R. van Wazer, and L. C. D. Groenweghe, ibid, 81, 6363 (1959).

30. M. P. Simmonnin, Bull. Soc. Chim. France, 1961, 401.

31. R. Bersbhn, Ann. Rev. Phys. Chem., 11, 369 (1960).

32. G. K. Fraenkel and B. Segal, ibid, 10, 435 (1959).

33. R. C. Axtmann, J. Chem. Phys., 30, 340 (1959).

34. R. Freeman, G. R. Murray, and R. E. Richards, Proc. Roy. Soc., A 242, 455 (1957).

35. S. S. Dharmatti and C. R. Kanehar, J. Chem. Phys., 31, 1436 (1959).

COMPLEX HYDRIDES OF THE TRANSITION METALS

Anastas G. Karipides May 23, 1961

INTRODUCTION

In recent years, there has been considerable interest in the hydrides of the transition metals both on structural grounds and because of their general chemical reactivity. Although iron carbonyl hydride and cobalt carbonyl hydride have been known for about 30 years, most of the progress in this area has been made only recently.

In addition to the metal carbonyl hydrides, hydride complexes of metal cyclopentadienyl compounds and phosphine and arsine hydrido complexes have been studied. A few types of other complexes containing metal-hydrogen bonds have also been described.

The chemical and physical properties of the complex transition metal hydrides are varied. Although some of these hydrides have been studied extensively from a synthetic point of view, there still is not an adequate description of the nature of the metal-hydrogen bond in these compounds, which will satisfactorily explain the observed chemical and physical properties. Thus, the cyclopentadienyl hydride complexes of rhenium, molybdenum, and tungsten are basic, whereas the carbonyl hydrides of iron and cobalt are acidic. Others, such as $HMn(CO)_5$ are relatively neutral. Also the paucity of information on hydrides of the transition elements prior to about 1955 has been due to the notion that the metal-hydrogen bond in unstable. This was substantiated for iron and cobalt carbonyl hydrides, which decompose readily above -50° and -20°, respectively. But some recently prepared hydrides are much more stable. For example, $Pt(PEt_3)_2HCl$ melts at 82° and can be distilled unchanged at $130^{\circ}/.01$mm.(1) Other hydrides have still higher melting points.

The only unifying feactures of these hydrides from a spectroscopic viewpoint are that the metal-hydrogen stretching frequency in the IR is around 2000 $cm.^{-1}$ and that the proton chemical shifts are very large--ranging from 10 ppm to 40 ppm (relative to water).

CARBONYL HYDRIDES

The metal carbonyl hydrides are prepared by acidification of the alkali salts of the corresponding metal carbonyls. The latter result on reduction of the carbonyl with Na/Hg in tetrahydrofuran or sodium in liquid ammonia. (2) Thus,

$$Co_2(CO)_8 \xrightarrow[T.H.F.]{Na/Hg} NaCo(CO)_4 \xrightarrow{H^+} HCo(CO)_4 \quad (3,4,5,6)$$

$$Re_2(CO)_{10} \xrightarrow[T.H.F.]{Na/Hg} NaRe(CO)_5 \xrightarrow{H^+} HRe(CO)_5 \quad (7)$$

$$Mn_2(CO)_{10} \xrightarrow[e.q.NH_3]{Na} NaMn(CO)_5 \xrightarrow{H^+} HMn(CO)_5 \quad (8,9,10)$$

$$Fe(CO)_5 \xrightarrow[H_2O]{NaOH} Na[HFe(CO)_4] \xrightarrow{H^+} H_2Fe(CO)_4 \quad (11,12)$$

Rhodium carbonyl hydride has been prepared by treatment of anhydrous $RhCl_3$ with CO and H_2 at 200 atm. and 200° for 24 hours (13). The mononuclear carbonyl hydrides are all highly volatile gases or liquids at room temperature. The compound $HRh(CO)_4$ is stable below its boiling point -10°, but $HMn(CO)_5$ and $HRe(CO)_5$ are stable at room temperature as colorless liquids. (13,9,10,7)

Only $H_2Fe(CO)_4$ and $HCo(CO)_4$ have been studied thoroughly from a synthetic point of view. Since $HMn(CO)_5$ and $HRe(CO)_5$ are much more stable and also highly reactive, interest in these compounds should increase. The mononuclear hydrides of chromium, molybdenum, tungsten, osmium, and iridium have been described, but the properties of these compounds have not been studied in any detail and in some cases a few have not been well characterized. (14,15,16,17).

