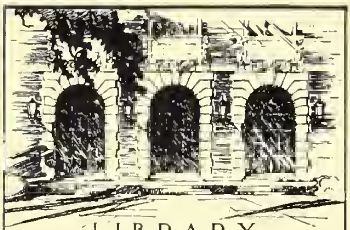


[redacted]

INORGANIC SEMINARS

1951 - 1952

TABLE OF CONTENTS

1951 - 1952

TABLE OF CONTENTS

*****

TETRANITROGEN TETRASULFIDE (N_4S_4)

P. Kippur September 25, 1961

Standard inorganic textbooks list three sulfides of nitrogen, namely, NS_2, nitrogen disulfide, N_4S_4 tetranitrogen tetrasulfide and N_2S_5, dinitrogen pentasulfide. The compound N_2S_4, dinitrogen tetrasulfide, has been isolated recently and its absorption spectra found to be identical with that of nitrogen disulfide and of dinitrogen pentasulfide which would indicate that the latter are actually dinitrogen tetrasulfide (1).

Tetranitrogen tetrasulfide was first prepared by Gregory in 1835 (2). Although subsequent investigations have contributed a great deal to our present knowledge of tetranitrogen tetrasulfide, the exact nature of this compound with respect to many of its properties and reactions is still undetermined.

Physical Properties

Tetranitrogen tetrasulfide is an orange-red crystalline material with a melting point of 179°C. It is not wet by water, but it is soluble in such solvents as carbon disulfide, benzene, chloroform and liquid ammonia.

Tetranitrogen tetrasulfide and most of its derivatives, with the exception of cyclotetrathiatetrimine ($N_4S_4H_4$), are sensitive to heat and shock; investigations have been carried out with respect to its possible use as a priming agent (3)(4)(5)(6)(7)(8)(9)(10). It has been found to be inferior to such materials as mercury (II) fulminate and is therefore not utilized for this purpose.

Structure

The structure of tetranitrogen tetrasulfide, which is in agreement with most of the available data, may be represented as an eight-membered puckered ring with alternating sulfur and nitrogen atoms. (11)(12)(13).

Preparation

There are two general modes of preparation:

1. The reaction of either sulfur monochloride or sulfur dichloride with gaseous ammonia (14)(15)(16)(17)(18)(19)(20)(21)(22)(23)(24)(25)(26)(27)(28)(29). These reactions are usually carried out in a non-aqueous solvent (i.e. CCl_4, C_6H_6), and the by-products are sulfur, iminosulfur (S_7NH), and ammonium sulfide and/or polysulfide.

2. The reaction of sulfur and liquid ammonia (30)(31).

$$10\ S + 16\ NH_3(liq.) \rightleftharpoons N_4S_4 + 6(NH_4)_2S$$

This reaction is a balanced one and the equilibrium may be shifted to the right by the addition of silver iodide which precipitates the sulfide ion.

Reactions

Tetranitrogen tetrasulfide reacts with the chlorides of Ti(IV), Sb(V), Mo(V), W(VI) and Se(I) in solvents, such as, chloroform and carbon tetrachloride, to produce addition compounds (32)(33).

The reaction of tetranitrogen tetrasulfide and lead (II) iodide in liquid ammonia produces the compounds $Pb(NS)_2 \cdot NH_3$ in concentrated solution and PbN_2S. $N_4S_4 \cdot 3NH_3$ in dilute solution (16)(34). With mercury (II) iodide only the compound $HgN_2S \cdot NH_3$ is formed. (16)

Treatment of tetranitrogen tetrasulfide with chlorine in non-aqueous media produces trithiazyl trichloride $(NS)_3Cl_3$. (34)(35)(36)(37). The corresponding bromine compound has also been prepared (38). These compounds were first reported to be tetrameric, but were later shown to be trimeric (34).

Thiotrithiazyl chloride $(NS)_3SCl$ is produced when tetranitrogen tetrasulfide reacts with either sulfur monochloride or thionyl chloride in a non-aqueous solvent (33)(39)(35)(40). The corresponding bromide is produced in a similar manner (33)(35). The iodide has also been prepared (35)(41). These compounds behave as though the thiotrithiazyl group $(NS)_3S$ is a monovalent cation; treatment of thiotrithiazyl chloride with nitric acid, sulfuric acid and thiocyanate ion yields the corresponding nitrate, bisulfate and thiocyanate(35). Further evidence for the ionic character of these materials is their insolubility in most organic solvents (39).

Tetranitrogen tetrasulfide may be reduced in benzene solution to cyclotetrathiatetrimine $(NSH)_4$ upon treatment with an alcoholic solution of tin(II) chloride at 60°C. (33). This material is unusual as it is the only member of this group of compounds that is not sensitive to heat or shock (33)(42).

In strongly alkaline solution, tetranitrogen tetrasulfide undergoes hydrolysis to produce ammonia, thiosulfate and sulfite (42). However, in neutral or weakly alkaline solution trithionate, thiosulfate and ammonia are formed (12).

Tetranitrogen tetrasulfide undergoes ammonalysis in liquid ammonia with the formation of ammonosulfurous and ammonothiosulfuric acids. This is evidenced by the formation of $Pb(NS)_2$ and HgN_2S upon the addition of lead(II) or mercury(II) iodide to the above solution (16)(43).

Uses

1. Insecticide (18)(44)(45)(46)(47)(48)(49)(50)(51)
2. Fungicide (18)(44)(52)(53)(54)
3. Ignition promoter for diesel fuels (55)(56)
4. Accelerator in the vulcanization of rubber (57)
5. Indicator in the titration of acids in non-aqueous solvents (58)(59).

The utilization of tetranitrogen tetrasulfide as an insecticide and fungicide is by far its most important practical application.

Bibliography

1. Goehring and Kaloumenos, Z. anorg. Chem., 263, 137-44 (1950).
2. Gregory, J. de Pharm., 21, 315-17 (1835).
3. Berthelot and Vieille, Ann. Chim. Phys., (5) 27, 262 (1882).
   Ibid., Bull. Soc. Chim., (2) 37, 388 (1882).
4. Ibid., Compt. Rend., 92, 1307-09 (1881).
   Ibid., J. B. (Liebig), 1114 (1881).
   Ibid., Ber., 14, 1558 (1881).
5. Hoitsema, Z. physik. Chem., 21, 136-48 (1896).
6. Koettnitz, Z. Elektrochem., 34, 768-83 (1928).
7. Muraour, Bull. Soc. Chim., 51, 1152-66 (1932).
8. Ibid., Mem. Artillerie France, 18, 895-7 (1939).
9. Wöhler and Matter, Z.f.d.ges. Schiess u. Sprengstoffwesen, 2, 203-6, 244-7, 265-69 (1907).
10. Wöhler, Z. angew. Chem., 24, 2089-99 (1911).
11. Lu and Donohue, J. Am. Chem. Soc., 66, 818-27 (1944).
12. Goehring, Ber., 80, 110-22 (1947).
13. Arnold, Hugill, and Hutson, J. Chem. Soc., 1645-49 (1936).
14. Voznesenskii, J. Russ. Phys. Chem. Soc., 59, 221-32 (1927).
15. Schenck, Ann., 290, 171-85 (1896).
16. Ruff and Geisel, Ber., 37, 1573 (1904).
17. Arnold and Perry, (to Imp. Chem. Ind. Ltd.) U.S. Patent 2,382,845, Aug. 14, 1945; C.A. 185 (1946).
18. Arnold, (to Imp. Chem. Ind. Ltd.) U.S. Patent 2,372,046, Mar. 20, 1945; C.A. 3862 (1946).
19. Carl, U.S. Patent 2,337,798, Dec. 28, 1943; C.A. 3428 (1944).
20. Van Valkenburgh and Bailar, J. Am. Chem. Soc., 47, 2134-37 (1925).
21. Macbeth and Graham, Proc. Roy. Irish Acad., 36B, 31-40 (1923).
22. Burt and Usher, Proc. Roy. Soc. London, Series A, 85, 82-98 (1911).
23. Fernelius, Can. Patent 398,365; C.C. Part II, 1503 (1942).
24. Ibid., U.S. Patent 2,207,791, July 16, 1940; C.A. 8190 (1940).
25. Arnold and Perry, (to Imp. Chem. Ind. Ltd.), Brit. Patent 542,912, Feb. 2, 1942; C.A. 4680 (1942).
26. Ibid., U.S. Patent 2,364,414, Dec. 5, 1944; C.A. 4203 (1945).
27. Ibid., Brit. Patent 552,987, May 4, 1943; C.A. 4392 (1944).
28. Swinehart, (to Harshaw Chemical Co.) U.S. Patent 2,190,177, Feb. 13, 1940; C.A. 4242 (1940).
29. (to Imp. Chem. Ind. of Australia and New Zealand Ltd.) Australia Patent 115,492, July 23, 1942; C.A. 980 (1946).
30. Bergstrom, J. Am. Chem. Soc., 48, 2319-27 (1926).
31. Ruff and Geisel, Ber., 38, 2659-67 (1905).
32. Davis, Proc. Chem. Soc., 22, 261 (1906).
    Ibid., J. Chem. Soc., 89, 1575 (1906).
33. Wolbling, Z. anorg. Chem., 57, 281-89 (1908).
34. Meuwsen and Holch, Ber., 64B, 2301-15 (1931).
35. Muthmann and Seitter, Ber., 30, 627 (1897).
36. Andreocci, Z. anorg. Chem., 14, 246-50 (1897).
37. Demarcay, Compt. Rend., 91, 854 (1880).
    Ibid., Ber., 13, 2412 (1880).
38. Clever and Muthmann, Ber., 29, 340-43 (1896).
39. Meuwsen, Ber., 65, 1724-33 (1932).

40. Demarcay, Compt. Rend., 91, 1066-68 (1880)
Ibid., Ber. 14, 253 (1881).
41. Mac Diarmid, Nature, 164, 1131-32 (1949).
42. Meuwsen, Ber., 62B, 1959-69 (1929).
43. Franklin, "Nitrogen System of Compounds", pp. 172-175.
44. Fulton and Fernelius, U.S. Patent 2,101,645, May 25, 1937.
45. (to Imp. Chem. Ind. Ltd.), Fr. Patent 866,312, July 28, 1941; C.A. 4807 (1949).
46. (ti Imp. Chem. Ind. Ltd.), Fr. Patent 882,652, July 7, 1941.
47. Fulton, J. Econ. Entomol., 32, 545 (1938).
48. Charlton and Woodward, (to Imp. Chem. Ind. Ltd.), Brit. Patent 543,459, Feb. 26, 1942; C.A. 4661 (1942).
49. Arnold, (to Imp. Chem. Ind. Ltd.), Brit. Patent 544,577, April 17, 1942; C.A. 6744 (1942).
50. Wiesmann, Landw. Jahrb. Schweiz, 55, 657-75 (1941).
51. Lean and Bovingdon, (to Imp. Chem. Ind. Ltd.), Brit. Patent 542,937, Feb. 3, 1942; C.A. 4662 (1942).
52. Appleby, Rayner, Arnold and Perry, (to Imp. Chem. Ind. Ltd.), Brit. Patent 544,926, May 4, 1942; C.A. 7225 (1942).
53. Lean and Brian, (to Imp. Chem. Ind. Ltd.), U.S. Patent 2,417,115, Mar. 11, 1947; C.A. 3581 (1947).
54. Ibid., (to Imp. Chem. Ind. Ltd.), Brit. Patent 542,523, Jan. 14, 1942; C.A. 3905 (1942).
55. Paulsen and Collins, (to Standard Oil Development Co.), U.S. Patent 2,280,716, April 21, 1942; C.A. 5637 (1942).
56. (to N.F. de Bataafsche Petroleum Maatschappij), Fr. Patent 764,721, May 26, 1934; C.A. 5968 (1934).
57. Romani, Caoutchouc et Guttaperche, 19, 11626-11629 (1922).
58. Voznesenskii, J. Russ. Phys. Chem. Soc., 61, 1317, 1323 (1929).
59. Skvortzov, J. Gen. Chem. (USSR), 2, 569-75 (1932).

THE HALOGENS AND INTERHALOGENS AS SOLVENTS

Niels C. Nielsen October 9, 1951

Since the publication of "Die Chemie in Wasserähnlichen Lösungsmitteln", much exploratory work has been done in establishing other solvent systems. In addition to Dr. Jander's work in liquid iodine, comprehensive surveys have been made of the solvent properties of iodine (V) fluoride, iodine (I) chloride, iodine (I) bromide and bromine (III) fluoride. Dr. H. J. Emeléus and his associates have provided most of the experimental information which is available for these new systems. Table I lists the pertinent properties of these solvents.

TABLE I

Property	I_2	IF_5	ICl	IBr	BrF_3
M. P.	113.6	-8	27.20	40-41	-2
B. P.	183	97	97.4	119	127
Density	3.918 at 133.5°	3.13 at 45°	3.7343 at 50°		
Spec. Cond.	1.7×10^{-4} (140°)	1.53×10^{-5} (25°)	4.6×10^{-3} (30°)	10.4×10^{-4} (55°)	8.1×10^{-3} (15°)
Diel. Const.	12.98 at 168°				
Visc.	1.414×10^{-2} at B.P.		3.74 (35°)		
Trouton Const.			27.5		25.3

Liquid iodine (5) readily dissolves the alkali iodides, and a few other metallic and non-metallic elements and compounds. (See Tables III and IV). Quantitative values are available only for KI which dissolves to the extent of 22 mole percent at 113° with an increase to 24 mole percent at 184°. The influence of cation size upon the solubility of various compounds is evident both in liquid iodine and in the other interhalogen solvents. Although AlI_3 and FeI_3 have small cations, they are soluble in iodine due to the formation of dimers.

The conductivity of liquid iodine has been attributed to the ionization:

$$2I_2 \rightleftharpoons I^+ + (I \cdot I_2)^- \rightleftharpoons I^+ + I_3^-$$

From these equilibria, it is to be anticipated that all soluble iodides will behave as bases while substances such as ICl or IBr

will behave as acids in this solvent. Evidence for such behavior has been found by conductivity measurements and neutralization reactions. The conductivity of 4 mole percent solutions of RbI or KI in liquid iodine is equivalent to the conductivity of a 2 mole percent solution of KCl in water. All of the alkali iodides except Na(and possibly Li) act as strong electrolytes in this solvent. Neutralization reactions were shown by conductometric and potentiometric titrations and by isolation of the salts which formed:

$$KI + ICl \longrightarrow KCl + I_2$$
$$HgI_2 + 2IBr \longrightarrow HgBr_2 + 2I_2$$
$$BiI_3 + 3ICl \longrightarrow BiCl_3 + 3I_2$$

Examples of amphoterism, solvolysis, and solvation are also known in this solvent.

In comparison to the studies made in liquid iodine, only a small amount of information is available with respect to iodine (V) fluoride as a solvent (21,24). Among the compounds known to be soluble in this medium are SbF_5, BF_3, SO_3, KIO_3, AsF_3, BrF_3, and HF. Its conductivity may be due to the ionization:

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

A one-hundred-fold increase in conductivity results when SbF_5 is added to this solvent, and the further addition of KF produces a typical neutralization reaction:

$$KF + IF_5 \rightleftharpoons K^+(IF_6)^- \qquad \text{(base)}$$
$$SbF_5 + IF_5 \rightleftharpoons (IF_4)^+(SbF_6)^- \qquad \text{(acid)}$$
$$KIF_6 + IF_4SbF_6 \longrightarrow KSbF_6 + 2IF_5$$

Solvolysis appears to occur quite readily in IF_5 and has prevented more careful studies of the system.

As might be anticipated, iodine (I) chloride (6,7,10,11) and iodine (I) bromide (12,13) have similar solvent properties with the latter being the poorer solvent in all respects. Both compounds will readily dissolve a large number of elements and compounds which may easily be classified as acids and bases, especially in ICl. (See Tables III and IV) The chlorides and bromides of the heavier alkali metals are basic anhydrides while the corresponding tin, antimony, and phosphorus halides may behave as acid anhydrides. The following reactions indicate the ionization of these solvents and typical reactions in the two systems:

<u>ICl</u>

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$
$$KCl + ICl \rightleftharpoons K^+ICl_2^-$$
$$SbCl_5 + ICl \rightleftharpoons I^+SbCl_6^-$$
$$KICl_2 + ISbCl_6 \longrightarrow KSbCl_6 + 2ICl$$

<u>IBr</u>

$$2IBr \rightleftharpoons I^+ + IBr_2^-$$
$$RbBr + IBr \rightleftharpoons Rb^+IBr_2^-$$
$$SnBr_4 + IBr \rightleftharpoons (I^+)_2SnBr_6^=$$
$$2RbIBr_2 + I_2SnBr_6 \longrightarrow Rb_2SnBr_6 + 4IBr$$

Numerous studies of the solvent properties of bromine (III) fluoride have indicated its usefulness in the preparation of many compounds and in the investigation of their physical and chemical properties. As a solvent, it appears to be a little less effective than iodine if one considers only the solubility of fluorides. However, the reactivity of $\mathrm{BrF_3}$ results in its serving as a solvent for a much wider range of substances which are first converted to fluorides before dissolving (8,18). (See Tables III and IV) The ionic equilibrium in solution is: (1)

$$\mathrm{2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-}$$

Basic and acid anhydrides are well-known in this system and follow the general pattern of the other interhalogen solvents. Neutralization reactions are represented by the following equations:

$$\begin{array}{ccccccc} \text{Acid} & + & \text{Base} & = & \text{Salt} & + & \text{Solvent} \\ \mathrm{BrF_2NbF_6} & + & \mathrm{KBrF_4} & \longrightarrow & \mathrm{KNbF_6} & + & \mathrm{2BrF_3} \end{array}$$

$$\begin{array}{ccccccc} \text{Acid Anhydride} & + & \text{Base} & = & \text{Salt} & + & \text{Solvent} \\ \mathrm{VF_5} & + & \mathrm{AgBrF_4} & \longrightarrow & \mathrm{AgVF_6} & + & \mathrm{BrF_3} \end{array}$$

$$\begin{array}{ccccccc} \text{Acid} & + & \text{Basic Anhydride} & = & \text{Salt} & + & \text{Solvent} \\ \mathrm{BrF_2TaF_6} & + & \mathrm{LiF} & \longrightarrow & \mathrm{LiTaF_6} & + & \mathrm{BrF_3} \end{array}$$

$$\begin{array}{ccccc} \text{Acid Anhydride} & + & \text{Basic Anhydride} & = & \text{Salt} \\ \mathrm{VF_5} & + & \mathrm{LiF} & \longrightarrow & \mathrm{LiVF_6} \end{array}$$

Solvolysis is prevalent in $\mathrm{BrF_3}$ and, in many cases, has prevented the isolation of pure products (16). In a typical reaction:

$$\mathrm{2KBrF_4 + (BrF_2)_2TiF_6 \rightleftharpoons K_2TiF_6 + 4BrF_3}$$

The reversibility is shown by incomplete combination of the starting materials, by X-ray analysis indicating the presence of $\mathrm{BrF_4^-}$ ion in the product isolated, and by noting the occurrence of partial decomposition when a pure sample of $\mathrm{K_2TiF_6}$ was treated with $\mathrm{BrF_3}$. Some displacement reactions are indicated, but more favorable compound formation has been obtained through neutralization reactions (20).

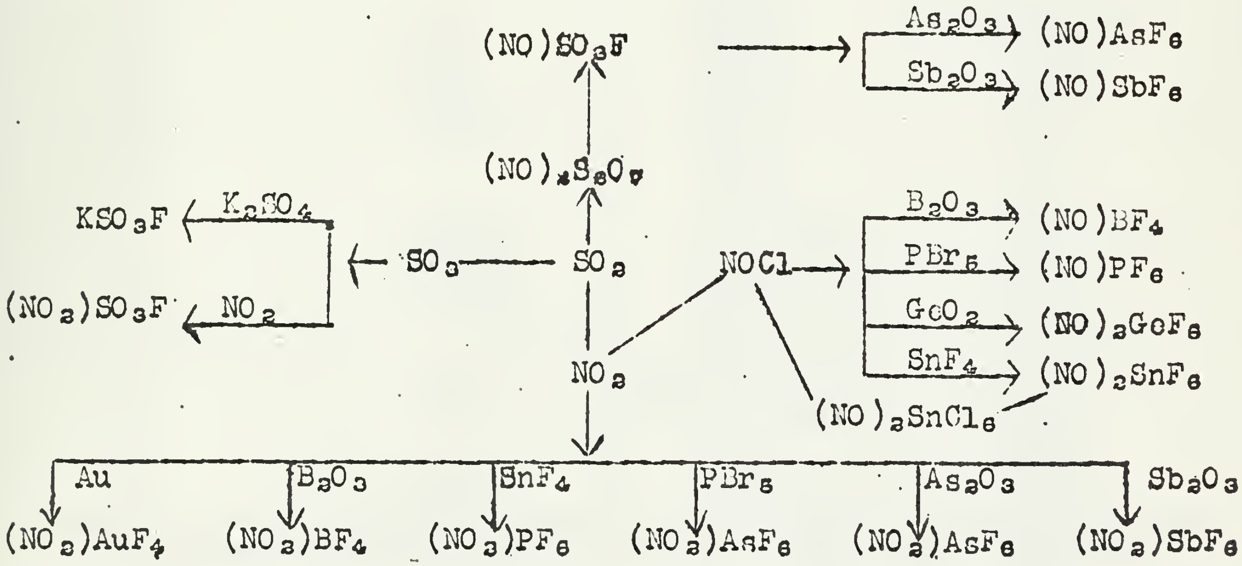
Many complex fluorides, whose thermal instability negates their formation in good yield by other procedures, have been prepared in $\mathrm{BrF_3}$ using mixtures of metals, oxides, oxy-salts, and halides (16,17,20,24). The reactions of numerous oxides have been investigated and the results are indicated in Table II (8).

TABLE II: Behavior of Oxides in BrF_3

Oxide	Compound Formed	% Yield
BeO	BeF_2	20
MgO	MgF_2	25-30
HgO	HgF_2	7
ZnO	ZnF_2	23
CdO	CdF_2	30
B_2O_3	BF_3	100
Al_2O_3	AlF_3	7
Tl_2O_3	TlF_3	100
PbO_2	PbF_4	70-90
SnO_2	SnF_4	20
ZrO_2	ZrF_4	13
Sb_2O_3	$SbBrF_8$	100
As_2O_3	AsF_5	100
Bi_2O_3	BiF_3	41-87
SeO_2	SeF_6	100
I_2O_5	IF_5	100
MoO_3	MoF_6	100

Among the many unusual reactions in BrF_3 are those involving the preparation of nitrosyl and nitronium complex fluorides and various fluorosulphonates. The following diagram illustrates the scope of these reactions (20).

PREPARATION OF NITROSYL AND NITRONIUM COMPLEX FLUORIDES AND FLUOROSULFPHONATES IN BrF_3*



*Arrows indicate reactions taking place in BrF_3

TABLE III: BEHAVIOR OF ELEMENTS IN VARIOUS SOLVENTS

	Solubility or Compound Formed* in		
Element	I_2	ICl	IBr
Na		$NaCl$	$NaBr$
K		$\underline{KICl_2}$	$\underline{KBr\text{-}KIBr_2}$
Cu	Insol.	$CuCl_2$	$\underline{CuBr_2}$
Ag	Insol.	$\underline{AgCl}$	$AgBr$
Au		$\underline{AuCl_3}$	$\underline{AuBr_3}$
Mg	Insol.	$MgCl_2$	$MgBr_2$
Ca		$CaCl_2$	$CaBr_2$
Ba		$\underline{BaCl_2}$	$BaBr_2$
Zn	Insol.	$\underline{ZnCl_2}$	$ZnBr_2$
Cd	Insol.	Insol.	Insol.
Hg		$\underline{HgCl_2}$	$\underline{HgBr_2}$
B		Insol.	Insol.
Al	AlI_3	$\underline{AlCl_3}$	$\underline{AlBr_3}$ (?)
In		$InCl_3$ (?)	(Surface react.)
Ti		$\underline{TiCl_4}$	$\underline{TiBr_4}$ (?)
Zr		Insol.	Insol.
C		Insol.	Insol.
Si		Insol.	Insol.
Ge		$\underline{GeCl_4}$(?)	$\underline{GeBr_4}$ (?)
Sn	SnI_4	$\underline{SnCl_4}$	$\underline{SnBr_4}$
Pb	Insol.	Insol.	Insol.
V		$\underline{VCl_3}$	$\underline{VBr_3}$
Nb		Insol.	Insol.
Ta		Insol.	Insol.
P		$\underline{PCl_5}$	$\underline{PBr_5\text{-}PBr_5 \cdot IBr}$
As	AsI_3	$\underline{AsCl_3}$	$\underline{AsBr_3}$ (?)
Sb	SbI_3	$\underline{SbCl_5}$	$\underline{SbBr_3}$
Bi	BiI_3	$\underline{BiCl_3}$	$\underline{BiBr_3}$
Cr	Insol.	Insol.	Insol.
Mo		Insol.	Insol.
W		Insol.	Insol.
S	Soluble	$\underline{S_2Cl_2}$ (?)	$\underline{S_2Br_2}$ (?)
Se	Soluble	$\underline{SeCl_4}$ (?)	$\underline{SeBr_4}$ (?)
Te	Soluble	$\underline{TeCl_4}$	$\underline{TeBr_4}$
Mn		$MnCl_2$	$MnBr_2$
Fe	FeI_3	$\underline{FeCl_2\text{-}FeCl_3}$	$\underline{FeBr_3}$
Co		$CoCl_2$	$CoBr_2$
Ni	Insol.	$NiCl_2$	$NiBr_2$
Pt	Insol.	Insol.	Insol.

* Underlined compounds formed in yields equal to or greater than 50%

TABLE IV: SOLUBILITY OF HALIDES IN VARIOUS SOLVENTS

Cation	Iodide in I_2	Chloride in ICl	Bromide in IBr	Fluoride in BrF_3
Li^+	soluble	slightly sol.	very sl. sol.	slightly sol.
Na^+	soluble	slightly sol.	very sl. sol.	soluble
K^+	soluble	very soluble	very soluble*	soluble
Rb^+	soluble	very soluble	very soluble	soluble
Cs^+	soluble	very soluble	very soluble	soluble
NH_4^+	soluble	very soluble	very soluble	
Cu^{+2}				insoluble
Ag^+		insoluble		soluble
Ag^{+2}				insoluble
Au^{+3}				soluble
Be^{+2}	insoluble			insoluble
Mg^{+2}	insoluble			insoluble
Ca^{+2}	insoluble			very sl. sol.
Sr^{+2}	insoluble	insoluble	mod. soluble	
Ba^{+2}	insoluble	insoluble	mod. soluble	
Zn^{+2}			mod. soluble	insoluble
Cd^{+2}				insoluble
Hg^{+2}	soluble			insoluble
B^{+3}				soluble
Al^{+3}	soluble	soluble	mod. soluble	insoluble
Ga^{+3}				insoluble
In^{+3}				insoluble
Tl^+	soluble			
Tl^{+3}				insoluble
Ti^{+4}		mod. soluble		soluble
Zr^{+4}				insoluble
Ce^{+3}				insoluble
Ce^{+4}				soluble
Th^{+4}				insoluble
Si^{+4}		soluble		soluble
Ge^{+4}				soluble
Sn^{+4}	soluble	soluble	very sl. sol.	
Pb^{+2}	soluble (?)			insoluble
Pb^{+4}				insoluble
V^{+4}		soluble		
V^{+5}				soluble
Nb^{+5}		soluble	insoluble	soluble
Ta^{+5}			insoluble	soluble
P^{+3}	soluble	soluble	very soluble	
P^{+5}		soluble	very soluble	soluble
As^{+3}	soluble			
As^{+5}				soluble
Sb^{+3}	soluble		mod. soluble	
Sb^{+5}		slightly sol.		soluble
Bi^{+3}	soluble			insoluble
Bi^{+5}				soluble

* KI also very soluble

Cation	Iodide in I_2	Chloride in ICl	Bromide in IBr	Fluoride in BrF_3
Cr^{+3}				insoluble
Mo^{+2}			mod. soluble	
W^{+2}			mod. soluble	
SO^{+2}		soluble**	insoluble	
Mn^{+2}				insoluble
Mn^{+3}				insoluble
Fe^{+3}	soluble			insoluble
Co^{+2}				insoluble
Co^{+3}				insoluble
Ni^{+2}			insoluble	insoluble

**Miscible in all proportions.

BIBLIOGRAPHY

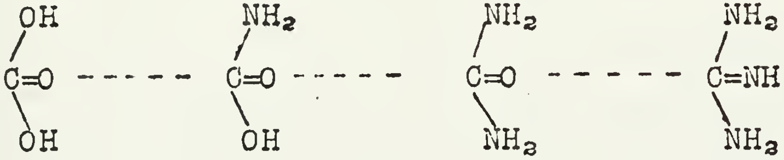
1. Banks, A. A., Emeleus, H. J., and Woolf, A. A., J. Chem. Soc., 1949, 2861.
2. Emeleus, H. J. and Gutmann, V., J. Chem. Soc., 1949, 2979.
3. Emeleus, H. J. and Sharpe, A. G., J. Chem. Soc., 1949, 2206.
4. Emeleus, H. J. and Woolf, A. A., J. Chem. Soc., 1950, 164.
5. Jander, G. and Klemm, W., "Anorganische und Allgemeine Chemie" Vol. I, G. Jander, "Die Chemie in Wasserahnlichen Losungsmitteln". Berlin: Springer-Verlag, 1949, pp. 192-208.
6. Greenwood, N. N. and Emeleus, H. J., J. Chem. Soc., 1950, 987.
7. Gutmann, V., Research 3, 337 (1950).
8. Gutmann, V., Angew. Chem., 62A, 312 (1950).
9. Gutmann, V., Monatsh., 81, 1155 (1950).
10. Gutmann, V., Z. anorg. u. allgem. Chem., 264,151 (1951).
11. Ibid, 264,169 (1951).
12. Gutmann, V., Monatsh., 82, 156 (1951).
13. Ibid, 82, 280 (1951).
14. Gutmann, V. and Emeleus, H. J., J. Chem. Soc., 1950, 1046.
15. Sharpe, A. G., J. Chem. Soc., 1949, 2901.
16. Ibid, 1950, 2907.
17. Ibid, 1950, 3444.
18. Sharpe, A. G. and Emeleus, H. J., J. Chem. Soc., 1948, 2135.
19. Sharpe, A. G. and Woolf, A. A., J. Chem. Soc., 1951, 798.
20. Woolf, A. A., J. Chem. Soc., 1950, 1053.
21. Ibid, 1950, 3678.
22. Woolf, A. A. and Emeleus, H. J., J. Chem. Soc., 1949, 2865.
23. Ibid, 1950, 1050.
24. Woolf, A. A. and Greenwood, N. N., J. Chem. Soc., 1950, 2200.

CYANATE ADDITION REACTIONS[9]

James W. Currier — October 16, 1951

I. Introduction

Cyanic acid may be regarded as a mixed aquo ammono carbonic acid. The relationship is most readily apparent from Figure 1 in which the successive replacement of OH and O of carbonic acid by the analogous nitrogen containing groups has been effected (4). Cyanic acid is a desolvation product of either carbamic acid or urea.



$$HNCO \rightleftharpoons (HNCO)_3$$

Figure 1. The Mixed Aquo Ammono Carbonic Acids

The reverse reactions of hydration and ammonation are possible as indicated in Figure 1. Cyanic acid furthermore undergoes a wide variety of solvation reactions which are presented in Figure 2 and lead to useful and interesting classes of compounds. These are often called ureido derivatives.

$HNCO + ROH \longrightarrow NH_2COOR$ (urethanes)

$HNCO + RNH_2 \longrightarrow NH_2CONHR$ (N-substituted ureas)

$HNCO + R_2NH \longrightarrow NH_2CONR_2$ (NH_2CONR_2 (N-disubstituted ureas)

$HNCO + NH_2OH \longrightarrow NH_2CONHOH$ (oxyureas)

$HNCO + N_2H_4 \longrightarrow NH_2CON_2H_3$ (semicarbazide)

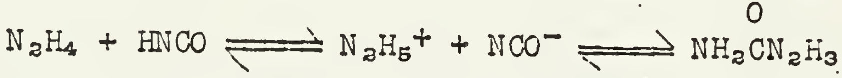
$HNCO + N_2H_3R \longrightarrow NH_2CON_2H_2R$ (N-substituted semicarbazides)

Figure 2. Solvation Reactions of Cyanic Acid

The relationships outlined in Figure 2 indicate that it should be possible to prepare ureido derivatives (N-substituted ureas and semicarbazides) by the direct action of the corresponding nitrogen compounds with cyanic acid. It is significant, however, that such reactions do not proceed through direct addition but involve a more complicated mechanism.

II. Mechanism of the Reaction

In a study of the transformation of hydrazine cyanate into semicarbazide in aqueous solution, Gilbert and Baker (5) came to the conclusion that the rate determining step involves the interaction of the $N_2H_5^+$ and NCO^- ions as represented in the following equilibria:



$$N_2H_4 + HNCO \rightleftharpoons N_2H_5^+ + NCO^- \rightleftharpoons NH_2\overset{O}{C}N_2H_3$$

This conclusion was based upon two significant experimental observations. 1. The reaction proceeds most rapidly under those conditions where the pH is adjusted to give the maximum value for the product of the concentrations of the reacting ions, $N_2H_5^+$ NCO^- . 2. The reaction rate diminishes in solution of increasing ionic strength. Other investigators have shown that these same factors apply to the formation of urea from ammonium cyanate (7,8). This same ionic mechanism might therefore be expected in all cyanate addition reactions of amine and hydrazine derivatives.

III. Cyanate Addition Reactions in Aqueous Solution

From a consideration of the ionic reaction mechanism one can determine the conditions which would favor the amine and hydrazine reactions with cyanic acid in aqueous solutions. Since cyanic acid is a weak acid (K_a=1.2 x 10^{-4}), the concentration of cyanate ion will be repressed in solutions of very low pH. Consequently the addition reaction would not be expected to take place rapidly in such solutions. Similarly, the onium ion concentration afforded by substituted amines or hydrazines, most of which are weak bases, will be effectively repressed in solutions of high pH. At some intermediate pH the reaction will be favored since the product of the concentrations of the reacting species reaches a maximum. The optimum pH is clearly that of the amine or hydrazine salt in solution. From this it is apparent that an increased basic character on the part of the amine or hydrazine compounds will facilitate the ionic rate determining step (3). A further consideration of the equilibria involved in the overall reaction indicates that an insoluble or nonionic product will shift the reaction toward completion.

In addition to the factors dictated by the nature of the reaction mechanism, several side reactions influence the cyanate addition reaction by decreasing the available amount of cyanic acid in solution (1). First, the cyanate ion undergoes hydrolysis in solution. The hydrolysis is enhanced by elevated temperatures and acidic solutions.

$$2NCO^- + 2H_2O \longrightarrow NH_2CONH_2 + CO_3^{=}$$

Secondly, cyanic acid in concentrated solutions polymerizes to form cyanic acid.

A group of synthetic procedures may be found in the literature for the preparation of the ureido derivatives of various amine and hydrazine compounds. These procedures differ principally with respect to the source of cyanic acid. Compounds which have been used successfully for this purpose include potassium cyanate, urea, and nitrourea.

1. Potassium Cyanate -- This reagent may be added to a solution of an amine or hydrazine salt (1).

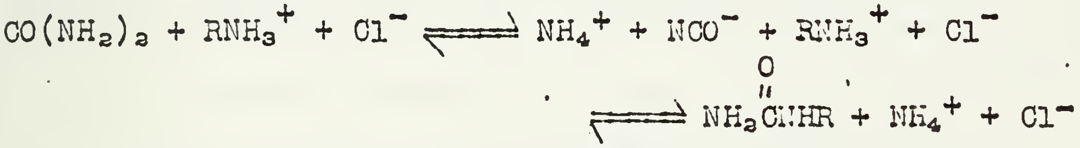
$$KNCO + RNH_2.HCl \longrightarrow K^+ + Cl^- + RNH_3^+ + NCO^- \longrightarrow RNH\overset{O}{\overset{\|}{C}}NH_2 + K^+ + Cl^-$$

When the nitrogen compound is a relatively strong base the salts of strong acids are generally quite satisfactory. However, if the compound is a weak base it is desirable to buffer the solution in order to maintain the hydrogen ion concentration at a pH in the range 5-7. An acetate buffer is usually satisfactory for this purpose.

2. Urea -- The reaction by which urea is formed from ammonium cyanate is reversible at elevated temperatures. This is evidenced by the fact that potassium cyanate is produced by heating an alcoholic solution of potassium hydroxide and urea (2).

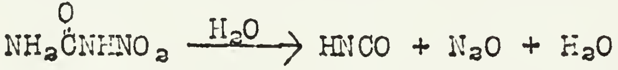
$$KOH + CO(NH_2)_2 \longrightarrow KNCO + NH_3 + H_2O$$

In a similar reaction an aqueous solution of urea and a salt of an amine or hydrazine compound is heated for a period of time. On cooling the solution the resulting equilibrium is shifted toward the formation of the corresponding ureido derivative of the amine or hydrazine compound providing this product is sufficiently insoluble.



$$CO(NH_2)_2 + RNH_3^+ + Cl^- \rightleftharpoons NH_4^+ + NCO^- + RNH_3^+ + Cl^-$$
$$\rightleftharpoons NH_2\overset{O}{\overset{\|}{C}}NHR + NH_4^+ + Cl^-$$

3. Nitrourea -- This compound affords a unique source of cyanic acid in aqueous media. The isolated compound which is formed by the dehydration of urea nitrate, is an explosive. However, in aqueous solutions heated above 60°C. it derranges to produce cyanic acid, water, and nitrous oxide (3).

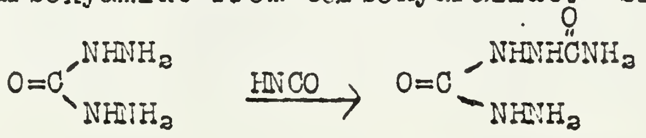


$$NH_2\overset{O}{C}NHNO_2 \xrightarrow{H_2O} HNCO + N_2O + H_2O$$

Since the nitrous oxide is evolved as a gas, a solution of cyanic acid free from contaminants is formed. Davis and Blanchard (3) applied this method to the preparation of a number of N-substituted ureas simply by warming the solution of nitrourea and the corresponding amine.

$$NH_2CONHNO_2 + RNH_2 \longrightarrow NH_2CONHR + H_2O + N_2O\uparrow$$

In order to evaluate these three synthetic approaches and the conditions under which the cyanate addition reaction can be effected each of the procedures was adapted to the synthesis of carbohydrazide-N-carboxyamide from carbohydrazide. Since carbo-



Carbohydrazide Carbohydrazide-N-carboxyamide

hydrazide-N-carboxyamide had previously been prepared and its properties studied, it was felt that the preparation of this compound might suggest what approach would be most feasible in preparing the ureido derivatives of other amine or hydrazine compounds.

These experimental studies showed that each of the outlined procedures for effecting cyanate addition reactions was pH dependent as indicated by the proposed reaction mechanism. In each case addition of an excess of an alkali hydroxide or strong acid completely inhibited the reaction. While under the careful pH control each of the procedures produced a maximum yield of the ureido derivative of carbohydrazide. The largest yields of carbohydrazide-N-carboxyamide were obtained by reacting potassium cyanate and carbohydrazide in the presence of an acetate buffer. Somewhat smaller yields were produced by this same method if the theoretical amount of hydrochloric acid was used in place of the buffer. The maximum yield obtained by using nitrourea as a source of cyanic acid for the reaction with carbohydrazide was considerably smaller than the comparable yield obtained from the potassium cyanate procedure. This difference is apparently due to the increased hydrolysis of cyanic acid brought about by heating the nitrourea solution. The yields of carbohydrazide-N-carboxyamide obtained by using urea as a source of cyanic acid were considerably smaller than the yields obtained using either nitrourea or potassium cyanate. However, this might be expected since the ureido derivative of carbohydrazide is in equilibrium with urea.

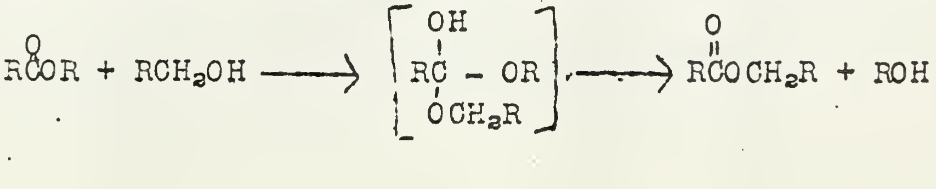
IV. Cyanate Addition Reactions in Non-aqueous Media

Urea has also been employed as a source of cyanic for effecting the preparation of various ureido derivatives in non-aqueous media. Urethanes for example may be prepared by heating a urea dissolved in an excess of the appropriate alcohol. Similarly, the ureido derivatives of certain high boiling amines have been prepared by heating urea in the presence of an excess of the amine.