POLYNUCLEAR CARBONYL HYDRIDES

In addition to the mononuclear compounds, a large number of polynuclear carbonyl hydrides have been prepared for iron(18,19, 20,21,22), chromium(23), molybdenum(24), and tungsten (25,26). These compounds are formed by the reaction of the corresponding metal carbonyl with a strong base (KOH) in alcoholic solution or, in the case of the iron derivatives, reaction with pyridine or ammonia. (2)

$$Cr(CO)_6 \xrightarrow{OH^-, H_2O,\ \text{ethanol}} [Cr_2(CO)_6(OH)_3H]^{\ominus}$$

$$Mo(CO)_6 \xrightarrow[\text{ethanol}]{OH^-} [Mo_2(CO)_6(OH)_3]^{-3} \xrightarrow[H_2O]{H^+} [Mo_2(CO)_6(OH)_3H_3]$$

$$Fe(CO)_5 \xrightarrow[h\nu]{py\ 85^{\circ}} [Fepy_6][Fe_4(CO)_{13}] \xrightarrow{H^+} H_2Fe_4(CO)_{13}$$

With iron an entire series of compounds has been found--$H_2Fe(CO)_4$, $H_2Fe_2(CO)_8$, $H_2Fe_3(CO)_{11}$, $H_2Fe_4(CO)_{13}$. These all behave as dibasic acids and salts have been isolated. Recently, the proton magnetic resonance has been measured for these compounds, and the results indicate that they contain iron-hydrogen bonds.(2) However, similar verification of metal-hydrogen bonds in the other polynuclear carbonyl hydrides has not yet been obtained.

Hieber and Schuster (27) have reported an anionic dinuclear rhenium carbonyl hydride $K(Re_2(CO)_8O_2H)$, which results in almost quantitative yield from the reaction:

$$Re(CO)_5Cl \xrightarrow[CH_3OH]{KOH} K[Re_2(CO)_8O_2H]$$

The above species has an inert-gas configuration and is diamagnetic. The anion may be precipitated by $Ni(o\text{-}phen)_3^{+2}$. The NMR has not yet been examined.

Behrens and Lohoffer(28) prepared the binuclear nickel carbonyl hydride, $Ni_2(CO)_6H_2$. The properties and structure have not been investigated, and it appears obvious that this is worthy of further study. The hydrogens appear to be non-acidic.

One major source of interest in the iron and cobalt carbonyl hydrides arises from their ability to transfer a hydrogen atom. This is particularly significant in organic chemistry where many hydrogenation reactions are considered to be intermediates in these processes. (29) The hydrides also can transfer CO and H_2 in certain reactions. A good review of this area of chemistry may be found in reference 30.

CYCLOPENTADIENYL CARBONYL HYDRIDES

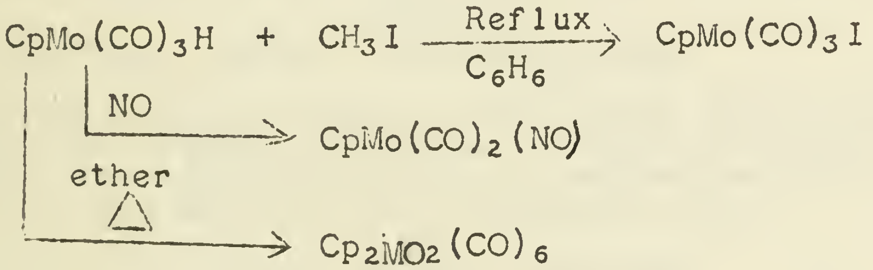
The hydrides $CpM(CO)_3H$ (M=Cr,Mo,W) are formed on acidification of a solution of the corresponding cyclopentadienyl metal carbonyl anion. (31,32,33)

$$M(CO)_6 \xrightarrow{NaCp} CpM(CO)_3^{\ominus} \xrightarrow{HOAc} CpM(CO)_3H$$

The tungsten derivative is the most stable of the three, being stable in air. The compound $CpMo(CO)_3H$ is slowly decomposed by air, whereas $CpCr(CO)_3H$ is instantly oxidized by air as a solid or in solution. (32) Thermal decomposition of the hydrides results in the formation of the binuclear cyclopentadienyl metal carbonyl ~~hydrides~~.~~they react with carbon tetrachloride~~. *

$$CpM(CO)_3H + CCl_4 \rightarrow CpM(CO)_3Cl + CHCl_3$$

The corresponding chloride is precipitated quantitatively. Other reactions are:



$$CpMo(CO)_3H + CH_3I \xrightarrow[C_6H_6]{Reflux} CpMo(CO)_3I$$

$$CpMo(CO)_3H \xrightarrow{NO} CpMo(CO)_2(NO)$$

$$CpMo(CO)_3H \xrightarrow[\triangle]{ether} Cp_2Mo_2(CO)_6$$

$2CpM(CO)_3H + Hg(CN)_2 = Hg(CpM(CO)_3)_2 + 2HCN$ (31). These mercury derivatives are soluble in organic solvents.

The corresponding cyclopentadienyl iron carbonyl hydride has also been made as a yellow liquid (m.p. -5°) (39,32)

$$CpFe(CO)_2Cl \xrightarrow{NaBH_4} CpFe(CO)_2H$$

* These hydrides behave as weak acids (29) and as with all metal hydrides they react with carbon tetrachloide.

CYCLOPENTADIENYL HYDRIDES

Cyclopentadienyl metal hydrides which contain no carbonyl groups have also been prepared. The first example of such a hydride is the classic biscyclopentadienyl rhenium hydride. (35,36) This compound results when $ReCl_5$ is treated with NaC_5H_5 in tetrahydrofuran at 0°. Sublimation from the reaction product gives Cp_2ReH as lemon yellow crystals (mp. 161°) soluble in benzene. The compound is thermally stable to at least 250° and sublimes in a vacuum above 80°. (36) Probably the most characteristic property of the substance is that it is basic in contrast to the previously known metal hydrides of the transition metals. Thus, it reacts with HCl to form the white salt $(CpReH_2)^+Cl^-$ and may be regenerated by treatment of the latter with base. (36) The pKb value of Cp_2ReH at 25° has been found to be 8.5. (36)

Since the intial discovery of Cp_2ReH, a number of other "basic" hydrides have been described. Borohydride reduction of the dicyclopentadienyl halides of molybdenum and tungsten leads to the dihydrides, Cp_2MoH_2 and Cp_2WH_2. (37,38)

$$Cp_2MoCl_2 \xrightarrow{NaBH_4} Cp_2MoH_2$$

These hydrides are yellow crystalline materials which can be readily sublimed. The compounds are rapidly oxidized by air, although the tungsten compound is noticeably more stable (38,37) As with Cp_2ReH, they react with dilute HCl to form the corresponding cations:

$$Cp_2WH_2 + H^+Cl^- \rightarrow Cp_2WH_3^{\oplus} Cl^-$$

Very recently, McCleverty and Wilknson (39) have prepared the neutral dicyclopentadienyl tantalum trihydride by the reaction,

$$Cp_2TaCl_3 \quad NaBH_4 \xrightarrow{T.H.F.} Cp_2TaH_3$$

The trihydride is a white crystalline solid, stable in air, and soluble in organic solvents. It does not act as a base towards acids. The structure of this compound and the related Mo, W and Re compounds will be discussed later.