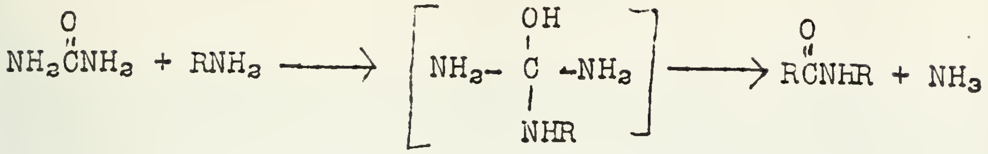
$$ROH + OC(NH_2)_2 \longrightarrow NH_2COOR + NH_3$$

$$RNH_2 + OC(NH_2)_2 \longrightarrow NH_2CONHR + NH_3$$

In a very few instances these procedures have been adapted to the reactions of solid amine and hydrazine compounds. In these latter modifications, the nitrogen compound is fused with an excess of urea. Urea may therefore be considered as a solvent for the reaction in such cases. The mechanism by which an amide group of urea is replaced by another group in non-aqueous media has not been determined. One might propose an ionic mechanism such as that previously indicated for the reactions in aqueous solution. However, it would be difficult to show how such a mechanism would apply to the formation of urethanes since alcohols have little tendency to act as bases. Instead, the mechanism may be anaalogous to that generally accepted for the exchange of alcohols by esters.



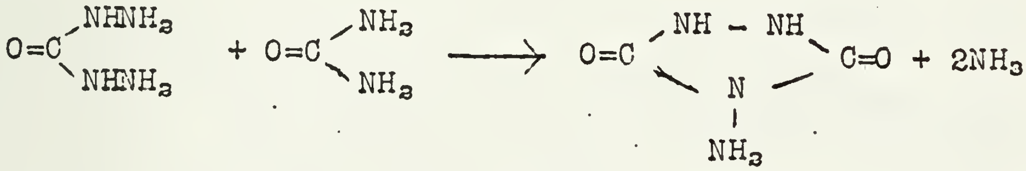
$$R\overset{O}{C}OR + RCH_2OH \longrightarrow \left[\begin{array}{c} OH \\ | \\ RC - OR \\ | \\ OCH_2R \end{array}\right] \longrightarrow R\overset{O}{\overset{\|}{C}}OCH_2R + ROH$$



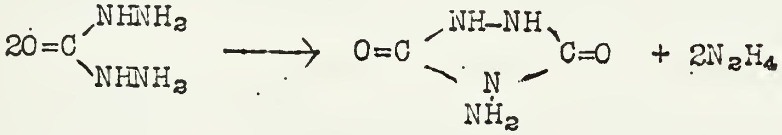
$$NH_2\overset{O}{\overset{\|}{C}}NH_2 + RNH_2 \longrightarrow \left[NH_2-\underset{NHR}{\overset{OH}{C}}-NH_2 \right] \longrightarrow R\overset{O}{\overset{\|}{C}}NHR + NH_3$$

In either case, however, the reaction mechanism furnishes little information concerning the conditions under which the reactions might best be carried out. Such factors as time and temperature of reaction seem to be limited only by the stability of the reactants and the product. A consideration of the deammonation reactions of urea therefore indicates that these reaction should be carried out under the mildest conditions possible particularly when urea is in excess.

The fusion reactions of urea are particularly interesting since Guha and De (6) have claimed that urazine was obtained by heating a mixture of carbohydrazide at 120°C. for four or five hours.



In attempts to reproduce these results no urazine could be isolated from the reaction mixture, but carbohydrazide-N-carboxyamide was isolated. The absence of urazine indicated that the urazine found by Guha and De might have been formed by dehydrazination of carbohydrazide.



In a further investigation of the fusion reaction of urea and carbohydrazide variables altered in order to determine the conditions under which the optimum yields of carbohydrazide-N-carboxyamide could be produced.

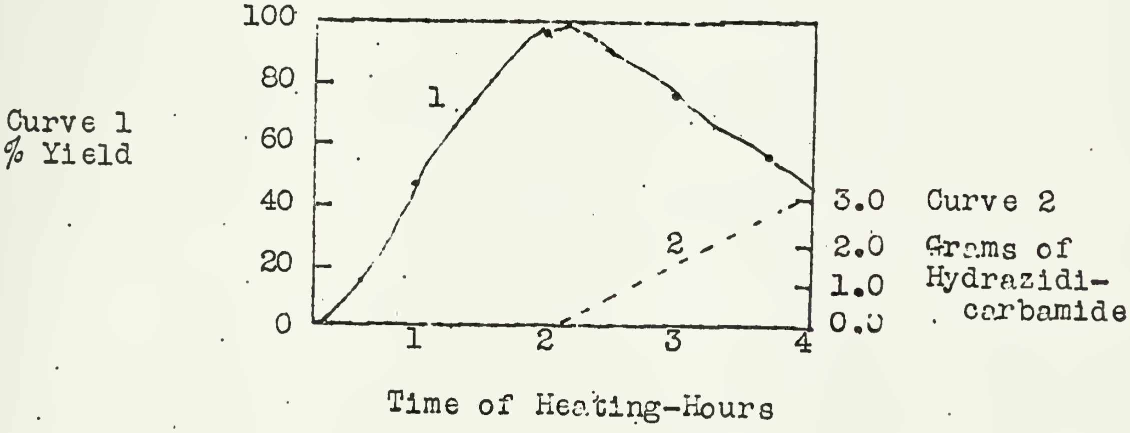
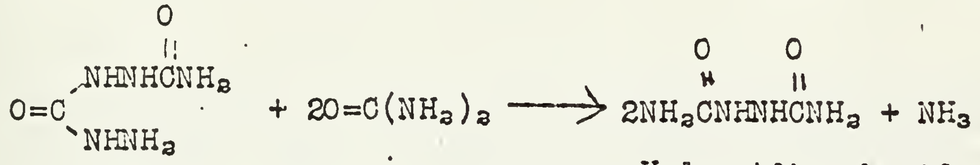


Figure 3. Preparation of carbohydrazide-N-carboxyamide by Fusion at 120°C. - Carbohydrazide, 0.1 mole; urea, 0.3 mole.

Figure 3 indicates as a function of time the per cent yield of carbohydrazide-N-carboxyamide obtained by heating a 1:3 mixture of carbohydrazide and urea at 120°C. The decrease in the per cent yield after two hours is due to a secondary reaction in which hydrazidicarbamide is formed.



$$O{=}C\begin{matrix}\nearrow NHNH\overset{O}{\overset{\|}{C}}NH_2 \\ \searrow NHNH_2\end{matrix} + 2O{=}C(NH_2)_2 \longrightarrow 2NH_2\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}NH_2 + NH_3$$

Hydrazidicarbamide

Bibliography

1. "Potassium Cycanate", American Cyanamide Company, New Products Bulletin No. 4.
2. Butler, thesis University of Illinois (1936).
3. Davis and Blanchard, J. Am. Chem. Soc., 51, 1790-1801 (1929).
4. Franklin, "The Nitrogen System of Compounds" Reinhold Publishing Corp., New York, 1935, pp. 108-11.
5. Gilbert and Baker, J. Am. Chem. Soc., 64, 2777-80 (1942).
6. Guha and De, J. Chem. Soc., 105, 1215 (1924).
7. Werner and Stitt, J. Am. Chem. Soc., 55, 4807-12 (1933).
8. Werner and Warrick, J. Am. Chem. Soc., 57, 1491-5 (1935).
9. This seminar is based upon experimental work taken up in detail in the following theses:

    a) J. W. Currier, "Cyanate Condensation Reactions", University of Illinois (1951).
    b) R. G. Fessler, "Compounds of High Nitrogen Content" University of Illinois (1951).

STEREOCHEMISTRY OF SOME BORON COMPOUNDS

R. O. Kerr October 23, 1951

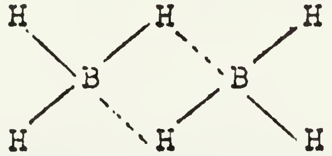
I. Introduction

Most boron compounds are believed to assume a planar trigonal configuration. Exceptions to this generalization arise when boron compounds act as Lewis acids in which event the structure tends to become tetrahedral.

II. Boron Hydrides

Since four recent seminars have dealt with the boron hydrides (1)(2)(3)(4) only those data which are covered in the latest articles will be presented.

The structure of diborane can be depicted as follows:

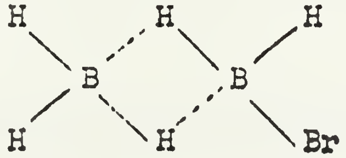


Hydrogen bridges are assumed to represent the bonds between the boron atoms. By means of the electron diffraction method Hedbërg and Schomaker (5) calculated the following bond lengths for diborane and ethane.

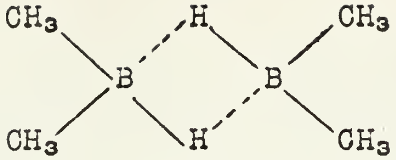
Diborane		Ethane	
B-B	1.770 Å	C-C	1.538 Å
B-H	1.187 "	C-H	1.114 "
$B-H_{br}$	1.334 "		

The fact that two different B-H bond distances were obtained was cited as evidence for a bridge structure.

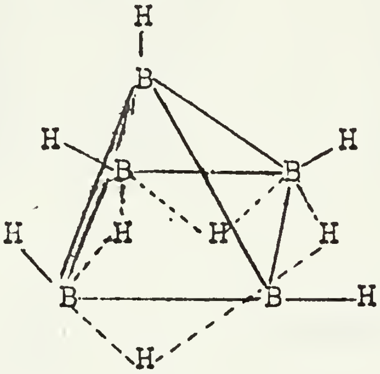
From microwave spectra Cornwell proposed the following structure for bromodiborane:



Cowan (7) found further evidence for hydrogen bridging from an interpretation of the infrared absorption spectrum of tetramethyldiborane. The absence of normal B-H bonds and the appearance of the B-H-B bond would make the following structure appear probable:

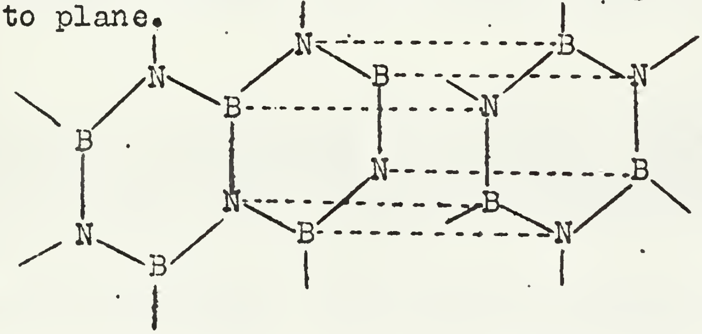


Various structures for the higher boranes have been suggested previously by several workers. Recently, however, two groups of investigators have postulated the same configuration for pentaborane (B_5H_9). (8)(9)



III. Boron Nitrides

The structure of boron nitride may be represented as consisting of parallel planes which are made up of six membered rings of boron and nitrogen, based upon X-ray diffraction measurements of Hassel (10) and more recently by Pease. (11) The rings are packed one above another with boron and nitrogen atoms alternating from plane to plane.

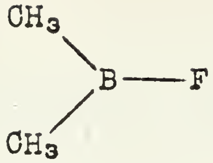


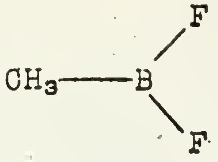
The chemistry of borazols has been reported in a recent seminar. (12)

IV. Boron halides and alkyls

Diffraction data and dipole movement measurements demonstrate that the planar structures may be assigned to the boron halides. (13)(14)(15)

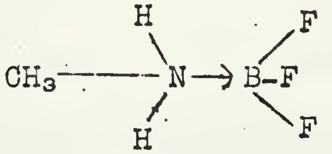
Trimethyl boron has also been found to be planar. (13) Dimethyl boron fluoride and methyl boron difluoride have been found to be planar with angle CBF = 121°. (16)

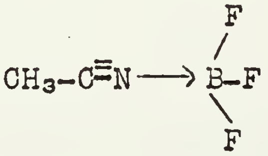




Geller and Hoard (17) used the x-ray diffraction procedure to calculate data on complexes of boron trifluoride:

BF_3	CH_3-NH_2-BF_3		CH_3-C≡N-BF_3	
-	B-N	1.58 Å	B-N	1.64 Å
B-F 1.30 Å	B-F	1.37 "	B-F	1.32 "
	BNC	114°		
	FBF	111°	FBF	114°
	FBN	108°	FBN	103°





The longer B-N bond in the methyl cyanide complex is due to a weaker bond. The amine is more basic than the cyanide. This also explains why there is less distortion from the normally planar BF_3 in the cyanide complex compound.

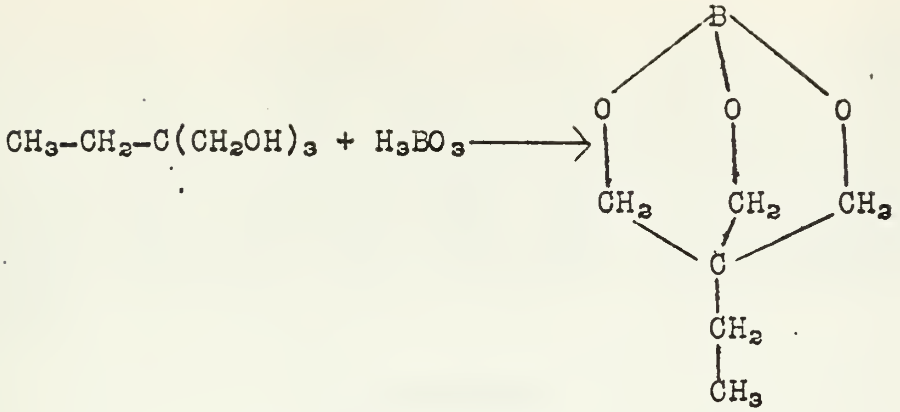
Borine carbonyl, CO-BH_3, has a similar structure. (18)

V. Borates

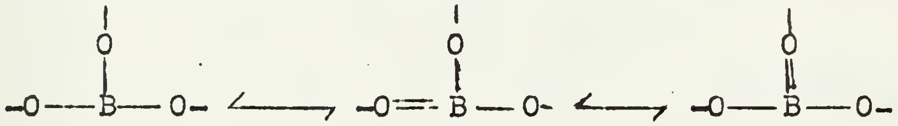
Borates and boric acids usually exhibit a planar tricovalent linkage with oxygen. (19)(20)(21) Exceptions are noted in glasses and boron oxide resins. (21)(22) When alkali, Na_2O, is added to a glass containing boric oxide, the boron becomes tetracovalent and a three dimensional system is formed.

Arbuzou and Vinogradova (23) prepared several boric acid esters and found them to be planar.

Since all of the simple boron compounds studied so far have proved to be planar in character and since many predictions have been made on the ease of sitorting these bonds, Brown and Fletcher (24) have attempted to prepare a compound in which boron bonding angles would have to be nonplanar without the formation of a complexed boron atom. This could be accomplished by preparing a compound with boron at the bridgehead of a bicyclic structure. Borate esters were chosen for these experiments because they are more stable and more readily made than alkyl borons. The following reaction was attempted:

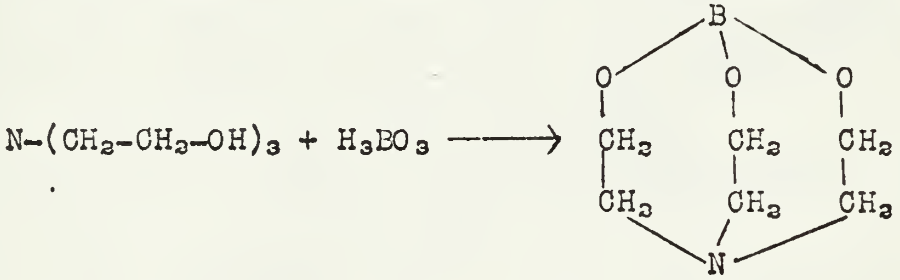


The resulting products were polymers. No monomers could be isolated even on distillation at high temperature and low pressure. The failure to isolate a monomer may be ascribed to the strain involved in passing from the planar to the tetrahedral form, or to the part resonance plays in stabilizing the esters.

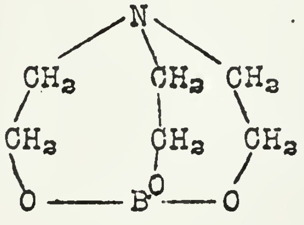


If resonance plays an important part then the formation of the monomer is highly improbable if Bredts rule can be applied.

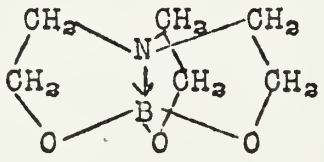
When triethanolamine reacts with boric acid a monomer is formed.



The resulting compound had a sharp melting point, 236.5-237.5°; the analysis and the molecular weight corresponded to that of monomer. Formation of triethanolamine borate does not necessarily show that the boron atom can be nonplanar. A model of the compound can take two relatively strainless forms.



I



II

The structure represented by Figure I seems to be the more logical one. Since it has a planar construction about the boron atom, and since Bredts rule does not apply to bicyclic compounds having eight membered rings, resonance would be possible. Furthermore borate esters do not ordinarily complex with amines. Bridgehead nitrogen atoms generally react rapidly with alkyl iodides; triethanolamine borate, on the other hand, reacts slowly with methyliodide. This slow rate of reaction can be explained by structure II.

BIBLIOGRAPHY

1. M. Kramer, Inorganic Seminar University of Illinois, Jan. 9, 1945.
2. M. Kramer, " " " " " , Oct. 23, 1945.
3. H. Jonassen, " " " " " , Oct. 23, 1945.
4. N. Miller, " " " " " , Mar. 8, 1949.
5. K. Hedberg and V. Schomaker, J. Am. Chem. Soc., <u>73</u>, 1482, (1951).
6. C. Cornwell, J. Chem. Phys., <u>18</u>, 1118 (1950).
7. R. Cowan, J. Chem. Phys., <u>17</u>, 218 (1949).
8. K. Hedberg and M. Jones, J. Am. Chem. Soc., <u>73</u>, 3538 (1951).
9. W. Dulmage and W. Lipscomb, J. Am. Chem. Soc., <u>73</u>, 3539 (1951).
10. O. Hassel, Norsk. Geol. Tids., <u>9</u>, 266 (1926).
11. R. Pease, Nature, <u>165</u>, 722 (1950).
12. R. Mohr, Inorganic Seminar, University of Ill. Mar. 22, (1949).
13. H. Levy and L. Brockway, J. Am. Chem. Soc., <u>59</u>, 2085 (1937).
14. M. Rollier, Gazz. chim. ital., <u>77</u>, 372 (1947).
15. C. Bailey and J. Hale, Proc. Roy. Soc. A <u>161</u>, 107 (1937).
16. S. Bauer and J. Hastings, J. Am. Chem. Soc., <u>64</u>, 2686 (1942).
17. S. Geller and J. Hoard, Acta Cryst., <u>3</u>, 121 (1950).
18. S. Bauer, J. Am. Chem. Soc., <u>59</u>, 1804 (1937).
19. G. Carpeni, Bull. soc. chim. France, <u>1949</u>, 344.
20. M. Sen and A. Gupta, Indian J. Physic, <u>9</u>, 433 (1935).
21. G. Carpeni, Bull. soc. chim. France, <u>1950</u>, 1280.
22. I. Weyl, Glass Ind., <u>29</u>, 200 (1948).
23. B. Arbuzou and Vinogradova, Compt. rend. acad. sci. U.R.S.S. <u>55</u>, 411 (1947). (In French)

24. H. Brown and E. Fletcher, J. Am. Chem. Soc., <u>73</u>, 2808 (1951).

ORGANOMETALLIC COMPOUNDS OF GROUP III

John F. Walker October 23, 1951

I. Preparation and Properties

There are three general methods of preparing organometallic compounds which are applicable to Group III metals (1).

a) Reaction of a metal and an alkyl halide.
b) Reaction of a metal with an organometallic compound. The latter are generally the dialkyl or diaryl compounds of mercury or zinc. The reactions proceed to form a more reactive product.
c) Reaction of a metal halide with an organometallic. This process employs the active but accessible "Grignard" or organolithium reagents and leads to a less reactive product.

In nearly all cases the reaction must be carried out in the absence of air or moisture; nitrogen or carbon dioxide atmospheres are usually employed.

Organometallics of scandium and yttrium are little known; they have been made using method c (2).

Organometallics of boron have been studied extensively. They are best prepared by the action of a "Grignard" reagent on boron trifluoride.

$$3\ R\ MgX + BF_3 \longrightarrow BR_3 + 3MgFX \quad (3).$$

$$3\ \phi\ MgX + BF_3 \longrightarrow B\phi_3 + 3MgBrF \quad (4).$$

another method employs the alkyl halide and aluminum.

$$3RX + 2Al + BF_3 \longrightarrow R_3B + AlXF_2 + AlX_2F \quad (4).$$

Trialkylborons are slowly hydrolysed by water and are spontaneously inflammable in air with the activity decreasing as the chain length of the alkyl group increases (4). The triarylborons fume in air but do not ignite. All unite readily with donor molecules such as ammonia, ether, and the phosphines. This acid base reaction has been used to study the basicity of amines in non aqueous solvents (5).

Arylboronic acids tend to form trimeric or dimeric anhydrides readily (6).

The organometallics of boron have planar trigonal configuration and are monomeric, normal covalent compounds (4).

Aluminum organometallics have been prepared using mercury alkyls and aryls (1) but they are best prepared by use of aluminum metal and an alkyl halide (7). Trimethylaluminum reacts with donor molecules as expected (1); with dimethylamine the addition product loses methane readily (8).

$$Al_2Me_6 + HNMe_2 \longrightarrow Me_3\bar{Al}-\overset{+}{N}HMe \xrightarrow{\Delta} (Me_2AlNMe_2)_2 + CH_4$$

Aluminum trimethyl has been shown to be a dimer both in the vapour state and in solution. The triethyl and triisopropyl derivatives are also highly associated but triisopropylaluminum exists only as a monomer (7)(9).

Zinc dimethyl and gallium halides or mercury dimethyl and gallium metal are used to prepare gallium trimethyl. It inflames in air even at -80°C. and is rapidly hydrolyzed by water (10)(11). Donor molecules add readily; both etherates and ammines are more stable to air and moisture than the parent trimethyl compound. Monamminodimethylgallium chloride is a covalent compound but it will absorb ammonia at room temperature to form a salt-like compound.

$$\begin{aligned} Me_3GaCl.NH_3 + NH_3 &\longrightarrow NH_4^+ \left[Me_2GaNH_2Cl\right]^- \\ &\xrightarrow{HCl} MeGaCl_2 + CH_4 + NH_4Cl. \end{aligned}$$

In liquid ammonia both trimethylgallium and dimethylgallium chloride are reduced by metallic sodium (10).

$$\begin{tikzcd} 2Na + 2Me_3\bar{Ga}-\overset{+}{N}H_3 \arrow[r, "Na", "NH_3"'] & Me_3\bar{Ga}-\bar{Ga}-Me_3 + 2NH_3 + 2Na^+ \arrow[d, "NH_4Br"] \\ & Me_3\bar{Ga}-\overset{+}{N}H_3 + HBr \end{tikzcd}$$

$$\begin{tikzcd} Me_2GaCl + Na \arrow[r, "NH_3"] & NaCl + Me_2Ga \arrow[d, "evaporate"] \\ & Me_2GaNH_2 \end{tikzcd}$$

Dimeric methylhydrides of gallium, like those of aluminum, are formed by the action of a glow discharge on a mixture of trimethylgallium and hydrogen; these disproportionate with triethylamine to give digallane. (12)

$$3Ga_2H_2Me + 4NEt_3 \longrightarrow Ga_2H_6 + 4Me_3\bar{Ga}-\overset{+}{N}Et_3.$$

Indium trimethyl can be prepared from indium metal and mercury dimethyl. A similar method gives indium triphenyl (13)(15). It has been reported that indium trimethyl exists as a tetramer in benzene (13) but later work indicates that it exists only as a monomer (9). The electron deficiency of the molecule is apparently slight since no stable ammines or etherates of the trimethyl are known. It is spontaneously inflammable in air at room temperature but at lower temperatures the oxidation may be controlled (13). Indium triphenyl yields amorphous oxides on oxidation;

treatment with bromine gives various salt-like phenylindium bromides (15).

<u>Dialkyl- and diarylthallium halides</u> are reaily prepared.

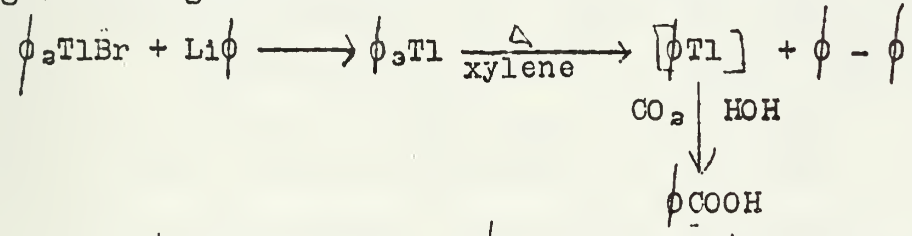
$$TlCl_3 + RMgX \longrightarrow [R_2Tl]^+ X^-$$

These are true salts and the cation is isoelectronic with dialkyl and diaryl mercury compounds and is quite stable. The corresponding hydroxide is a strong base, absorbing CO_2 from the atmosphere. There is a slight tendency for these cations to form four-covalent compounds with substances like salicylaldehyde and acetylacetone (16). Triethylthallium can be prepared by the action of lithium ethyl on diethylthallium chloride.

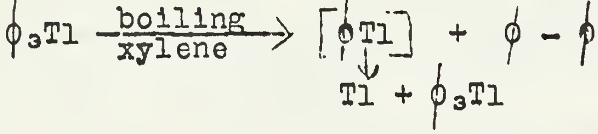
$$Et_2TlCl + LiEt \xrightarrow[\text{pet. ether}]{50^\circ} Et_3Tl + LiCl$$

The compound is readily hydrolyzed to the diethylthallium salt. Although triethylthallium is soluble in ether no etherates or ammines have been described (17).

There is some evidence for the existence of monophenylthallium which is a compound only slightly less reactive than a "Grignard" reagent.



$$\phi_2TlBr + Li\phi \longrightarrow \phi_3Tl \xrightarrow[\text{xylene}]{\Delta} [\phi Tl] + \phi - \phi$$
$$[\phi Tl] \xrightarrow{CO_2 \mid HOH} \phi COOH$$



$$\phi_3Tl \xrightarrow[\text{xylene}]{\text{boiling}} [\phi Tl] + \phi - \phi$$
$$[\phi Tl] \longrightarrow Tl + \phi_3Tl$$

II. Structures

The organometallics of Group III are monomeric except for the lower alkyls of aluminum (9). Trimethyl, triethyl, and tripropylaluminum are dimeric but triisopropylaluminum is monomeric (7). Early electron diffraction data led to the proposal of an ethane-like structure for the dimers (19), but Raman spectra, infra-red spectra, and later electron diffraction data all give evidence for a bridge structure (20)(21)(22). Polymers other than the dimer do not appear to be present (7).

A polar bond has been postulated for the bridged dimer, but there are many drawbacks to this type of bond (23). The most satisfactory proposal suggests the formation of a bridge containing "five covalent carbon" using three sp^2 bonds and two p "half bonds". This gives rise to two resonating structures which can account for the observed properties of the compounds (1)(23).

This type of bonding is the same as that proposed for the transition state of an SN^2 reaction at a carbon atom, and it may be significant that the bond strengths appear to be of the same order of magnitude (24).

Interstitial compounds are apparently bonded by "half bonds". It is therefore not surprising that gallium, indium, and thallium do not form dimeric organometallics since they do not form interstitial carbides; that is they do not tend to form "half bonds". Boron organometallics do not dimerize due to geometric considerations even though boron is capable of forming half bonds (23).

Bibliography

1. Coates, Quart. Rev. 4, 217 (1950).
2. Plets, Compt. Rend. Acad. Sci. U.R.S.S. 20, 27 (1938). C.A. 33, 2105 (1938).
3. Krause and Nitsche, Ber. 54B 2784 (1921).
4. Booth and Martin, "Boron Trifluoride and Its Derivatives", John Wiley and Sons, Inc., New York, N.Y., 1949, pp. 35-38.
5. Brown, Taylor and Gerstein, J. Am. Chem. Soc. 66, 431 (1944).
6. Berg, J. Am. Chem. Soc. 62, 2228 (1940).
7. Pitzer and Gutowsky, J. Am. Chem. Soc. 68, 2204 (1946).
8. Brown and Davidson, J. Am. Chem. Soc. 64, 316 (1942).
9. Laubengayer and Gilliam, J. Am. Chem. Soc. 63, 477 (1941).
10. Kraus and Toonder, J. Am. Chem. Soc. 55, 3547 (1933).
11. Wiberg, Johannsen, and Stecker, Z. anorg. Chem. 251, 114 (1943).
12. Wiberg and Johannsen, Angew Chem. 55, 38 (1942).
13. Dennis, Work, Rochow, and Charnot, J. Am. Chem. Soc. 56, 1047 (1934).
14. Pauling and Laubengayer, J. Am. Chem. Soc. 63, 480 (1941).
15. Schumb and Crane, J. Am. Chem. Soc. 66, 306 (1938).
16. Menzies, Sidgwick, Cutcliffe, and Fox, J.C.S., 1288 (1928).
17. Birch, J. C.S., 1132 (1934).
    Rochow and Dennis, J. Am. Chem. Soc. 57, 486 (1935).
    Groll, J. Am. Chem. Soc. 52, 2998 (1930).
18. Gilman and Jones, J. Am. Chem. Soc. 62, 2357 (1940).
19. Brockway and Davidson, J. Am. Chem. Soc. 63, 3287 (1941).
    Skinner and Sutton, Nature 156, 601 (1945).
20. Kohlrausch and Wagner, Z. Physik. Chem. B52, 185 (1942).
21. Pitzer and Steline, J. Chem. Phys. 16, 552 (1948).
22. Bell and Longuet-Higgins, Proc. Roy. Soc. (London) 183, 357 (1945).
23. Rundle, J. Am. Chem. Soc. 69, 1327 (1947).
24. Gorin, Kauzmann, Walter, and Eyring, J. Chem. Physics 7, 633 (1949).

VITAMIN B_{12} - PART I

James M. Quinn October 30, 1951

Introduction - In 1926 Minot and Murphy (1) discovered that pernicious anemia could be treated therapeutically with whole liver. Soon after this epoch-making discovery, various groups of investigators began to fractionate liver extracts for the purification of the principle which is active in the therapy of pernicious anemia. Cohn and Minot and their associates described their notable work during the period of about 1927 to 1930. West and Dakin and their associates apparently studied fractionation over the longest period of time. Other groups of investigators were Laland, Klem, Strandell, and associates (1935-36), Wilkinson (1932-40), and Karrer and his associates (1937-38). SubbaRow and Jacobson reported their first studies during 1935-38 on a multiple factor hypothesis. Castle and his associates worked on the extrinsic and intrinsic factors.

Isolation - It was discovered in 1942 (2) that there was a growth factor for chicks in cow manure and that this could be transmitted through the egg to the chick by the hen (3)(4). Shorb (5) discovered that there were unidentified growth factors in refined liver extracts for Lactobacillus lactis Donner (LLD). In 1946 Emery and Parker (6) isolated two fractions from liver by chromatography that were active in human pernicious anemia at 1 mg. per single dose. Two years later Smith and Parker (7) purified proteolyzed ox liver extract by successive chromatograms and obtained a red crystalline substance that was 37 times more intense in color than Emery and Parker's product. In the same year Folkers and co-workers (8) isolated a red crystalline compound which they designated vitamin B_{12}. The new vitamin was found to be clinically active when a single dose of 3 to 6 mg. was injected intramuscularly in patients with pernicious anemia. In Smith's article he had also reported the isolation of a second anti-pernicious anemia factor with a cobalt-phosphorous ratio of 1 to 3 but this was subsequently to be found in error (9) and a corrected ratio of 1 to 1 was reported which is the same as that for B_{12}.

Properties - B_{12} shows a microbiological activity of 11 million LLD units/mg., or 1.3×10^{-6} micrograms per milliliter supports half-maximal growth. Its refractive indexes were found to be α, 1.616; β, 1.652; γ, 1.664. The hygroscopic dark-red crystals, when exposed to air, may absorb about 12% water. They darken at 210-220° but do not melt below 300°. The molecule (10) is levorotary, $[\alpha]^{33}_{5\mathring{8}8} = -59 \pm 9°$ obs., and shows absorption maxima at 2780, 3610, 5500 Å which do not shift much with pH change. It has a molecular weight of 1490±150 by ebullioscopic means. Numerous micro-analyses lead to the empirical composition $C_{61-64}H_{86-92}N_{14}O_{13}PCo$. In water it gives the following absorption maxima 550 mμ ($E^{1\%}_{1\ cm.} = 63$), 361 mμ ($E^{1\%}_{1\ cm.} = 204$), 278 mμ ($E^{1\%}_{1\ cm.} = 115$). One gram dissolves in about 80 ml. of water giving a neutral solution

with maximum stability in the pH range 4.5 to 5; solution in this pH range may be autoclaved for 20 min. at 120°. B_{12} is soluble in alcohol and insoluble in acetone, chloroform and ether.

Assay - Four methods have been outlined in the literature for the assay of B_{12}. In the first (11), the weakly bound cyanide group is released by illumination with visible light releasing free cyanide ions which may be determined colorimetrically. The second method (12) is based on the separation of B_{12} from B_{12a} by paper chromatography and followed by microbiological analytical methods. A third method, with several variations, (13)(14)(15)(16) is based upon the response of L. lactis Donner to B_{12} as measured by the lactic acid formed from the dissimilation of glucose. The fourth method, the officially approved one, (17)(18)(19)(20) is based on the titration with sodium hydroxide of the acid produced after 72 hours by Lactobacillus leichmannii ATCC 7830 and B_{12} culture.

Commercial Preparation - Vitamin B_{12} was first prepared commercially by isolation from liver. Within the last two years however, it has been produced by the fermentation of a Streptomyces griseus culture (21) and also by the fermentation of Streptomyces aureofaciens culture (22). In both cases the cultures are adsorbed on charcoal followed by elution and chromatography upon silicic acid columns. The pink bands are further purified by chromatography and recrystallization. It has also been found (23) that injection of cobalt nitrate into the culture increased the yield of B_{12}. Radioactive Co^{60} (24)(25) can also be introduced in this manner. An attempt (26) to exchange the cobalt in B_{12} with radioactive cobalt while in solution has failed. It was also reported (27) that B_{12} suffers very little loss in biological activity when subjected to radiation by a Co^{5} (n, γ)Co^{60} reaction.

Derivatives - At the present time four compounds very similar to B_{12} have been reported in the literature (28). These are B_{12a}, B_{12b}, B_{12c}, and B_{12d}. B_{12a} and B_{12b} are produced upon hydrogenation of B_{12} with three moles of hydrogen; it has been proven that these two compounds are actually the same (31). B_{12b} has been obtained as one of the co-products in neomycin fermentation (32) and also from cultures of Streptomyces griseus (33). The cyanide group on B_{12b} may be caused to leave or return depending upon whether light is or is not present (34)(35), whether acidic or basic (36) and upon the cyanide ion concentration. B_{12c} was isolated from cultures of Streptomyces griseus (37) and has the following composition: $C_{63}H_{97}O_{22}N_{14}PCo$ which shows that it is more highly oxygenated than B_{12} although it gives the same degradation fragments and has about the same activity. Although B_{12b} and B_{12d} have the same spectrum they produce different types of growth in biological tests and are separable by chromatography. B_{12d} has the same biological activity as B_{12}.

When B_{12} is treated with hydrogen peroxide (38) in strongly alkaline solution, the cyano group is transformed to an acid group and the activity of the compound is reduced between 60 and 80%. The addition of slightly more than eight moles of perchloric acid to a solution of B_{12} in glacial acetic acid solution forms an amorphous orange-colored precipitate (39). B_{12a} responds in a

similar manner except that the resulting salt is red-colored. These are the first simple salts of the unchanged vitamins in which six moles of perchloric acid are added.

Activity of Degradation Fragments - Since several fragments of the B_{12} molecule have been isolated (40) their activity was compared (41)(42) to that of B_{12} itself. 5,6-Dimethylbenzimidazole and 1,2-diamino-4,5-dimethyl-benzene have been found to show B_{12}-like growth activity when fed to rats. 5-Methylbenzimidazole showed significantly high activity although in these three cases the activity was about a thousandth of that of B_{12}. α-Ribazole (1-α-D-ribofuranosido-5,6-dimethylbenzimidazole) was also found to be about one four-hundredth as active as B_{12} when fed to rats.

B_{12} and the Intrinsic Factor - In the past (43)(44) it has been thought possible that B_{12} (extrinsic factor) reacts with some unknown intrinsic factor in human gastric juice in the small intestine to form the antianemic principle. However no evidence has been found (45) to show that a major structural change has taken place in the B_{12} molecule. But the results do support a previously derived hypothesis that the effect of the intrinsic factor is due to its ability to promote the absorption of the small amounts of B_{12} or its equivalent which occur in natural foods.

Biological and Therapeutic Effects - The biological aspects of B_{12} may be separated into at least two categories; (a) nutrition of Poultry and animals, (b) therapeutic treatment of human diseases.

B_{12} has been shown to be one of the essential growth factors (46-52) for chicks, rats and rabbits.

The minimum effective dosage for therapeutic treatment of pernicious anemia is thought to be about one microgram daily, or multiples of this dose at longer intervals. The dose for proper remission has been estimated at 100 μg. (53). Alternatively, 3 μg. daily for six weeks, and the 1 μg. daily for a maintenance dose has been suggested (54). No evidence of toxicity from B_{12} has been reported although a question has been raised as to its carcinogenic properties. It has been found (55) that certain effects attributed to it are in reaility due to certain impurities in the liver extracts.

B_{12} has hematopoietic activity for the following diseases which are associated with anemia: pernicious anemia (uncomplicated and with neurologic involvement), nutritional macrocytic anemia, certain cases of macrocytic anemia of infancy, sprue (tropical and nontropical). It is being studied in certain diseases which are unassociated with anemia. In five cases of amyotrophic lateral sclerosis, injections of B_{12} resulted in great subjective improvement. It was not curative (56). In some cases it has been reported (57) that thymidine may replace B_{12} when used in large doses. It is an interesting fact that B_{12} is destroyed by vitamin C (ascorbic acid) (58)(59).

The amazing fact about B_{12} is that doses which are almost too small to be seen by the unaided eye are effective in curing a major disease. Outside of a few extremely deadly poisons, B_{12} is the only compound which can have such a profound effect upon the human body when administered in only microgram amounts.