PHOSPHINE AND ARSINE HYDRIDO COMPLEXES

A new series of hydrogen metal complexes has been reported which has greatly extended this area of research. These compounds are prepared by the reduction of phosphine and arsine metal complexes. NMR has confirmed the presence of metal-hydrogen bonds in these derivatives. The first compound of this type to be described was $(PEt_3)_2PtHCl$, obtained from the reaction:

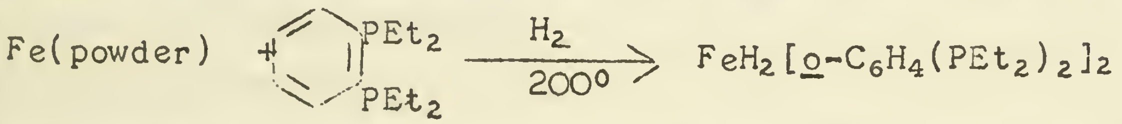
$$\begin{matrix}\underline{\text{cis-}}\\ \underline{\text{trans-}}\end{matrix} \quad (PEt_3)_2PtCl_2 \xrightarrow[T.H.F.]{LiAlH_4} (PEt_3)_2PtClH$$

This compound is very stable and can be distilled unchanged. It is not oxidized by air and is stable towards water. (40,41) Other phosphine platinum hydrides have been described as well as the bis-triethylarsine compound.(40)

Stable hydrido complexes of iron(42,43), osmium (42,44,45, 46,47), ruthenium (44,45,46,47,48), rhodium (49,48,47), iridium(49, 48,50,47,51), and palladium (52) have also been described. These may be prepared in general by reduction of the halophosphine or haloarsine metal complexes with sodium borohydride or lithium aluminumhydride. For example,

$$FeCl_2[\underline{o}\text{-}C_6H_4(PEt_6)_2]_2 \xrightarrow{LiAlH_4} FeH_2[\underline{o}\text{-}C_6H_4(PEt_2)_2]_2$$

This iron derivative may also be prepared by treating iron powder with ortho-phenylene-bis-diethylphosphine in a hydrogen atmosphere at 200°.



The hydride $(C_2H_4(PEt_2)_2)_2FeHCl$ has a proton chemical shift of 39.1 ppm (relative to water), which is the highest shift known for any substance. (42).

Chatt and Shaw (48,47) have described a novel route to hydride complexes. They found that when phosphine metal halide complexes were boiled with alcoholic KOH solution, hydrides resulted. Thus,

$$PtCl_2(PEt_3)_2 + KOH + C_2H_5OH \xrightarrow{\text{boil}} \underset{(85\%)}{PtHCl(PEt_3)_2} + CH_3CHO + KCl + H_2O$$

Similarly, $IrCl_3(PEt_3)_3$ boiled with alcoholic KOH, gives a 90% yield of $IrHCl_2(PEt_3)_3$. (48)

In some instancescarbonyl groups are also introduced into the product. Thus, boiling $RhCl_3(PEt_3)_3$ with alcoholic KOH for 1.5 hours, followed by acidification, gives only the carbonyl derivative $RhCl(CO)(PEt_3)_2$ in 80% yield. (48) On boiling $[Ru_2Cl_3(PEt_2\Phi)_6]$ Cl with KOH in ethanol for 1 hour, the colorless hydridocarbonyl $RuHCl(CO)PEt_2(C_6H_5)$ is obtained. (48). In the same way treatment of $(NH_4)_2OsCl_6$ with diethyl-phenyl phosphine and subsequent boiling with ethanolic KOH gives the hydrido-carbonyl, $OsHCl(CO)PEt_2(C_6H_5)$.(47) The presence of base is not necessary when allyl alcohol is used. Other alcohols may be used in these reactions, although 2-methoxyethanol is the only other one investigated. For example--

$$\begin{tikzcd}
(NH_4)_2IrCl_6 + P(C_6H_5)_3 + \text{aq. } CH_3OCH_2CH_2OH \arrow[r, "100^\circ"] \arrow[dr, "190^\circ"'] & IrHCl_2(P(C_6H_5)_3)_3 \quad (95\%) \\
 & IrH_2Cl[P(C_6H_5)_3]_3{}^{*} \arrow[u, "HCl"'] \arrow[d, "Cl_2"] \\
 & IrCl_3(P(C_6H_5)_3)_3
\end{tikzcd}$$

$$IrHCl_2[P(C_6H_5)_3]_3 \xrightarrow[\text{T.H.F.}]{LiAlH_4} IrH_3[P(C_6H_5)_3]_3$$