Bibliography

1. Folkers, Chem. and Eng. News, 28, 1634 (1950).
2. Hammond, J. Poultry Sci., 21, 554-559 (1942).
3. Rubin, Max and Bird, J. Biol. Chem., 163, 387-391 (1946).
4. ibid, 163, 393-400 (1946).
5. Shorb, J. Biol. Chem., 169, 455-456 (1947).
6. Emery, Parker, Biochem. J., 40, iv (1946).
7. Smith and Parker, Biochem. J., 43, viii (1948).
8. Rickes, Bink, Koniusky, Wood and Folkers, Science, 107, 396-97 (1948).
9. Smith, J. Pharm. Pharmacol., 1, 500 (1949).
10. Brink, Wolf, Kaczka, Rickes and Folkers, J. Am. Chem. Soc., 71, 1854-1856 (1949).
11. Boxer and Richards, Arch. Biochem., 30 (2) 392 (1951).
12. Woodruff and Foster, J. Biol. Chem., 183 (2), 569 (1950).
13. Foster, Lally and Woodruff, Science, 110, 507-09 (1949).
14. Caswell, Koditschek and Hendlin, J. Biol. Chem., 180 (1), 125-131 (1949).
15. Hendlin and Soars, J. Biol. Chem., 188 (2), 603-610 (1951).
16. Caswell, Koditschek and Hendlin, J. Biol. Chem., 180, 125-131 (1949).
17. Skeggs, Huff, Wright and Bosshardt, J. Biol. Chem., 176, 1459-1460 (1948).
18. Skeggs, Nepple, Valentik, Huff and Wright, J. Biol. Chem., 184, 211-221 (1950).
19. Brownlee, A.C.S. Abstracts of 119th Meeting, 21A (1951).
20. Soars and Hendlin, J. Bact., 62 (1), 15-17 (1951).
21. Rickes, Brink, Koniuszy, Wood and Folkers, Science, 107, 396 (1948); 108, 134, 634 (1948).
22. Pierce, Page, Stokstad and Jukes, J. Am. Chem. Soc., 72, 2615 (1950).
23. Hendlin and Ruger, Science, 111, 541-42 (1950).
24. Chaiet, Rosenblum and Woodbury, Science, 111, 601-02 (1950).
25. Rosenblum and Woodbury, Science, 113, 215 (1951).
26. Baldwin, Lowry and Harrington, J. Am. Chem. Soc., 73, 4968 (1951).
27. Anderson and Delaborre, J. Am. Chem. Soc., 73, 4051 (1951).
28. Anslow, Ball, Emery, Fantes, Smith and Walker, Chem. and Ind., 29, 574 (1950).
29. Brockman, Pierce, Stokstad, Broquist and Jukes, J. Am. Chem. Soc., 72, 1042 (1950).
30. Kaczka, Wolf, Folkers, J. Am. Chem. Soc., 71, 1514 (1949).
31. Kaczka, Denkewalter, Holland and Folkers, J. Am. Chem. Soc., 73, 335 (1951).
32. Jackson, Whitfield, De Vries, Nelson and Evans, J. Am. Chem. Soc., 73, 337 (1951).
33. Fricke, Lanius, De Rose, Lapidus and Frost, Fed. Proc. 9, 173 (1950).
34. Veer, Edelhausen, Wijmenga and Lens, Biochim. Biophys. Acta, 6, 225 (1950).

35. Boxer, Richards, Rosenblum and Woodbury, Arch. Biochem., 30 (2), 470-71 (1951).
36. Wijmenga, Veer and Lens, Biochim. Biophys. Acta, 6, 229 (1950).
37. Buchanam, Johnson, Mills and Todd, Chem. and Ind., 29, 426 (1950).
38. Schindler, Helv. Chim. Acta, 34, 101 (1951).
39. Alicino, J. Am. Chem. Soc., 73, 4051 (1951).
40. Kaczka, A.C.S. Abstracts, 119th Meeting, 19A (1951).
41. Emerson, Brink, Holly, Koniuszy, Heyl and Folkers, J. Am. Chem. Soc., 72, 3084 (1950).
42. Emerson, Holly, Shunk, Brink and Folkers, J. Am. Chem. Soc., 73, 1069 (1951).
43. Ternberg and Eakin, J. Am. Chem. Soc., 71, 3858 (1949).
44. Beck, Castle and Welch, New Eng. J. Med., 239, 911-13 (1948).
45. Wolf, Wood, Valiant and Folkers, Pro. Ex. Biol. and Med., 73, 15-17 (1950).
46. Hogan and Parrott, J. Biol. Chem., 132, 507-517 (1940).
47. Whitson, Hammond, Titus and Bird, Poultry Sci., 24, 408-416 (1945).
48. Babcock and Hollister, Arch. Biochem., 16, 115-129 (1948).
49. Nichol, Dietrich, Cravens and Eluehjem, Proc. Soc. Exptl. Biol. Med., 70, 40-42 (1949).
50. Schaeffer, Salmon and Strength, Soc. Proc. Exptl. Biol. Med., 8, 395 (1949).
51. Emerson, Proc. Soc. Exptl. Biol. Med., 70, 392-94 (1949).
52. Abbott, Fed. Proc., 10, 153 (1951) .
53. Spies, Swarez, Lopez, Milanes, Stone, Toca, Aramburu and Kartus, Southern Med. J., 42, 528-531 (1949); 43, 206-08 (1950).
54. Jones, Darby and Tillman, Am. Internal Med., 30, 374-380 (1949).
55. Berk, Brown and Finland, NewEng. J. Med., 239, 328-330 (1948).
56. Spies and Stone, Intern. Z. Vit., 21, 328-340 (1949); 21, 347-353 (1949).
57. Wright, Skeggs, Huff, J. Biol. Chem., 175, 475 (1948).
58. Gakenheimer and Feller, J. Am. Pharm. Assoc., 38 (12), (1949).
59. Trenner Buhs Bacher and Gakenheimer, J. Am. Pharm. Assoc., 39 (6), (1950).

VITAMIN B_{12} - PART II

Sheldon E. Frey October 30, 1951

Introduction - The chemistry of vitamin B_{12} may be extended by observing various degradation studies as well as discussing the coordination involved in this complex cobalt compound.

Preliminary Data - Cobalt and phosphorus were found to be present in B_{12} by emission spectrographic analysis (1)(2). B_{12} has 4.5% cobalt which corresponds to a minimum molecular weight of 1300 while the experimental value was observed to be about 1490. It is a polyacidic base as shown by its titration in glacial acetic acid (3). This last property is emphasized by the fact that a perchloric acid derivative has been obtained corresponding to six moles of acid per mole of B_{12} indicating the presence of six weakly basic amino groups (4). Two empirical formulas agree excellently with analytical results, $C_{62}H_{88-90}N_{14}O_{13}PCo$ and $C_{63}H_{88-92}N_{14}O_{13}PCo$ (3). Using the Ilkovic equation in conjunction with polarographic studies indicate that two electrons are involved in the reduction at the dropping mercury electrode, probably the reduction from Co (III) to Co (I) (5).

Degradation Studies - No amino acids were obtained by acid hydrolysis which rules out the possibility of polypeptides. The distillate from alkali fusion was tested with Ehrlich reagent and the typical red color characteristic of pyrroles and certain cyclic five-membered nitrogen-containing compounds resulted (3).

Acid hydrolysis of B_{12} gave a crystalline product melting at 205-206°. By observing the absorption spectra, analysis, potentiometric titration of equivalent weight, as well as preparing derivatives, this product was characterized as 5,6-dimethylbenzimidazole (6). Two other products were characterized in the acid hydrolysate as being 1,5,6-trisubstituted benzimidazoles (7)(8). A positive carbohydrate test facilitated the characterization of 1-α-D-Ribofuranosido-5,6-dimethylbenzimidazole as a degradation product which was verified by synthesis (9). This fragment was further characterized by the isolation of a barium salt which indicated the presence of a substituted phosphoric acid. Further tests indicated that the phosphoryl group was on either the 2 or 3 carbon atom of the sugar molecule (10).

Acid hydrolysis was found to liberate the phosphorus as phosphate, a ninhydrin active product, as well as ammonia (11). The product reacting with ninhydrin was first thought to be 2-aminopropanol but later was shown to be Dg-1-amino-2-propanol (12). The ratio of aminopropanol to phosphorus was 2 to 1 while the ratio of ammonia to phosphorus was 4 to 1 (13).

The infra-red spectrum of B_{12} shows a band which is characteristic for a C-N triple bond. Potassium permanganate oxidation, or heating B_{12} solutions with hydrochloric or oxalic acid causes the evolution of hydrogen cyanide. Only slight liberation is noted with sulfuric acid since there is less tendency for the sulfate ion to coordinate with the cobalt. Using oxalic acid the cyanide liberated corresponds to 0.96 moles per mole of B_{12} (14). An improved method of determining cyanide ion has been reported (15). The photochemical release of the cyano group by exposure to visible light at room temperature is the better of two methods given.

Coordination in B_{12} - Both B_{12} and B_{12b} are reported (16)(17)(18) to be diamagnetic which would indicate that a d^2sp^3 hybrid of tripositive cobalt exists in these molecules. It should be noted that a limited number of cobaltous compoundshave the property of reversibly absorbing and releasing molecular oxygen. In these compounds the deoxygenated forms are paramagnetic while the oxygenated forms are diamagnetic (17). Calculations from the empirical formula and Pascal's constants rule out the possibility that the cobalt might be paramagnetic and yet have this effect obscured by a large diamagnetic organic molecule (17).

Certain incomplete coordination structures have been considered partly on the basis of the degradation studies and partly on the basis of reactions of B_{12} and B_{12b} (19). These authors point out that Co (III) possesses the same number of electrons as Fe (II) and one might expect certain analogies between B_{12} and the ferroporphyrins.

The relationship between B_{12} and B_{12b} was established by spectral and reaction studies in which it was determined that B_{12b} contains the hydroxyl group coordinated in place of the cyano group in B_{12} (14). An aqueous solution of B_{12b} has a pH of about 9 and to explain the spectral shifts observed with varying pH it is postulated that the aquocobalamin cation exists in equilibrium with the hydroxocobalamin (19).

It has been observed that in the presence of excess cyanide a purple complex of dicyanocobalamin is formed (19). The absorption spectra of this derivative in the benziminazole region together with that of B_{12} and B_{12b} give some weight to the idea that the 3-nitrogen atom is coordinated to the cobalt in B_{12} and B_{12b}. The enhanced stability of cyanocobalamin over hydroxocobalamin may be explained by the ideas of resonance and the contribution of the form containinga Co-C double bond (20). Two possibilities may be considered for the structure of the dicyanocobalamin, either a hepta-covalent or a hexacovalent structure. These transformations parallel those reported in the porphyrin series. Further studies of the equilibrium between B_{12} and cyanide ion indicate that two cyanide ions may add stepwise but in overlapping stages (21).

The reaction between ammonia and B_{12b} likewise has its parallel in the porphyrins. The product formed is called ammonia cobalichrome in which ammonia replaces the hydroxyl of B_{12b} to give a cation (19). This observation and evidence that the B_{12} factors exist partly in combined form in certain natural materials

(22) has lead to a suggested scheme of a possible role of B_{12} in metabolic processes (19).

Some Analogs of Vitamin B_{12} - Since the characterization of B_{12} as a cyanocobalamin and B_{12b} as a hydroxocobalamin other derivatives have been made in which the cyano group in B_{12} has been exchanged with the chloro and sulfato groups (23). Reaction of hydrogen sulfide introduces a sulfur-containing group that does not appear to be sulfido, sulfito, or sulfato (23). The thiocyanate analog of B_{12} has been prepared as dark purple-red needles by treatment of B_{12a} with potassium thiocyanate (24). Other derivatives include the bromo, nitro, and cyanato-cobalamin (25).

BIBLIOGRAPHY

1. Rickes, E. L., Brink, N. G., Koniuszy, F. R., Wood, T. R., and Folkers, K., Science, 108, 134 (1948).
2. Folkes, K., Chem. Eng. News, 28, 1634 (1950).
3. Brink, N. G., Wolf, D. E., Kaczka, E., Rickes, E. L., Koniuszy, F. R., Wood, T. R., and Folkers, K., J. Am. Chem. Soc., 71, 1854, (1949).
4. Alicino, J. F., ibid., 73, 4051 (1951).
5. Diehl, H., Morrison, J. I., and Sealock, R. R., Experienta, 7, 60 (1951).
6. Brink, N. G. and Folkers, K., J. Am. Chem. Soc. 71, 2951 (1949), 72, 4442 (1950).
7. Holiday, E. R. and Petrow, V., J. Pharm. Pharmacol., 1, 734 (1949).
8. Beaven, G. R., Holiday, E. R., Johnson, E. A., Ellis, B., Manalis, P., Petrow, V., and Sturgeon, B., ibid., 1, 957 (1949).
9. Brink, N. G., Holly, F. W., Shunk, C. H., Peel, E. W., Cahill, J. J., and Folkers, K., J. Am. Chem. Soc. 72, 1866 (1950).
10. Buchanan, J. G., Johnson, A. W., Mills, J. A., and Todd, A. D., Chem. and Ind., 22, 426 (1950).
11. Ellis, B., Petrow, V., and Snook, G. F., J. Pharm. Pharmacol., 1, 287, 735, 950 (1949).
12. Wolf, D. E., Jones, W. H., Valiant, J., and Folkers, K., J. Am. Chem. Soc., 72, 2820 (1950).
13. Chargaff, E., Levine, C., Green, C., and Kream, J., Experientia, 6, 229 (1950).
14. Brink, N. G., Kuehl, F. A., and Folker, K., Science, 112, 354 (1950).
15. Boxer, G. E. and Richards, J. C., Arch. Biochem. 30, 372,382 (1951).
16. Grun, F. and Menasse, R., Experientia, 6, 263 (1950).
17. Diehl, H., Vander Haar, R. W., Sealock, R. R., J. Am. Chem. Soc., 72, 5312 (1950).
18. Wallmann, J. C., Cunningham, B. B., and Calvin, M., Science, 113, 55 (1951).
19. Cooley, G., Ellis, B., Petrow, V., Beaven, B. H., Holiday, E. R., and Johnson, E. A., J. Pharm. Pharmacol., 3, 271 (1951).
20. Pauling, L., "Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 254.
21. Conn, J. B., Norman, S. L., and Wartman, T. G., Scienoc, 113, 658 (1951).

22. Scheid, H. E, and Schweigert, B. S., J. Biol. Chem., 185, 1 (1950).
23. Kaczka, E. A., Wolf, D. E., Kuehl, F. A., and Folkers, K., Science, 112, 354 (1950).
24. Buhs, R. P., Newstead, E. G., and Treuner, N. R., ibid., 113, 625 (1951).
25. Kaczka, E. A., Wolf, D. E., Kuehl, F. A., Folkers, K., J. Am. Chem. Soc. 73, 3569 (1951).

MOLECULAR ADDITION COMPOUNDS OF STANNIC CHLORIDE[‡]

Wm. C. Smith November 4, 1951

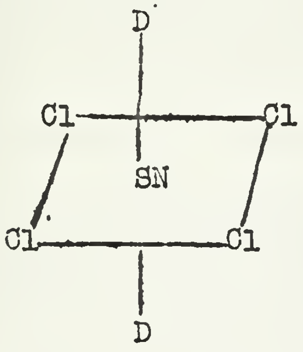
I. INTRODUCTION

The current interest in molecular structure and the nature of bonding forces has prompted a widespread study of molecular addition compounds.

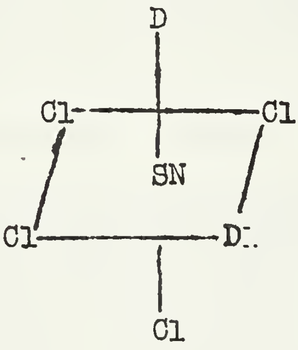
Systems of this kind in which one pair of electrons from the donor atom is added to the valence shell of the acceptor atom to give a 1:1 ratio of donor and acceptor molecules are well known. The systems of this type that have been the subject of particularly thorough investigations are those in which boron trifluoride acts as the acceptor molecule (1). Very little is known about reactions in which two donor molecules combine with a given acceptor molecule. For this reason a study of this type of system was chosen for investigation.

II. STANNIC CHLORIDE AS AN ACCEPTOR MOLECULE

Stannic chloride was selected as the acceptor molecule because its ability to attain a coordination number of six has been widely recognized, the case of the chlorostannate ion, $SnCl_6^{=}$, being the best example. In the stannic chloride molecule the 5s and 5 p orbitals are filled to give a tetrahedral configuration for the molecule, and the two pairs of added electrons might be expected to enter 5d orbitals to give an octahedral configuration. Structural features of such a molecule offer interesting possibilities because of the opportunity for cis-trans isomerism to occur.



<u>trans</u>- form



<u>cis</u>- form

D = donor molecule

Since increased electronegativity and smaller size of the halogen atom favor an increased acceptor tendency for the tin halides, it might be assumed that stannic fluoride would be a more suitable acceptor molecule for these studies. This is not the case, however, for stannic fluoride is a solid and presumably ionic in character.

[‡] Work done in partial fulfillment of the requirements for the Master of Science degree at Cornell University.

III. CHOICE OF DONOR SYSTEMS

The selection of the donor systems for this investigation was governed by several considerations. It was of primary concern that donor molecules be selected which would not lend themselves readily to a condensation reaction with stannic chloride involving the elimination of hydrogen chloride. The spatial configuration of the donor molecule should be such that the donor atom could easily approach close enough to the acceptor atom to form the desired coordinate covalent bond. The presence of electron-releasing groups on the donor atom and a low electronegativity of the donor atom would also be expected to enhance its donor ability. In line with these factors trimethylamine, tri-n-butylamine, pyridine, diethyl ether and ethyl alcohol were chosen as the donor molecules. Although the latter molecule listed would seem to lend itself readily to hydrogen chloride elimination, it was studied because preliminary studies indicated that its reaction with stannic chloride resulted in crystal formation.

Reactions of stannic chloride with tri-n-butylamine (2) pyridine (3)(4), ethyl alcohol (5)(6)(7)(8)(9)(10) and diethyl ether (11)(12)(13)(14)(15) were previously reported, but in most cases the information was sketchy and often incomplete. The literature contains no report of a reaction between stannic chloride and trimethylamine.

IV. EXPERIMENTAL

Stannic chloride and the majority of the compounds prepared were extremely susceptible to hydrolysis and for this reason a vacuum train was employed for certain phases of the work. The reactants were carefully purified and dried in each case. The reactions themselves were carried out in an atmosphere of dry nitrogen and extreme precautions were necessary throughout the course of the investigation to avoid attack by atmospheric moisture.

A. System: Trimethylamine-Stannic Chloride

A reaction between trimethylamine and stannic chloride in the gas phase resulted in a finely divided white solid. No satisfactory solvent could be found for the material and attempts at purification by a vacuum sublimation procedure were unsuccessful. Since no purification technique was satisfactory, elemental analyses for tin, chlorine, nitrogen, carbon and hydrogen were carried out on the unpurified material and they showed good agreement with the empirical formula $[(CH_3)_3N]_2SnCl_4$. The reaction product seemed reasonably stable to the atmosphere. It melted with partial decomposition at 171°C. and was shown to have a characteristic x-ray powder diffraction pattern. It was not investigated further because its observed insolubility in solvents of widely varying dipole moments ruled out any possible cryoscopic or dipole moment studies.

B. System: Tri-n-butylamine-Stannic Chloride

A liquid phase reaction was used in the attempted preparation of a molecular addition compound of tri-n-butylamine and stannic chloride using carbon tetrachloride as a solvent. An oil formed in this reaction and all attempts to bring about its crystallization were unsuccessful. It might be postulated that the solid addition compound did not form because the larger n-butyl groups prevented the close proximity of donor and acceptor atoms necessary for coordinate covalent fond formation.

C. System: Pyridine-Stannic Chloride

A white solid material resulted from the reaction of pyridine and stannic chloride in carbon tetrachloride. This product was attacked slowly by atmospheric moisture, was insoluble in a wide variety of solvents, and was not conducive to purification by a vacuum sublimation technique. Although not visibly crystalline, it gave a sharp x-ray powder diffraction pattern. The unpurified material was analyzed for all elements present and the results were in good agreement with the empirical formula $(C_5H_5N)_2SnCl_4$. The product melted at a temperture of 360°C.

D. System: Ethyl Alcohol -Stannic Chloride

The reaction of stannic chloride and ethyl alcohol with petroleum ether as solvent resulted in a white product that was very susceptible to hydrolysis. This material could be crystellized as large needles from ethyl alcohol or hot benzene but decomposed with purification by a vacuum sublimation technique was tried. After drying the recrystallized material to constant weight in an Alederhalden dryer it was subjected to elemental analysis for tin, chlorine, carbon and hydrogen. On the basis of these results the empirical formula may be represented as $(C_2H_5OH)(C_2H_5O)SnCl_3$. This would correspond to the formula $(C_2H_5OH)_2SnCl_4$ from which one molecule of hydrogen chloride had split out. A similar conclusion was reached by Rosenheim and Coworkers (10) on the basis of tin and chlorine analyses only, and they reported further that rapid analyses of a solid material formed at 0°C. indicated the formation of the true molecular addition compound at that temperature. This latter observation was not reinvestigated since the formation of this relatively unstable compound at lower temperatures would not favorably lend itself to an extensive investigation of its physical properties.

The solid condensation product obtained in the reaction at room temperature melted at 187°C. but apparently underwent some decomposition at this temperature. It gave a satisfactory X-ray powder diffraction pattern. Although the material was quite soluble in hot benzene, it was found as a result of attempted cryoscopic studies not to be sufficiently soluble in this solvent at room temperature to permit an accurate determination of its molecular weight. The cryoscopic results did indicate qualitatively, however, that it is associated to some extent in benzene solution.

Infra-red studies were made on this compound. Qualitative interpretation of the data indicated shifts in the C-O, C-C, C-H stretching, CH_3-bending and CH_3-rocking frequencies that would be expected as a consequence of complex formation.

E. System: Diethyl Ether-Stannic Chloride

The reaction of diethyl ether and stannic chloride in petroleum ether as solvent resulted in a white, extremely hygroscopic material that fumed on exposure to atmospheric moisture. It could be readily sublimed in the vacuum train by cooling the receiver with liquid nitrogen, and it was purified in this manner. Samples for analysis were prepared in a "dry box", as were the samples for the capillary melting point determination and the X-ray powder diffraction pattern.

The analyses for tin, chlorine, carbon and hydrogen agreed very well with the empirical formula $[(C_2H_5)_2O]_2SnCl_4$. A satisfactory and characteristic X-ray powder diffraction pattern was obtained for the material. A sealed capillary melting point value of 80.6°C. was obtained. In addition to being soluble in several materials because of an apparent reaction it was found to be soluble in benzene. Cryoscopic studies in this latter solvent using a cell adapted for use on the vacuum train indicated that the compound is partly dissociated into the reactant molecules. Extrapolation of the molecular weight values indicated essentially complete dissociation at infinite dilution.

An all-glass "sickle" cell of the type described by Laubengayer and Schirmer (16) was used in the measurement of vapor pressure and vapor density values for the addition compound. The results of this study are as follows:

1) The melting point was shown to be 80.3°C. and a normal boiling point of 83.7°C. obtained by extrapolation.

2) Nearly complete, reversible dissociation occurred in the vapor phase.

3) Using the integrated form of the Clausius-Clapeyron equation the apparent heat of sublimation was calculated to be 19.1 kcal/mole, and the apparent heat of vaporization was calculated as 7.1 kcal/mole. This letter value corresponds closely to the value of 6.7 kcal/mole reported by Hieber and Reindl (17).

4) The apparent heat of fusion, obtained by difference, was 12.0 kcal/mole.

5) The region of solid-vapor equilibrium may be expressed by the equation

$$\log_{10} P_{mm} = (-3766/T) + 13.435$$

The equation

$$\log_{10} P_{mm} = (-1706/T) + 7.613$$

represents the region of liquid-vapor equilibrium.

V. DISCUSSION

Although three molecular addition compounds involving stannic chloride were prepared during the course of this investigation, in no case was it definitely established that the empirical formula corresponded to the molecular formula. That this is the case for each of the molecular addition compounds prepared, however, seems a logical assumption to make. In a structural representation of the molecular formula the tin atom may be assumed to have achieved its maximum coordination number of six, and it seems impossible to devise any reasonable dimeric or more condensed polymeric system.

On the assumption that the molecule is monomeric, it is possible to reason from structural considerations that the cis-form of molecular addition compounds having a donor to acceptor atom ratio of 2:1 would be favored (15)(16). In the tetrahedral stannic chloride molecule three of the four chlorine atoms may be considered as being in a plane. The addition of the first donor molecule might be postulated to result in a hypothetical trigonal bipyramid intermediate. It can be seen that the addition of the second donor atom to this intermediate should involve the least shifting of atoms and corresponding smaller energy requirement in the case where the cis-isomer formed.

VI. BIBLIOGRAPHY

1. Booth and Martin, "Boron Trifluoride and Its Derivatives", John Wiley and Sons, New York (1949).
2. George, Mark and Wechsler, J. Am. Chem. Soc., 72, 3896 (1950).
3. Pfeiffer et. al., Z. Anorg. Chem., 17, 82 (1898).
4. Pfeiffer, ibid., 71, 97 (1911).
5. Davy, Phil. Trans., 102, 169 (1812).
6. Meyer and Tarnan, Ber., 42, 1163 (1909).
7. Holmberg, Z. Anorg. Chem., 56, 385 (1908).
8. Thiessen and Koerner, ibid., 195, 88 (1931).
9. Hieber and Reindl, Z. Electrochem., 46, 559 (1940).
10. Rosenheim, Schnabel and Bilecki, Ber., 38, 2778 (1905).
11. Levy and Kuhlman, Ann. chim. phys., 16, 303 (1846).
12. Pfeiffer and Halperin, Z. Anorg. Chem., 87, 335 (1914).
13. Tzionev, J. Russ. Phys. Chem. Soc., 48, 550 (1916).
14. Sanwei Ai, J. Soc. Chem. Ind., Japan, 37, supplementary binding, 107 (1934).
15. Ulich, Hertel and Nespital, Z. physik, Chem., B17, 21 (1932).
16. Laubengayer and Schirmer, J. Am. Chem. Soc., 62, 1578 (1940).
17. Brockway and Jenkins, ibid., 58, 2036 (1936).

RARE EARTH SEPARATIONS UTILIZING COMPLEXING AGENTS

Robert H. Marshall November 6, 1951

Introduction

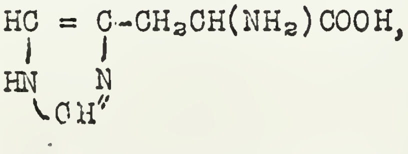
Separations of rare earths are foremost among the classical examples of long and painstaking fractional crystallizations. The present trend is to recognize the limitations of the older purely cationic fractionation procedures and to develop processes which involve more or less stable anionic complexes. Some of the classical procedures, such as crystallization of double salts or dimethyl phosphates, in reality do involve weak complex formation. However, this discussion is centered around some of the more recent developments in fractional crystallization and in ion-exchange procedures.

Since the usual valence of the rare earths is three, they have a normal coordination number of six. The rare earths do not have a great tendency to form complexes, however, and they do so only with the more powerful complexing agents. There is a gradual decrease in ionic size as one moves from the lighter to the heavier lanthanons, and thus one would expect the heavy members to form the more stable complexes. Experiments have shown this to be true.

Fractional Crystallization Procedures

Beck found nitrilotriacetic acid, $N(CH_2COOH)_3$, to be quite effective in rare earth separations (1)(2)(3). The complex is easily formed by dissolving lanthanon oxalates in a solution of ammonium "trilo". The heavier lanthanons give the more stable complexes, and the lighter members may then be precipitated in a variety of ways. Gradual lowering of the pH by the addition of acid gave Beck a 75% yield of pure La_2O_3 from a sample originally 90% La_2O_3. Addition of cupric ions removes "trilo" from the lanthanon complexes and thus promotes fractional precipitation. When a solution of the complex is heated for a period of time with undissolved lanthanon oxalates, the lighter members concentrate in the solid phase.

Vickery has conducted fractionations using various amino acids as complexing agents (4). Of those tried, histidine,

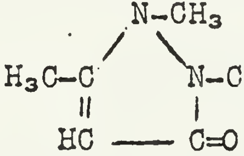


proved most effective, glycine, H_2NCH_2COOH, was next, and the others were of little value. Using histidine and a sample con-

taining lighter earths minus cerium, approximately 60% of the lanthanum was recovered in the head fraction with an increase in purity of from 40% to 95%, whereas in the sixth and final fraction samarium had increased from 5% to 50%. Some separation of praseodymium and neodymium was also observed. If only enough amino acid solution to dissolve the lanthanon oxides is used and the resulting solution is treated with oxalic acid, the order is reversed and the heavier earths are precipitated first. In the latter instance there is probably a lesser degree of complexing than in the former, but the exact nature of the bonding has not been explained.

Many years ago Urbain observed that alkali lanthanon sulfates are soluble in ammonium acetate solution (5). Vickery has used this complex formation to advantage in separating lanthanum from praseodymium and neodymium (6). The addition of small portions of sulfuric acid to the hot solution breaks the complex of the most basic lanthanum first, and this lanthanum is precipitated as the alkali sulfate. Although the procedure removed lanthanum quite effectively, the separation of praseodymium and neodymium was poor.

Ethylenediaminetetraacetic acid or "etna", $(HOOCCH_2)_2NCH_2CH_2N$-$(CH_2COOH)_2$, has become quite popular as a complexing agent. Its ability for forming chelate rings with various metals has been discussed in a previous seminar (7). Marsh has found the application of this reagent to be superior to the classical alkali double sulfate precipitation as a first step in the separation of a crude lanthanon mixture (8). The procedure concentrates the lighter members in the head fractions as well as the sulfate method, erbium and ytterbium are better concentrated in the tail fractions, and the oxalates obtained require little processing to again be fractionated. Marsh has also reported "etna" to be quite effective in separating erbium from yttrium (9). Vickery found that when the light lanthanons are fractionally precipitated with this reagent, lanthanum can be obtained in good concentration, and there is some separation of praseodymium, neodymium, and samarium (10).

Antipyrine,  has received consideration as a complexing agent in rare earth separations (11). Marsh found that when this compound was added to a solution of the heavier lanthanon iodides, a good initial separation of hexa-antipyrine lutetium iodide resulted. This separation appears to be based more upon complexing strengths than solubility differences among the complexes. Marsh has also accomplished a separation of lutetium from thulium by fractional crystallization of the complexes but the process still required nearly 3000 crystallizations (12).

An interesting note on the precipitations with antipyrine is that yttrium takes a place between erbium and thulium. Although yttrium is known to migrate through various positions in the series (13), this is the first report in which it has migrated this far. Marsh advances the explanation that six antipyrine groups are

probably the largest and heaviest assemblage known to coordinate with rare earth positive ions, and the greater compressiblity of the yttrium ion would account for this position (12).

Ion-exchange Procedures

Formation of anionic complexes has also been utilized in ion-exchange methods of separation. Most of the research in this area has dealt with samples of a few milligrams or less. However, in a recent communication Spedding reports stepping up the process to pilot plant scale (14). Resin beds of 6 x 30 inches were filled with a high capacity resin, Dowex 50 (trade name Nalcite HCR). Samples were eluted with 0.1% citrate at a pH of 6.1 and a flow rate of 0.5 cm./min. Under these conditions he was able to obtain a 73.8% yield of 99.9% pure Nd_2O_3 from a 250 g. original sample of 76% Nd_2O_3, 11% Sm_2O_3, 9% Pr_6O_{11}, and 4% other R_2O_3. In the process a total of 3050 liters of eluant was required. Excellent results were also obtained from a crude Pr_6O_{11} sample. Some success has been obtained in separating certain of the heavier earths in amounts of a few grams.

In an experiment using a 3.2 x 160 cm. bed of Amberlite IR 120, Fitch and Russell were quite successful in treating didymium oxide (15). They used nitrilotriacetic acid, iminodiacetic acids, $RN(CH_3COOH)_3$, and hydrazinodiacetic acid, $H_2NN(CH_3COOH)_3$ with the first described as being the most effective.

Elution with 0.5% "trilo" and 0.25% ammonium acetate as a buffer gave a good separation of praseodymium and neodymium. Samarium and traces of other heavier earths were eluted first and lanthanum remained absorbed on the resin bed under these conditions.

Although the large volumes of eluting solution and the close attention required make ion-exchange procedures unattractive for the laboratory, it is likely that the future trend in commercial rare earth separations will be in this direction.

Bibliography

1. Beck, G., Helv. Chim. Acta 29, 357 (1946).
2. Beck, G., Mikrochemie ver. Mikrochim. Acta 33, 344 (1948).
3. Beck, G., and Gasser, A., Anal. Chim. Acta 3, 41 (1949).
4. Vickery, R. C., J. Chem. Soc. 1950, 2058.
5. Urbain, G., Bull. soc. chim. Paris (3) 15, 347 (1896).
6. Vickery, R. C., J. Chem. Soc. 1950, 1101.
7. Dalton, R. L., Inorganic Seminar, University of Illinois, October 11, 1949.
8. Marsh, J. K., J. Chem. Soc. 1950, 1819.
9. Marsh, J. K., J. Chem. Soc. 1951, 1461.
10. Vickery, R. C., J. Chem. Soc. 1951, 1817.
11. Marsh, J. K., J. Chem. Soc. 1950, 577.
12. Marsh, J. K., J. Chem. Soc. 1951, 1337.
13. Marsh, J. K., J. Chem. Soc., 1947, 1084.
14. Spedding, F. H., *et al.*, J. Am. Chem. Soc. 73, 4840 (1951).
15. Fitch, F. T., and Russell, D. S., Can. J. Chem. 29, 363 (1951).

THE ART OF ELECTROPLATING

Ernest H. Lyons, Jr. November 13, 1951

Introduction

Early in the investigation of electrical phenomena it was observed that when direct current passes through a solution containing a suitable metal salt, the metal appeared on the negative electrode. Faraday's study of the process led him to formulate the laws we know by his name, which now form one of the fundamental concepts basing our theory of matter. Attempts were soon made to apply the process in coating metals, an application which has now reached the scale of tons of metal being electrodeposited every day.

The purpose of any coating is to alter the surface properties of an object. For example, steel, one of the cheapest and strongest materials of construction, rusts so readily that almost always some sort of surface coating is necessary. The new surface however, will not necessarily have the properties of the coating metal.

For instance, copper is not rapidly corroded in most atmospheres but copper-plated steel always rusts sooner or later; and not infrequently it rusts more rapidly than uncoated steel. The reason for this behavior is found in the existence of numerous microscopic openings or pores in the coating. At each pore, both steel and copper are exposed to the corrosive agents, and since steel is anodic to copper, corrosion of the steel occurs, and is accelerated by the electrolytic couple set-up.

On the other hand, if the coating metal is anodic to the steel, like zinc, the steel is cathodically protected from corrosion. This protection is absolute so long as the zinc remains; even bare spots several millimeters across are protected. However, the protection is the result of the corrosion of the zinc. Eventually the zinc will be removed and the steel will rust. Furthermore, the initial bright appearance of the coating is soon lost.

Where appearance is important, nickel, chromium, and silver are commonly used. The effect of the pores may be reduced by making the coatings very thick, which closes some of the openings and narrows others.

Although nickel does not corrode seriously in the customary atmospheres, it does tarnish readily. A thin coating of chromium avoids this tarnish, since chromium is normally passive. Chromium itself, as ordinarily plated, has such a poor structure that it is almost without value in protecting steel. The protective value of a so-called chromium plate depends almost entirely on the soundness of the nickel beneath.

Nickel is usually applied to steel after the steel is first copper plated. Now that nickel is scarce, chromium is being applied directly over heavy copper coatings. Whether these are as effective as nickel will have to be determined after a few years of service, as laboratory corrosion tests are difficult to evaluate.

The Plating Process

The steps, or mechanisms, by which metal is tranformed from the ionic state in solution to the metallic state on the cathode are unknown. It has commonly been assumed that the positively charged ions are attracted electrically to the cathode, there take on electrons, and crystallize as the metal.

Ionic migration is, of course, well understood, but its importance in electroplating is but poorly known. At the cathode surface, the density of the solution is lowered by loss of metal ions by deposition; this results in an upward convection current, while at the anode there is a downward convection current. Consequently any concentration of metal ions above the average value for the whole bath will be found in the bottom of the plating cell, and not in the regions predicted from consideration of migration.

Further, agitation of the electrolyte or the cathode is advantageous in most plating processes, and is common practice. In the tank as a whole, then, migration effects are obscured.

The Cathode Film

Most investigators (1) have assumed that at the cathode surface there is a film of electrolyte not subject to movements of convection, and which differs to more or less degree in composition from the bulk of the solution. Entrance of metal ions to this film is thought to be by diffusion and migration, and the essential steps of the deposition process occur within the film.

Under this assumption, with the further supposition that the concentration gradient across the layer is linear, application of Fick's law gives the rate of diffusion of metal ions into the film. In the presence of indifferent electrolytes, so that migration of themetal ions in carrying the current is neglibly small, it can readily be shown that there is a limiting diffusion current given by

$$I_d = cDzF/d$$

where c is the bulk concentration of the metal ion, D is its diffusion coefficient, z its charge, F the Faraday equivalent, and d is the thickness of the film. Likewise, it can be shown that the potential of the electrode is

$$E = E° + \frac{RT}{zF} \ln \frac{I_d}{I_d - I}$$

where E° is the molar electrode potential and I is the current passing. This equation has been thoroughly tested (2) and holds satisfactorily; indeed it is fundamental to the branch of analytical chemistry known as polarography. From such measurements it has been concluded that the thickness of the cathode film, in unstirred aqueous solutions at room temperature, is fairly constant at about 0.03 cm. (3). It is, of course, reduced very considerably by agitation and rise of temperature.

In electroplating, indifferent salts are usually not present in amounts sufficient to make the equatioms given above valid. The potential is then given (4) by:

$$E = E^\circ + \frac{RT}{zF} \ln \frac{1}{1 - Id(1-T)/cDzF}$$

where T is the transference number of the metal ion. Under these circumstances, the limiting current is not a diffusion current and its interpretation is not clear, but it is seen that migration reduces concentration polarization and increases the limiting current except when the metal ion is a complex anion. In the latter case, the transference number is negative so that the polarization is increased and the limiting current is reduced, but the limiting current depends on the diffusion of the complex ion and may remain quite high. This has been observed in deposition from cyanide solutions (5).

For these reasons, quantitative studies have not demonstrated clearly the existence of the cathode film in electroplating solutions. Furthermore, if the ions approach the electrode by ordinary diffusion processes, there is no indication that such a film should be set up in a short time and remain in a stationary state (6). However, if the convective processes are also taken into account, it has been shown by B. Levich (7) that a diffusion layer is in general established, in analogy to the polarographic case.

Efforts have been made to demonstrate the existence of the film and to determine its composition by drawing off samples of the electrolyte, by drainage (7a) through a pin-hole in the cathode (8), and by freezing the solution next to the polarized cathode, machining off known thicknesses of the frozen solution, and analyzing the various layers (9). In general the results show changes of composition; in each case the change in the anticipated directions, but it has not yet been possible to determine the composition of the layer at the cathode surface itself.

Accordingly, although the evidence is not conclusive, the concept of the cathode film or diffusion layer has been almost universally adopted in considering electrode mechanisms, and is generally considered to account satisfactorily for the concentraion polarization of the electrode (1).

The Discharge Process

Within the cathode film, migration must play a minor role. The deposition of metal from complex anions is well-known, and occurs despite the powerful repulsion which must exist between the anion and the negatively charged cathodes. In such cases, deposition is usually ascribed to simple ions resulting from dissociation of the complex.

In the case of the cyanide copper plating bath, the cathode potential is in the neighborhood of -1.0v., according to rough measurements performed by the writer, whereas the potential of the copper-cuprous ion electrode is about 0.5 volts. This shift of about 1.5 volts in potential corresponds to a concentration change of 10^{25} x 6 x 10^{23}, or about 0.06 ions per liter.

A reasonable practical plating rate with this bath is 1 amp./sq.dm. (9.3 amp./sq.ft.). This is 1/96,500 faradays per sec., or 6 x 10^{23}/96,500, ions discharged per second per sq.dm., and amounts to about 6 x 10^{18} ions per second. It is difficult to imagine that the complex ion can be dissociated so rapidly as to supply 10^{18} free or aquated cuprous ions per second from a solution which at any instant contains less than one-tenth of an ion per liter.

It therefore seems necessary to conclude that copper is desposited directly from the complex ion or at least from a related complex which may be positively charged (9a). Another argument for this view has been supplied by Bailar: cobalt is deposited from optically active complexes which have a negligible rate of racemization; if appreciable free cobalt ion ixisted in equilibrium with the complex in appreciable quantities, racemization should proceed. Finally, plating from the chromate and stannate ions may be cited; the existence of free chromium VI ion or tin IV ion in equilibrium with the anions is not admitted, however useful the concept may be in thermodynamic calculations.

The existence of a double layer at the electrode surface has been postulated and its electrical capacity measured for oxygen and hydrogen discharge (10). However, if electrostatic attraction of the positive outer portion of the double layer is invoked to explain the approach of anions to the cathode surface, then another mechanism must be provided for the approach of cations, which deposit with great ease.

In most instances, the overvoltage measured at the cathode is greater than can be accounted for by concentration polarization. This is attributed to activation energy required for the slow stage in the mechanism of discharge and deposition (10). In the discharge of hydrogen or oxygen, the evidence has been variously interpreted to indicate that the slow process is the discharge or a subsequent step. In the deposition of metals, activation overvoltages are usually low, and some authors have considered discharge and incorporation into the metal lattice to be simultaneous (11). However, in the case of nickel, cobalt, and iron, activation overpotentials are considerable. This may perhaps be correlated with the irreversibility of these metals as electrodes.

Effects of Other Substances

The deposition process leaves a sheath of ions recently liberated from the complex, as well as the indifferenct ions which have accompanied the metal ion as the Debye-Huckel ionic atmosphere. The next ions discharged must either penetrate or displace these indifferent ions. Thus, it comes about that every detail of the ionic and non-ionic composition has an effect on the structure of the cathode. Thus, in baths of the simple salt, so-called, the nature of the anion is quite important. Sulfates, for example, are almost always superior to chlorides, and it has been claimed that fluoborates and organic sulfonic acids are better yet. Pyrophosphate baths contain complex pyrophosphates of the metals.

Any polar substance is apt to be absorbed at the cathode surface and exert its effect on the structure of the deposit. This is undoubtedly the explanation of the grain-refining type of addition agent (12). Unfortunately, while the theory is plausible, it does not lend itself to quantiative verification, and predictions are not possible. Consequently addition agent research is Edisonian in nature.

Recently addition agents have been used which produce a remarkable levelling of the surface of the deposit, making it bright and shiny without the necessity of mechanical polishing. A common example is the use of traces of zinc or cadmium in a nickel sulfate bath. A good bright nickel bath will contain at least one addition agent of the grain-refining type, and one of the levelling or primary type. The presence of one type enhances the action of the other. No explanation has been offered as to the action of the levelling type of brightener.

It has been suggested (12) that the lack of response of certain metals to the presence of addition agents is the result of very heavy hydration of the ions, resulting in excessive dilution of the interface where the discharge occurs. Thus, tin and silver are little affected by addition agents, while smaller ions, presumably less highly hydrated, are more strongly affected. In the absence of reliable evidence as to the degree of hydration, it is not possible to confirm this suggestion.

It is striking that the metals which can be plated from aqueous solution are with few exceptions metals which readily form complex ions, and it is understood, of course, that even in simple salts the plating proceeds from aquated ions. However, by no means all complex ions are suitable for plating. Thus, while cyanide complexes are suitable for copper, cadmium, zinc, silver, gold, and indium, no deposit is obtained from cyanide complexes of iron, nickel, or cobalt. One might say that the activation overpotential for deposition from the latter exceeds the hydrogen overvoltage. If a relation between the electronic states of metal complexes and the ease of plating could be found, it would throw light on the mechanism of discharge.

The task of the electroplater is to arrange conditions of the bath so that the deposit will have a desirable structure and form. Because of ignorance of the cathode processes, this can be done at present, only by empirical research. Accordingly, although the art of electroplating has been immeasurably aided by the comparatively recent attention of trained workers, in many respects it is still a "black art". Instead of concealing himself in a locked closet while he prepares corrective additions for his bath, the plater now admits that the process itself remains in the locked closet of ignorance. It is to be hoped that this situation will not long remain.

Types of Bath

The larger part of total metal plated is deposited from solutions of simple salts, almost entirely from the sulfates. In solution, even simple sulfates may contain complex ions; see Wolter and King, J. Am. Chem. Soc. 71, 576-8 (1949). In such baths the maximum permissible current density is higher than in complex baths; this is doubtless the effect of higher metal concentration. For example, zinc may be plated at 2000 amp./sq. ft. from the sulfate bath, while 100 amp./sq.ft. is high for the customary cyanide bath. This higher plating rate permits substantial savings in costs of equipment and space.

Further, in the cyanide zinc bath for example, the consumption of cyanide is relatively high, sometimes amounting to one pound of sodium cyanide for every pound of zinc deposited. At the present time the cost of sodium cyanide is comparable to that of zinc; (around 20 cents per pound); in the past it has usually been several times higher than that of zinc. The reactions by which cyanide is lost are not completely understood; they include hydrolysis, electrolysis, reaction with carbon dioxide from the atmosphere, and "drag-out" in the film of solution clinging to the plated material as it is removed from the bath. Cyanide consumption in other baths seems to be less than in zinc baths.

Complex baths usually show superior throwing power; to simple salt baths that is, they deposit metal in recesses on the cathode. The trowing power of a bath is a number of factors including conductivity, polarization, and cathode efficiency. Efforts to express throwing power quantitatively (14) have not met with general acceptance because the value depend on the dimensions of an arbitrary experimental set up and do not always correspond with results observed in practice. With a cyanide zinc bath, the best conditions for throwing into one type of recessed cathode are sometiies not satisfactory for another type of recess, according to plant experience of the writer.

Where both cyanide and sulfate baths are available, the cyanide solution will be employed where throwing power is needed. Moreover silver and cadmium deposits from simple salts are so coarse that the cyanide bath is always preferred. In plating copper on steel it is necessary to use the cyanide bath to avoid the loose immersion deposit which results from displacement of copper in other baths. Even the cyanide bath under some conditions will plate copper on steel by immersion.

Although most commercial plating baths are based on sulfates or cyanides, tin is frequently plated from the stannate bath and chromium from chromic acid only. To a limited extent, fluoborates, complex pyrophosphates, and complex amines have been used.

General Plating Procedures

The surface to be coated must always be cleaned before plating. The usual procedure is (1) alkaline cleaning, to remove grease and other fatty substances;,(2) rinse; (3) acid dip or "pickle", to remove oxides; (4) rinse; (5) electroplating (6) rinse; (7) dry. Only the first step is apt to prove troublesome. Cleaning solutions usually contain sodium hydroxide, sodium phosphate, and sodium silicate. They are kept at temperatures close to boiling, and agitation is important. Agitation is often provided by passing current through the bath, with the object to be cleaned either anodic or cathodic. Gas is evolved at the surface and provides a scrubbing action. Generally anodic cleaning is preferred, because most soils seem to be positively charged and are thrown off. In the writer's experience, however, he has rarely been able to distinguish between anodic and cathodic cleaning as to effectiveness.

It is frequently claimed that surfaces must be chemically clean in order to accept an adherent plate; but this is an impossible and unnecessary requirement, as the writer has shown (16). The question of how surface films are displaced by an electrodeposit has important implications in the theory and practice of electroplating.

The time required to deposit a spcified thickness of plate may be calculated by Faraday's law, correcting for the cathode efficiency of the bath. Allowance must also be made for the nonuniform thickness resulting from variations in current distribution on irregular cathodes. Even on a flat plate, current is concentrated on the edges, where the deposit may be from two to six times as thick as on the flat surfaces. With baths giving satisfactory plates over only narrow current density ranges (as chromium) it may be necessary to make the current distribution uniform by the use of shields and auxiliary anodes and cathodes. Such practice requires considerable skill and experience. The calculation of current distribution from the theory of the potential is not usually a practical procedure.

Bibliography

1. Agar and Bowden, Proc. Roy. Soc. A 169, 206 (1938); A. A. Noyes and W. R. Whitney, Z. phys. Chem. 23, 689 (1897); W. Nernst, ibid. 47, 52 (1904), and 53, 235 (1905); Brunner, ibid. 47, 56, 1904 and 58, 1 (1906); Weigert, ibid. 60, 513 (1907); Rosebrugh and Miller, J. Phys. Chem. 14, 816 (1910); Wilson and Youtz, Ind. Eng. Chem. 15, 603 (1923); Glasstone, Trans. Electrochem. Soc. 59, 277 (1931).

2. Kolthoff and Laitinen, J. Phys. Chem. 45, 1062 (1941).
3. Ibid.; also J. Am. Chem. Soc. 61, 3344 (1939):, Hickling and Wilson, Nature 162, 489 (1948).
4. A. Hickling, Quarterly Rev. 3, 95-125 (1949).
5. F. Foerster, Z. Electrochem. 13, 561, (1907); Glasstone, J. Chem. Soc. 1929, 690, 702.
6. Hickling, ref. 4.
7. B. Levich, Faraday Soc. Discussions 1, 37 (1947); see also A. Eucken, Z. Elektrochem. 38, 341 (1932), and J. N. Agar, Faraday Soc. Discussions 1, 26 (1947).
7a. H. E. Haring, Trans. Electrochem. Soc. 41, 351 (1922).
8. Graham, Heiman, and Read, Proc. Am. Electroplaters Soc. 1939, p. 95; Read and Graham, Trans. Electrochem. Soc. 78, 279 (1940).
9. Brenner, Proc. Am. Electroplaters soc. 1940, 95.
9a. Thompson, M.R., Trans. Electrochem. Soc. 79, 417 (1941).
10. Hickling, ref. 4.
11. Blum and Rawdon, Trans. Electrochem. Soc. 44, 397, (1923); Frolich and Clark, Z. Elektrochem. 31, 649 (1925).
12. L. E. Hunt, J. Phys. Chem. 36, 2259 (1932)
13. For reliable information on practical electroplating, see Blum and Hogaboom, "Principles of Electroplating and Electrorefining," McGraw-Hill, various ed. 1924, 1930, 1949. "Modern Electroplating", The Electrochemical Society, 1941. See also Trans. Electrochem. Soc. 80, 387 (1941) for the same papers. For a recent review on electrode processes, see ref. (4).

FERROELECTRIC CRYSTALS

Laurence F. Dempsey November 20, 1951

I Introduction

Rochelle salt, or "sel de Seignette", possesses properties which are peculiar to a class of compounds referred to as "Seignette-electric", "Rochelle-electric", or "ferroelectric", the latter term being derived by analogy from the term ferromagnetic. The study of ferroelectric crystals is only about thirty years old, and that of barium titanate, one of the most important of these crystals, only about ten or fifteen years old. Faraday has been reported as having sought an example of a ferroelectric material, and although unsuccessful, as being convinced that such compounds should exist.

In ferroelectric crystals there are regions or domains containing electric dipoles in exactly the same manner that regions of magnetic dipoles exist in ferromagnetic crystals.

II Discussion

Of the ferroelectric crystals, barium titanate has been studied most intensively during the past few years; the reason for the study of this ceramic material is probably its very high dielectric constant, which often approaches 12,000.

In order to understand the origin of electric dipoles in such a material, the structure of $BaTiO_3$ must be considered. Above 120°C, the unit cell is a cube with the corner positions occupied by barium ions, the face-centered positions by oxygen ions, and the body-centered position by a titanium ion. The electrostatic bond strengths are less than unity, having the values of 2/12 and 4/6 respectively for the Ba-O and the Ti-O coordination polyhedra. Since the bond strengths are less than unity, the crystal is assumed to be isodesmic; that is, ionic with no discrete groups of of complexes.

As the temperature falls below 120°C, however, cubic symmetry disappears, and the unit cell becomes tetragonal; the titanium ion moves closer to one of the oxygen ions, and although the volume of the unit cell remains constant, the length of the axis along which the titanium ion has moved becomes greater, and the other two axes become smaller.

This departure from cubic symmetry cannot be explained by steric considerations alone. In all cubic compounds of the type $A^{+2}B^{+4}O_3$, the cell dimensions are determined by the network of linked BO_6 octahedra, the large cation accomodating itself in the space between the octahedra. In the case of $CaTiO_3$, or perovskite itself, the calcium ion is too small, and the result is that the TiO_6 octahedral framework collapses in such a manner that the octahedra become tilted, and the structure is not cubic, but monoclinic; in the case of $SrTiO_3$, the radii of the Sr^{--} and O^{--} ions are nearly alike, and the 12-coordination of strontium can occur without distortion; but in the case of $BaTiO_3$, the barium ions are too large for the available space, and the oxygens around the titanium ion are forced apart leaving abnormally large Ti-O distances. The titanium ion can "rattle" in its oxygen octahedron. On purely steric grounds one might expect either the retention of a cubic lattice with all distances equally too large, or the formation of a tetragonal structure in which some distances would remain normal. Since one axis is lengthened, while the other two are shortened, it must be assumed that the bonds have a partial covalent character superimposed upon their predominantly ionic character. Above 120°C, thermal vibration is sufficient to overcome this covalent character and to make each of the oxygens equivalent, but below that temperature the covalent character should assume increasing importance and the tetragonal structure will occur.

The spontaneous formation of these dipoles gives $BaTiO_3$ its ferroelectric character. When an external field is applied, the system of dipoles tends to line up; this effect is brought about by the reorientation of a proportion of the dipoles, coupled with the growth of some preferred domains at the expense of others.

The outstanding characteristic of ferroelectric crystals is the temperature dependence of permittivity or dielectric constant; as the temperature approaches 120°C, the permittivity rises to a sharp maximum and then falls off rapidly. By analogy, this temperature is called the "curie-point", the possession of which is the basic criterion for including any crystal among the ferroelectrics. Other characteristics are the variation in specific heat with temperature, a maximum in the refractive index at the curie-point, and a disappearance of birefringence at the curie-point.

Other double tartrates such as $NH_4NaC_4H_4O_6 \cdot 4H_2O$, $RbNaC_4H_4O_6 \cdot 4H_2O$, or $TlNaC_4H_4O_6 \cdot 4H_2O$ are quite normal in their dielectric behavior, and exhibit no ferroelectric properties down to the lowest temperatures investigated; if they do have curie-points, these must come at very low temperatures. Other materials, however, such as $NH_4H_2PO_4$, KH_2PO_4, KH_2AsO_4,

$NH_4H_2AsO_4$, KD_2PO_4, $PbTiO_3$, and WO_3 do exhibit ferroelectric properties.

Recently Matthias postulated that ferroelectric properties are accidental since not all double tartrates nor all alkaline earth titanates exhibit such properties, and that all crystals would be ferroelectric, regardless of valency, if the metal-oxygen octahedra are of the same size and of the same electronic configuration as the TiO_6 octahedra in barium titanate. Niobium (V) and Tantalum (V) have a noble gas configuration similar to Titanium (IV), and have the same octahedral radii; $NaNbO_3$, $KNbO_3$, $NaTaO_3$, and $KTaO_3$ crystals have been obtained, and verification of their ferroelectric behavior has been published. The curie-point of $NaTaO_3$ at about 475°C is the highest so far observed, but that of $KTaO_3$ is around room temperature.

In the fourth row of the periodic table Gallium (III) might be considered, though it is slightly smaller than is Titanium (IV), and though it has not a noble gas structure; for $LaGaO_3$, x-rays show a tetragonal deviation from the cubic system; the crystals show a marked optical transition between 90° and 100°C, and the dielectric constant shows a discontinuity at the transition temperature. Similarly, $LaFeO_3$, although x-rays show no deviation from the cubic structure, does appear to be optically anisotropic, but with increasing temperature, the birefringence of $LaFeO_3$ crystals gradually decreases and finally disappears at 200°C; no dielectric measurements could be made on the ferrate because of the high electrical conductivity.

III Uses

Originally, the shortage of natural mica, the demand for high power capacitors, and the interest in miniature radio components have fostered the developement of high permittivity materials. Although it has the highest permittivity of the alkaline earth titanates, barium titanate is not as good a dielectric material as the others because of the complications arising from its ferroelectric nature; it has, however a valuable field of application where the highest permittivity is desirable and the non-linearity can be tolerated. Thus it has been used successfully for miniature by-pass condensers in radios.

An important recent development which is reaching commercial importance is the piezoelectric behavior of barium titanate. All crystals and in fact all solid insulators will mechanically deform upon application of an electrostatic field. This effect is known as electrostriction and is analogous to magnetostriction in ferromagnetic substances.

Normally such deformation is very minute, but in some ferroelectric substances, and in particular, barium titanate, the effect is of the same large magnitude as the piezoelectric effect in piezoelectric crystals. Since the deformation is proportional to the square of the applied field, application of an alternating field would result in a vibration of double the frequency of the applied voltage. This effect could be avoided by applying a large direct current polarizing bias, but barium titanate retains a large polarization after the temporary application of about 30,000 volts per centimeter, and the direct current is no longer needed. The following advantages have caused the replacement of quartz by barium titanate in many industrial applications:

1. barium titanates ease of formation into many shapes;
2. its independence of many environmental conditions, such as humidity;
3. its wider operating temperature range; and
4. its ability to produce the same power output as does quartz at only 1/70 the voltage which would have been required by quartz.

Some of these applications are its use in microphones, in record-player pick-ups, in ultrasonic generators and detectors, and in vibration and pressure detectors of all kinds.

IV Conclusion

The importance of this field is attested by the very large number of papers published in the last five years. Although the synthesis and study of these materials is more properly the work of a ceramist, the results of these investigations should be of interest to the inorganic chemist, and should add to his store of information concerning inorganic chemistry.

V Bibliography

1. U.S. 2,165,819 "Electric Insulator and Method of Making Same" by E. Albers-Schonberg.
2. "Relation of Electrical Conductivity to Chemical Composition of Glass" by A.E.Badger and J.F.White, J. Am. Cer. Soc. 23 271-4 (1940).
3. "The Dielectric Properties of the Rutile Form of TiO_2" by Berberich and Bell, J. Applied Phys. 11 681-92 (1940).
4. U.S. 2,328,410 "Ceramic Insulating Material", G. Berger.
5. "Preparation and Investigation of Barium Titanate Single Crystals", H.Blattner, W. Kanzig, and W.Merz, Helv. Phys. Acta 22 35-65 (1949)
6. "Dielectric Materials", Brit.Pat. 590,183
7. "Specific Heat Anamalies in Barium Titanate", Helv. Phys. Acta 21 210-12 H. Blattner and W. Merz

8. "The Dielectric Properties of Barium Titanate at Low Temperatures", Phys. Rev. 76 1202-4 (1949) R.F.Blunt
9. "Physics of Ferroelectric Barium Titanate" A.P.DeBretteville Ceramic Age 54 363-4 376-9 (1949)
10. "Anamalous Effects of Hysteresis Loops of a Single Crystal of $BaTiO_3$" Phys. Rev. 73 807-8 (1948) A. DeBretteville
11. "Oscillographic Study of the Dielectric Properties of Barium Titanate", A. DeBretteville, J. Am. Cer.Soc.29 303
12. "Properties of Barium-Magnesium Titanate Dielectrics" E.N.Bunting, G.R.Shelton, Bull.Am.Cer.Soc.26 83 (1947)
13. "Properties of Barium-Strontium Titanate Dielectrics" Bunting, Creamer, and Shelton, J. Am.Cer.Soc., 30 114-25 ('47)
14. "Hyper Sonic Division" The Brush Development Company 34-5 Perkins Avenue, Cleveland 14, Ohio
15. "Electrical Conductivity and Index of Refraction of Barium Titanate" Phys.Acta., 21 212-15 (1948) Busch,Flury, and Merz.
16. "X-ray Investigations of the Binary Systems TiO_2-MgO, ZrO_2-MgO, ZrO_2-TiO_2" Bussem, Schusterius, and Ungewiss Ceramic Abstracts, 17 366 (1938)
17. "The Electromechanical Behavior of $BaTiO_3$ Single Domain Crystals" M.E.Caspari, Report XXX Lab. for Inc. Res. M.I.T.
18. "Frequency Multiplier Network" U.S.Pat.2,443,094 by Carlson
19. "Single Unit Capacitor and Resistor", U.S.Pat. 2,528,113 by W.L.Carlson and R.L.Harvey
20. "Piezoelectric Effect in Polycrystalline Barium Titanate" W.L.Cherry in Phys. Rev. 72 981 (1947)
21. "Theory of Barium Titanate", A.F.Devonshire, Phil.Mag. 40 1040-63 (1949)
22. "Barium Titanate and Barium-Strontium Titanate Resonators" R.C.A. Rev. 9 No.2 218-28 (1948)
23. "Effect of Field Strength on Dielectric Properties of Barium-Strontium Titanate", R.C.A.Rev. 8 539-53 (1947) H.L.Donley
24. "The Electrical Conductivity of TiO_2" M.Earle Phys.Rev. 61 55-62 (1942)
25. U.S.2,398,088 "Electrical Capacitor and Dielectric for Same" G. Ehlers and R.Roup (1946)
26. "Phase Change in Barium Titanate Crystals Induced by Infra-red Radiation Absorption" Phys.Rev.72 1119-20 (1947) Normal J. Field, A.P.DeBrettsville, and E.H.D.Williams
27. Domain Structures and Phase Transitions in Barium Titanate" P.W.Forsbergh, Phys.Rev., 76 1187-1201 (1949)
28. "On High Dielectric Constants" F.C.Frank, Trans.Faraday Soc., 38 513-23 (1937)
29. "The Relation Between the Power Factor and the Temperature Coefficient of the Dielectric Constznt of Solid Dielectrics" M.Gevers, Philips Research Reports, 1 197-224 (1946)
279-313
361-79
447-64
30. "The Properties of Crystals of Seignettoelectric Substances and of Barium Titanate" V.Ginsberg, J. Exp. Theor. Phys., U.S.S.R. 15 739-49 (1945)
31. U.S. 2,270,872 "Making Ceramic Insulators" by Goede et al.
32. "Curie Constant of Barium Titanate Single Crystals" H. Graicher, Helv. Phys. Acta 22 395-7 (1949)

33. "Curie Point of Barium Titanate" Harwood and Popper Nature 160 160-1 (1947)
34. "Influence of Firing Temperatures on the Preparation of Barium Titanate", Nature V. 165 73 (1950) M.G.Harwood
35. "Research on Barium Titanate in USSR" Housner, H. Ceramic Age 50 162-4, 190 (1947)
36. "Ceramic Phonograph Pickup", L.G.Heckter, Electronics page 94, December 1949
37. "Phase Transitions in Barium Titanate" A. von Hippel Techn. Rept. XXVIII Lab for Insulation Res. M.I.T.
38. "Properties of Electromechanical Ceramics", Hans Jaffe Electronics page 128 July 1948
39. "Titanate Ceramics for Electromechanical Purposes" Jaffe, Ind. and Eng. Chem., 42 264 (1950)
40. "Properties of Barium Titanate in Connection with its Crystal Structure", Science 109, 632-5 (1949) G.H.Jonker
41. "The Dielectric Properties of Titanates of the Perovskite Type" Chem. Weekblad., 43 672-9 (1947) Jonker
42. "Preparations and Properties of Crystals of Barium Titanate" Acta Cryst. 1 229-37 (1948) H.F.Kay
43. "Symmetry Changes in BaTiO$_3$ at Low Temperatures and Their Relations to its Ferroelectric Properties", Kay and Vousden Phil. Mag., 40 1019-40 (1949)
44. "Transducer and Method of Making Same"., U.S.Pat. 2,486,560
45. "Dielectric Properties of Barium Titanate at High Frequencies" Phys. Rev. 74 987-8 (1948)

OXIDATION STATES OF THORIUM

Philip A. Horrigan November 26, 1951

Thorium has for a long time been considered to be a member of Group IV of the Periodic Table. Recently (1), it has also been classified as the first member of a second rare earth series, called the actinide series.

I. Apparent Lower Oxidation States of Thorium

Compounds represented by the formulas, ThH_2 (2), ThN (3), and ThC (3) would seem to lead to the conclusion that thorium is capable of existing in lower valence states. However, this is not the case. These compounds are interstitial compounds, resembling alloys; in general, the hydrides, nitrides and carbides of all the heavy metals are of this type. Crystallographic work on ThO (3) has been reported; the author refers to this substance as an interstitial compound. Studies of the thorium-sulfur system at high temperatures (ca. 2000°C) reveal the formation of ThS, Th_2S_3, Th_7S_{12}, ThS_2 (2) as well as other intermediate compositions. ThS is said to be a semi-metallic compound; the evidence with respect to Th_2S_3 is not clear.

The best evidence for lower oxidation states of thorium comes from J. S. Anderson and R. W. M. D'Eye (4) (English), who reported the preparation of thorium(III) and thorium(II) iodides, and from E. Hayek, Th. Rehner and A. Frank (5) (Austrian), who reported the preparation of thorium(III) and throium(II) chlorides, bromides, and iodides. Neither of these two groups have prepared any of these compounds in the pure state; only partial evidence for their existence is presented.

II. Formation of Impure Lower Halides of Thorium

A. Work of Anderson and D'Eye (4)

Preparation of Impure Thorium(III) and (II) Iodides

These compounds were prepared using the method employed by DeBoer and Fast (6) for zirconium(II) iodide.

$$Th^\circ + 3ThI_4 \xrightarrow{450-550^\circ} 4ThI_3 \text{ (black)}$$
$$Th^\circ \quad ThI_4 \xrightarrow{450-550^\circ} 2ThI_2 \text{ (black)}$$

The reaction of thorium metal with thorium(IV) iodide was carried out in an evacuated tube, the thorium(IV) iodide being sublimed from one chamber into the other, containing the metal. Prior to the reaction, the thorium metal was degassed in a vacuum. In general, for formation of thorium(III) iodide, the components were mixed in the ratio ThI_4/Th of 3 mols/1 atom and for thorium (II) iodide, 3 mols/3.6 atoms. The mixtures were heated for

12-144 hours at 450-550°C. Both products were deeply colored and reacted violently with water. Analysis was effected in each case by reaction with water and determination of the amount of hydrogen evolved in accordance with the following equations:

$$2ThI_3 + 2H^+ \longrightarrow 2Th^{+4} + H_2 + 6I^-$$
$$ThI_2 + 2H^+ \longrightarrow Th^{+4} + H_2 + 2I^-$$

The results can be seen in the following table.

	Th / I / H		H + I
ThI_3	1 /3.40/.70	4.10	70.0 (%ThI_3)
ThI_2	1 /2.36/1.63	4.00	64 (%ThI_2)

B. Work of Hayek, Rehner and Frank (5)

1. Preparation of Impure Thorium(III) and (II) Iodides

Two methods were employed by the Austrian investigators. They are as follows: 1. Reduction of thorium(IV) iodide by thorium metal and 2. Direct union of the elements. Impure thorium metal was used in all experiments. Activation by addition of traces of iodine or mercury seemed to give better results.

$$Th^\circ + 3ThI_4 \xrightarrow{\text{vac.}} 4ThI_3 \text{ (black-violet)}$$
$$2Th^\circ + 3I_2 \xrightarrow{650^\circ} ThI_3$$

See the end of Section B for the tabulation of results

Thorium(II) iodide was prepared by decomposition of thorium (III) iodide at 550-600°C. This reaction was also noted by Anderson and D'Eye.

$$2ThI_3 \xrightarrow{550-600^\circ} ThI_2 + ThI_4$$

The product resembled thorium(III) iodide.

2. Preparation of Impure Thorium(III) and (II) Bromides

Thorium(III) bromide was prepared by heating together thorium metal and bromine in the atomic ratio 1/3. The mixture was heated in an evacuated atmosphere of cacbon dioxide at 600° for 20 hours. The product was brownish-black and was not only hygroscopic, but also pyrophoric, burning with a bright light.

The disproportionation of thorium(III) bromide at 595°C. yielded impure thorium(II) bromide.

3. Preparation of Impure Thorium(III) and (II) Chlorides

Thorium(III) chloride was formed by heating thorium metal and chlorine together in a vacuum at 620° for 20 hours. The metal and chlorine were mixed in the ratio Cl/Th of 3/1. The same product was obtained by heating "thermally activated" metal with thorium(IV) chloride in the presence of mercury.

Impure thorium(II) chloride was prepared by the disproportionation of thorium(III) chloride in a vacuum at 670°.

III. Place of Thorium in the Periodic Table

	Th / X / H
ThI_3-Method 1.	1 /2.78/0.88
" " 2.	1 /2.94/1.02
ThI_2	1/2.13/1.83
$ThBr_3$	1/2.80/0.83
$ThBr_2$	1/2.11/1.75
$ThCl_3$	1/3.03/0.76
$ThCl_2$	1/2.05/1.42

III. Place of Thorium in the Periodic Table

Assuming that the work described above and the conclusions drawn therefrom are accurate, the position of thorium in the Periodic Table may now be argued. Similarity of thorium to cerium and to actinium, protoactinium and uranium should place thorium as the first member of an actinide series (similar to the lanthanide series), as Seaborg (1) would have it. On the other hand, if thorium can be shown similar to zirconium and hafnium and dissimilar to the above mentioned elements, the , thorium should be placed in Group IV. Thorium has been shown by M. Haissinsky (9) to resemble zirconium and hafnium with respect to hydrolysis of compounds, complex formation, basicity, stability of peroxides and electrochemical behaviour. It has also bee pointed out (9) that actinium, thorium, protactinium and uranium differ quite markedly from each other in their stable oxidation state. The discovery of oxidation states of +3 and +2 for thorium further demonstrates the similarity to zirconium and hafnium. The instability and deep colors of the lower halides of thorium are in direct relation to what is found in zirconium and hafnium. On the other hand, cerium has no oxidation state of +2. Therefore, it begins to look as if the original position of thorium is the correct one.

References

1. G. T. Seaborg, Chem. Eng. News 23, 2190 (1945).
2. E. D. Eastman, Leo Brewer, LeRoy A. Bromley, Paul W. Gillis and Norman L. Lofgen, J. Am. Chem. Soc. 72, 4019-23 (1950).
3. R. E. Rundle, Acta Cryst. 1, 180- 7 (1948).
4. J. S. Anderson and R. W. M. D'Eye, J. Chem. Soc., Suppl. No. 2, S241-8 (1949).
5. E. Hayek, Th. Rehner and A. Frank, Monatsh, 82, 576-587 (1951). and E. Hayek and Th. Rehnrer, Experimentia, 5, 114 (1949).
6. DeBoer and Fast, Z. anorg. Chem. 187, 177 (1930).
7. H. Wartenberg, Z. Electrochem. 15, 836 (1909).
8. O. Honigschmid, Z. Elektrochem. 22, 19 (1916).
9. M. Haissinsky, J. Chem. Soc. (London), Suppl. No. 2, S239-240 (1949).

PURIFICATION OF HYDROCARBONS BY MEANS OF INORGANIC REAGENTS

J. P. Freeman November 27, 1951

Introduction

Ever since petroleum refining was put on a sound, scientific basis, industrial chemists have searched for methods of purifying the various fractions by separation into their constituents. Distillation procedures cannot hope to do a complete job, and these investigators have attempted to find chemical processes to improve this separation. Their experiments have led them to a consideration of some inorganic reagents, and a few of these will be discussed here.

Urea

In 1940, a German patent application (1) announced rather mutely that urea has the remarkable property of forming easily obtainable crystalline adducts with straight chain organic compounds. Evidently this work was interrupted by the war because no more was heard of this interesting discovery until the original workers announced a reinvestigation of their work (2). At that time, they pointed out the value of this property in separating linear compounds from branched chain or cyclic ones. Since such crystal formation is especially attractive in connection with the paraffin hydrocarbons, where any other derivatives are unknown, this adduct formation has been investigated avidly by various oil companies. As will be shown, separations, which otherwise are only difficultly accomplished by distillation, have been effected readily.

The urea adducts are formed by all types of straight chain organic compounds regardless of the functional groups present, but not by cyclic compounds and only by those branched chain compounds which are so at or near the end of a long chain. For example, compounds with a single methyl branch form complexes when the linear chain approaches twenty (3). It is interesting to note that some branched chain compounds which do not form stable complexes themselves may do so when straight chain paraffins are precipitated from a mixture. This is especially true of long chain hydrocarbons with branching near the end (4). In order to insure the best efficiency in removing straight chain paraffins from petroleum, the process should be conducted over a fairly long period at relatively low temperatures with excess urea and should be followed by a minimum of washing.

Thermodynamically, this adduct formation more closely resembles adsorption than any other familiar process. The formation is exothermic and the heat developed (800-1300 cal/mole urea) is of the order expected from van der Waal forces. This heat of adduct formation is about the same as the calculated energy of

hydrogen bonding in ammonia crystals. It has been shown that these adducts are not merely adsorption products because upon evaporation of some of the less stable adducts the vapor pressure remains constant until complete dissociation has occurred.

These adducts conform to no stoichiometric ratio of urea to hydrocarbon, but in a homologous series the mole ratio of organic compound to urea increases linearly with the length of carbon chain. For paraffins of from seven to thirty-two carbon atoms, the number of moles of urea per carbon atom remains constant at about 0.8.

There are four facts to be considered in attempting to assign structures to these adducts.

a) Shape is the determining factor in their formation
b) The adducts are characterized by no simple ratio of urea to linear molecule or carbon atom.
c) Only portions of some molecules are involved.
d) The heat of formation is large for these adducts.

These facts suggest that the carbon chains are held within distorted urea crystals. Debye X-ray diagrams show that the adducts have identical lattice structures different from that of urea, but the hydrocarbons do not contribute to the interference pattern. Also, whereas most of the adducts are hexagonal, urea itself crystallizes in tetragonal prisms (5).

A structural analysis of the n-$C_{16}H_{34}$-urea adduct indicated that the hydrocarbon in its extended form lies in the central lumen canal of the changed urea prismatic lattice the cross section of which can accommodate the hydrocarbon (5). Branching on a secondary carbon atom prevents the lattice from accommodating the molecule except by distending itself which leads to a breakdown in the crystal. Apparently the attraction in the lattice is caused by hydrogen bonding between the paraffin and the oxygen atom of urea. When these adducts form with hydrocarbons, it has been shown that the urea lumen lattice is 2.4 Å longer than the central molecule.

Other examples are known of the separation of molecules not on the basis of physical or chemical property but because of their shape.

The zeolitic materials, analcite, and chabazite, the structures of which are characterized by long interstitial channels, have been shown to occlude linear hydrocarbons up to eight carbon atom length (14). All hydrocarbons with side chains were excluded. The affinity between the n-paraffins and the zeolite lattices is considerable (ΔH is fairly high) and increases with chain length.

Dutch workers have demonstrated that long-chain hydrocarbons may be separated from naphthenic and aromatic ones by passing the mixture in pentane solution through a column of Floridin earth. This earth consists mostly of an attapulgite structure containing long channels with a diameter from 4-6.5A° (15).

Quite recently reports have been made to the effect that the urea process of purifying hydrocarbons is now at the pilot plant stage. In one of the processes (6), methyl isobutyl ketone is used as the solvent since it is available commercially and is suitable for a hydrocarbon mixture ranging from heavy naphtha to lubricating oils. A rapid reaction is effected when a saturated aqueous solution of urea is mixed with a solution of the hydrocarbon feed in the ketone. Water and ketone and urea and ketone are only slightly soluble in each other, but even this slight solubility serves to reduce the reaction rate barrier which exists between the two phases. Saturating the water solution with urea at a higher temperature than that at which the reaction is run insures a constant saturation of the urea layer. The adduct can then be separated, washed free of contaminants, and decomposed.

The efficiency of such a process can be seen from the tables below which show results in three different fractions of petroleum.

	Naphtha		Light Stove Oil		Heavy Stove Oil	
	Feed	Extract	Feed	Extract	Feed	Extract
Yield, %vol of feed	---	8.1	---	10.9	---	13.7
n-paraffin, %vol	9.9	96.8	11	97.0	13	95

The use of a polar solvent seems necessary since attempts to form these adducts in hydrocarbon medium failed (7). Apparently there is some inhibitor in the hydrocarbon, possibly sulfur or peroxides which must be destroyed if reaction is to occur.

Several practical applications have been suggested for this process in the literature (6).

1) Recovery of n-paraffin mixtures in nearly pure form. These can be used as odorless solvents, special lubricants and raw material.

2) Production of low pour point distillate fuels---removal of n-paraffins from Diesel fuels.

3) Raising octane number.

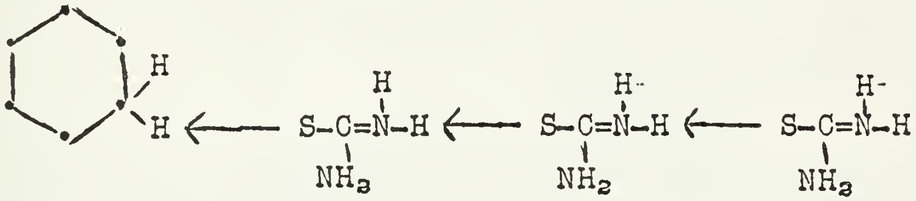
4) Improvement of cetane number. (Straight chain are extracted from low quality short chain).

5) Extraction of straight chain olefins.

Thiourea

Thiourea also forms crystalline adducts but in contrast to urea, it forms them only with so-called compact hydrcarbons (8). Thus, adducts are formed with cyclohexane and its derivatives and with highly branched aliphatic hydrocarbons such as hexamethylethane and isooctane. (Tetramethylmethane or ethane do not form adducts and neither do aromatic compounds.) Angla (8) claimed

that olefins do not form these adducts because of mutual repulsions between the molecules, but a recent patent claims adduct formation with iso- and cyclo-olefins (9). It may be possible to use both urea and thiourea to complete the purification of hydrocarbon fractions. Angla proposed a structure based upon the observation that the adducts are usually characterized by a 1:3 ratio of thiourea to hydrocarbon.

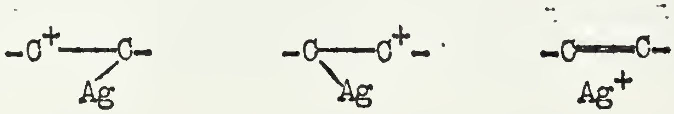


This structure seems to give no explanation for the fact that the straight chain adducts are unstable. It is probable that the structures of these adducts are much the same as those of the urea adducts except that the central canals in thiourea have a larger diameter.

Formation of Complexes with Silver Nitrate

It has been known for many years that olefins combine with aluminum, silver, cuprous, mercuric, platinous, and ferrous salts. The majority of these adducts seem to be ordinary molecular compounds which are easily resolved into their components (10).

In 1938, the reaction of ethylenic compounds with aqueous silver nitrate solutions was investigated (11). It was found that they react rapidly and reversibly with the salt and are thus extracted into the water layer. In the complex there is one silver ion to one molecule of olefin. The chemical change that takes place is probably the replacement of a coordinated water molecule by an olefinic molecule. If the strength of the coordinate bond holding the water is much greater than of that holding olefinic compound, there is no tendency to complex. Solid addition compounds of cyclopentadiene and biallyl have been isolated. When the double bond is deeply buried in the molecule, the complex is less stable. Probably it is more difficult for the silver ion to approach the π-electrons of the double bond. The proposed structure is a resonance hybrid of the following classical forms having a resonance energy of 10 kcal/mole:



Aromatic hydrocarbons also can be argentated with silver nitrate (12). Although this reaction is of less practical significance than others mentioned in this article, an investigation of the structures of these molecules may throw some light on the structures of the olefin complexes.

The reaction of aromatic hydrocarbons can be expressed as two equilibrium reactions:

$$(1)\ Ag^+ + Ar \rightleftharpoons AgAr^+ \qquad K_1 = (AgAr^+)/(Ag^+)(Ar)$$
$$(2)\ AgAr^+ + Ag^+ \rightleftharpoons Ag_2Ar^{++} \qquad K_2 = (Ag_2Ar^{++})/(AgAr^+)(Ag^+)$$

$K = K_1 + K_1K_2(Ag^+)$, where K is a constant defined in terms of the several species postulated as present.

If reaction (1) were the only one contributing to complex formation, K should equal K_1 and values of K should be independent of silver ion concentration. However, it was found that K increased with increasing silver ion concentration. Thus reaction (2) contributes appreciably. If (1) and (2) account for all complexes, a plot of K vs. (Ag^+) should give a straight line, which it does.

The silver ion is pictured as being above the ring equidistant from the six carbon atoms in a position to use the π electrons to form covalent bonds with any of the atoms. The structure then is a hybrid of eighteen singly bonded structures and two no-bond structures. The loss of ring resonance is compensated by the resonance energy of the complex. In the doubly argentated complex the second silver ion is below the plane of the ring.

Recently an important process has been developed for the removal of small amounts of saturated hydrocarbons from olefins (13). This involves the addition of anhydrous crystalline silver nitrate to the liquid hydrocarbon under pressure. In the case of propylene and 1-butene, a separate liquid phase forms. This is miscible with water but insolbule in hydrocarbons. It is very stable when kept in contact with some liquid hydrocarbon, but decomposes upon prolonged exposure to the atmosphere. Since propane and other paraffins are insoluble in this liquid phase, formation of this liquid complex provides a method for purifying propylene of 70-99% purity. (The complex is not formed from a hydrocarbon containing less than 70% propylene).

After the complex is formed at 0°C. the undissolved hydrocarbon is separated under pressure. The propylene is then evolved from the complex completely either by slight reduction or pressure or by warming.

It is interesting to note that ethylene, 2-butene, isobutene, and mixed pentenes do not form any complex. Evidently their dissociation pressures exceed the vapor pressures of the olefins at all temperatures.