All these derivatives have high melting points and are quite stable The arsine and stibine derivatives have also been synthesized.(50,51)

Stable arsenic complexes of [illegible]

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Chatt and Shaw [illegible]

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Similarly, [illegible]

In some [illegible]

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All [illegible]

Hypophosphorus acid, H_3PO_2, has also been used as a reducing agent in the preparation of transition-metal hydrides. (49)

The possibility of hydride and carbonyl formation when a transition-metal complex is in contact with an alcoholic medium should always be considered, especially if the solution is basic.(47)

There appears no reason why these reactions should be restricted to tert-phosphine or arsine complexes. Recently, Wilkinson (53) has described the formation of a hydride species in solution when aqueous $Rhen_2Cl_2$ is treated at 0° with $NaBH_4$. The NMR of this solution showed a line which was a sharp doublet at 22.2ppm. (splitting 31c/s)

CYANIDE COMPLEX HYDRIDES

Griffiths and Wilkinson have found that solutions obtained upon dissolving Co(II) salts in CN^- solutions gave a large proton chemical shift. This resonance is not observed at CN^-/Co^{++} rations less than 3.5, and it is not affected by excess CN up to a CN^-/Co^{++} ratio of 8.(54,55) A formula $Co(CN)_5H^{-3}$ has been proposed for the ion although attempts to isolate it in solid form have failed. (54) A rhodium cyano-hydride has also been described and the NMR shows the expected doublet. (54)

TETRAHYDRORHENATE ION

The question of existence of the so-called "rhenide" ion has always been interesting. Wilkinson(56) and Miller and Ginsberg (57) have shown that the rhenide ion is actually a hydride species. Floss and Grosse have made a careful study of the system and have found that the hydride is actually $KReH_4$ rather than $KReH(H_2O)_3$ as originally proposed. (58,59)

A corresponding technetium hydride has been detected (60)

AN UNUSUAL RHODIUM-HYDROGEN COMPOUND

An unusual hydride has been recently described by Farr(61). When LiH and rhodium metal are heated together to about 600°, a liquid phase appears with no gas evolution. At room temperature, this liquid phase solidified to a hard, black crystalline material, X-ray diffraction patterns show the absence of LiH, LiOH, Li_2O, LiRh, and Rh metal. The reaction proposed is:

$$4LiH \ + \ Rh(powder) \xrightarrow[Ar]{600^\circ} Li_4RhH_4$$

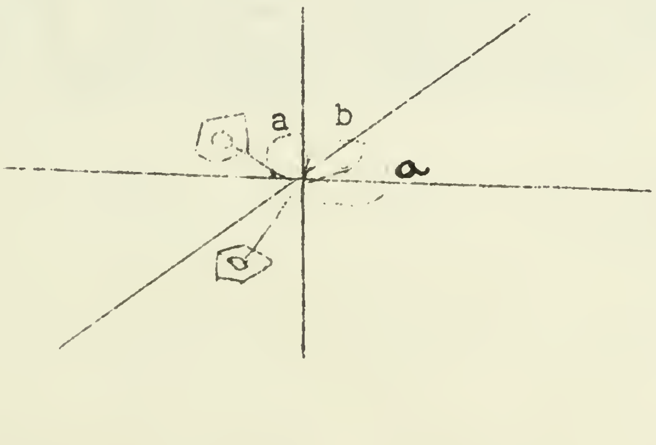
If the reaction is carried out in a hydrogen atmosphere, a black solid of composition Li_4RhH_5 is formed. (61) More work in this area is needed before these interesting derivatives can be well characterized.