BIBLIOGRAPHY

1. F. Bengen, German patent appl. O. Z. 12438 (1940).
2. F. Bengen and W. Schlenk, Experientia, 5, 200 (1949).
3. W. J. Zimmerscheid, R. A. Dinerstein, A. W. Weitkamp and R. F. Marschner, J. Am. Chem. Soc., 71, 2947 (1949).
4. O. Redlich, C. M. Gable, A. K. Dunlop and R. W. Millar, J. Am. Chem. Soc., 72, 4153 (1950).
5. W. Schlenk, Ann., 565, 204 (1949).
6. W. A. Bailey, R. A. Baumrot, L. C. Fetterly and A. G. Smith, Ind. Eng. Chem., 43, 2125 (1951).
7. W. J. Zimmerscheid, R. A. Dinerstein, A. W. Weitkamp and R. F. Marschner, Ind. Eng. Chem., 42, 1300 (1950).
8. B. Angla, Ann. chim., 12 4, 639 (1949).
9. L. C. Fetterly, U.S.P. 2,499,820 (1950).
10. C. Ellis, "The Chemistry of Petroleum Derivatives", The Chemical Catalog Co., New York, 1934, Vol. 1, p. 582.
11. S. Winstein and H. J. Lucas, J. Am. Chem. Soc., 60, 836 (1938).
12. L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc., 71, 3644 (1949).
13. A. W. Francis, J. Am. Chem. Soc., 73, 3709 (1951).
14. R. M. Barrer and D. A. Ibbitson, Trans. Faraday Soc., 40, 195 (1944).
15. G. W. Nederbragt and J. J. DeJong, Rec. trav. chim., 65, 831 (1946).

PROCESS DEVELOPMENT OF INORGANIC CHEMICALS

Roger W. Sanftner December 4, 1951

It is the purpose of this discussion to illustrate, by means of some specific and general examples, the applications of inorganic chemistry and chemical engineering, one to the other, to achieve a desired end. The characteristic approaches of the chemist and of the chemical engineer will be illustrated and compared.

1. The Chemico sulfuric acid process

It is well known that the chamber process necessitates the use of 98 percent sulfuric acid for absorbing the SO_3. If water, or less concentrated acid is used, a mist or fog is produced. If more concentrated acid is used the SO_3 ceases to be absorbed. In the Chemico process the use of a venturi scrubber in series with a cyclone eliminates the need for using 98 percent sulfuric acid, and in addition, makes it possible to obtain acid strengths up to 95 percent directly (7).

2. Spray drying

The drying of oxidizable or heat sensitive materials is difficult, even on a laboratory scale. However, it is possible to obtain dry materials, e.g. $FeSO_4$ or $FeCl_3$, from a spray drier which contain less oxidized material than can be produced by conventional methods (3).

3. Continuous counter current ion exchange

A continuous ion exchange system has been constructed on a laboratory scale which demonstrates (a) that such an operation is feasible, and (b) that it can compete commercially with a fixed bed type. Essentailly counter current flow is obtained in the exhaustion and regeneration columns. Hydraulic classification enables the use of a fluidized exhaustion column (8).

4. Holland evaporator for sodium sulfate

Many methods for the dehydration of sodium sulfate have been suggested, but because of the inverted solubility relationship, none has been fully successful. The Holland evaporator uses a combination spray and rotary evaporator. This eliminates the scale formation on hot surfaces which has plagued all other driers when producing an anhydrous material exhibiting retrograde solubility (5).

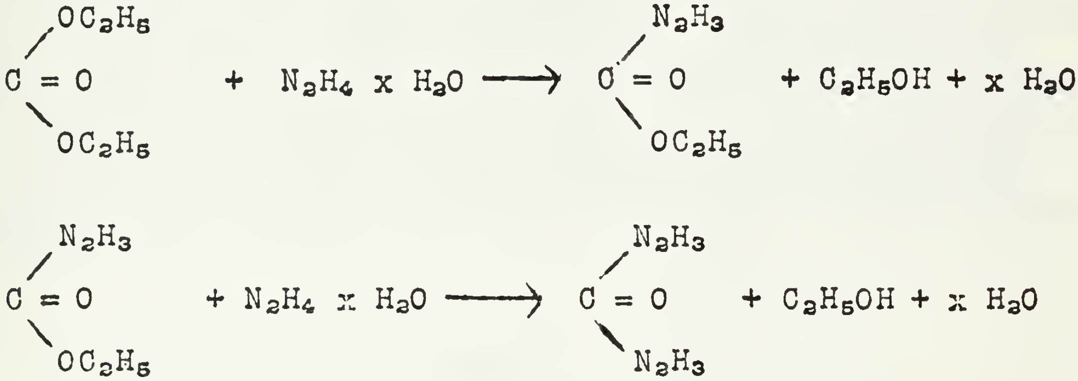
5. The carbohydrazide project

The development of a test tube reaction into a continuous process has been accomplished, chiefly by the use of a packed column to remove diluting reaction products. This development

is illustrative of the approach used by the chemical engineer in converting a laboratory synthesis into a commercial process. It is discussed in detail: (1)(2)(4).

Considerable attention has been given recently to the potential use of polyfunctional hydrazine derivatives in the preparation of polymers, pharmaceuticals, and explosives. Carbohydrazide, is such a molecule. However, the cost of production is still so prohibitive that no program on any such line can yet be seriously considered. Recently a continuous process for the production of carbohydrazide from diethyl carbonate and hydrazine has been investigated, although the present cost of the reactants dictates a relatively high cost for carbohydrazide, the new process does point to the possibility of producing carbohydrazide in limited amounts at reasonable costs. Further, if an economic synthesis of hydrazine is developed the process would make available a potential by useful product at a price commensurate with cost of the raw materials.

Carbohydrazide can be prepared by several methods, e.g. the reaction of urea, or the diphenyl or diethyl esters of carbonic acid with hydrazine hydrate. Of the above, the best procedure is that described by Beck (2) using diethyl carbonate and hydrazine hydrate. Presumably this is a two step reaction:



$$C(=O)(OC_2H_5)_2 + N_2H_4 \; x \; H_2O \longrightarrow C(=O)(N_2H_3)(OC_2H_5) + C_2H_5OH + x \; H_2O$$

$$C(=O)(N_2H_3)(OC_2H_5) + N_2H_4 \; x \; H_2O \longrightarrow C(=O)(N_2H_3)_2 + C_2H_5OH + x \; H_2O$$

This is indicated by the formation of a simple phase with the evolution of considerable heat from the originally immiscible diethyl carbonate and hydrazine hydrate. Beck concluded that the optimum results for this reaction were obtained by refluxing the reaction mixture for no less than two days and by using a 25-50 percent excess of hydrazine hydrate. Under these conditions a yield of 80 percent was obtained.

Such a laboratory syntheses would hardly seem to be suitable for commercial production, even on a batch-wise basis. At least two factors would militate against this process from a commercial standpoint (1) the relatively low yield, (2) the long reaction period. For this reason, study to modify the procedure was desirable.

It had been shown that the temperature of the reaction mixture decreases with an increase in time of reaction. This is caused by the formation of lower boiling diluents in the course

of the reaction. It is a known fact that a rise in temperature increases the reaction rate. This rise in temperature could possibly be realized by removing the low boiling diluents. Further, if this removal could be attained, the equilibrium would at the same time be favorably displaced to the right.

This approach was first investigated on a batch-wise scale. A packed tower was employed for removing the ethanol and water as they were formed. It was found that, as the lower boiling diluents were removed and a steady state was reached, the reaction temperature increased from 97° to 120°C. As a result, it was found that after a period of slightly over two hours, a yield of greater than 60% was obtained while using only an excess of 10 percent of hydrazine hydrate. From this work it was concluded and subsequently shown that the process could be adapted to a semi-continuous and a continuous process by removing the bottom products, crystallizing the carbohydrazide from the reaction liquor, and recycling the mother liquor with a premixed solution of diethyl carbonate and hydrazine hydrate. Although only relatively short runs have been attempted, the indication is that the reaction is practical on a commercial scale.

It should be pointed out, however, that the success of the adaptation of the reaction to a continuous basis is not a complete criterion of its actual adoption as a commercial preparative method. Newer processes might make this method obsolete over night or the condition of the product obtained from this reaction might be such that specifications could not be met at reasonable cost. The latter appears to be of little concern in this case since the best medium for recrystallization of carbohydrazide is a water-ethanol mixture, and this is produced as the overhead in the reaction itself.

Bibliography

1. Barger, B.D. and Hyman, M.L., Chem. Eng. Rept. 6 (1948-9).
2. Beck, E.C., B.S. Thisis, University of Illinois (1948).
3. Bullock, K. and Lightbrown, J.W., The Industrial Chemist 19, 455 (1943).
4. Brazaitis, J. and Tarika, E., Chem. Eng. Rept. 8 (1948-9).
5. Holland, A.A., Chem. Eng. 58, No. 1, 106 (1951).
6. Kamenko, G.C. and Rabin, E., Chem. Eng. Rept. 13 (1950).
7. Olive, T.R., Chem. Eng. 57, No. 10, 102 (1950).
8. Selke, W.A. and Bliss, H., Chem. Eng. Prog. 47, 529 (1951).
9. Walker et. al. "Principles of Chemical Engineering", McGraw-Hill Book Co., New York (1937).

ADDITION PRODUCTS OF BORON TRIFLUORIDE WITH SALTS OF OXY-ACIDS

Paul G. Gordon December 11, 1951

This seminar is based upon a thesis entitled "Ueber die Anlagerungsprodukte von Borfluorid an Salze sauerstoffhaltiger Mineralsäuren" submitted to the University of Berlin by Heinz Hennig (4) in 1939. A copy was recently received by the University of Illinois and is on file in the Department of Chemistry Library.

I. Introduction

Boron trifluoride and sulfur trioxide have been shown to posses similar electronic configurations (6), and to undergo similar chemical reactions (2,4).

$$H_2O + SO_3 \longrightarrow HOSO_3H$$
$$H_2O + BF_3 \longrightarrow HOBF_3H$$
$$NaF + SO_3 \longrightarrow NaSO_3F$$
$$NaF + BF_3 \longrightarrow NaBF_4$$
$$SO_4^{=} + SO_3 \longrightarrow S_2O_7^{=}$$
$$SO_4^{=} + BF_3 \longrightarrow \left[SO_4\cdot BF_3\right]^{=} \quad (1)$$

Since sulfur trioxide had been shown to coordinate with salts of various oxy-acids, a study was made of the preparation and properties of addition products of these same salts with boron trifluoride.

Reactions were carried out by passing borontrifluoride over the heated salts at various temperatures. The boron triluforide was prepared using methods of Schiff (5) and of Hellriegel (3); sulfur trioxide was prepared from oleum.

II. Addition Products of Boron Trifluoride with Sulfates

A. Alkali Metal Sulfates

	Relative Rates
1. $Li_2SO_4 + BF_3 \xrightarrow{500°} Li_2SO_4\cdot\frac{1}{x}BF_3$	very slow
2. $Na_2SO_4 + BF_3 \xrightarrow{310°} Na_2SO_4\cdot BF_3$	slow
3. $K_2SO_4 + BF_3 \xrightarrow{290-300°} K_2SO_4\cdot 1.7BF_3$	faster
4. $Cs_2SO_4 + BF_3 \xrightarrow{250°} Cs_2SO_4\cdot 2BF_3$	fastest

B. Other Metal Sulfates

1. $MSO_4 + BF_3 \xrightarrow{500°}$ N.R. M = Alkaline Earth Metals
2. $Tl_2SO_4 + BF_3 \xrightarrow{250°} Tl_2SO_4\cdot BF_3$
3. $Ag_2SO_4 + BF_3 \xrightarrow{500°}$ N.R.

The reactivity of the alkali metal sulfates increases with increasing atomic weight. The boron trifluoride adducts are clear glass-like melts which solidify on cooling. When the products are heated in the dry state they give up all of the boron trifluoride, Debye-Scherrer patterns show that these compounds are amorphous. Sulfur trioxide is more reactive, for it will combine with <u>all</u> of the above mentioned salts in the neighborhood of 100°C.

III. Reactions of Boron Trifluoride with Carbonates

Interaction of boron trifluoride with potassium carbonate at 350°C gave product which contained no CO_2. The presence of KBF_4 was established by x-ray diffraction. The following reactions were hypothesized to explain this finding.

1. $K_2CO_3 + BF_3 \xrightarrow{350°} K_2CO_3\cdot BF_3$
2. $K_2CO_3\cdot BF_3 \xrightarrow{350°} K_2O\cdot BF_3 + CO_2\uparrow$
3. $2K_2O\cdot BF_3 + 2BF_3 \xrightarrow{350°} 3KBF_4 + KBO_2$

or $2K_2CO_3 + 4BF_3 \xrightarrow{350°} 3KBF_4 + KBO_2 + 2CO_2\uparrow$

Analogous reactions have been found to take place in the following cases:

$$\left.\begin{array}{c} CaO \\ Na_2SO_3 \\ KNO_3 \end{array}\right\} + BF_3 \longrightarrow \left\{\begin{array}{c}\text{Metal fluoborate + metal}\\ \text{metaborate}\end{array}\right\} \begin{array}{l} +SO_2\uparrow \\ +N_2O_5\uparrow \end{array}$$

IV. The Addition Products of Boron Trifluoride with Phosphates

A. $\text{Meta-}MPO_3 + BF_3 \xrightarrow{400°} MPO_3\cdot\frac{1}{3}BF_3$ $\qquad M = Na$ and K

$$\left.\begin{array}{ll} \text{B.} & \text{Ortho-}M_3PO_4 + 3BF_3 \xrightarrow{300-400°} M_3PO_4\cdot 3BF_3 \\ \text{C.} & \text{Pyro-}M_4P_2O_7 + 4BF_3 \xrightarrow{300-400°} M_4P_2O_7\cdot 4BF_3 \end{array}\right\} \xrightarrow[\text{to } BF_3]{\text{long exposure}} \left\{\begin{array}{l} \cdot 4BF_3 \\ \cdot 5BF_3 \end{array}\right.$$

The alkali ortho- and pyrophosphates react readily at 300°-400°C; the metaphosphate only slowly. There is no difference in the activity of the sodium and potassium salts as was noted with the sulfates. The resulting products are amorphous glass-like materials. All are hygrscopic, except $K_4P_2O_7\cdot 4BF_3$, and all dissolve in cold water. Although a small amount of light yellow precipitate appears on the addition of Ag^+ to such solutions it is not until they are heated that appreciable quantities of yellow Ag_3PO_4 are obtained. The phosphate adducts do not release boron triluforide completely on heating to red heat.

D. $K_3PO_4\cdot 3BF_3 \xrightarrow{\Delta} 66.8\%$ of its $BF_3\uparrow$

E. $K_4P_2O_7\cdot 4BF_3 \xrightarrow{\Delta} 68.5\%$ of its $BF_3\uparrow$

F. $Na_4P_2O_7\cdot 4BF_3 \xrightarrow{\Delta} 84.2\%$ of its $BF_3\uparrow$

The glassy products remaining after heating to fusion and cooling dissolved in cold water; they give an immediate quantitative precipitation of Ag_3PO_4 in cold solution. No further precipitation is obtained if the filtrate is then heated.

It had previously been shown that pyrophosphates and sulfur trioxide react in accordance with the following equation:

$$K_4P_2O_7 + 6SO_3 \rightleftharpoons 2K_2S_3O_{10} + P_2O_5$$

It was therefore considered possible that the products obtained by interaction of phosphates with BF_3 might consist of mixtures, rather than addition complexes. The following analogous reactions were proposed:

G. $K_4P_2O_7 + 4BF_3 \rightleftharpoons P_2O_5 + 3KBF_4 + KBO_2$

H. $2K_4P_2O_7 + 4BF_3 \rightleftharpoons 4KPO_3 + 3KBF_4 + KBO_2$

I. $4K_3PO_4 + 12\ BF_3 \rightleftharpoons 2P_2O_5 + 9KBF_4 + KBO_2$

J. $2K_3PO_4 + 4BF_3 \rightleftharpoons 2KPO_3 + 3KBF_4 + KBO_2$

H and J were ruled out since these compounds were found to take up four and three moles of BF_3 respectively per mole of salt. G was ruled out for the product was not hygroscopic. The products were all soluble in cold water, thus showing that the slightly soluble salts, KBF_4 and KPO_3, were absent. Debye-Scherrer diagrams gave no evidence for the presence of KBF_4 in any of the products.

V. Reaction of KF with BF_3; KBF_4 and KF with SO_3

A. $KF + BF_3 \xrightleftharpoons{400°} KF \cdot BF_3$

B. $KBF_4 + BF_3 \xrightleftharpoons{\Delta}$ No R.

C. $KBF_4 + SO_3 \xrightarrow{R.T.} KF \cdot SO_3 + BF_3$

D. $KF + 2SO_3 \xrightarrow{R.T.} KF \cdot 2SO_3$

VI. Bibliography

1. P. Baumgarten and E. Müller: B., 69, 2688 (1936).
2. C. Brandenburg: Thesis, University of Berlin (1939).
3. W. Hellriegel: B., 70, 689 (1937).
4. H. Hennig: Thesis, University of Berlin (1939).
5. H. Schiff: A. Suppl., 5, 172 (1867).
6. W. H. Zachariasen: J.A.C.S., 53, 2129 (1931).

THE STRUCTURES OF THE IRON CARBONYLS

Donn D. Darsow December 11, 1951

Introduction

Carbon monoxide forms stable addition compounds with several of the transition metals. These compounds are called metallic carbonyls and are not comparable to any other metallic compounds.

VI	VII	VIII		
$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$CO_2(CO)_8$ $CO_4(CO)_{12}$	$Ni(CO)_4$
$Mo(CO)_6$		$Ru(CO)_5$ $Ru_2(CO)_9$ $Ru_3(CO)_{12}$	$Rh_2(CO)_8$ $[Rh(CO)_3]n$ $[Rh_4(CO)_{11}]m$	
$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_2(CO)_9$	$Ir_2(CO)_8$ $[Ir(CO)_3]x$	

Table 1. Known Metallic Carbonyls[1] according to Periodic Group

The structures of iron pentacarbonyl $Fe(CO)_5$[13] and of iron enneacarbonyl $Fe_2(CO)_9$[14] are known; that of iron tetracarbonyl $Fe_3(CO)_{12}$ is still in doubt.

Preparation and Properties

$$\underset{\text{Finely divided}}{Fe^\circ} + CO \xrightarrow[\text{20-200 atm}]{173^\circ} Fe(CO)_5 \xrightarrow[\text{light}]{\text{u.v.}} \underset{+\ CO}{Fe_2(CO)_9} \xrightarrow[\text{heat}]{\text{toluene}} \underset{+\ CO}{Fe_3(CO)_{12}}$$

$Fe(CO)_5$	colorless liq. diamagnetic	M.P. 19.5°; B.P. 102.5°	sol ether, decomp H_2O, alk, H_2SO_4
$Fe_2(CO)_9$	or-yel hex plates diamagnetic	Decomp 100°	insol org. solvents insol H_2O
$Fe_3(CO)_{12}$	green-blk sq plates diamagnetic	Decomp 140°	sol most org solvents, insol H_2O

Structure of $Fe(CO)_5$

$Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ were first prepared, respectively, in 1891, 1891 and 1905[9]. Some of the first structures proposed for $Fe(CO)_5$ were the following :

L. Mond, 1892 A. von Werner, 1909

Blanchard and Gilliland, 1926 Manchot, 1929

Fig. 1

The correct symmetrical trigonal bipyramidal structure, Fig. 2, was determine in 1939 by Ewens and Lister[13] by electron diffraction of gaseous $Fe(CO)_5$.

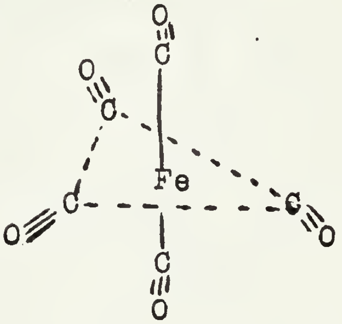


Fig. 2

Structure of $Fe_2(CO)_9$

Brill[12] made an x-ray diffraction study of $Fe_2(CO)_9$ but was able to say with certainty only that the nine CO groups were arranged in three planes separatint the Fe atoms as in Fig. 3.

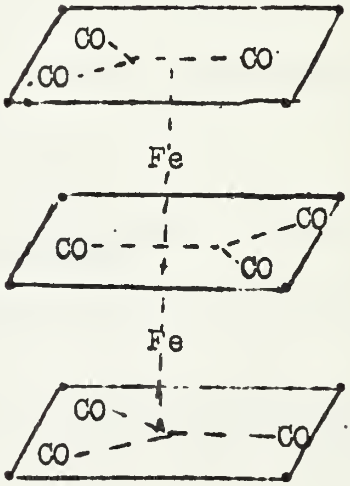


Fig. 3

Sidgwick and Bailey proposed a formula extending the effective atomic number (EAN) concept to polymetallic carbonyls. The structure depicted in Fig. 4 was deduced therefrom.

Sidgwick's EAN formula is as follows:

$$G - \frac{xM + 2y}{x} = x - 1$$

G = at. no. of nearest inert gas
M = at. no. of the metal
x, y = subscripts in the carbonyl formula $M_x(CO)_y$
x-1 = deficiency of electrons of each metal atom from that of the EAN of gas G.

(See Emeleus and Anderson[3] for further explanation.)

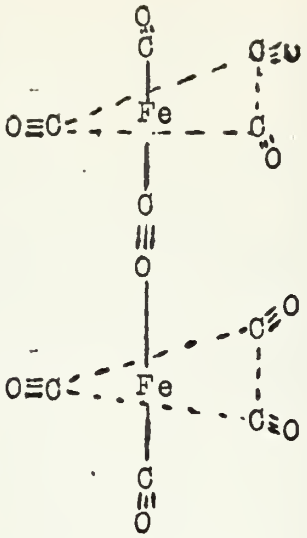


Fig. 4

The currently accepted structural arrangement (Fig. 5) of $Fe_2(CO)_9$ was established by Powell and Ewens[14] in 1939. They confirmed Brill's work by a more comprehensive x-ray diffraction analysis (using Weissenberg type photographs and applying Patterson and Fourier analyses).

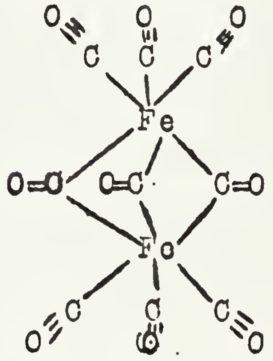


Fig. 5

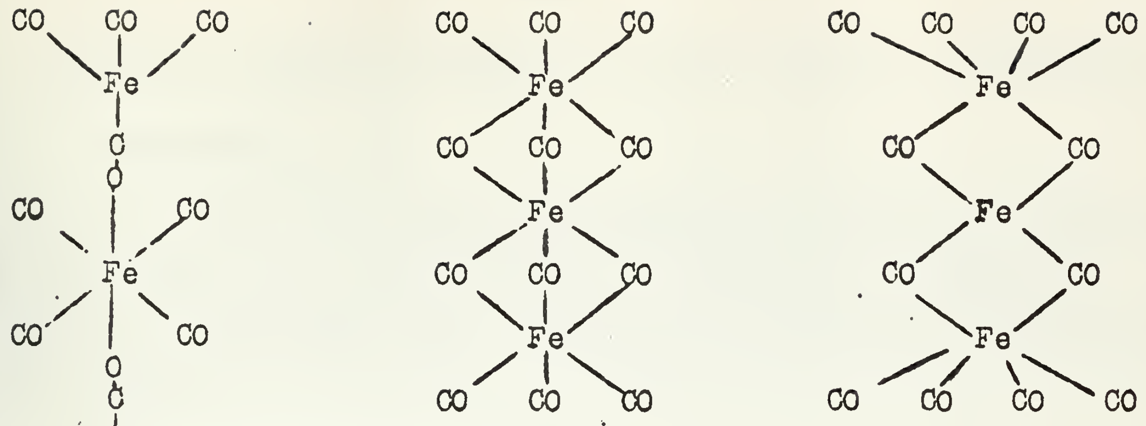
In addition they came to the following conclusions:

1. The terminal CO groups are linear and are true carbon monoxide type.
2. The central CO groups are ketone-like.
3. In both type CO groups it is the carbon atom and not the oxygen atom that is bonded to the Fe.
4. The Fe-Fe distance is slightly greater than twice the covalent radius of iron.

Powell and Ewens did not postulate a covalent Fe-Fe bond; Pauling[5] and Sheline[4], on the other hand, believe such a bond to be indicated.

Structure of $Fe_3(CO)_{12}$

Without x-ray data Hieber and Becker[15] in 1930 proposed the structures given in Fig. 6.



(a) (b) (c)

Fig. 6

Brill[16] in 1930 subsequently performed the only x-ray diffraction studies made to date on $Fe_3(CO)_{12}$ and found that all three of Hieber's structures possess some correspondence to the crystal structure requirements but that structure (c) is the most logical. He proposed the spatial arrangement depicted in Fig. 7.

Sidgwick and Bailey[11] applied their EAN formula and concluded that the structure should be represented as in Fig. 8. They even claimed that Brill's x-ray data could be interpreted to substantiate their proposed structure.

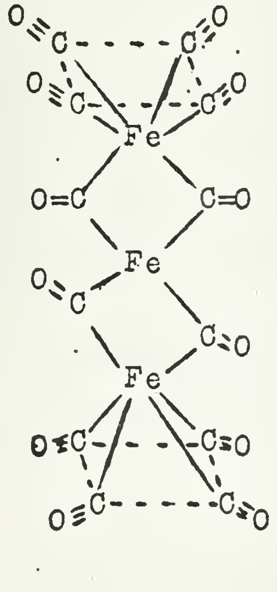


Fig. 7

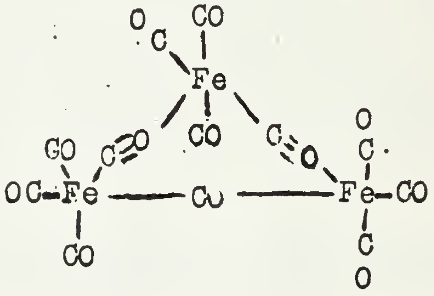


Fig. 8

Sheline[8] in 1951 gives the following arguments supporting the structure depicted in Fig. 7.

1. Diamagnetic Data

In contradiction to J. S. Anderson who states that the structure in Fig. 7 is highly improbable because it would "certainly be paramagnetic, and $Fe_3(CO)_{12}$ is definitely diamagnetic," Sheline points out that the structure depicted therein would actually be diamagnetic and that Fig. 6 (b) (and apparently 6 (a) also) would be paramagnetic. Therefore Sheline rules out Fig. 6 (a) and (b).

2. Infra Red Spectra Data

Strong absorption bands are shown at 2020 cm^{-1} and 2043 cm^{-1}. Bands at these frequencies are observed for carbon monoxide type carbonyl groups in other carbonyls. A definite but less strong band is observed at 1833 cm^{-1}. This corresponds very closely to the 1828 cm^{-1} band in $Fe_2(CO)_9$ known to be due to its ketone type bridging carbonyl groups. Thus all structures such as Fig. 8 which do not contain ketone-type bridging carbonyls are ruled out.

3. Ultra Violet Spectra Data

A weak but definite band occurs at 2835 Å, precisely where one expects a "forbidden nonbonding electron transition ($n \longrightarrow n^*$) for ketone carbonyls." This band does not appear in $Fe(CO)_5$, which has no ketone type carbonyls. This evidence for ketone carbonyls also rules out Fig. 8.

4. Solubility Differences between Fe_2CO_9 and $Fe_3(CO)_{12}$

The fact that $Fe_3(CO)_{12}$ is soluble in so many organic solvents, whereas $Fe_2(CO)_9$, also a solid containing both ketone and carbon monoxide type carbonyls, is so insoluble in organic solvents is notable. Sheline suggests that Fig. 7 could account for this difference in that the three empty 4p orbitals of the central Fe atom could be expected to offer to the solvent convenient sets of empty orbitals by which the $Fe_3(CO)_{12}$ molecule could solvate. In Fig. 8 or Fig. 6 (a) and (b) there are not as many empty Fe orbitals available, making solvation more difficult.

5. Physical Property Variation

The diversity of physical properties of the three carbonyls suggests the diversity of structure as in Figs. 2, 5, 7.

References

1. J.S. Anderson, Quart. Rev. 1, 355, (1947).
2. H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry", (1938), p. 414.
3. W. Hieber and E. Becker, Ber. 63B, 1406, (1930).
4. R. K. Sheline and K. S. Pitzer, J. Amer. Chem. Soc. 72, 1107, (1950).

5. L. Pauling, "The Nature of the Chemical Bond", p. 254 (1939).
6. A. A. Blanchard, Chem. Rev. 26, 409-21, (1940).
7. A. A. Blanchard, Chem. Rev. 21, 3-38, (1937).
8. R. K. Sheline, J. Amer. Chem. Soc. 73, 1615, (Apr. 1951).
9. W. E. Trout, Jr., J. Chem. Ed. 14, 575-81, (1937).
10. R. Brill, Z. Krist, 77, 36-42, (1930).
11. N. V. Sidgwick and R. W. Bailey Proc. Roy. Soc., 144, 52, (1934).
12. R. Brill, Z. Krist. 65, 89, (1927).
13. R. V. G. Ewens and M. L. Lister, Trans. Faraday Soc. 35, 681 (1939).
14. H. M. Powell and R. V. G. Ewens, J. Chem. Soc., (1939), p. 286.

DISPOSAL OF RADIOACTIVE WASTES

S. J. Bodnar December 18, 1951

Radioactive materials are not new but much of the knowledge about them is new and the quantities now available for use are much greater than in the past. (1) This greater usage produces wastes which must be disposed so that they can not be of harm to man.

There are two general ways in which to do this:(2)

(1) Wastes can be rendered harmless by diluting and dispersing them until the concentration of the radioactive components is too low to damage animal tissue.

(2) Wastes can be separated, concentrated to a convenient volume and stored until time can destroy them by natural decay. Oak Ridge National Laboratory, a large producer of radioactive wastes, uses a combination of both the above methods. As much activity as possible is precipitated in storage tanks. The activity remaining in solution is decanted, diluted with non-active process waste and dispersed in a natural stream.

The Knolls Atomic Power Laboratory disposes active wastes entirely by evaporation and storage at a total cost of about eleven cents per gallon (3).

Los Alamos produces wastes containing plutonium (4). Since plutonium is adsorbed on almost any surface, a number of mineral adsorption agents, which include celite, kaolin, pumice and tuff, have been studied. Required efficiencies were not obtained unless a serial adsorption process was used. This method was found to be undurable since it results in the accumulation of large amounts of contaminated material. Activated carbon was tried next and worked satisfactorily except when citrates were present.

Work on adsorbents was abandoned altogether when concurrent investigations carried on with coagulating agents promised to be more successful. Nature of the process operative in the use of coagulants may include (1) coprecipitation (2) adsorption by the floc produced or (3) flocculation of suspended or colloidal plutonium present in the waste. Good results were obtained by either adding $Al_2(SO_4)_3$ or $FeCl_3$ and adjusting the pH (6-10) with NaOH, lime, or NH_4OH. It was finally decided to use a lime and iron combination for the following reasons:

(1) The floc produced by this method seemed to settle better and filter more readily.

(2) It was believed that the use of iron would permit the use of a wider pH range if such proved desirable. Very high pH values could be used with iron but not with aluminum.

(3) It was hoped that high pH treatment with lime and iron might result in adequate fluoride removal since the waste contained an excessive amount of fluoride from the public health standpoint.

Final results obtained before the erection of a disposal plant showed -

(1) One half of the results obtained were less than 100 counts per minute per liter. Final count desired was 70, indicating the need for serial coagulation.

(2) Average of suspended solids of the flocculated mixtures was about 25% of the average untreated wastes. Evaporation would remove more of the solid material than coagulation.

(3) 8330 lbs (1000 gals) of liquid wastes were finally reduced to 3.09 lbs of dry active wastes.

(4) The fluoride content of the treated solution was too high to discharge into streames or ground where fluoride content of the area is relatively high. Fluorides were finally removed by the anion exchanger Fluorex.

(5) pH of wastes ranged from 2-4 during working hours and from 7.8-8.3 at night.

(6) Presence of citrates and phosphates which probably would complex plutonium to a high degree had no effect on removal of plutonium if the pH was approximately 12.

For the treatment of mixed fission products a calcium phosphate floc was chosen in preference to aluminum or ferric hydroxide because the number of insoluble phosphates of the iron present exceeds the number of insoluble hydroxides (5). The flocs were formed by adding a solution of either potassium dihydrogen phosphate or tri sodium phosphate and the radio isotope to a solution of calcium hydroxide. The pH was adjusted 11.3 by addition of dilute sodium hydroxide. The ratio of Na_3PO_4 to $Ca(OH)_2$ was 2.2:1. On analysis of a mixture of mixed fission products is given below (Except iodine).

Trivalent rare earths	43.5
Cerium	27.0
Strontium	17.4
Barium	5.1
Luthenium	2.9
Cesium	1.1
Total	97.0

The remaining three percent consists of traces of a large number of isotopes with low fission yields.

The use of radioactive tracers results in large amounts of liquid wastes having a low level of activity. Ion exchange is applicable to this type of waste (6). The following factors enter into this process:

(1) Determination of capacity of various resins. Limiting Capacity was taken when the ratio of the concentration of the ion in the effluent to the feed solution was 0.02.

(2) Determination of operating curves under set conditions for various ions. It was found that amphoteric ions were more efficiently removed by anion exchange resins. Radio colloids could also be removed by ion exchangers.

(3) Determination of amount of leakage or efficiency of ion exchange resin in order to estimate decontamination factor.

$$\text{Decontamination factor} = \frac{\text{no. of counts per min. per liter before treatment}}{\text{no. of counts per min. per liter after treatment}}$$

(4) Effect of reagents which might cause precipitation or complexing. If the pH was low enough these caused no trouble.

(5) Effect of solvents, greases, detergents, or precipitates. These also had little effect on the efficiency.

(6) Possible concentration by incineration since resins could not be regenerated.

There are three applications possible with this general method.

(1) Two-bed deionization in which the solution is first led through a cation exchanger and then through an anion exchanger.

(2) Monobed deionization in which the cation and anion exchangers are mixed and placed in one column.

(3) Cation or anion exchanger which is to be used only when either active cations or anions are present but not to be used when both are present.

It is important that when radioactive wastes are burned no active gases are discharged to the atmosphere. It was found that by using a steam nozzle which removes particles from moving gas streams by the condensation center effects (i.e. - the particles act as nuclei for the condensation of water droplets) removals greater than 99.9 percent could be obtained.

Suggested uses for radioactive wastes are in radiological warfare (8) and the following industrial usages- activation of phosphors for luminous signs and markers; static eliminators for a variety of industrial processes; cold sterilization of drugs and foods; and portable low level power sources.

Bibliography

(1) James H. Jensen, "National Committee on Radiation Protection" Ind. Eng. Chem. 43 no. 7, 1500 (1951).
(2) Frank N. Browder, "Liquid Waste Disposal at Oak Ridge National Laboratory" ibid., pg. 1502-1505.
(3) G. E. McCullough, "Concentration of Radioactive Liquid Waste by Evaporation" ibid., pg. 1505-1509.
(4) C. W. Christenson, M. B. Ettinger, G. G. Robeck, E. R. Hermann, K. C. Kohr, and J. F Newell, "Removal of Plutonium from Laboratory Wastes" ibid., 1509-1515.
(5) R. A. Laserderdale, "Treatment of Radioactive Water by Phosphate Precipitation" ibid., 1538-1540.
(6) John A. Ayres, "Treatment of Radioactive Waste by Ion Exchange" ibid., 1526-1531.
(7) P. J. Schauer, "Removal of Submicron Aerosol Particles from Moving Gas Streams" ibid., pg. 1532-1538.
(8) Hans Therring, Time, pg. 43, December 3, 1951.
(9) T. Keith Glennan, Time, pg. 87, December 10, 1951

BORIDES

Walter E. Thatcher January 8, 1952

Many of the early investigations concerning borides are of questionable value, mainly because of the unsatisfactory methods of preparation and the low purity of commercial boron used as starting material, and the great difficulties encountered in isolating and studying the intermediary phases by classical chemical methods.

An investigation on the borides of the transition elements as binary systems was started by Roland Kiessling in 1945. These investigations have been reported in "Acta Chemica Scandinavica", from which this summary is primarily taken. The borides of chromium, manganese, molybdenum, nickel, niobium, tantalum, thorium, tungsten, zirconium, and the alkaline-earths and rare-earths (8-15) have been studied.

I. Preparation of Boron (9,18,19)

Commercial boron has a low degree of purity, varying between 65 and 80% of boron and containing such impurities as the oxides of boron, aluminum, magnesium, and iron, borides of aluminum and magnesium, and silicon compounds. Some of these impurities may be removed by treating the boron crude product with acids and potassium hydroxide followed by heat treatment in vacuum, but the boron still contains impurities amounting to 5-15%.

Laubengayer et al. (19) prepared pure crystalline boron by reducing boron tribromide with hydrogen on a hot tungsten or tantalum filament. All older methods (18), gave only very small amounts of boron; most of these procedures required a rather complicated apparatus. The method worked out by Kiessling (9) consists essentially of the vapor phase reduction of boron tribromide in a quartz tube at 750-800°C. The use of a quartz tube has the advantage of giving a much greater hot surface than a filament; at the temperatures used quartz suffers no attack. The yield of 1-2 grams of boron for each run is not high, but the apparatus can be constructed for greater capacity.

The apparatus consists of two reaction tubes and two condensation vessels. As boron tribromide is decomposed by even slight traces of moisture, the apparatus must be carefully dried by a stream of pure, dry hydrogen (passed over copper at 500°C and dried over cooled silica gel and phosphorous pentoxide). Boron tribromide is prepared by the action of dry bromine on commercial boron at 700°C. The bromide, having a boiling point of about 90°C, is condensed in the first vessel, which is cooled by a salt-ice mixture. The procedure is interrupted and all the bromine is carefully driven out with hydrogen. The temperature of the vessel containing the BBr_3 is allowed to come to room temperature; the stream of hydrogen is adjusted to carry the vapors of the bromide

into the reduction chamber, where the reduction is carried out at 800°C. The unreduced bromide is "caught" in the second condensing vessel and this is interchanged with the first, and the reduction is carried out as before. (Note - the deposited boron catalyzes the reduction reaction and so it is not removed immediately from the reduction chamber).

The product is washed with hot water to remove traces of the bromide and dried. To determine the boron content, a sample is completely oxidized by 1:1 nitric acid, and the resulting boric acid is titrated in the presence of mannitol in the usual way. The mean values of the analyses of the final product are:

Element	Weight %
B	98.9
Al	0.4
Si	0.1
Mg	<.1
O	<.1
H	<.1

II. Preparation of Borides (1,6,8,10-15,16,17,18,19)

The borides of calcium, barium, and strontium were first obtained by reducing the borates with aluminum in an arc furnace. An improved method involves the electrolysis of a molten mixture of the borate and fluoride of the metals in question at 1000°C. This method is also used for the preparation of the borides of the alkaline-earth and rare earth elements. Many borides prepared by sintering or melting a mixture of the constituents either in evacuated silica tubes at 1100-1200°C or in vacuum furnaces at 1200-2000°C. Two different vacuum furnaces were used a) a resistance furnace with a graphite tube as heating element and b) a high frequency induction furnace. Sometimes single crystals could be obtained by prolonged heating in the sintering process. In Lafferty's work with the alkaline earth and rare earth borides (17), the borides were prepared from the metal or metal hydride and amorphous boron. The metal and boron were pressed into bars and packed with boron powder into a graphite crucible. This was fired in an electric furnace in a pure dry hydrogen atmosphere for one hour at 1375°C. The boron was removed and the firing continued for 20 minutes at 1800°C in an induction furnace. The product was crushed, washed with HCl, rinsed with water, and then powdered. This material was washed in concentrated HCl to remove any free metal, metal oxide, and boric oxide. The boride, being 2.5 times as dense as amorphous boron, is further separated from boron by stirring with water and decanting the water layer, before the powder has settled completely. Spectroscopic tests on the final product (made with 85% boron) showed that silicon is present, but only traces of iron, aluminum, magnesium, and manganese.

Alloys were prepared for analysis by dissolving them in perchloric acid or fusing with sodium peroxide or nitrate-carbonate mixtures.

To investigate phase relationships among the boride mixtures of the metal and boron in different proportions were heated. Phase analyses of the products were carried out by x-ray methods; selected alloys were analyzed chemically. The structures of the pure phases were determined by powder or single crystal methods.

III. Properties of the Borides (8,10-15,17,20)

The strong bonding forces between the boron atoms, especially among the alkaline earth and rare earth alloys, lead to very refractory compounds with very high melting points. The hexaborides are also very stable chemically; moisture, oxygen, and even hydrochloric acid do not affect them. The hexaborides are characteristic of the boron structure and not of the metal atoms. They are opaque and vary in color from black, brown to purple. The metallic character of these compounds is evident from their high electrical conductivity. When the hexaborides are heated to a sufficiently high temperature the metal atoms at the surface evaporate away. They are immediately replaced by diffusion of metal atoms from the cells below. The boron framework remains intact. Diffusion occurs only when there is a vacancy at the surface. This process therefore provides a mechanism for constantly maintaining an active cathode surface. This characteristic together with the high electrical conductivity and high thermal and chemical stability, gives a cathode material with ideal properties.

It is of interest to compare the best boride emitter, LaB_6, with some of the conventional cathode materials (such as W, Mo, Ta, Nb, Th-W, ThO_2, and BaO). Emission from LaB_6 is surpassed only by BaO at low temperatures; in the high current density range, LaB_6 is superior to any of the conventional materials now available (17).

IV. Structures of the Borides (2,8,10-15,17)

The following table represents a summary of borides which have been prepared and have either proposed or proven structures.

Table of Borides (in atomic percent)$^{+, ++, +++}$

20%	33.3%	40%	50%	57%	60%	66.7%	70%	85.7%
Mn_4B(8) (orthorhombic)	Mo_2B (4) W_2B Fe_2B Co_2B Ni_2B Mn_2B (tetragonal) Cr_2B (orthorhombic)	Ni_3B_2 (?)	MnB (4) FeB CrB NbB TaB NiB (orthorhombic) MoB (8) WB (tetratonal)	Ta_3B_4 (2) Mn_3B_4 Nb_3B_4 Cr_3B_4 (orthorhombic)	Ni_2B_3 (?)	ZrB_2(4) CrB_2 NbB_2 TaB_2 AlB_2 (hexagonal) TiB_2 (cubic)	Mo_2B_5 (3) (rhombohedral) W_2B_5(2) (hexagonal)	MB_6 Alkaline and rare-earths and Th.

Table of Borides (continued)

+The subgroups are isomorphous within each other, but the whole group may not be isomorphous (e.g. the 50% group).

++The numbers in parentheses are the number of molecules per unit cell

+++ The crystal systems are placed under each subgroup.

It will be noted that the bonding between the boron atoms becomes of increasing importance in the structure as the boron content increases. The boron atoms have a marked tendency to first form chains, then rings and finally a three dimensional lattice. Four arrangements may be distinguished; based upon structural studies.

1. In the 33.3% phase, M_2B, the boron atoms are present as isolated units in the lattice.

2. In the 48-51% phase, MB, the boron atoms form zig-zag linear aggregates running through channels in the lattice and form a partial network.

3. In the 67-70% phase, M_2B_5, they form partly hexagonal networks and partly two-dimensional sheets.

4. In the 85% phase, MB_6, the boron atoms form a three dimensional network which is very stable.

V. Special Comments

The borides of the rare earths, the alkaline earths, and thorium all have the same formula MB_6 and the same crystal structure consisting of a three-dimensional boron framework in whose interlattice spaces the metal atoms are embedded. The valence electrons of the metal atoms are not accepted by the B_6-complex (17), thus giving rise to the presence of free electrons which impart a metallic character to these compounds. If the hexaborides are operated at high temperatures in contact with refractory metals, boron diffuses into the metal lattices of the latter to form interstitial boron alloys. When this occurs, the boron framework which holds the alkaline earth or rare earth metal atoms collapses, permitting the latter to evaporate. However, the hexaboride cathodes may be operated at high temperatures in contact with tantalum carbide or graphite. LaB_6 cathodes are especially useful in applications where high current densities are required. They are also suitable for high voltage applications because they stand up well under positive ion bombardment. Since they are atmospherically stable and activate easily, they have found wide use in experimental demountable systems.

Bibliography

1. Andrieux, L., Compt. rend. 189, 1279-81 (1929).
2. Buddery, J. H. and Welch, A.J.E., Nature 167, 362 (1951).
3. Cambell, I. E., Powell, C. F., Nowicki, D. H., and Gonser, B. W. J. Electrochem. Soc. 96, 318-33 (1949).
4. Hägg, G. and Laurent, T., J. Sci. Instru. 23, 155-57 (1946).
5. Hesse, R., Acta Cryst. 1, 200-07 (1948).
6. Heusler, F. and Take, E., Trans. Faraday Soc. 8, 169-84 (1912).
7. Jack, K. H., Proc. Roy. Soc. (London) A 195, 41-55 (1948).
8. Kiessling, R., Acta Chem. Scand. 1, 893-916 (1947).
9. Kiessling, R., ibid 2, 707-12 (1948).
10. Kiessling, R., ibid 3, 90-91 (1949).
11. Kiessling, R., ibid 3, 595-602 (1949).
12. Kiessling, R., ibid 3, 603-15 (1949).
13. Kiessling, R., ibid 4, 146-59 (1950).
14. Kiessling, R., ibid 4, 160-64 (1950).
15. Kiessling, R., ibid 4, 209-27 (1950).
16. Lafferty, J. M., Phys. Rev. 79, 1012 (1950).
17. Lafferty, J. M., J. Applied Phys. 22, 299-309 (1951).
18. Laubengayer, A. W., Newkirk, A. E., and Brandaur, R. L., J. Chem. Education 19, 382-5 (1942).
19. Laubengayer, A. W., Hurd, D. T., Newkirk, A. E., and Hoard, J. L., J. Am. Chem. Soc. 65, 1924-31 (1943).
20. McKenna, P. M., Ind. Eng. Chem. 28, 76771 (1936).
21. Pauling, L., J. Am. Chem. Soc. 69, 542-53 (1947).
22. Pauling, L., Proc. Roy. Soc. (London) A 196, 343-62 (1949).
23. Tucker, S. A. and Moody, H. R., Proc. Chem. Soc., 17, 129-30 (1901).
24. Tucker, S. A. and Moody, H. R., J. Chem. Soc. 81, 14-17 (1902).
25. Winslow, E. H. and Liedhafsky, H. A., J. Am. Chem. Soc. 64, 2725-6 (1942).

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS CONTAINING ORGANIC MOLECULES

THE PARTIAL RESOLUTION OF RACEMIC MIXTURES OF SOME ORGANIC ACIDS BY MEANS OF DIFFERENT STABILITIES OF ISOMERS OF COMPLEX IONS AND THE PRINCIPLE OF PREFERENTIAL COORDINATION

Thesis Report

Allan D. Gott January 15, 1952

Introduction

There is considerable evidence (1,2) to support the theory that in a complex ion containing optically active ligands, the more stable and more symmetrical form of the complex is the one in which all of the optically active groups have the same sterical configuration. It seems reasonable to assume, therefore, that some "selectivity" would be exhibited in the introduction of an optically active molecule or ion into a coordination sphere which contains other coordinated groups of like configuration.

A great amount of evidence has been obtained in this laboratory for the selectivity of this type of reaction (3,4,5,6). The resolution of racemic-tartaric acid, begun in earlier years (4,5) has now been extended and the resolution of racemic-mixtures of organic acids containing one asymmetric carbon atom has been developed.

Experimental and Discussion

The partial resolution of racemic-tartaric acid by the reaction of excess levo-propylenediamine with racemic-tartrato-bis-levo-propylenediamine cobalt (III) chloride was reported by Jonassen (4). This resolution was repeated, but under different experimental conditions than those previously reported. An aqueous solution of the racemic-tartrato complex, prepared by the reaction of racemic-tartaric acid with carbonato-bis-levo-propylenediamine cobalt (III) chloride, was heated at 70°C with an excess of levo-propylenediamine. At various time intervals the solution was poured into ice-cold methanol, causing the tartrate ion to precipitate, probably as $[Co(l\text{-}pn)_3]$ Cl tart. The solution was filtered and the filtrate reheated for another time interval. The precipitate was recrystallized from methanol, dissolved in water and the tartrate precipitated as calcium tartrate. The calcium tartrate was dissolved in enough hydrochloric acid to make the resulting solution one molar in tartaric acid. Optical rotations from one of these runs are given in the following table:

Experiment I

Time of Heating	Temperature	Obs α
50 hrs.	70°C	-0.03
146 hrs.	70°C	+0.04

Conclusive evidence was obtained to indicate that the complex containing the dextro-tartrate ion was more stable than the complex containing the levo-tartrate ion, since the latter was much more readily liberated from the coordination sphere by the action of the levo-propylenediamine on the tartrato complex. When an aqueous solution of either complex is treated with levo-propylenediamine and the pH of the solution measured, the basicity should be a direct function of the amount of uncoordinated propylenediamine present. As the propylenediamine entered the coordination sphere the pH should decrease and any difference in the rate of decrease when the two tartrato complexes were allowed to react with levo-propylenediamine would establish a difference in stabilities of these complexes. The pH of the solution containing the levo-tartrato complex showed a considerable decrease within the first hour and a gradual decrease thereafter whereas the pH of the solution containing the dextro-tartrato complex showed no decrease in the first hour and only a gradual decrease thereafter.

Attempts were made to establish the difference in stability of the dextro-tartrato-bis-levo-propylenediamine cobalt (III) complex and the levo-tartrato-bis-levo-propylenediamine cobalt (III) complex by a spectrophotometric study of the reaction rates of the individual complexes with excess levo-propylenediamine. The results obtained were inconclusive, because the high absorption of the complexes involved in the reaction necessitated working with very dilute solutions. However, some insight into the course of the reaction was obtained. It is apparent that "hydroxolation" took place, with the formation of a hydroxo-tartrato-bis-levo-propylenediamine cobalt (III) complex. The reaction does not proceed to the complete liberation of the tartrate ion and the formation of the tris-levo-propylenediamine cobalt (III) ion unless a large excess of levo-propylenediamine is present in a highly concentrated solution.

The method of resolution of racemic-tartaric acid proposed by Hamilton (5) was also investigated. Since some difficulty had been encountered in attempts to verify Hamilton's results (6), a slightly different procedure was employed. The former procedure consisted of treating racemic-tartrato-bis-levo-propylenediamine cobalt (III) chloride with excess racemic-tartaric acid. A partial resolution resulted when the dextro-tartrate ion displaced the coordinated levo-tartrate ion in the formation of the more stable complex. It was thought that the selectivity of this type of reaction might be increased by treating a solution of carbonato-bis-levo-propylenediamine carbonate with a one hundred percent excess of racemic-tartaric acid. In this way both the dextro-tartrate ion and the levo-tartrate ion would have an equal opportunity to enter the coordination sphere, the dextro-isomer presumably coordinating preferentially. This would not involve the displacement of the levo-tartrate ion.

A solution containing the carbonato-complex and a 100% excess of racemic-tartaric acid was evaporated to dryness on the steam-bath and subsequently ovendried for four days at 90°C to insure complete reaction of the tartrate ion. When this somewhat powdery mass was dissolved in a small amount of water and a large excess

of a saturated solution of barium hydroxide added, the uncoordinated tartrate fraction was precipitated as barium tartrate and removed by filtration. Sufficient excess barium hydroxide remained in the filtrate to effect complete precipitation of the preferentially coordinated tartrate fraction upon standing for about four days.

In Experiment II, the two barium tartrate precipitates were dissolved in dilute hydrochloric acid and the solutions diluted to twenty-five milliliters. The rotations obtained for these tartaric acid solutions are recorded in the following table, the weight of tartaric acid having been calculated from the weight of the barium tartrate precipitates.

Experiment II

	Wt. Tart'c acid	obs α	$[\alpha]_D$
1. Initial Ba-tart Precipitate	1.337 g.	−0.044°	−0.412°
2. Final Ba-tart Precipitate	1.762 g.[+]	+0.033°	+0.234°

[+] The barium tartrate precipitate from which this weight of tartaric acid was calculated is believed to have contained a considerable amount of barium carbonate because of effervescence noted upon the addition of acid. Barium carbonate would precipitate if the solution absorbed carbon dioxide from the air.

In order to determine the extent of resolution achieved, a known weight of barium-*dextro*-tartrate, prepared from commercial *dextro*-tartaric acid, was dissolved in dilute hydrochloric acid, diluted to twenty-five milliliters and the rotation determined. The specific rotation of this solution indicated that about an eight percent resolution had been obtained by the above procedure.

An investigation of some of the factors which might affect the rotation of a solution of optically active tartaric acid showed that the rotation of the acid was considerably decreased by the presence of barium ions, calcium ions and concentrated sulfuric acid. This suggested the removal of the barium ions from the optically active tartaric acid solutions. Since concentrated sulfuric acid also decreased the rotation of the acid, Hamilton's procedure (6) of grinding the barium tartrate precipitates with excess concentrated sulfuric acid and removing the barium sulfate by filtration, proved unsatisfactory. It was found that barium chloride has a low solubility in concentrated hydrochloric acid whereas tartaric acid is very nearly as soluble in this medium as in water. By treating the barium tartrate precipitates with concentrated hydrochloric acid, and removing the precipitated barium chloride by filtration, the barium ion content was reduced to an extent which produced no decrease in the rotations of the optically active tartaric acid solutions.

In Experiment III, exactly the same procedure was used as in Experiment II, except that most of the barium ions were removed

by the hydrochloric acid treatment just described. The weights of tartaric acid were again calculated from the weights of the barium tartrate precipitates.

Experiment III

	Wt. Tart'c acid	Obs α	$[\alpha]_D$
1. Initial Ba-tart Precipitate	1.370 g.	-0.075°	-0.685°
2. Final Ba-tart Precipitate	1.115 g.	+0.057°	+0.640°

The results of the partial resolution indicated that more than a one-hundred percent excess of barium hydroxide was necessary to effect complete precipitation of the "uncoordinated" tartrate fraction. This observation was also reported by Hamilton (5), who concluded that the levo-tartrate ion must be attached to the central cobalt (III) ion as well as the more firmly coordinated dextro-tartrate ion. This would necessitate either monodentate coordination of both the dextro- and levo-tartrate isomers, the former being more firmly held, or a coordination number greater than six for the central cobalt (III) ion.

Even though only 8% percent resolution was obtained, the experiment lends considerable support to the utilization of "preferential coordination" as a means of resolving racemic-mixtures of organic acids.

The possibility of resolving racemic- mixtures of organic acids which contain one asymmetric carbon atom and which are monodentate coordinating agents, by the method of preferential coordination, was intriguing. The resolution of racemic-lactic acid by the usual methods is very tedious and the resolutions of racemic-α-chloropropionic acid and racemic-α-bromopropionic acid have received very little attention. It was desirable to develop a perfectly general procedure for the resolution of these three acids by preferential coordination. Since all common salts of these three acids are quite soluble or tend to decompose in water, the acids were recovered by extraction with ether.

A mixture of a one-hundred percent excess of the racemic-acid and a carbonate solution of carbonato-bis-levo-propylenediamine cobalt (III) complex was evaporated to dryness. The residue was then dissolved in a small amount of water and the uncoordinated acid extracted with ether. An aqueous solution of the extracted acid was prepared by evaporating the ether on a steambath. In order to recover the fraction of the acid which had entered the coordination sphere it was necessary to decompose the complex by sodium sulfide, remove the precipitated cobalt sulfide by filtration, acidify with sulfuric acid, and extract with ether. The acid fractions recovered in this way were optically active. The results of one of the resolutions of racemic-α-chloropropionic acid are recorded in the following table, the amount of acid having been determined by titration with standard sodium hydroxide solution:

Experiment IV

	Wt. Acid	Obs α	$[\alpha]_D$
1. Initial Extract	0.575 g.	+0.050°	+1.088°
2. Final Extract	0.400 g.	-0.058°	-1.812°

In order to determine the percent resolution achieved for α-chloropropionic acid, which was the acid most thoroughly investigated, it was necessary to determine the specific rotation of the pure, optically active acid which had been resolved by standard methods. *Racemic*-α-chloropropionic acid was resolved by recrystallization of the cinchonine salt. The salt was decomposed by the addition of sodium hydroxide and the precipitated alkaloid removed by filtration. The specific rotation was determined on the filtrate after acidification, the average value being 3.40° at room temperature and the D line of sodium.

The resolution of *racemic*-lactic acid was attempted in an effort to determine the configuration of the α-chloropropionate ion which preferentially entered the coordination sphere of the complex. As in the resolution of α-chloropropionic acid the levorotatory lactic acid isomer, which is known to possess a *dextro*- configuration with a specific rotation of about 3.80° (7), preferentially coordinated. Since the structures of these two molecules are very similar it is assumed that the levorotatory isomer of α-chloropropionic acid also possesses a *dextro*-configuration.

Both *racemic*- lactic acid and *racemic*- α-chloropropionic acid were resolved to an extent of greater than thirty percent by this procedure. The partial resolution of α-bromopropionic acid was studied only qualitatively since the specific rotation of the pure optically active acid is not known. The results obtained are significant and are of both theoretical and applied interest, since the procedure employed is much simpler than the usual methods of alkaloid salt recrystallizations and could be adapted to a much larger scale than is possible with enzymatic resolutions.

The selectivity of this type of reaction is valuable in determining the sterical configuration of optically active isomers of organic molecules. In the resolutions of *racemic*-tartaric acid, *racemic*-lactic acid, and *racemic*-α-chloropropionic acid it was always the *dextro*- form of the acid which preferentially entered the coordination sphere, even though the *dextro*- forms of the latter two are levorotatory whereas *dextro*- tartaric acid is dextrorotatory. The *dextro*- forms of these acids must then have the same configuration as *levo*-propylenediamine, as proposed by Jonassen (4).

Conclusion

At present it is not possible to explain why the reactions involving coordination by optically active groups are selective especially in the case of mondentate groups. It is entirely possible that a coordination number greater than six for the

central cobalt (III) ion is involved but further study is necessary to confirm this supposition. The results of these investigations are of both theoretical and practical importance and provide a basis for future studies.

Bibliography

1. Smirnoff, Helv. Chim. Acta., 3, 177 (1920).
2. Hürliman, Dissertation; Jaeger, "Optical Activity and High Temperature Measurements," pp. 167-168, McGraw-Hill, N.Y. (1930).
3. Stiegman, Thesis, University of Illinois, 1937.
4. Jonassen, Thesis, University of Illinois, 1946.
5. Hamilton, Thesis, University of Illinois, 1947.
6. Sister Martinette, Thesis, University of Illinois, 1949.
7. Karrer, "Organic Chemistry," Third Edition, p. 253, Elsevier Publishing Co., Inc., N.Y. (1947).

THEORY OF OVERPOTENTIAL IN ELECTRODEPOSITION

Ernest H. Lyons Jr. February 5, 1952

During electrodeposition, the potential between cathode and solution differs from that measured when no current is flowing. The difference, called overpotential overvoltage, or polarization represents three terms, potential due to concentration changes, that due to ohmic resistance, and that due to slowness of the electrode reactions.

Concentration overpotential

In a still solution, the concentration of metal ions steadily decreases and a varying concentration gradient is established (1). Usually, however, convection currents resulting from the density differences maintain the metal ion concentration at a uniform value a small distance from the electrode, as has been shown by hydrodynamic considerations (2-5) To a good approximation it may be assumed that within this distance the concentration gradient is linear (6-13), and ions are transferred only by diffusion and migration. In the presence of an excess of indifferent electrolyte, the tranference number of the metal ion is negligibly small, and migration may be ignored. At the steady state, where I is current

$$\frac{I}{nF} = \frac{D(c_o-c_e)}{\delta} \qquad (1)$$

D the diffusion coefficient, ce and co the metal ion concentrations at the electrode surface and in the bulk of the solution, is the thickness of the diffusion layer, in the number of charges on the ion, and F the faraday equivalent. The limiting current density is searched when c_e is zero, so that

$$I_o = nFDc_o/\delta \qquad (2)$$

In stirred solutions, is independent of the rate of diffusion, and

$$\frac{c_e}{c_o} = 1-\frac{I}{nFDc_o} = 1-\frac{I}{I_o} \qquad (3)$$

This relation is approximately correct for unstirred solutions also (14).

When migration cannot be neglected, (1) must include a correction for the number of ions transferred through the layer:

$$\frac{I}{nF} = \frac{D(c_o c_e)}{\delta} + \frac{t_A I}{nF} \qquad (4)$$

where t_A is the transference number of the metal ion;

$$\frac{c_e}{c_o} = 1-\frac{(1-t_A)}{DnFc_o} = 1-\frac{I}{I_o} \qquad (5)$$

where the limiting current is given by

$$I_o = DuFc_o\ (1-t_A)$$

Equation (5) is an approximation since t_A depends upon the concentration; but tje errpr os mpt serious. (14)

The concentration overpotential is that of a concentration cell with concentrations c_o and c_e, or more precisely a_o and a_e. If migration is not important the liquid junction potential is negligible, and the overpotential is

$$\eta_c = \frac{RT}{nF}\ \mathrm{lu}\ \frac{c_e}{c_o} = \frac{RT}{nF}\ \mathrm{lu}\ (1-\frac{I}{I_o}) \qquad (7)$$

Equation(7) accounts for a large body of experimental data (17)(18)

Resistance Overpotential

$$\eta_r = R_oI + \int_o^{\delta} \frac{I}{c_x} dx \qquad (8)$$

The first term represents resistance due to the bulk of the solution, R_o being a constant for the cell and solution; the integral represents resistance due to the diffusion layer, where c_x is the concentration at distance x from the electrode, and is the equivalent conductance. Noting that c_x is linear, and assuming is constant, we have from (5),

$$\eta_r = R_oI + \frac{DF}{(1-t_A)}\ \mathrm{lu}\ (1-\frac{I}{I_o}) \qquad (9)$$

where $I_o = -DFc_o/\delta\ (1-t_A)$. Since D is proportional to the mobility (15) (16),

$$D = \frac{2RT}{F_2}\ t_A\ (1-t_A) \qquad (10)$$

$$\eta_r = R_oI + \frac{2RT}{F}\ t_A\ \mathrm{lu}\ (1-\frac{I}{I_o}) \qquad (11)$$

Comparing the last term in (11) with (7), it appears that resistance due to concentration changes in the diffusion layer is of the same order of magnitude, and varies in the same manner, as concentration overpotential.

Activation Overpotential

Overpotential remaining after the resistance and concentration overpotentials have been deducted is ascribed to a slow step in transferring ions from the solution to their final position in the metal crystal lattice. Such overpotential raises the energy of the reacting ions so that they may surmount a potential carrier in passing to the cathode, and therefore is called activation or chemical overpotential.

It may be treated by the usual kinetic methods. Thus Agar and Bowden (19) suppose that the activation energy, W, is proportional to the overpotential, that is, $W = \alpha\eta_aF$. In Maxwellian distribution, the number of ions reacting per second is

$$N = N_0 \exp - (W - \alpha\eta_a F)/RT \qquad (12)$$

If N is measured by the current density, I, (12) becomes

$$\ln I = \text{const.} + \alpha F/RT \qquad (13)$$

This has the form of the Tafel equation, frequently observed in hydrogen overvoltage.

Glasstone, Laidler, and Eyring (20-22) reach (13) from the theory of absolute reaction rates, but when the overpotential is very small so that the rate of the reverse reaction is significant, find

$$\eta_a = K(RT/F)I \qquad (14)$$

If, however, the rate determining step occurs after discharge of the ions, as when the atoms are seeking lattice positions, activation energy is unaffected by the potential. The accummulation of atoms not yet incorporated into the metal lattice would set up its own electrode potential (23). Where thermodynamic data are available, the potential can be calculated, and often (24) has the form of equation (13).

Among steps postulated as rate-controlling are

a. Slow decomposition of complex or hydrated ions. (25-27,33,54, 60,61). For example (28), if in cyanide solutions, silver is deposited from so-called free silver Ions, the rate of their production is $d(Ag^+)/dt = k_1[Ag(CN)_2^-] - k_2[Ag^+][CN^-]^2 = k_1[Ag(CN)_2^-] - k[Ag^+]$ since the concentration of cyanide ions is constant. The rate of decomposition is I/F, and in the steady state the concentration of the simple ion will fall to $[Ag+]-z'$ Thus:

$$I/F = k_1 [Ag(CN)_2^-] - k([Ag+] - z).$$

If equilibrium is preserved in the dissociation of the complex,

$$I/F = \text{constant} + k\,a \qquad (15)$$

The activation overpotential is given by

$$\eta a = \frac{RT}{F} \ln \frac{[Ag+] - z}{[Ag+]} = \frac{RT}{F} \ln\left(1 - \frac{z}{[Ag+]}\right) = \frac{RT}{F} \ln\left(1 - \frac{I}{k[Ag+]}\right) \qquad (16)$$

b. Passage of Ions through films and other obstructions. These may be (28): i- porous, semi-permeable, or impermeable films; congregation of undischarged cations; iii- removal of a portion of the discharging ion before it reaches the cathode. Colloids (27) and basic material (29,30, 59) are known to offer obstruction. Glasstone, Laidler and Eyring, (22) propose passage through the double layer as the slow step, but Bockris (62) discounts the explanation.

c. Lateral movement of ions on the cathode to a "favorable spot" before discharge. (31-34,44).

d. Hindrance to discharge. Contact with the cathode may be insufficient. This hypothesis has been fruitful in considering hydrogen overpotentials, and Volmer (40) considers it important in depositing iron, nickel and cobalt.

e. Migration after discharge to positions in existing lattices.

This concept conforms to present ideas of crystallization from vapor and liquid phases. The discharged atoms not yet incorporated in lattices are considered as a supersaturated solution which sets up its own potential (55-58). Erdey-Gruz and Volmer (41) assume little supersaturation to start a new layer; and very much higher to start a new grain. They obtained the following relations for the three cases. respectively:

$$\eta_a \propto I, \quad \eta_c \propto \frac{1}{\log I}, \quad \eta_c \propto \frac{1}{(\log I)^{\frac{1}{2}}} \qquad (17)$$

and observed these relationships experimentally (42;43) in different cases.

f. Obstruction to crystal growth by adsorbed or codeposited non-metallic matter. (39,45,50).

g. Simultaneously, slow discharge of ions and incorporation into the metal lattice. (51, 52).

Since many of these considerations lead to logarithmic functions it is not possible to distinguish the various components of the overpotential from the potentail-current curve alone. In particular, pressing the tip of the reference electrode against the cathode surface does not eliminate resistance overpotential, due to the diffusion layer, as commonly assumed. (63). Activation overpotential may be distinguished from concentration overpotential as follows: (14)

1. Stirring will decrease concentration overpotential but will not affect activation.
2. Concentration overpotential is not influenced by the nature and catalytic activity of the cathode surface, as is activation.
3. The effect of temperature is obtained by differentiating equation (7):

$$\left(\frac{\partial \eta_c}{\partial T}\right)_I = \frac{\eta_c}{T} - \frac{RT}{1=} \frac{I}{(I-I_0)} \left(\frac{\partial \, \mathrm{lu}\, I_0}{\partial \; T}\right) \qquad (18)$$

At relatively small values of I, so that $I \gg - I_0$, approximately

$$\left(\frac{\partial \eta_c}{\partial T}\right) = \left(\frac{\eta_c}{T}\right) - \frac{RT}{1=} \quad \frac{\partial \, \mathrm{lu}\, I_0}{\partial \; T}$$

($\partial\, \mathrm{lu} I_0/\partial T$) is approximately 0.04 per degree in a large number of cases. (14) . ($\partial \eta_c/\partial T$) is typically about -0.5×10^{-3} V./deg., and the corresponding coefficient for activation is ordinarily several times higher.

4. The limiting current, I_0, is approximately proportioned to con-to concentration of the discharging ion; in many cases this does not apply to activation. (53)
5. Concentration overpotential is a logarithmic function of current density; activation may have other relationships.
6. Activation overpotential generally increases linearly with time to a steady value (54), while concentration overpotential has a lower rate of growth, giving an apparent "capacitance" of the electrode several hundred times larger than for activation overpotential. (14).

REFERENCE

1. Kolthoff and Laitinen, J. Am. Chem. Soc. 61, 334 (1939).
2. Eucken, Z. Elektrochem. 38 341 (1932).
3. Wood and Tordai, J. Chem. Physics 14, 453 (1946).
4. Agar, Faraday Soc. Discussions 1, 26, (1947).
5. Levich, ibid. 37.
6. A. A. Noyes and W. R. Whitney, Z. physik. Chem. 23, 689 (1897).
7. Nernst, ibid. 47, 52 (1904).
8. Bruner, ibid. 56.
9. Nernst and Merriam, ibid. 53, 235, (1905).
10. Weigert, ibid. 60, 513 (1907).
11. Rosebrugh and Miller, J. Phys. Chem. 14, 816 (1910).
12. Wilson and Youtz, Ind. Eng. Chem. 15, 603 (1923).
13. Glasstone, Trans. Electrochem. Soc. 59, 277 (1931).
14. Agar and Bowden, Proc. Roy. Soc. 169A, 206 (1938).
15. Nernst, Z. physik. Chem. 2, 612 (1888).
16. Haskell, Phys. Rev. 27, 145 (1903).
17. Kolthoff and Laitinen, J. Phys. Chem. 45, 1062 (1941).
18. Kolthoff and Lingane, "Polarography", New York, 1946, Chap. 9
19. Agar and Bowden, Ann. Reports 35, 90, (1938).
20. Kimball, J. Chem. Phys. 8, 199 (1940).
21. Eyring, Glasstone, and Laidler, ibid. 7, 1053 (1939).
22. Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," New York, 1941, p. 575.
23. Hickling and Salt, Trans. Faraday Soc. 38, 474, (1942).
24. Hickling, Quart. Revs. 3, 95 (1949).
25. Foerster, Z. Elektrochem. 13, 561 (1907).
26. Brdika, Coll. Czech. Chem. Commun. 2, 489, 545 (1930); 3, 396 (1931).
27. Kolthoff and Lingane, loc. cit. (18), p.183

28. Gardam, Faraday Soc. Discussions 1, 182 (1947).
29. Macnaughtan, Gardam, and Hammond, Trans. Faraday Soc. 29, 729, 755, (1933).
30. Macnaughtan and Hothersall, ibid. 24, 387 (1928).
31. Hunt, J. Phys. Chem. 36,1006, 2259 (1932).
32. Hunt, Trans. Electrochem. Soc. 65, 413 (1934).
33. Thon, Compt. rend. 197, 1312 (1932).
34. Thon, "L'Ectrolyse et la Polarization Electrolytique," Paris, 1934
35. Glasstone, " Electrochemistry of Solutions," London, 1937.
36. Bowden, Proc. Roy Soc. 120A, 59 1.(1928).
37. Baars, Z. physik. Chem. 142A, 97 (1929).
38. Volmer, ibid. 150, 203 (1930)
39. Gurney, Proc. Roy Soc. 134A, 137 (1931).
40. Volmer, Phys. Z. 4, 346 (1933).
41. Erdey-Gruz ibid. 172, 157 (1935).
42. Erdey Gruz and Volmer, Z. physik Chem. 157, 165, 182 (1931)
43. Erdey-Gruz and Volmer, ibid. 178, 255, 266 (1936).
44. Hoekstra, Rec. trav. chim. 50, 339 (1931).
45. Kasper, Bur. Standards J. Research 9, 351 (1932); 14, 693 (1935)
46. Adcock, J.Iron and Steel Inst. 115, 369 (1927).
47. Weisberg, Alexander's "Colloid Chemistry", vol. 6, New York, 1946, pp. 579-587.
48. Hendricks, Trans. Electrochem. Soc. 82, 237 (1942)
49. Kohlschutter, Z. Elektrochem. 19, 181 (1913).
50. Sand and Black, Z. physik. Chem. 70, 496 (1909).
51. Blum and Rawdon, Trans. Electrochem. Soc. 44, 397 (1923).
52. Frolich and Clark, Z. Electrochem. 31, 649 (1925).
53. Bowden, Trans. Faraday Soc. 24, 473 (1928.)
54. LeBlanc, Abh. Bunsen Gex. 1910, No. 3; Trans. Faraday Soc. 9, 251 (1914).

55. Hughes, D.S.I.R. Bull. No. 6, 1922 (referred to in J. A. V. Butler, "Electrocapillarity," London, 1940, p. 166).

56. Aten and Boorlaage, Rec. trav. chim. 39, 720 (1920).

57. Volmer, Z. physik. Chem. 139, 597 (1928).

58. Brandes, Z. physik. Chem. 142. 97 (1929).

59. O'Sullivan, Trans. Faraday Soc. 26, 89 (1930).

60. LeBlanc and Schick, Z' physik. Chem. 46, 636 (1903).

61. LeBlanc and Schick, Z. Electrochem. 9, 213 (1903)

62. Bockris, J. Electrochem. Soc. 98, No. 11, 156C (1951).

63. Luggin, Z. physik. Chem. 32, 208 (1900).

SUPPLEMENTARY REMARKS ON OVERPOTENTIALS

Ernest H. Lyons, Jr. February 5, 1952

With respect to electrolytic behavior, metals may be classified into three groups. The classification was first made by Piontelli (64, 65) on the basis of the electrode potentials in the absence of any impressed external voltage, and has been extended by him to overpotentials and other properties. The classification corresponds to certain phenomena observed in electroplating.

Metals which readily set up a constant, reproducible potential with respect to solutions containing their ions, also show relatively low overpotentials, and behave normally in displacement reactions. Such metals are termed "normal". e.g. lead, thallium, tin, mercury, cadmium.

Metals which do not readily reach an exchange equilibrium with their solvated ions do not show constant electrode potential, have relatively high overpotentials, and do not behave as expected in displacement reactions. These are termed "inert" , e.g. iron, cobalt, nickel, manganese, platinum, rhodium, palladium.

A third class shows intermediate properties; e.g. copper, silver, gold, arsenic, antimony, bismuth.

"Normal" metals have the following general characteristics: 1- large atomic volume; 2- open structure lattices; 3- low or medium melting point; 4- heat of sublimation below 80 Cal. per mol; 5- low recrystallization temperature; 6- low mechanical strength; 7- low surface tension in liquid state; 8- high mobility and diffusion coefficient of solvated ion; 9-satisfactory agreement with the law of Dulong and Petit; 10- large thermal vibration amplitude; 11- stable electrode potentials, not much affected by history of the electrode; 12- anode and cathode overpotentials nearly equal and relatively low; 13- Electrodeposits are usually of large crystals or grains; 14--form of electrodeposit is difficultly influenced by addition agents in the bath; 15- anode and cathode efficiencies tend to be high; 16- high hydrogen overvoltage; 17- poor catalytic activity in hydrogenation reactions; 18- low capacity for absorbing hydrogen; 19- readily form amalgams; 20- good correlation between position in electromotive series and behavior in displacement reactions; 21- normal behavior in concentration cells; 22- rapid exchange between metal and hydrated ion, as shown by radioactive tracer experiments (67) reversible polarographically.

The characteristics of the "inert" metals are diametrically opposite. Further, the inertness persists to large degree when the metals are deposited on mercury cathodes, showing that difficulties in crystallization are not the important factors. Inert metals are, moreover, good

as reduction-oxidation electrodes, so that there is no great transfer resistance to the passage of electrons, and sluggish electrolytic behavior is not due to a surface condition.

Inertness increases gradually in the groups Fe-Co-Ni, Ru.-Rh-Pd. Ag-Cu-Au, Bi-Sb-As. Inert metals have incomplete d-shells, high hydration energy of the ions, and low interatomic distance in the metallic state. According to Pauling (66), as the metal-oxygen bonds in the aquo complexes become more covalent in character, the stability of the hydration complex is more pronounced, and this appears to be parallel with increasing inertness.

Comparing the electrolytic behavior of various simple salts of the same metal shows certain regularities (64). For any metal, the halide salts show the lowest overpotentials, the perchlorates and nitrates, the highest overpotentials, and others such as sulfates, sulfamates, and fluborates are intermediate. The overpotential has no relationship with the electrode potential, the ionic strength of the solution, nor the ionic activity of the metal ion.

To interpret the influence of the anion as an inhibition requires that perchlorate be the most effective inhibitor, particularly on the more negative surfaces. It is more reasonable to regard the halides as having a sort of catalytic effect which is absent from the perchlorates. In fact, the deformability of the anion appears to be decisive; it is suggested that a chloro- substituted aquo complex is more deformable than the aquo complex itself.

From these considerations it is plausible that adsorption on the electrode surface with subsequent deformation of the complex in the intensified electric field at the interface is an essential part of the electrode reaction. Ultimate dissociation of the complex to permit the stripped ion to enter the metal lattice is perhaps the extreme of this deformation.

Cathode deposits from halide solutions are least affected by addition agents, and those from perchlorate solutions are the most profoundly affected, while sulfate solutions are intermediate. Just as in comparing different metals, high overpotentials correspond to fine crystals in the deposits and the greatest influence of addition agents. Furthermore, halide solutions often show higher anode and cathode efficiencies, which may be correlated to the catalytic effect.

In effecting the orientation and deformation of the complex ions at the electrode-solution interface, it is suggested that the strong, directed, predominantly covalent bonds characterizing the inert metals project less markedly

from the metal surface than the more electrostatic, longer range bonds of normal metals. This difference results in lower field strength at the interface for inert metals, as well as in the high hydration energy of the ions and the low stability of the metal itself, so that electrodeposition and metal-metal ion interchange is more difficult for the inert metals.

64. Piontelli. Z. Elektrochem. 55, 128 (1951); J. chim. phy-
 45, 115 (1948).

65. Piontelli and Poli. Gazz. chim. ital, 78, 717 (1948);
 79, 210, 814. 538, 635, 642, 863 (1949); 80, 107
 (1950).

66. Pauling, Vol. Commem. Victor Henri, Leige, 1947-8 P. 1

67. Haissinsky, Colloque Internat. sur les exchanges
 isotopiques, Paris, 1948, p. 70.

The "Half-Bond" and Its Application to the Structure of Electron Deficient Compounds

Niels C. Nielsen February 12, 1952

In forming a simple covalent bond, it is necessary to have available certain combinations of energy levels (orbitals) and electrons which, in most cases, are paired. Examples of one-electron and three-electron bonds are also known. An important characteristic of such bonding, as far as the following discussion is concerned, is the fact that, except in the case of the three-electron beond, sufficient orbitals are available for all of the electrons involved in the bonding to be paired in accordance with the Pauli exclusion principle. Coordinate covalent complexes present a slightly different situation. Rather than having each species involved supply approximately equal numbers of orbitals and electrons, the metal furnishes a comparatively large number of stable orbitals whereas the coordinating group furnishes the bulk of the electrons involved in the bonding. The structure and properties of such compounds are intimately related to the number of stable orbitals available and to the number of unpaired electrons which remain after such bonds are formed.[1]

Another familiar type of bonding arises in metals which have an excess of stable orbitals with respect to the number of electrons available for filling these orbitals. The general tendency seems to be that of having the electrons using as many orbitals as possible giving rise to the Brillouin zones.[2] To emphasize the differences involved, the following classification may be made with respect to a bond between two species A and B:

Type I: A and B have approximately equal numbers of stable orbitals, and electrons for bonding. (Covalent)

Type II: A furnishes more stable orbitals than B whereas B supplies most of the electrons used in bonding. (Coordinates covalent.)

Type III: Bonding in pure metals where excess stable orbitals are available. (Metallic)

From a theoretical point of view, a fourth possibility man occur which appears, logically, to be intermediate between the coordinate covalent bond and the metallic bond. This would involve a bond between an atom with excess stable orbitals and another atom which did not possess sufficient electrons to fill these orbitals completely. The electron deficient compounds belong to this category and may better be classed as "excess orbital" compounds.[3] Metals of the scandium, titanium, vanadium, and chromium families have

numerous unfilled stable orbitals. On the other hand, hydrogen and the first row elements: boron, carbon, nitrogen, and oxygen have an apparent lack of stable orbitals and electrons for sharing in any bond which may be formed. However, these two groups of elements do combine to give the carbides, nitrides, borides, and oxides. (In the present discussion compounds containing principally ionic bonds will not be considered.) A study of the structure of these compounds will indicate the nature of this fourth type of bonding which appears possible.