STRUCTURE AND BONDING IN TRANSITION METAL COMPLEX HYDRIDES

Perhaps the most fascinating aspect of the hydride complexes (and also other hydrides) is the problem of their structure. Although the literature contains many papers concerning the bonding and structure of metal carbonyl hydrides, we must still regard the problems in this area as unsolved. Indeed, with the exception of $PtHBr(PEt_3)_2$, which has been examined by X-rays, the exact configurations of all the hydrides are largely unknown. A number of models have been proposed for the structure of $HCo(CO)_4$, but a recent investigation by Edgell has shown that the hydrogen atom lies on the C_3v axis of the molecule. (62,63,64,65,66,67, 68,69,70,71,72,73) Ewens and Lister (74) earlied have shown the tetrahedral disposition of the CO groups in iron and cobalt carbonyls. Iron carbonyl hydridesis probably the most perplexing of the hydrides. Wilkinson and Cotton(64) report that the protons are equivalent from the NMR, although the possibility of equivalence by exchange cannot be ruled out. Stammreich(75) recently has looked at the Raman spectra of $HFe(CO)_4^-$ and has found that the proton is also on the C_{3v} axis. Wilkinson has proposed that if one hydrogen is on the C_{3v} axis, the only ways to put two equivalent hydrogen atoms into the molecule is to have dissimilar CO groups. (76,64) However, there is no reason to suppose that in $H_2Fe(CO)_4$ one hydrogen must lie on the C_3v axis. A C^{13} NMR study would indicate the presence of dissimilar CO groups although a similar lack of splitting may result in $H_2Fe(CO)_4$ as in the C^{13} NMR of iron pentacarbonyl. (77) An infrared analysis of $HMn(CO)_5$ has shown that this molecule has very low symmetry. (78,79,80)

These three are the only carbonyl hydrides studied from a structural point of view. It is obvious that additional work in this area should be fruitful.

The cyclopentadienyl hydrides of Re, Mo, W, and Ta have been correlated by one model by Wilkinson. (39) The structure proposed is:



where <u>a</u>, <u>b</u> and α are three hybrid orbitals in the xy-plane. Two of these orbitals are equivalent. All three orbitals in Cp_2TaH_3 are utilized in bonding with hydrogens. The NMR indicates two types of hydrogens. (39)

However, in Cp_2MoH_2 and Cp_2WH_2, only orbitals a are occupied since both hydrogens in these compounds are equivalent. The cations $Cp_2MoH_3^+$ and $Cp_2WH_3^+$ have two different hydrogens. (2) In $Cp_2ReH_2^+$, the hydrogens are equivalent and occupy the two a orbitals. Recently, other cyclopentadienyl compounds such as ferrocene, ruthenocene, and others, (39,81,82,83) have been protonated, and the structure of these species may be similar to that indicated by the above model.

Since the phosphine and arsine hydrido complexes are quite stable in contrast to the unstable carbonyl compounds, the problem of their structures is more easily approached. Only the compound $HPtBr(PEt_3)_2$ has been examined by X-ray diffraction. The results indicate it to be trans-square planar with a P-Pt-Br angle of 94°. (84) The Pt-P distance is 2.26A. and the Pt-Br distance is 2.56A. (84)

The other phosphine complexes should have similar structures. Thus, the series of compounds IrH_3R_3, IrH_2ClR_3, and $IrHCl_2R_3$ are all probably octahedral. ($R=P(C_6H_5)_3$) It is interesting to note that no isomers have been isolated as yet.

Besides the tremendous interest in the structure of these hydrides, another aspect is the nature of the metal to hydrogen bond. The most striking aspect of this bond is the large proton chemical shift observed for all the transition metal hydrides. Any bonding model must also be consistent with the observed chemical properties (acidities). The metal-hydrogen stretching frequencies in the IR are near 2000 cm.$^{-1}$ for most of the complex hydrides. The large chemical shifts are characteristic of only transition metals. The NMR of Et_2SiH_2 indicates a shift of only 3.2 ppm. (32) and in alkyl substituted tin hydrides small shifts are also observed. (2)

CONCLUSION

An attempt has been made to outline in brief fashion the preparation and properties of complex transition metal hydrides. A further attempt has been made to indicate the paucity of information regarding the known structures of these exciting compounds. It can be certain that this area of chemistry will be exploited to a greater extent in the future.