The usual explanation for the structure of the interstitial compounds is that a particular crystal lattice is determined by the metal. The small atoms of the non-metal are then inserted between the metal atoms forming a solid solution. As a first consequence of this proposal, it is normally found that there is a small expansion of the metal's crystal structure in order to accommodate the foreign atoms. This is shown by Table I.[4]

TABLE I: Metal-metal distances in metals and interstitial phases, MX*

	Metal	Carbide	Nitride	Oxide
Sc	3.20	--	3.14	--
La	3.75	--	3.73	--
Ce	3.64	--	3.54	--
Pr	3.64	--	3.65	--
Nd	3.64	--	3.64	--
Ti	2.93	3.05	2.99	2.99
Zr	3.19	3.32	3.27	--
Hf	3.16	3.15	--	--
Th	3.59	3.75	3.68	3.71(?)
V	2.63	3.03	2.920	2.91
Nb	2.85	3.16	3.12	2.96
Ta	2.85	3.14	--	--
Cr	2.71	--	2.75(Hex.) 2.93(?Cubic)	--
Mo	2.72	2.90	2.86	--
W	2.74	2.91	3.03	--
U	2.97(C.N. 8) 2.80 3.27(C.N. 12)	3.50	3.45	3.47

*Sources of information and comments regarding certain values are given in reference 4.

In the rare earth nitrides, there is no increase in metal-metal distances whereas the volume of uranium carbide is thirty-three percent greater than that of uranium metal. Increased metal-metal distances should result in weakening of these bonds, yet most interstitial compounds melt at a temperature higher than that of the metal itself.

As a second consequence of the solid solution concept, no change in the fundamental crystal structure of the metal would be anticipated. Table II compares the lattice of each metal with that of its various interstitial compounds.[4] It is interesting to note that the sodium chloride lattice is preferred by almost all of the interstitial compounds. In such a structure, each non-metallic atom would have a total of six nearest neighbors, thus implying that six equivalent bonds are formed. The appearance of an octahedral configuration, despite the fact that the first row elements have only four low energy orbitals available, led Pauling to suggest that these four bonds were able to "resonate" among the six possible positions in the lattice.[1]

TABLE II: Structure of metals and of interstitial phases, MX*

	Metal	Carbide	Nitride	Oxide
Sc	A1	--	B1	--
La	A1	--	B1	--
Ce	A1	--	B1	--
Pr	A3	--	B1	--
Nd	A3	--	B1	--
Ti	A3	B1	B1	B1
Zr	A3	B1	B1	B1
Hf	A2, A3	B1	--	--
Th	A1	B1	B1	B1
V	A2	B1	B1	B1
Nb	A2	B1	B1	B1 (distorted)
Ta	A2	B1	--	--
Cr	A2	Hex. (?)	Hex. (B1 ?)	--
Mo	A2, A3	Hex.	Hex.	--
W	A2	Hex.	Hex. (?)	--
U	A2	B1	B1	B1

KEY: A1, cubic closest-packed A3, hexagonal closest-packed
A2, body-centered cubic B1, sodium chloride type

*Sources and comments on these structures are given in Reference 4.

The brittle nature of the interstitial compounds is another property in which they may differ considerably from the parent metals. In addition to requiring bonds between the metal and non-metal, this property would indicate that the bonds have a certain amount of directional character. However, they should not be completely localized for the electrons must be free enough to account for the conductivity of the interstitial compounds. Thus, the nature of any bonding proposed for the interstitial compounds must account for four distinct properties:[3,4]

1. Preference for a NaCl lattice
2. Hardness and melting point
3. Brittleness
4. Conductivity

Octahedral bonding in the interstitial compounds may be accounted for in the following manner.[3,4] The metals in Tables I and II all have several stable orbitals available for bonding whereas carbon, nitrogen, and oxygen can, at the most, use one 2s- and three 2p-orbitals. If three p-orbitals containing six electrons (three electron pairs) are used, they will be required to furnish six bonds. When one orbital containing one electron pair is used to form two bonds, each of these bonds is called a "half-bond". The possibility of a p-orbital forming two bonds is due to the bidirectional nature of the electron distribution in such an orbital. Similarly, a symmetrical s-orbital might conceivably provide for two bonds.[5] A third possibility would involve hybridization to give sp-orbitals which are also bidirectional.[4] In any case, some or all of the six bonds will be "half-bonds". It is important to note that, by this type of bonding, an atom which would not have enough electrons to use all the available low energy orbitals if normal bonding took place, can use all of these orbitals by "half-bonding".

The existence of "half-bonds", as indicated in the preceding paragraph, rests on a purely hypothetical basis. However, evidence is available which strongly suggests that the "half-bond" is a reality rather than an arbitrary designation of bond formation. By calculations involving wave mechanics, it can be shown that, in most cases, two "half-bonds" are of lower energy (greater bond strength) than a normal single bond plus an unused low energy orbital.[5] It can also be shown that the bond numbers obtained by assuming "half-bonds" agree, in general, with those calculated by using Pauling's rule for the calculation of bond number.[6] If three p-orbitals are used to form six bonds, each of which is a "half-bond", it is obvious that the bond number for any of these bonds will be one-half. On the other hand, if sp-hybridization takes place to give two normal single bonds, and the two remaining two p-orbitals form four "half-bonds", the bond number will be:

$$\frac{2 \times 1}{6} + \frac{4 \times \frac{1}{2}}{6} = \frac{2}{3}$$

The results obtained from Pauling's data are shown in Table III.[4]

TABLE III: Determination of bond number in interstitial phases, MX

Bond	D(Bond length)	R(radii for single bond)	D-R	Probable** Bond No.
Ti-C	2.158	2.095	0.063	2/3
Zr-C	2.344	2.225	0.219	1/2
Hf-C	2.229*	2.213	0.016*	2/3*
Th-C	2.645	2.423	0.222	1/2
V-C	2.068	1.995	0.073	2/3

Table III (continued)

Bond	D(Bond length)	R(radii for single bond)	D-R	Probable** Bond No.
Nb-C	2.231	2.112	0.119	2/3
Ta-C	2.223	2.114	0.109	2/3
Mo-C	2.17	2.06	0.11	2/3
W-C	2.20	2.07	0.13	2/3
U-C	2.476	2.192	0.274	1/2 or less
La-N	2.64	2.39	0.25	1/2 or less
Ce-N	2.506	2.346	0.16	1/2
Pr-N	2.578	2.348	0.23	1/2
Nd-N	2.571	2.342	0.23	1/2
Ti-N	2.11	2.02	0.09	2/3
Zr-N	2.315	2.15	0.165	1/2
Th-N	2.60	2.35	0.25	1/2 or less
V-N	2.065	1.925	0.14	2/3-1/2
Mo-N	2.165	1.999	0.166	1/2
U-N	2.44	2.12	0.32	1/2 or less
Ti-O	2.11	1.98	0.13	2/3-1/2 (?)
Th-O	2.62*	2.31	0.31	1/2 or less
V-O	2.06	1.88	0.18	1/2
Nb-O	2.09	2.00	0.09	2/3(?)
U-O	2.45	2.08	0.33	1/2 or less

*Data questioned by Rundle.

** If D-R is 0.10, bond number is 2/3

If D-R is 0.18, bond number is 1/2

It should be noted that the more electropositive metals give interstitial compounds with bond number one-half since the non-metal would tend to <u>keep</u> an unshared pair of electrons in the 2s-orbital and bonding would involve three p-orbitals. An examination of Table III will also show that nitrogen has a greater tendency than carbon to hold its 2s-electrons with the result that the carbides have a bond number two-thirds (sp-hybridization) while the nitrides have a bond number one-half. The apparent anomaly of the titanium and niobium oxides may be due to a predominance of ionic character in these bonds.[4]

From the previous discussion it is possible to establish the nature of the "half-bond" more definitely. The formation of "half-bonds" depends upon certain characteristics of the combining atoms:[3]

1. One element, A, must have more stable orbitals than valence electrons. (Class A)

2. Another element, B, must have relatively few orbitals available for bonding. (Class B)

3. The electronegativities of A and B must not differ to the extent that the bonding is essentially ionic.

As mentioned previously, the above conditions will lead to the formation of compounds in which all the orbitals of A are not used unless B, by forming "half-bonds", uses an orbital for more than one bond.

Using the above criteria, it is possible to select those atoms which will combine to give structures containing "half-bonds". Hydrogen, carbon, nitrogen, and sometimes oxygen belong to Class B(See above). Class A includes most of the metals in Groups IIIB, IVB, VB, and VIB of the periodic table. If a metal has four sp^3-orbitals, normal tetrahedra will be formed. This is true in the case of gallium, indium, and thallium nitrides. If a metal has more than four stable orbitals, it will tend toward a d^2sp^3 configuration, but, if the non-metal with which it combines does not have sufficient electrons for this bonding, the non-metal "over-extends" the use of its orbitals; i.e., the non-metal must use a single orbital for more than one bond. Therefore, metals in the scandium, titanium, and vanadium families form MX types of interstitial compounds with a sodium chloride structure involving "half-bonds". For the chromium and manganese families and the Group VIII elements, the interstitial compounds are more complex in character. This may be due to the appearance of one or more electron pairs in the d-orbital.

The concept of the "half-bond" is useful in accounting for the structures and properties of the interstitial compounds. In addition, however, it can be used to explain the structure of electron deficient compounds such as tetramethyl platinum,[3] the aluminum alkyls,[3] the beryllium alkyls,[6,7] and the boron hydrides.[3] Early reports of "half-bonds" in uranium hydride were later disproved by a more accurate structure determination.[8,9]

As has been indicated, the first row elements, having a maximum of four stable orbitals, may form "half-bonds" with metals having more than four stable orbitals. On the other hand, since the hydrogen atom and methyl groups have only one stable orbital, they will form "half-bonds" with first row elements in which case the latter group possesses the excess orbitals required for this type of bonding.

The structure of tetramethylplatinum shows that the compound is a tetramer with an essentially cubic lattice.[3,10]

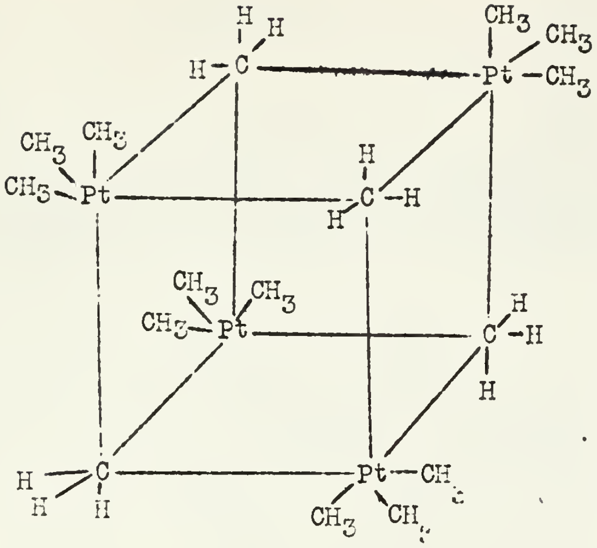


Figure 1: Structure of tetramethylplatinum

In this structure, the carbon in the bridging groups uses three p-orbitals to form six "half-bonds" with each p-orbital used to bond a platinum and a hydrogen atom. The possibility of sp-hybridization as in the metal carbides also exists. In any case, it is necessary to assume that the H-C-H angle in the bridging groups is approximately 90° instead of the normal tetrahedral angle.

The dimerization of aluminum alkyls which will occur if a minimum of two hydrogen atoms are present on one alkyl group may be explained by utilizing "half-bonds". Three sp^2-hybrids and one p-orbital are involved leading to two possible bridge-type structures in which one of these orbitals provides for two "half-bonds"[3]

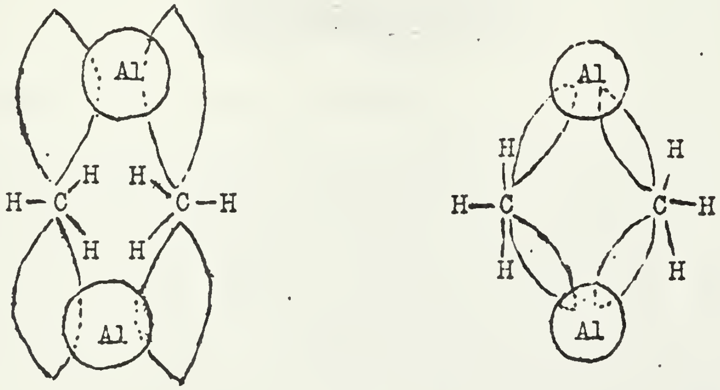


Figure 2: Possible structure of aluminum alkyl dimers.

That this type of bonding prevails and is responsible for dimerization is partly substantiated by the fact that gallium and indium alkyls do not dimerize; neither do they form the types of interstitial compounds previously mentioned.

Dimethyl beryllium also involves bridging through methyl groups with the formation of "half-bonds". In this case, tetrahedral sp^3 bonds prevail and it is postulated that one sp^3-orbital from carbon overlaps tetrahedral orbitals from each of two beryllium atoms.[6,7]

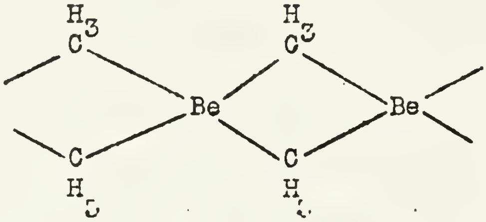


Figure 3: Possible bonding in dimethylberyllium

This would imply some contribution from Be-Be bonding to the stability of the structure, and bond lengths tend to substantiate this deduction.

Another interesting application of the "half-bond" has been its use in the clarification of the so-called "protonated double bond" in the boron hydrides. The hydrogen bridges which exist may be interpreted as being formed by hydrogen using one electron pair and its 1s-orbital to bond two boron atoms.[3]

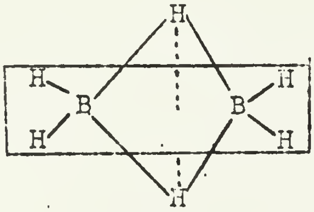


Figure 4: Nature of bridge in boron hydrides

Boron would tend to maintain tetrahedral orbitals and, since the molecule is not planar, the bridging hydrogens are situated above and below the plane of the boron atoms. If "half-bonds" are involved, angle H-B-H would be less than the normal tetrahedral angle. This may not occur because of the repulsion of the two hydrogen atoms. The physical properties as interpreted by the "protonated" or the "half" bond remain the same, and the major gain by considering the boron hydrides as examples of "half-bonding" is that of enabling their classification with other electron deficient compounds.

Bibliography

1. L. Pauling, "The Nature of the Chemical Bond", 2nd ed., Cornell University Press, Ithaca, N. Y., 1948.
2. H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry", D. Van Nostrand Company, New York, 1948.
3. R. E. Rundle, J. Am. Chem. Soc., 69, 1327 (1947).
4. *ibid*, Acta Cryst., 1, 180 (1948).
5. *ibid*, J. Chem. Phys., 17, 671 (1949).
6. R. E. Rundle and A. I. Snow, J. Chem. Phys., 18, 1125 (1950).
7. A. I. Snow and R. E. Rundle, Acta Cryst., 4, 348 (1951).
8. R. E. Rundle, J. Am. Chem. Soc., 69, 1719 (1947).
9. *ibid*, J. Am. Chem. Soc., 73, 4172 (1951).
10. E. J. Holman and R. E. Rundle, J. Am. Chem. Soc., 71, 3264 (1949).

DEVELOPMENTS IN TECHNETIUM CHEMISTRY

Therald Moeller February 12, 1952

Among the more abundant products of the slow neutron fission of uranium - 235 is technetium ($Z=43$), the fission yield being some 6.2 atoms of technetium per 100 atoms of fissioned uranium. Work at Oak Ridge has lead to the comparatively large scale extraction of technetium, and at last reports some 544 g. of the metal have now been prepared (1). Technetium is available from the Oak Ridge National Laboratory in the form of ammonium pertechnetate, NH_4TcO_4, in aqueous ammonia as the 99-isotope, a material of half-life some 5.5×10^5 yr. The recent price reduction (2) from $250 to $50 per milligram in 1-10 mg. quantities and from $100 to $25 per milligram for amounts in excess of 10 mg. should stimulate outside research on the chemistry of the element.

Work at Oak Ridge has centered in an evoluation of the chemistry of technetium. A recent report (3) indicates that like rhenium, technetium is oxidized to M_2O_7 by dry oxygen. Reaction at 400-600° gives a yellowish oxide which dissolves in water to pink solution. This solution can be titrated with alkali as a strong mon-basic acid. Data indicate conclusively that the oxide Tc_2O_7 is formed and gives TcO_4^- in solution. From such solutions red-black crystals of $HTcO_4$ have been obtained by room temperature evaporation over sulfuric acid. Pertechnetate ion absorbs at 2470 A. and 2890 A. and may be detected and determined spectro-photometrically. The possibility of the natural occurrence of technetium is also being pursued at Oak Ridge. The possibility of a long-lived 98-isotope has not been completely eliminated (1).

A recent non-A.E.C. report (4) establishes the composition of the sulfide precipitated by hydrogen sulfide from TcO_4^- solutions 2-4 N in hydrochloric acid as Tc_2S_7. Unlike the rhenium analog, this sulfide cannot be precipitated from 9 N hydrochloric acid.

A non-technical review (5) of technetium chemistry may be consulted with profit.

References

1. Anon.: Chem. Eng. News, 29, 3967 (1951).
2. U.S. Atomic Energy Commission: Isotopics, 2, Jan. 1952.
3. G. E. Boyd, J. W. Cobble, C. M. Nelson, and W. T. Smith: J. Am. Chem. Soc., 74, 556 (1952).
4. C. L. Rulfs and W. W. Meinke: J. Am. Chem. Soc., 74, 235 (1952).
5. J. C. Hackney: J. Chem. Education, 28, 186 (1951).

THE IMINE RADICAL[1]

Melvin Tecotzky   February 19, 1952

The thermal decomposition of hydrogen azide is presumed to take place according to the equation:

$$HN_3 \rightarrow NH + N_2$$

The decomposition is brought about by the passage of hydrogen azide at pressures in the range of 0.05-0.2 mm; through a quartz tube heated to about 1000°C. The imine radical can be frozen out by allowing it to condense on a cold finger containing liquid nitrogen. The liquid nitrogen cooled surface becomes covered with a blue deposit having the composition $(NH)_n$. When allowed to warm up to -125°C, a sharp transition occurs to a white compound. Comparison with a known sample of ammonium azide in the mass spectrometer and chemical analysis proved this white compound to be ammonium azide.

The blue material was found to have a small vapor pressure below its transition point and to be insoluble in the following liquified gases: nitrogen, air, ethylene, propane, and butane. Heat is evolved at the transition temperature, since volatile compounds condensed on the blue material were found to vaporize at this point. It was found to be paramagnetic and a non conductor of electricity.

It was found to be unreactive toward different substances. There is no formation of aniline when benzene is deposited on the material and warmed. In contrast to the solid, the imine radical in the vapor state was found to be quite reactive. By passing carbon monoxide containing 1% hydrogen azide through a furnace at 450°C, one can obtain a test for cyanic acid, HNCO. An attempt to prepare ethylene imine in this manner by reacting ethylene and hydrogen azide failed. Ammonia and small amounts of hydrazine were obtained by passing hydrogen at atmospheric pressure containing 1% hydrogen azide through a furnace at 450°C. The imine radical does not show the Paneth effect with mirrors of lead, antimony, tellurium, and carbon. The half life of the imine radical was calculated to be approximately 9×10^{-4} Sec.

Three suggestions have been offered as to the constitution of the blue material.

1. The blue material is the imine radical in the solid state in which each individual NH radical is loosely coupled to its neighbor.
2. The blue material is diimide HN=NH. The fact that the blue material is paramagnetic is consistant with this idea since diimide may have an electronic structure similar to oxygen.

3. The blue material may consist of a mixture of the monomer and dimer or of still higher polymers.

At present the best approach to the solution of this problem would appear to be an X-ray diffraction study below -125°C, the transition temperature.

Bibliography

1. Rice, F. O. and Freamo, M., J, Am. Chem. Soc. 73, 5529 (1951).

FIRST ISOLATION OF CURIUM

Dale E. Woerner February 19, 1952

Alpha bombardment of ^{239}Pu in the Berkeley cyclotron led to the discovery of the 242 isotope of curium. This isotope has a half life of some 162 days and it decays via alpha emission. In an attempt to produce and isolate this element, Werner and Perlman (1) subjected 4.48 mg of americium oxide to slow neutron bombardment for a period of one year. The curium and americium were separated from the nuclear reaction products and were obtained in a hydrochloric acid solution. This solution contained approximately 150 micrograms of curium. Separation of curium from americium was difficult due to the great similarity in ionic sizes. Oxidation states other than positive three were unknown for americium at the time of this investigation.

The curium was separated from americium by an ion exchange procedure using Dowex 50 cation exchanger. This separation was conducted in a column 8 mm. in diameter and 50 cm. in length. The two actinides were adsorbed at pH = 1 and were eluted by a citrate solution at pH=3. The curium is eluted first (the progress of elution being followed by counting alpha activity) and by repeated fractionation, 50 ml of solution was obtained containing 115 micrograms of curium.

Concentration of the curium was effected by readsorption and elution by citrate at a higher pH. The citrate was destroyed by evaporation with nitric and sulfuric acids, the residue was dissolved, and the addition of ammonia caused the precipitation of light yellow curium hydroxide.

Only the oxidation state of positive three was observed in aqueous solutions for curium, which would be expected if one considers curium to be an actinide counterpart of gadolinium; each should have seven f electrons.

The absorption spectrum of curium in hydrochloric acid solution shows no absorption in the visible range (note the similarity to gadolinium) but it has a high absorption in the ultraviolet at 3300 A°.

Curium fluoride is insoluble in 3M hydrofluoric acid. Concentrated ammonia will convert the fluoride to the hydroxide, the latter being soluble in 0.1M hydrochloric acid. After this series of reactions, the solution was found to have lead as an impurity to the extent of approximately 10%.

References

1. L. B. Werner and I. Perlman, J. Am. Chem. Soc., 73, 5215 (1951).

SEPARATION OF LANTHANONS BY ION EXCHANGE

Philip A. Horrigan March 11, 1952

During World War II great emphasis was placed on the study of the lanthanons, which were produced in relatively large quantities in nuclear reactions. The problem, which necessarily preceded the others in this study, was the separation of these elements. The method of preferentially desorbing the lanthanons from the surface of an organic resin was soon discovered. Many articles were published on the early exploratory work (1-7) and since then, Dr. Spedding of Iowa State College has published a number of further articles dealing with the subject. This paper will treat only those articles published by Dr. Spedding within the last two years.

I. Studies with Amberlite IR-100 and a 0.5% Citrate Eluant (8)

1. Elution of pure Sm and pure Nd in pH range 3.80 to 4.20

It was observed that decreasing the pH increased the eluant volume; increasing the flow rate increased the volume.

2. Effect of temperature on elution of pure Sm at pH 3.80

The break-through volume increases from 0° to 25° C. but remains constant from 25° to 50°. The break-through volume also increased for increased flow rate.

3. Effect of particle size on elution of pure Nd at pH 3.80

Finer mesh (-60+80) particles brought about a quicker break-through volume than the larger mesh (-30+40).

4. Separation of Sm and Nd in pH range 3.80 to 4.20

pH of Eluant	Elution Vol.	% recovered 99.5% pure Sm_2O_3	% recovered 99.5% pure Nd_2O_3
4.20	161	81	79
4.00	27	90	96
3.80	50	96	96

It can be seen that decreasing the pH brings about better separation, although requiring a larger elution volume. It may be noted that, under the conditions of this experiment, 40 liters of eluate corresponds to 17 days of constant operation.

5. Separation of Nd and Pr in pH range 3.80 to 4.20

		% recovered 99.5% pure	
pH of Eluant	Elution Vol.	Nd_2O_3	Pr_6O_{11}
3.80	901	84	82
4.00	35	55	48
4.20	20	57	55

Again, decreasing pH improves the separation and increases the volume of eluant required.

II. Studies with Nalcite HCR and a 0.1% Citrate Eluant[9]

1. Effect of column length on separation of Nd from crude Nd_2O_3.

Increasing the column length gradually from 30 cm. to 60 cm. brought about great improvement in separation, but increases beyond this length caused no further improvement.

2. Effect of proportionate increase in column load and length on separation of Nd from crude Nd_2O_3

Starting with a bed length of 20 cm. and a load of 2.50 g. of R_2O_3, the % yield of pure Nd_2O_3 increased from 0% to 54.4% at a length of 80 cm. and a load of 10.00 g. Beyond this increase the % yield dropped (poor packing was suggested as the reason for this).

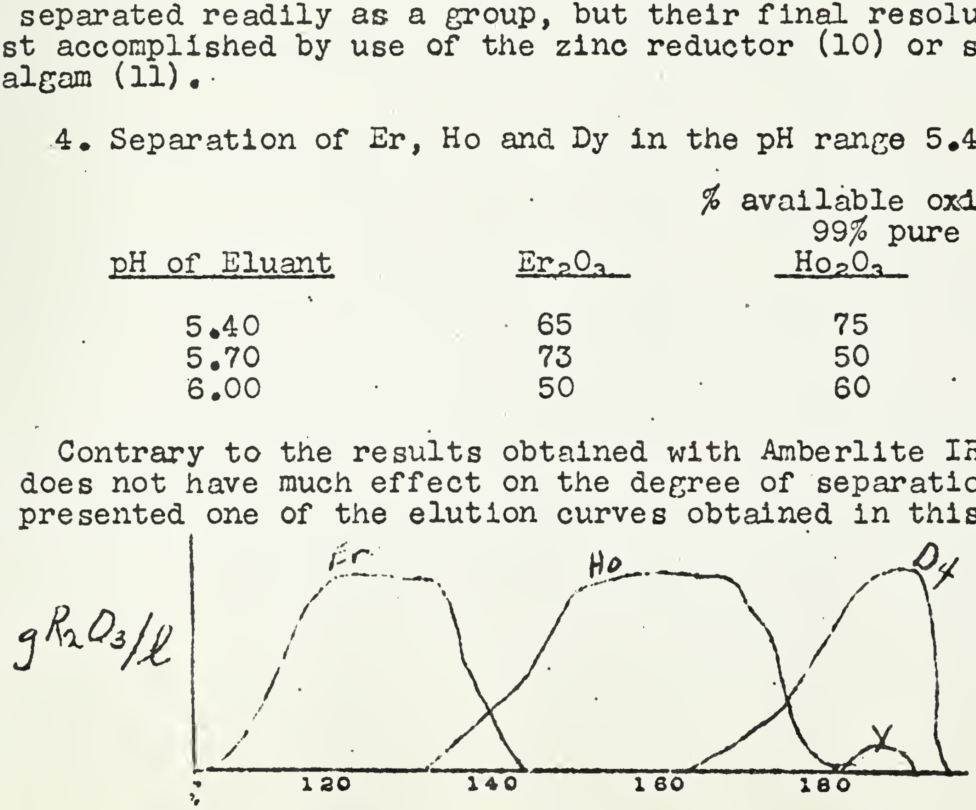
3. Separation of Sm and Eu in the pH range 5.80 to 6.20

Mixtures of Sm and Eu were eluted at pH values of 5.80, 6.00 and 6.20. Lowering the pH caused a greater eluate volume but resulted in no improvement in separation. Gd, Eu and Sm can be separated readily as a group, but their final resolution is best accomplished by use of the zinc reductor (10) or sodium amalgam (11).

4. Separation of Er, Ho and Dy in the pH range 5.40 to 6.00

	% available oxides 99% pure		
pH of Eluant	Er_2O_3	Ho_2O_3	Dy_2O_3
5.40	65	75	33
5.70	73	50	26
6.00	50	60	19

Contrary to the results obtained with Amberlite IR 100, the pH does not have much effect on the degree of separation. Below is presented one of the elution curves obtained in this experiment.



References

1. E. R. Tompkins, J. X. Khym, and W. E. Cohn, J. Am. Chem. Soc., 69, 2769-77 (1947).
2. F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, ibid., 2777-81.
3. F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, ibid, 2786-92.
4. D. H. Harris and E. R. Tompkins, ibid., 2792-2800.
5. B. H. Ketelle and G. E. Boyd, ibid., 2800-12.
6. F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, M. Gobush, P. E. Porter, J. E. Powell and J. M. Wright, ibid., 2812-18.
7. G. E. Boyd, L. S. Myers, Jr., and A. W. Adamson, ibid., 2849.
8. F. H. Spedding, E. I. Fulmer, T. A. Butler and J. E. Powell, ibid., 72, 2349 (1950).
9. F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and J. S. Yaffe, ibid., 73, 4840 (1951).
10. H. N. McCoy, ibid., 58, 2279 (1936); 63, 3432 (1941).
11. J. K. Marsh, J. Chem. Soc., 523 (1942); 531 (1943).

SOME RECENT ADVANCES IN THE CHEMISTRY OF THE HYDRIDES

Harold M. Foster March 4, 1952

INTRODUCTION

For the purpose of limiting the scope of this paper, a hydride will be defined as a stoichiometric compound containing a hydrogen to metal bond(1). Hydrides are generally classified into three principle groups:

(1) saline or salt-like hydrides
(2) metallic hydrides
(3) volatile or molecular hydrides.

At the present time two additional categories appear to be necessary:

(4) interstitial hydrides
(5) polymeric hydrides

A further classification into primary and complex hydrides may be useful.

Classification of Hydrides

Primary Hydrides	Name	Formula	Characteristics	Ref.
Saline	Sodium hydride	NaH	W. cryst., reacts violently with water.	2
	Calcium hydride	CaH_2	W. cryst.,reacts with water.	3
Metallic	Uranium hydride	UH_3	Brittle metallic pyrophoric powder, no react. with water.	1
	Zirconium hydride	ZrH_2	Brittle metallic powder, stable, no react. with water.	4,5
	Chromium hydride	CrH_3	Black powder, dissoc. at room temp.	6
Volatile	Silicon(silane) hydride	SiH_4	Colorless gas, odor strong, toxic.	1,7
	Tin(stannane) hydride	SnH_4	Colorless gas, odor toxic, dissoc. at room temp.	1,7
Interstitial	Palladium hydride	PdH_n	Gray, stable.	1
Polymeric	Aluminum hydride	$(ALH_3)_x$	W.powd., insol. in ether, reacts vigor. with water.	8,39

Complex Hydrides				
Saline	Sodium Borohydride	$NaBH_4$	W. cryst., no react. with water.	9
Volatile	Dimethyl aluminum hydride	$(CH_3)_2AlH$		11

There are four general methods which have been used for preparing hydrides:

(1) direct combination of the elements
(2) solvolysis of alloys or intermetallic compounds
(3) reaction of metallic halides with hydrogen in the presence of phenylmagnesium bromide
(4) various displacement reactions.

This paper will deal briefly with various aspects of these synthetic methods, with special emphasis on the recently reported investigations.

HYDRIDWS FORMED BY DIRECT COMBINATION OF THE ELEMENTS

The saline and the metallic hydrides are most generally prepared by direct combination of the elements. The recent advances which have been made are, for the most part, technological rather than chemical. For example a recent patent(12) indicates that alkali metal hydrides may be produced by treating the desired metal oxide with metallic aluminum in a reaction zone to reduce the alkali metal compound. The reduced alkali metal is distilled to a cooler part of the reaction chamber whence hydrogen is admitted to convert the metal to the hydride. A commercial grade of calcium hydride is prepared by heating a charge of magnesium pellets and calcium oxide in a reaction zone at 400° in an atmosphere of hydrogen(3).

Titanium and zirconium hydrides can be prepared by reacting an intimate mixture of the respective oxide with an excess of calcium hydride(5,13). The reaction is carried out above the dissociation temperature of the calcium hydride, and is, therefore, not a simple displacement reaction.

A recent report(14) indicates that magnesium hydride may also be prepared by the direct combination of the elements. If magnesium and hydrogen are heated together at 570° and 200 atmospheres in the presence of magnesium iodide, a 60% yield of magnesium hydride is said to result.

The saline hydrides have found limited use as reducing agents. For example, sodium hydride reduces sulfur dioxide to the hydrosulfite, $Na_2S_2O_4$ (2). The most important use of sodium hydride appears to be in the field of organic chemistry, where it has found wide application as an alkaline condensing agent. Calcium hydride is used as a source of hydrogen.

The metallic hydrides such as titanium hydride, zirconium hydride, thorium hydride, niobium hydride and tantalum hydride (produced and sold by Metal Hydrides, Incorporated) are stable at room temperature, and are nonhygroscopic. They can be preserved in air indefinitely. When heated in vacuum above 350°F. they decompose into pure hydrogen and free metal. The structure of these hydrides makes them especially suited for use in alloying operations.

HYDRIDES PRODUCED BY SOLVOLYTIC PROCEDURES

Various solvolytic procedures find limited application in the preparation of volatile hydrides. For example, acetylene is made by the hydrolysis of calcium carbide. One of the better methods developed for making silanes involves treatment of magnesium silicide with ammonium bromide in anhydrous liquid ammonia(15). Little work of significant nature has been accomplished recently, however.

HYDRIDES PREPARED BY REACTION OF THE METAL HALIDE, PHENYLMAGNESIUM BROMIDE AND HYDROGEN

This procedure has not found as widespread application as some of the other methods; nontheless, this method holds significant theoretical interest for it is the only presently known method for preparing stoichiometric hydrides of several of the transition elements. Nickel hydride, NiH_2, was prepared by treating dry powdered nickel chloride in ether with an etheral solution of phenylmagnesium bromide while passing hydrogen through the solution. The course of the reaction appears to be:

$$2\ C_6H_5MgBr + NiCl_2 \longrightarrow (C_6H_5)_2Ni + MgBr_2 + MgCl_2$$
$$(C_6H_5)_2Ni + 2\ H_2 \longrightarrow NiH_2 + 2\ C_6H_6$$

A small amount of biphenyl was detected among the products of the reaction. A cobalt hydride, CoH_2, an iron hydride, FeH_2, and a chromium hydride, CrH_3, were prepared by analogous reactions(6). These hydrides were produced in minute quantities and were not well characterized.

Some recent investigations of this procedure have conclusively demonstrated the existence of stoichiometric hydrides of nickel, cobalt, and iron(16,17,18). The latter workers isolated and characterized these hydrides.

A new hydride, FeH_3, was prepared by using ferric chloride instead of ferrous chloride.

$$2\ FeCl_3 + 6\ C_6H_5MgBr + 6\ H_2 \longrightarrow 2\ FeH_3 + 6\ C_6H_6 + 3\ MgBr_2 \\ 3\ MgCl_2$$

In studying the dissociation equilibria of these hydrides, the existence of various monohydrides was demonstrated.

$$2\ MH_n \rightleftharpoons 2\ MH + (n-1)\ H_2$$

Heats of formation were calculated from the dissociation pressure-temperature relationships (16,17,18).

Hydride	Dissociation Reaction	Transition Temperature-°C	Heat of Formation -cal per mole
NiH_2	$2\ NiH_2 \rightleftharpoons 2NiH + H_2$	54.8-56	7312
NiH	$2\ NiH \rightleftharpoons 2\ Ni + H_2$	>150	8835
CoH_2	$2\ CoH_2 \rightleftharpoons 2\ CoH + H_2$	44-45.8	9400
CoH	$2\ CoH \rightleftharpoons 2\ Co + H_2$	>150	12500

FeH_2	$2\ FeH_2 \rightleftharpoons 2\ FeH + H_2$	53-55.6	7178
FeH_3	$FeH_3 \rightleftharpoons FeH + H_2$	58-60.2	9365
FeH	$2\ FeH \rightleftharpoons 2\ Fe + H_2$	>150	10700

These hydrides were quantitatively decomposed by water and acid. With the nickel and cobalt hydrides the water acted merely as a catalyst.

$$MH_2 \xrightarrow{H_2O} M + H_2$$

The iron hydrides appeared to undergo more complete reaction.

$$FeH_2 + 2\ H_2O \longrightarrow Fe(OH)_2 + 2\ H_2$$

$$2\ FeH_3 + 4\ H_2O \longrightarrow 2Fe(OH)_2 + 5\ H_2$$

With acid, the reactions were more complete in all cases.

$$2\ MH_n + 4\ H^+ \longrightarrow 2\ M^{+2} + (n+2)\ H_2$$

The appearance of biphenyl among the products of these syntheses appears to be explicable in the light of some recent studies of the use of metal salts as catalysts in Grignard reactions(19).

HYDRIDES PREPARED BY DOUBLE DISPLACEMENT REACTIONS

The most recently developed method for preparing hydrides involves interaction of the respective metal halide or alkyl with a metal hydride such as lithium hydride, lithium aluminum hydride, sodium borohydride, and diborane, Several of these reagents will be discussed in some detail.

(1) <u>Diborane and borohydrides as hydrogenating agents</u>- Aluminum borohydride, beryllium borohydride, and lithium borohydride were originally prepared by interaction of diborane with the respective metal alkyl(20,21,22), <u>e.g.</u>,

$$4\ B_2H_6 + Al_2(CH_3)_6 \longrightarrow 2\ Al(BH_4)_3 + 2\ B(CH_3)_3$$

These compounds are more easily prepared by reaction of sodium borohydride with the respective metal halide(9), <u>e.g.</u>,

$$2\ NaBH_4 + BeBr_2 \longrightarrow Be(BH_4)_2 + 2\ NaBr$$

More recently a series of heavy metal borohydrides were prepared by reaction of the heavy metal compound with aluminum borohydride or lithium borohydride(23), <u>e.g.</u>,

$$NaHfF_5 + 2\ Al(BH_4)_3 \longrightarrow Hf(BH_4)_4 + 2\ AlF_2BH_4 + NaF$$

Another recent report(24) indicates that magnesium hydride may be prepared by reaction of excess diethylmagnesium with diborane.

$$3\ Mg(C_2H_5)_2 + B_2H_6 \longrightarrow 3\ MgH_2 + 2\ (C_2H_5)_3B$$

The use of excess diborane results in the formation of magnesium borohydride(40).

$$3\ Mg(C_2H_5)_2 + 4\ B_2H_6 \longrightarrow 3\ Mg(BH_4)_2 + 2\ (C_2H_5)_3B$$

Hydride	Starting Material	Hydrogenating Agent	Properties	Ref.
$Al(BH_4)_3$	$Al_2(CH_3)_6$	B_2H_6	m.p.,-64.5;b.p.,44.5; very reactive,inflam. spontan.in air, readily hydrolyzed.	20
	$AlCl_3$	$NaBH_4$		9
$Be(BH_4)_2$	$[Be(CH_3)_2]n$	B_2H_6	m.p.,123;b.p.,91.3:, very reactive,inflam. spontan.in air,readily hydrolyzed.	21
	$BeBr_2$	$NaBH_4$		9
$LiBH_4$	LiC_2H_5	B_2H_6 $Al(BH_4)_3$	d.,275;stable in dry air;salt-like; readily hydrolyzed	22
MgH_2	$Mg(C_2H_5)_2$	B_2H_6	d.,280-300;stable in dry air; readily hydrolyzed	24
$Mg(BH_4)_2$	$Mg(C_2H_5)_2$	B_2H_6	W.solid,insoluble in ether; readily hydrolyzed	40
$Th(BH_4)_4$	ThF_4	$Al(BH_4)_3$	m.p.,203;very salt-like;stable in dry air;similar to $NABH_4$	23
$Hf(BH_4)_4$	$NaHfF_5$	$Al(BH_4)_3$	m.p.,29;b.p.,118; moderately stable	23
$Zr(BH_4)_4$	$NaZrF_5$ $ZrCl_4$	$Al(BH_4)_3$	m.p.,28.7;b.p.,123; less stable than Hf analog	23
$Ti(BH_4)_3$	$TiCl_4$	$LiBH_4$	green solid,very unstable	23
$TiCl(BH_4)_2$	$TiCl_4$	$Al(BH_4)_3$	blue solid,unstable	23

(2) Lithium aluminum hydride as a hydrogenating agent-

A recent report(11) indicates that the relatively unknown hydrides of zinc, cadmium, beryllium, and magnesium can be prepared by reaction of an ethereal lithium aluminum hydride solution with an ethereal solution of the respective metal alkyl, *e.g.*,

$$Zn(CH_3)_2 + 2\ LiAlH_4 \xrightarrow{\text{ether}} ZnH_2 + 2\ LiAlH_3CH_3$$

Investigations of reactions of metal halides and alkyls with lithium aluminum hydride have led to the discovery of a large number of hitherto unknown hydrides and aluminohydrides. The rather considerable amount of work is best summarized in tabular form.