REFERENCES

1. J. Chatt, L.A. Duncanson, and B. L. Shaw: Proc.Chem.Soc.(1957)343.
2. M.L.H. Green: Angew. Chem. 72, 719 (1960).
3. G.W. Coleman and A.A. Blanchard: J.Am.Chem.Soc., 58, 2161(1936).
4. W. Hieber: Angew. Chem., 49, 463 (1936).
5. H.W. Sternberg, I. Wender, R.A. Friedel and W.Orchin: J. Am.Chem.Soc., 75, 2717 (1953).
6. W.Hieber, H. Schulten, and R. Morin: Z. anorg. allgem.Chem. 240, 261(1939).
7. W. Hieber and G. Braun: Z. Naturforsch., 14b, 132 (1959).
8. D. T. Hurd, G.W. Sentell, and F. J. Norton: J.Am.Chem.Soc., 71, 1899 (1949).
9. W. Hieber and G. Wagner: Z. Naturforsch., 12b, 478 (1957).
10. W. Hieber and G. Wagner: Ibid ., 13b, 339 (1958).
11. W. Hieber and F. Leutert: Naturwissenschaften, 19, 360 (1931).
12. W. Hieber and F. Leutert: Z. anorg. allgem. Chem., 204, 145 (1932).
13. W. Hieber and H. Lagally: Z. anorg. allgem. Chem., 251, 96 (1943).
14. M. G. Rhomberg and B. B. Owens: J. Am. Chem. Soc. 73, 5904 (1951).
15. H. Behrens and W. Hoag: Z. Naturforsch., 14b, 600 (1959).
16. J. S. Anderson: Quart. Revs., 1, 331 (1947).
17. W. Hieber and H. Lagally: Z. anorg. allgem. Chem.,245, 321 (1940).
18. W. Hieber and G. Brendel: Ibid ., 289, 324 (1957).
19. M.L.H. Green, L. Pratt, and G. Wilkinson: J. Chem. Soc., (1959), 3753.
20. W. Hieber, J. Sedlmeier, and R. Werner: Chem. Ber., 90, 278 (1957).
21. W. Hieber and N. Kahlen: Ibid, 91, 2234 (1958).
22. W. Hieber and R. Wagner: Ibid., 90, 286 (1957).
23. W. Hieber and K. Rieger: Z. anorg. allgem. Chem., 300 , 288 (1959).
24. W. Hieber, K. Englert, and K. Rieger: Ibid., 300, 304 (1959).
25. W. Hieber and K. Englert: Ibid., 300, 311 (1959).
26. W. Hieber, K. Englert, and K. Rieger: Ibid., 300 304 (1959)
27. W. Hieber and L. Schuster: Z. anorg. allgem. Chem., 285 205 (1956).
28. H. Behrens and F. Lohofer: Z. Naturforsch., 8b, 691 (1953).
29. J. Lewis: Sci. Progr., 49, 67 (1961).
30. H.W. Sternberg and I. Wender: Chem. Soc. Special Publication No. 13, 35 (1959).
31. E. O. Fischer, W. Hafner and H.O. Stahl Z. anorg. allgem. Chem., 282, 47 (1955).
32. T.S. Piper and G. Wilkinson: J. Inorg. Nucl. Chem., 3, 104 (1956).
33. E.O. Fischer and W. Hafner: Z. Naturforsch.,10b 140(1955).
34. M.L.H. Green, C.N. Street, and G. Wilkinson: Ibid., 14b, 738 (1959).
35. J.M. Birmingham and G. Wilkinson: J. Am. Chem. Soc., 77, 2022 (1955).
36. M.L.H. Green, L. Pratt, and G. Wilkinson: J. Chem. Soc., (1958), 3916.
37. M.L.H. Green: Angew. Chem., 72, 719 (196).
38. E.O. Fischer and Y. Hristidu: Z. Naturforsch., 15b, 135(1960).

39. J.A. McCleverty and G. Wilkinson: Chem. and Ind., (1961), 288.
40. J. Chatt, etal: Proc. Chem. Soc., (1957), 343.
41. J. Chatt and B.L. Shaw: Chem. and Ind., (1960), 931.
42. J. Chatt, F.A. Hart, and R.G. Hayter: Nature, 187, 55 (1960).
43. J. Chatt: Angew. Chem., 72, 40 (1960).
44. J. Chatt and R. G. Hayter: Proc. Chem. Soc. (1959) 153.
45. L. Vaska and J.W. DiLuzio: J.Am. Chem. Soc., 83, 1262 (1961).
46. J. Chatt and R.G. Hayter: Abstracts of Papers Presented at St. Louis, March 21-30, 1961, Div. of Inorg. Chem. of the American Chemical Society, page 26M.
47. J. Chatt and B. L. Shaw: Chem. and Ind., (1961), 290.
48. J. Chatt and B.L. Shaw: Chem. and Ind., (1960), 931.
49. J. Lewis, R.S. Nyholm, and G.N.K. Reddy: Chem. and Ind., (1960), 1386.
50. L. Vaska: J. Am. Chem. Soc., 83, 1259 (1961).
51. R.G. Hayter: J. Am. Chem. Soc., 83, 1259 (1961).
52. J. Chatt, L.A. Duncanson, and B.L. Shaw: Chem. and Ind., (1958), 859.
53. G. Wilksinson: Proc. Chem. Soc., (1961), 72.
54. W. P. Griffith and G. Wilkinson: J. Chem. Soc., (1959)2757.
55. W. P. Griffith, L. Pratt and G. Wilkinson: Nature, 182, 466 (1958).
56. R. Colton and G. Wilkinson: Nature, 183, 1755 (1959).
57. A. P. Ginsberg, J. M. Miller, J. R. Coronaugh and B. P. Dailey: Nature, 185, 528 (1960).
58. J.G. Floss and A.V. Grosse: J. Inorg. Nucl. Chem., 16, 36 (1960).
59. J.G. Floss and A.V. Grosse: Ibid., 9, 318 (1959).
60. J.G. Floss and A.V. Grosse: Ibid., 16, 44 (1960).
61. J.D. Farr: Ibid., 14, 202 (1960).
62. R. A. Friedel, I. Wender, S.L. Shufler and H.W. Sternberg: J. Am. Chem. Soc., 77, 3951 (1955).
63. W. F. Edgell, C. Magee and G. Gallup: Ibid., 78, 4185 (1956).
64. F. A. Cotton and G. Wilkinson: Chem. and Ind., (1956) 1305.
65. W. F. Edgell and G. Gallup. J. Am. Chem. Soc., 78, 4188 (1956).
66. W. Hieber and F. Seel: Chem. Ber., 85, 647 (1952).
67. W. F. Edgell and G. Gallup: J. Am. Chem. Soc., 77, 5762 (1955).
68. W. Edgell: Ann. Rev. Phys. Chem., 8 353 (1957).
69. L. Kirch and M. Orchin: J. Am. Chem. Soc., 80, 4428 (1958).
70. H. B. Jonassen etal.: Ibid., 80, 2586 (1958).
71. W. F. Edgell and R. Summitt: Ibid., 83, 1772 (1961).
72. A. D. Liehr: Z. Naturforsch., 12b, 95 (1957).
73. F. A. Cotton: J. Am. Chem. Soc., 80, 4425 (1958).
74. R. V. G. Ewens and M. L. Lister: Trans. Far. Soc., 35, 681 (1939).
75. H. Stammreich, K. Kawai, Y. Tavres, P. Krumholz, J. Behmoiras and S. Bril: J. Chem. Phys., 32, 1482 (1960).
76. E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards and G. Wilkinson: J. Chem. Soc., (1959), 2484.
77. F. A. Cotton, A. Danti, J. S. Waugh and R. W. Fessenden: J. Chem. Phys., 29, 1427 (1958).
78. W. E. Wilson: Z. Naturforsch., 13b, 394 (1958).

79. F. A. Cotton, J. L. Down, and G. Wilkinson: J. Chem. Soc., (1959), 833.
80. W. F. Edgell, G. Asato, W. Wilson and C. Angell: J. Am. Chem. Soc., 81, 2022 (1959).
81. T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards: J. Am. Chem. Soc., 82, 5249 (1960).
82. A. Davidson and G. Wilkinson: Proc. Chem. Soc., (1960), 356
83. M. Rosenblem: J. Am. Chem. Soc., 81, 5517 (1959).
84. P. G. Owston, J. M. Partridge, and J.M. Rowe: Acta. Cryst., 13, 246 (1960).