Hydride	Starting Material	Properties	Ref.
MgH_2	$Mg(C_2H_5)_2$	W. solid, insol. in ether, readily hydrol. obtained impure	11
BeH_2	$Be(CH_3)_2$	W. solid, insol. in ether, reacts violently with water, obtained impure	11
ZnH_2	$Zn(CH_3)_2$	W. solid, reacts violently with water, insol. in ether, stable at room temp.	11
	ZnI_2		25
CdH_2	$Cd(CH_3)_2$	W. solid, insol. in ether, decomposes at -20°, reacts violently with water	11
	CdI_2		26
HgH_2	HgI_2	W. solid, insol. in ether, decomposes at -125°	27
$Mg(AlH_4)_2$	$MgBr_2$	Soluble in ether, reacts quantitatively with water, very similar to $LiAlH_4$	28
$MgC_2H_5(AlH_4)$	C_2H_5MgBr	Not characterized	28
$Ga(AlH_4)_3$	$GaCl_3$	Soluble in ether; decomposes at 0°	30
$InCl_2(AlH_4)$	$InCl_3$	Insoluble in ether; stable up to 100°; salt-like	31
$In(AlH_4)_3$	$InCl_3$	Insoluble in ether; decomposes at -40°	31
$Al(AlH_4)_3$	$AlCl_3$	Soluble in ether; polymerizes readily to ether insoluble product	8
$Be(AlH_4)_2$	$BeCl_2$	Soluble in ether; readily hydrolyzed	29
$Sn(AlH_4)_4$	$SnCl_4$	Insoluble in ether; decomposes at -40°	32
$Ti(AlH_4)_4$	$TiCl_4$	Insoluble in ether; decomp. at room temp.	33

(3) Aluminum hydride as a hydrogenating agent-
Aluminum hydride is best prepared by treating an ether solution of aluminum chloride with lithium aluminum hydride(8).

$$3\ LiAlH_4 + AlCl_3 \longrightarrow Al(AlH_4)_3 + 3\ LiCl$$

The initially formed hydride is soluble in ether and may be easily freed from the ether insoluble lithium chloride. Aluminum

hydride readily polymerizes to an ether insoluble form. Addition of aluminum chloride prevents polymerization presumably by formation of an addition compound.

$$Al(AlH_4)_3 + 4\ AlCl_3 \longrightarrow 4\ AlH_3 \cdot AlCl_3$$

This addition compound has been used to prepare an indium and a thallium aluminum hydride, e.g. ,

$$TlCl_3 + 4\ AlH_3 \cdot AlCl_3 \longrightarrow Tl(AlH_4)_3 + 5\ AlCl_3$$

The existence of other halide derivatives of aluminum hydride has been demonstrated. Compounds having the empirical formulae $AlHI_2$(37), AlH_2I(37), $AlHBr_2$(38), AlH_2Br(38), and $AlHCl_2$(39) have been prepared and characterized.

Empirical Formula	Molecular Weight in Ether	Characteristics in Free State	Ref.
$AlCl_3 \cdot AlH_3$	159	Colorless liquid; b.p., 95°	8,39
$AlHI_2$	270	Colorless crystals; dimeric; m.p., 80° b.p.,110° in high vacuum	37
AlH_2I	154	Colorless crystals; dimeric; m.p.,35° disproportionates on heating	37
$AlHBr_2$	189	Colorless mobile oil;dimeric; m.p.,15° b.p., 95° in vacuum	38
AlH_2Br	110	Colorless liquid; dimeric; disproportionates above 35°	38
$AlHCl_2$	118	Not Characterized	39

(4) Lithium gallium hydride as a hydrogenating agent-
Lithium gallium hydride is best prepared by treating an ether solution of gallium chloride with excess finely pulverized lithium hydride(35).

$$GaCl_3 + 4\ LiH \longrightarrow LiGaH_4 + 3\ LiCl \quad (95\%\text{yield, } 99\%\text{ pure})$$

Lithium gallium hydride is a much less reactive reagent than is lithium aluminum hydride; a thallium gallium hydride has been prepared(36).

$$3\ LiGaH_4 + TlCl_3 \longrightarrow Tl(GaH_4)_3 + 3\ LiCl$$

MISCELLANEOUS HYDRIDES:

(1) Magnesium hydride- Magnesium hydride has been prepared by the pyrolysis of diethylmagnesium(34).

$$Mg(C_2H_5)_2 \longrightarrow MgH_2 + 2\ C_2H_4$$

(2) Copper hydride- A copper hydride, CuH, has been prepared by reduction of copper sulfate with sodium hypophosphite(34).

$$2\ Cu^{+2} + 3\ H_2PO_2^{-1} + 3\ H_2O \longrightarrow 2\ CuH + 3\ H_3PO_3 + H^{+1}$$

Copper hydride is stable to hydrolysis. Its heat of formation is -5120 calories per mole.

BIBLIOGRAPHY

1. Gibb, Trans. Electrochem. Soc., 93, 198-211 (1948).
2. Anon., Bulletin 507A, Metal Hydrides, Incorporated.
3. Archibald and Alexander, U.S. 2,401,326,June 4,1946 [C.A.,40, P5213 (1946)]
4. Davis, U.S. 2,411,524, November 26, 1946[C.A.,41, P575 (1947)]
5. Alexander, U.S. 2,427,339, September 16,1947[C.A.,42,P332 (1948)]
6. Weichselfelder, Ann., 447, 64 (1926)
7. Finholt, Bond and Schlesinger, J.Am.Chem.Soc.,69,1199 (1947).
8. Wiberg and Schmidt,Z. Naturforsch., 6b, 333-4 (1951).
9. Anon.,Bulletin 502A, Metal Hydrides, Incorporated.
10. Anon.,Bulletin 401A, Metal Hydrides, Incorporated.
11. Barbaras, Dillard, Finholt, Wartik, Wilzbach, and Schlesinger, J. Am. Chem. Soc., 73, 4585 (1951).
12. Alexander, U.S. 2,401,323, June 4, 1946 [C.A.,40, P5212 (1946)]
13. Alexander, U.S. 2,427,338, September 16, 1947[C.A.,42, P332(1948)]
14. Wiberg, Goltzer, and Bauer, Z. Naturforsch.,6b, 394-5 (1951).
15. Johnson and Hogness, J. Am. Chem. Soc., 56, 1252 (1934).
16. Sahai and Ray, J. Indian Chem. Soc., 20, 213 (1943).
17. Sahai and Ray, J. Indian Chem. Soc., 23, 61 (1946).
18. Sahai and Ray, J. Indian Chem. Soc., 23, 67 (1946).
19. Urry and Kharasch, J. Am. Chem. Soc.,66, 1438 (1944).
20. Schlesinger, Sanderson and Burg, J. Am. Chem. Soc.,62,3421 (1940).
21. Burg and Schlesinger, J. Am. Chem. Soc., 62, 3429 (1940).
22. Schlesinger and Brown, J. Am. Chem. Soc., 62, 3429 (1940).
23. Hoekstra and Katz, J. Am. Chem. Soc., 71, 2488 (1949).
24. Wiberg and Bauer, Z. Naturforsch., 5b, 396 (1950).
25. Wiberg, Henle and Bauer, Z. Naturforsch., 6b, 393 (1951).
26. Wiberg and Henle, Z. Naturforsch., 6b, 461 (1951).
27. Wiberg and Bauer, Z. Naturforsch., 6b, 461-2 (1951).
28. Wiberg and Bauer, Z. Naturforsch., 5b, 397-8 (1950).
29. Wiberg and Bauer, Z. Naturforsch., 6b, 171 (1951).
30. Wiberg and Schmidt, Z. Naturforsch., 6b, 172 (1951).
31. Wiberg and Schmidt, Z. Naturforsch., 6b, 172-3 (1951).
32. Wiberg and Bauer, Z. Naturforsch., 6b, 392 (1951).
33. Wiberg and Uson, Z. Naturforsch., 6b, 392-3 (1951).
34. Sieverts and Gotta, Ann., 453, 289 (1927).
35. Wiberg and Schmidt, Z. Naturforsch., 6b, 171-2 (1951).
36. Wiberg and Schmidt, Z. Naturforsch., 6b, 335 (1951).
37. Wiberg and Schmidt, Z. Naturforsch., 6b, 458-9 (1951).
38. Wiberg and Schmidt, Z. Naturforsch., 6b, 459-460 (1951).
39. Wiberg and Schmidt, Z. Naturforsch., 6b, 460-1 (1951).
40. Wiberg and Bauer, Z. Naturforsch., 5b, 397 (1950).

Ernest H. Lyons, Jr. March 4, 1952

Cyanide Complexes of Cobalt (II). Adamson, J. Am. Chem. Soc. 73, 5710 (1951). -- In solution, cobaltous ion reacts with only five cyanide ions, and gives a solid of composition $K_3Co(CN)_5$. It has been assumed that the complex ion actually contains a coordinated aquo group. The solid is diamagnetic, but the solution in excess KCN is paramagnetic and indicates an unpaired electron. Incorporation of the aquo group (or of a sixth cyanide) into the coordination sphere would require promotion of the unpaired electron. It is believed that this does not occur, for the following reasons:
1- no other instance of hexacovalent cobalt II has been recognized;
2- the instability expected of a promoted electron is not exhibited;
3- by analogy with Mn, Fe, and Co (III), the hexacyano complex should be as stable as the pentacyanoaquo complex; 4- $[Co^{III}(CN)_5H_2O]^{-2}$ undergoes a two electron reduction at the dropping mercury electrode, indicating that the corresponding cobalt II ion is not stable; 5- the cobalt (II) complex exchanges rapidly with radioactive cyanide ion, suggesting pentacovalency because exchange is slow with a number of hexacyanides, and rapid with tetracyanides. It is suggested that the pentacyano complex exhibits ionic type of bonding. The structure of the solid may be dimeric.

A REVIEW OF THE RUSSIAN CONCEPT OF CHEMICAL STRUCTURAL THEORY

Niels C. Nielsen February 26, 1952

At the request of the All-Union Communist Party and the All-Union Lenin Academy of Agricultural Sciences, Russian scientists have been requested to examine the present state of Chemical structural theory. The result of this examination has been reported (1) and two conclusions have been reached:

1. The only true and correct theory of chemical structure is that proposed the famous Russian chemist, Butlerov.
2. The theory of resonance, so completely accepted by scientists on both sides of the political fence, is not a true representation of the structure of molecules.

Butlerov, who has suddenly become the father of modern structural chemistry, is mentioned in a German history of chemistry published in 1873.(2) At that time his name was coupled with that Erlenmeyer as having contributed to the knowledge of chemical structure at that time. Mendeleev's text mentioned Butlerov in three footnotes. (3) Western science is more familiar with the work of Buterov's student, Markonikov. No major book on chemical structure, either Russian or Western, mentions Butlerov's work.

The theory of chemical structure, as stated by Buterov, is based on two tenets:

1. Chemical structure of molecules is real.
2. Chemical properties are caused by chemical structure.

After stating that each atom in a molecule exerts a chemical force, Butlerov continues

> "I designate as chemical structure the distribution of the action of this force by which the chemical atoms, indirectly or directly influencing one another, are united into a chemical particle."

One important fact is inherent in these statements. There is only one rational formula possible for each compound and this formula will represent all of the properties of that compound. It is also obvious that it would be incorrect to think that the idea of chemical structure and the method of writing structural formulas are equivalent. As Butlerov says, "What matters is not the form but the essence, the concept, the idea."

Most scientists today have interposed the theory of resonance between the"forms" for depicting chemical structure and the true Butlerovian "idea" of chemical structure. This has resulted in the virtual elimination of the "idea" and led to a tendency to replace Butlerov's concept of chemical structure by the structural formulas themselves. In addition, there has developed a mathematical fetishism leading to the creation of a concept of "quantum-mechanical resonance structures." Psi represents the real state of a molecule and is approximately represented by a sum of psi functions to each member of which is ascribed the meaning of a definite chemical structure. The resonance of these structures then produces the real state of the molecule.

> "These structures are considered as though they existed; in the words of the theory of resonance, in each molecule they 'are in a state of superposition'. When different structures are superimposed, there is formed a

> transitional structure which here plays an essential part, as it does in the hydrogen molecule, by causing a lowering of energy.... The only reason for introducing a transitional structure is the fact that, in the square of the binomial expression Ψa and Ψb, there appears the term $2\Psi a\Psi b$." The basic assertion of the resonance theory that 'resonance' in some way can determine the properties of molecules is devoid of meaning."

We get further away from reality by accepting these resonance structures and introducing physical concepts based upon them, such as:

1. Resonance energy: a certain specific energy which has its source in resonance structures.
2. Reactivity of certain compounds resulting from a single resonance structure.

The Butlerovian theory of chemical structure gives us the true concept. The resonance theory, on the other hand, gives us forms for picturing molecular structure, but, in doing so, it replaces the real "idea" of chemical structure and leaves us with a picture which does not agree with reality. The problem, then, is to find a method of representing structural formulas which will properly indicate Butlerov's idea of molecular structure. Present suggestions are not accurate, but

> "there is no doubt that Soviet chemists educated in the great traditions of the Russian Chemical science founded by Lomonosov, Butlerov, and Mendeleev, armed with the Marxist-Leninist world outlook, and guided by the great party of Lenin-Stalin will successfully attain the objectives before them."

Bibliography

1. D. N. Kursanov, M. G. Gonikberg, B. M. Dubinin, M. I. Kabachnik, E. D. Kaverzneva, E. N. Prilezhaeva, N. D. Sokolov, and R. Kh. Freidlina, Uspekhi Khimii 19, 529-544 (1950). Translated by I. S. Bengelsdorf, J. Chem. Education 29,1-13(1952).

2. H. Kopp, "Die Entwickelung der Chemie in der neueren Zeit" Munich, 1873. page 831.

3. Mendeleev, "Prinicples of Chemistry", 3rd English Edition, Translated by G. Kamensky, Edited by T. H. Pope. 1905. Vol. I, page 392; Vol. II, pages 11, 168.

ADDENDUM

A biographt appearing in the Journal of Chemical Education 17, 203 (1940) indicates that Butlerov was widely known and respected by his contemporaries. In 1876, he was elected an honary member of the American Chemical Society. In addition to studying numerous compounds and reactions in organic chemistry, Bulterov is noted for his theoretical approach to organic chemistry and is credited with the first use of the term "chemical structure" in this field.

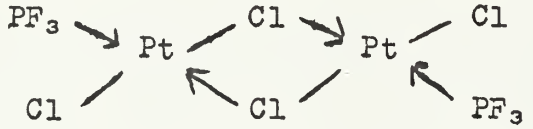
COORDINATION COMPOUNDS CONTAINING GROUP V HALIDES

Robert H. Marshall March 18, 1952

Recent investigations have been carried out with the intent of clarifying the nature of the coordinate link. This work has included the syntheses and characterization of several complexes which contain phosphorus trihalides as ligands. The preparation and properties of some of these compounds will be discussed.

COMPLEXES OF PHOSPHORUS TRIFLUORIDE WITH PLATINUM

Chatt and Williams found that two products may be obtained by passing phosphorus trifluoride through a plug of platinum (II) chloride at 200-220° (1). With an excess of phosphorus trifluoride, bis(trifluorophosphine) platinum (II) chloride, $(PF_3)_2PtCl_2$, is formed as colorless crystals which melt to a very pale yellow liquid at 102°. In a slow stream of gas some of this dichloride is formed, but in addition orange-yellow crystals are obtained which melt to a red liquid at 155-56°. This compound is apparently the dimeric bis(trifluorophosphine)-μ,μ'-dichlorodiplatinum (II) chloride with the probable structure



Refluxing the dichloride at 240° converts it into the tetrachloride which in turn decomposes at 285°. The tetrachloride can be distilled without decomposition at reduced pressures. Both compounds are readily hydrolyzed by water to give clear solutions which probably contain the corresponding phosphorous acid derivatives.

The dichloro compound was found to have a dipole moment of 4.4 D as contrasted to an expected moment of about 8-9 D for the *cis*-isomer. The authors suggest two explanations: 1) there may be an equilibrium mixture of *cis*- and *trans*- isomers in the benzene solution, or 2) there may be a large neutralization of the Pt-P coordinate link by an opposing drift of *d*-electrons from the metal.

The above evidence is in direct support of a theory that two distinct methods of coordination are possible: 1) the classical coordinate link involving an electron pair from a donor atom, and 2) an essentially covalent link, involving also filled *d*-orbitals of the acceptor atom and unfilled orbitals of the donor atom. This link is much less polar than the first, and is displayed particularly in complexes with platinum (II) and metals with zero valency. Chatt has suggested that such a link be called a "dative double-bond" (2).

There is additional evidence for bonding of the second type with certain metals.

1. Since d-orbitals are in planes at right angles to each other, it is only in the *cis*-isomer that different d-orbitals are available to bind each molecule of ligand. Use of phosphorus trifluoride as the ligand gives a much larger percentage of *cis*-isomer than the alkyl phosphines. Fluorine is much more electronegative than the alkyl group and thus d-orbitals must play a more significant part in binding phosphorus trifluoride than in binding alkyl phosphines to platinum.

2. Boron trifluoride is one of the strongest acceptor molecules known, yet it shows no tendency to combine with phosphorus trifluoride (3). Here there are no filled d-orbitals in the metal atom. With phosphorus trichloride the electron pair is less tightly held and the complex $BF_3 \cdot PCl_3$, decomposing at -6°, has been reported (4).

3. Ligands which show the greatest *trans* effect, e.g., PF_3, CN, C_2H_4, CO, NO_2, and PR_3, are those that possess vacant orbitals. The *trans* influence cannot be due only to an inductive effect, because the fluorine atoms of phosphorus trifluoride would lead to increased attachment of other ligands rather than a decrease.

4. Phosphorus trifluoride complexes with hemoglobin in a manner similar to that of carbon monoxide, but nitrogen trifluoride does not form the complex (5). This is attributed to the absence of vacant 2d-orbitals in the nitrogen atom.

COMPLEXES OF PHOSPHORUS TRIHALIDES WITH NICKEL

In 1936 Blanchard of MIT predicted that phosphorus trichloride should form a volatile analog of nickel tetracarbonyl. Preliminary attempts to prepare it by the reaction of phosphorus trichloride on finely divided nickel failed. However, tetrakis (trichlorophosphine) nickel, $Ni(PCl_3)_4$, has recently been prepared by direct action in the liquid phase of phosphorus trichloride on nickel tetracarbonyl (6). The phosphorus tribromide derivative could not be obtained by a similar method, but it has been prepared in 60% yield by warming $Ni(PCl_3)_4$ in phosphorus tribromide (7). A 50% yield of $Ni(PF_3)_4$ was obtained by treating either $Ni(PCl_3)_4$ or $Ni(PBr_3)_4$ with phosphorus trifluoride in a sealed tube at 50 to 100 atmospheres and 100° (7).

A summary of the properties of these derivatives is presented in Table 1.

TABLE I

	$Ni(PF_3)_4$	$Ni(PCl_3)_4$	$Ni(PBr_3)_4$
Appearance	Colorless, odorless, mobile and volatile liquid.	Thermochroic crystals, pale yellow at room temp., white at -30°.	Thermochroic crystals, deep orange-red at room temp., very pale yellow at -38°.
Physical constants	Density 1.800± 0.001 at 25° m.p. -55.0± 0.5° b.p. 70.7± 0.3° at 760 mm.	Decomp. thermally above 120°.	Decomp. thermally at about 80°.
Stability in water	Can be steam distilled with little hydrolysis.	Stable	Slow decomp.
Stability in cold mineral acids	Stable	Reacts very slowly	Decomp. in several hours.
Stability in hot mineral acids	Conc. H_2SO_4 causes decomp. to $NiSO_4$	Rapid decomp.	Probably very rapid decomp.
Stability in ammonium hydroxide	Rapid decomp. to give brown sol., warming causes reduction to metallic Ni	Reacts readily to give brown sol.	Not mentioned.
Stability in sodium hydroxide sol.	Yellow ppt. which reduces to Ni upon heating, and yields sol. of sodium phosphite	Reacts slowly to give a black ppt. and solution of sodium phosphite	Rapid decomp. to give brown ppt. of undetermined comp. and a sol. of sodium phosphite
Stability in inert solvents, room temp.	Soluble, no reaction	Soluble, very slow decomp.	Soluble, rapid decomp. to form pale yellow or white ppts. of undetermined comp.

Table I (continued)

	$Ni(PF_3)_4$	$Ni(PCl_3)_4$	$Ni(PBr_3)_4$
Stability in hot inert solvents	Not mentioned	Rapid decomp., black ppt. of Ni	Immediate blackening
Stability in oxygen containing organic solvents	Reacts to give colorless solution with hot ethanol	Rapid decomp, green and brown solutions	Rapid decomp.
Stability in carbon disulfide	No reaction	Rapid blackening	Not mentioned

$Ni(PF_3)_4$ has still other properties that are of interest (7). The vapor explodes forming metallic Ni when it is ignited in air or oxygen. There is no attack upon glass or mercury but the compound is slowly oxidized by strong oxidizing agents. Iodine slowly reacts with $Ni(PF_3)_4$ to give nickel iodide, and bromine reacts vigorously to give nickel bromide and probably phosphorus dibromotrifluoride. Heating the compound with phosphorus tribromide gives a volatile yellow compound, probably $Ni(PF_3)_3(PBr_3)$. Warm pyridine reacts to give a greenish-blue precipitate which is probably a partially substituted compound.

Wilkinson explains that the decreasing stability of $Ni(PX_3)_4$ from phosphorus trifluoride to phosphorus tribromide is probably due mainly "to decreasing availability of stable orbitals in the phosphorus atom and a consequent increase in the polar nature of the Ni-P bond"(7).

RELATED REACTIONS OF GROUP V HALIDES WITH CARBONYLS

Nickel tetracarbonyl reacts readily with arsenic trifluoride, arsenic trichloride, and arsenic tribromide in both liquid and vapor phases with the liberation of carbon monoxide (6). Black products are formed but they have not been identified.

Wilkinson has also reported that the interaction of nickel tetracarbonyl with excess antimony trichloride in cyclohexane solution gives a pale buff precipitate (8). Analyses indicate it to be $Ni(CO)_3(SbCl_3)$. A similar reaction between iron pentacarbonyl and antimony trichloride in benzene solution gives a pale yellow precipitate that appears to be $Fe(CO)_3(SbCl_3)_2$. Both of these compounds are photosensitive and darken upon exposure to light.

Phosphorus trichloride has been shown to react with molybdenum, tungsten, and chromium hexacarbonyls at temperatures up to 150° but no replacement compounds have been isolated (6). The products obtained appear to be mainly the metal phosphides.

REFERENCES

1. J. Chatt and A. A. Williams, J. Chem. Soc., <u>1951</u>, 3061.
2. J. Chatt, Nature <u>165</u>, 637 (1950).
3. H. S. Booth and J. H. Walkup, J. Am. Chem. Soc. <u>65</u>, 2334 (1943).
4. H. Baumgarten and W. Bruns, Ber. <u>80</u>, 517 (1947).
5. G. Wilkinson, Nature <u>168</u>, 514 (1951).
6. J. W. Irvine, Jr., and G. Wilkinson, Science <u>113</u>, 742 (1951).
7. G. Wilkinson, J. Am. Chem. Soc. <u>73</u>, 5501 (1951).
8. G. Wilkinson, J. Am. Chem. Soc. <u>73</u>, 5502 (1951).

VALENCE INDUCTIVITY

Stanley Kirschner March 25, 1952

Discussion:

While investigating the relationship between the magnetic properties and catalytic properties of transition metal compounds, Selwood and his co-workers noticed an interesting effect which took place when paramagnetic transition metal oxides were supported on diamagnetic substrates. If, for example, manganous nitrate is oxidized thermally, the usual oxidation product is MnO_2. However, if the $Mn(NO_3)_2$ is supported in low concentration on a diamagnetic γ-alumina substrate of high surface area (200 $m^2/g.$), and is then oxidized, the product contains manganese in the tri-positive oxidation state as Mn_2O_3. If the $Mn(NO_3)_2$ is supported instead on a high area rutile (TiO_2), and is then thermally oxidized, the resulting material is entirely pyrolusite (MnO_2), even at very low concentrations of manganese. These results suggest that the manganese oxide produced tends to assume the crystal structure of the support, even to the extent of an alteration of the usual oxidation state of the manganese (6,8).

The term Valence Inductivity has been offered by Selwood and his associates as a name for this phenomenon, and it is defined as ".... an induced change of valence brought about when a transition group ion is supported on a high area surface with which it may become isomorphous...." (6).

The same effect has been noted for other paramagnetic transition metal oxides. For example, if $Ni(NO_3)_2$ in low concentration is oxidized thermally on a high area magnesia (MgO) support, NiO is the product; if this is done on a high area γ-alumina (Al_2O_3), Ni_2O_3 results; and, if high area rutile (TiO_2) is used, there are indications that NiO_2, nickel in the tetra-positive state, occurs (6,1).

However, neither copper nor silver tends to assume a tri-positive oxidation state on γ-alumina, and it appears that this effect of Valence Inductivity is shown only when the supported positive ion may fairly readily assume a charge and radius similar to that of the supporting ion (6,10). A recent investigation (11) has shown that this Valence Inductivity phenomenon is not restricted in the case of alumina to the gamma form, but that any form may be used provided the area is kept large.

Another element exhibiting this effect is iron, which will tend to form in the tetra-positive state as FeO_2 if supported in low concentration on rutile; and this resulting oxide may even be used successfully in place of MnO_2 as a depolarizer in the Leclanché dry cell (9).

Theoretical:

The above discussion is somewhat over-simplified and needs additional refinement with regard to (1) the theories and methods used in the determinations of the oxidation states of the supported oxides, (2) the explanations offered to account for the appearance of the Valence Inductivity effect with certain transition metal oxides (e.g., the oxides of Fe, Ni, and Mn), and (3) the explanations offered for the apparent absence of the Valence Inductivity effect in the case of certain other elements (e.g., Cu, Ag and Mo).

1. Concerning the determination of the oxidation states of the elements, Selwood and his co-workers made use of the paramagnetic susceptibilities of these transition group metals (3,4). For paramagnetic elements, the magnetic moment (μ_{eff}) of an ion can be determined by using the equation:

$$(a) \quad \mu_{eff} = \sqrt{\frac{3k X_m T}{N\beta^2}} = 2.83 \sqrt{X_m T}$$

where X_m is the molar magnetic susceptibility (which can be determined experimentally by several methods (3), T is the absolute temperature, and 2.83 is the calculated value of

$$\sqrt{\frac{3k}{N\beta^2}}$$

where k is the Boltzman constant, M is Avogadro's number, and β is the Bohr Magneton ($\beta = 0.917 \times 10^{-20}$ ergs/oersted). (The above equation (a) is often given as:

$$(b) \quad \mu_{eff} = 2.83 \sqrt{X_m (T + \Delta)}$$

where Δ is an empirical constant which is added to the temperature. The latter equation sometimes gives better results than (a).) In addition, the magnetic moment (μ) is related to the number of unpaired electron spins by:

$$(c) \quad \mu_{eff} = \sqrt{n (n + 2)}$$

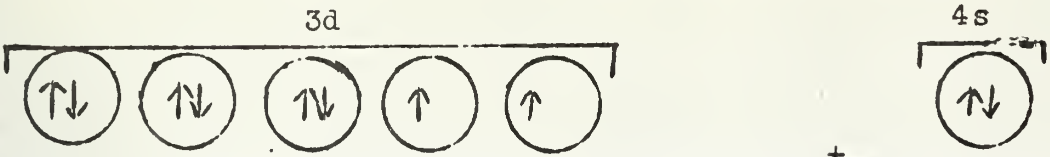
where n is the number of unpaired electron spins in an ion. Thus, by measuring the paramagnetic susceptibility of a compound at a known temperature, one may determine the magnetic moment of the compound, from which one can evaluate the number of unpaired electron spins in an ion by:

$$(d) \quad \mu_{eff} = \sqrt{X_m T} = \sqrt{n (n + 2)}$$

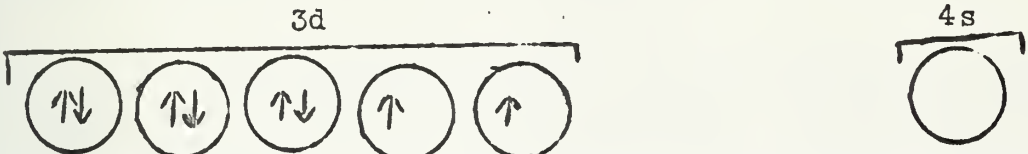
This is known as the "spin-only" formula, because all factors influencing the paramagnetic susceptiblity other than the unpaired electron spins are neglected; but, it nevertheless applies quite well in many cases (4,5).

With a knowledge of both the number of unpaired electrons and of the extra-nuclear structure of an atom, one can often determine the oxidation state of the atom. For example, in the case of nickel, if μ_{eff} were found to be 2.8 for a nickel compound, the number of unpaired electrons (from c) would be two, and, since the nickel atom has the following configuration for its outermost

electronic sub-shells (2), it is seen that the nickel in the com-



pound must be in the di-positive state as Ni^{+2} because this is the only state in which two unpaired electrons exist:



That this effect occurs frequently may be seen by a comparison of the calculated and observed magnetic moments determined from compounds of known oxidation state, as shown in the following table (5)

Ion	No. of unpaired electrons	Calculated Moment	Observed Moment
Cr^{+3}	3	3.87	3.8
Mn^{+2}	5	5.92	5.9
Fe^{+3}	5	5.92	5.9
Cu^{+2}	1	1.73	1.8
Mo^{+3}	3	3.87	3.7

However, this agreement (based on values calculated from equation d) is obtained only when the compounds examined are magnetically "dilute" (5), that is, the paramagnetic ions are far apart and exert little influence upon each other. Chromic sulfate hydrate would be an example of a magnetically dilute compound, while chromia (Cr_2O_3) is a magnetically concentrated compound, and the observed magnetic moment of chromia is much lower than the value calculated on the basis of the "spin-only" equation. However, if the chromia is deposited on γ-alumina, it is found that ".... the magnetic properties of a supported transition group oxide approach those of the same element at high magnetic dilution", that is, increased magnetic susceptibility results (5,7).

In addition to this magnetic method of determining oxidation states, Selwood and his associates also used chemical methods (8). These consisted of independently determining both the positive ion and the oxygen in the supported oxides by chemical wet methods (e.g., hydrogen reduction of NiO to determine oxygen; Mohr's salt titration to determine Mn in manganese oxides after oxidation of the manganese to permanganate by bismuthate, etc.) (8). Wherever possible similar chemical wet methods were used to support magnetic determinations of the oxidation states. Pronounced differences in color were also taken as supporting evidence of the formation of a different compound. For instance, NiO is black, while the tri-positive nickel oxide, Ni_2O_3, is pale blue (6), and the compound believed to be the tetrapositive oxide of nickel (NiO_2) is bright yellow in color (1).

2. Concerning the nature of the Valence Inductivity effect itself, Selwood interpreted his data to represent a situation in which the paramagnetic metal oxide is induced to deposit with a crystal structure similar to that of the supporting diamagnetic oxide, even to the extent of changing its usual oxidation state (6). This is probably more easily accomplished by the transition elements than by the representative elements because the former more readily undergo changes in oxidation state because of the relatively low energy involved in d shell transitions.

In addition, Selwood notes that the supported oxide must be present in low concentrations, or else the Valence Inductivity effect does not seem to take place (6). He has determined that deposition takes place with the probable formation of small clusters of the supported oxide, from two to four atoms deep, before the entire surface of the substrate is covered (1), and he declares that the low concentration is necessary because a supported ion which is not in its usual oxidation state will have a smaller inductive effect (with regard to orienting the molecules which deposit on top of it) than the diamagnetic substrate ion which is in its usual valence state; and, if the supported oxide should deposit rapidly and in large quantity, there is a possibility that the outer layers of the oxide will deposit in the usual oxidation state of the metal, rather than in the induced oxidation state (8). For example, in the case of iron oxide depositing on rutile (1), the most dilute sample gives iron in the oxidation state nearest to Fe^{+4}:

Weight % of Fe	Magnetic Moment	Oxidation State (Fe)
8.4	3.3	3.4
5.4	3.9	3.7
3.8	4.3	3.6
2.4	5.0	3.7
1.5	5.3	3.9

However, if dilute solutions are used, and the oxides are deposited slowly, one may build up concentrations as high as 10% Ni^{+3} on γ-alumina by means of multiple impregnations of nickel oxide on the alumina (6).

3. Finally, an explanation is needed to account for the apparent lack of the Valence Inductivity effect found for certain transition elements. For example, the Valence Inductivity effect is (10):

found for	not found for
chromium oxide on TiO_2	vanadium oxide on Al_2O_3
chromium oxide on Al_2O_3	vanadium oxide on TiO_2
iron oxide on TiO_2	copper oxide on Al_2O_3
nickel oxide on Al_2O_3	copper oxide on TiO_2
nickel oxide on TiO_2	silver oxide on Al_2O_3
	molybdenum oxide (1)

Hill and Selwood postulate that a partial covalent bond may exist between two paramagnetic metal ions, and they call this an intercation covalency (1). Such a bond would result in the lowering of the magnetic moment of a compound (compared with that calculated on the basis of the "spin-only" formula) due to the pairing or partial pairing of one or more unpaired electrons on each of two neighboring paramagnetic ions. The degree of this intercationic covalent bond formation may be expressed on a percentage basis. Thus, if μ (calculated) is 5.9 and μ (observed) is 3.6,

$$\% \text{ intercationic bond} = \frac{5.9 - 3.6}{5.9} \times 100$$

$$= 39\%$$

This effect would, of course, be dependent both on the number of unpaired electrons in a paramagnetic ion and on the distance from it to its nearest paramagnetic neighbor. For instance, Ni^{+2} and Mo^{+4} have the same number of unpaired electrons, but the percent intercationic bonding for the nickel ion is zero, and that for the molybdenum ion is about 100% (i.e., Mo^{+4} hardly seems to exhibit this Valence Inductivity effect at all), so one would predict that the molybdenum ions in MoO_2 would probably be unusually close to each other, and this was shown to be the case by Magnéli*.

This concept would also explain the reduced moment found in Cr_2O_3 (when not supported on a diamagnetic substrate) as compared with chromic sulfate hydrate (mentioned previously), because the chromium ions are closer to each other in the oxide than they are in the sulfate.

In addition, Selwood has indicated that this Valence Inductivity effect would not be expected to appear if the radius of the supported ion in its induced form differed from that of the diamagnetic supporting ion by more than about 30%, which would, perhaps, explain the fact that copper, silver, and vanadium do not exhibit this effect (10).

Selwood also feels that this concept may be very useful in helping to explain problems in catalysis (caused by transition metal ions), in coprecipitation, in promoter effects, and in mineralogical and crystallographic problems as well (6).

References

1. F. N. Hill and P. W. Selwood, J. Am. Chem. Soc., 71, 2522 (1949).
2. J. R. Partington, General and Inorganic Chemistry, Macmillan and Co. Ltd., London; p. 271.
3. P. W. Selwood, Magnetochemistry, Interscience Publishers, New York (1943).
4. P. W. Selwood, Chem. Rev., 38, 41 (1946).
5. P. W. Selwood, F. N. Hill, and H. Boardman, J. Am. Chem. Soc., 68, 2055 (1946).
6. P. W. Selwood, J. Am. Chem. Soc., 70 883, (1948).
7. P. W. Selwood and N. S. Dallas, ibid., 70, 2145 (1948).

---

*Magnéli, Ark. Kem. Mineral. Geol., 24A Nr. 2 (1946).

8. P. W. Selwood, T. E. Moore, M. Ellis, and K. Wethington, ibid., 71, 693 (1949).
9. P. W. Selwood, M. Ellis, and K. Wethington, ibid., 71, 2181 (1949).
10. P. W. Selwood and L. Lyon, Discussions of the Faraday Society, No. 8, pp. 222-230 (1950).
11. P. W. Selwood and L. Lyon, J. Am. Chem. Soc., 74, 1051 (1952).

SOME MOLECULAR ADDITION COMPOUNDS OF TRIMETHYLAMINE OXIDE AND TRIMETHYLOPHOSPHINE OXIDE

William C. Smith April 1, 1952

I. Introduction

In the early formulations of the higher oxides and oxy-acids of elements in Groups V, VI and VII the oxygen atoms attached only to a central atom were supposed to be held by double bonds. According to Lewis, however, they are held by coordinate or dative links,[1] and this view received some support from stereochemical investigations. Subsequent measurements of the bond lengths threw serious doubt on the later formulations for such compounds of elements not in the first short period, and suggested that the earlier ones were more correct. Electric dipole-moment data gave some support to this conclusion; for the first short period the bond lengths of various molecular addition compounds indicate coordinate links of nearly the length to be expected for a normal, single covalent link between the same two elements, but both bond lenght and dipole moment studies indicate that the bonds between elements of the second short period and later periods and the extra oxygen or sulfur atoms always are as short as or shorther than the normal double bond lenght.

Particularly extensive studies of this type were carried out by Phillips and co-workers.[2] They used the change in dipole moment that took place when a wide variety of donor molecules reacted with boron trifluoride or boron trichloride as a means of qualitatively evaluating the type of bond formed. Several general conclusions reached as a result of these studies were:

1) Coordinate links occur much less commonly than once thought, and when they do form, they appear to be relatively weak.
2) For elements of the second short period and succeeding periods, the bonds are thought to be partly or wholly double bond in character instead of the single, coordinate links formerly thought to exist.
3) Properties of the oxy-bonds in the higher oxides or oxy-acids of phosphorus, sulfur selenium and chlorine can be very well explained on the hypothesis that they are double.

Trimethylamine oxide, $(CH_3)_3NO$, is formally similar to trimethylphosphine oxide, $(CH_3)_3PO$, and it is of interest to consider similar addition products of these compounds in order to make a general comparison of the electron-donor power of the oxygen in the respective oxides.

II. Preparation of Materials

1. Trimethylamine oxide was preapred by treatment of trimethylamine with hydrogen peroxide and subsequent water removal by vacuum drying[3] [4]

2. Trimethylphosphine oxide was prepared by a Grignard-type reaction using $POCl_3$ and CH_3MgCl in ether solution.[5] [6] After removal of the ether by evaporation and precipitation of the magnesium with sodium carbonate, the $(CH_3)_3PO$ was extracted with the hot chloroform and purified by vacuum sublimation.

3. The molecular addition compounds were prepared by either a) passing the gas over the solid oxide or b) bubbling the gas through a benzene or chloroform solution containing the oxide. It is interesting to note that $(CH_3)_3POBF_3$ could also be prepared using water as the solvent for the oxide, this suggesting a greater stability for the BF_3 addition compound with $(CH_3)_3PO$ than for H_2OBF_3.

III. Properties of the Molecular Additions

The reactions of trimethylamine oxide and of trimethylphosphine oxide with boron trifluoride and sulfur dioxide have been studied.[6-9] These are best suited for a comparison of the donor ability of the oxygen atom in the two oxides and the properties described for these compounds are given in Table I.

Table I

	$(CH_3)_3NOBF_3$[8]	$(CH_3)_3POBF_3$[6]	$(CH_3)_3NOSO_3$[7]	$(CH_3)_3PO + SO_2$[6]
Appearance	White Solid	White Solid	White Solid	liquid with a saturation limit of 50 mole percent $(CH_3)_3PO$. Saturation pressure of SO_2 over this liquid scarcely one-tenth that expected in terms of Raoult's Law, indicating weak combination.
Stability in Water	soluble, but recovered unchanged with evaporation of the water	slowly dissolves with reversible removal of the BF_3 by water*	extremely soluble without decomposition	
Thermal Stability	begins to melt at 89°C with decomposition. Charring complete at 227°C.	melts at 148-150°C; sublimes cleanly in vacuo.	appears extremely stable; formation not reversed by heating in vacuo. Does decompose at 120° in Vacuo however	

* possible equilibrium:

$$(CH_3)_3POBF_3 + H_2O \rightleftharpoons (CH_3)_3PO + H_3O^+ + HOBF_3^-$$

A solid product was also obtained on treatment of $(CH_3)_3PO$ with sulfur trioxide,[6] but the corresponding product using $(CH_3)_3NO$ has not as yet been prepared, and the former can only be compared with $(C_2H_5)_3NOSO_3$. Unlike the triethylamine oxide - sulfur trioxide product, $(CH_3)_3POSO_3$ is very readily alcoholized, to form $(CH_3)_3POHOSO_2C_2H_5$ (m.p. 87°)

Another solid addition compound has been prepared in which silicon tetrachloride presumably act as the Lewis acid,[8] but it has not been completely characterized. Trimethylphosphine oxide also forms solid products when treated with acids such as HCl and with salts such as ZnI_2 and $CuCl_2$.[5]

IV. Discussion

$(CH_3)_3NOBF_3$ and $(CH_3)_3POBF_3$ seem to be quite comparable in their stabilities. While $(CH_3)_3NOSO_3$ is well characterized and extremely stable, pressure - composition isotherms indicate only a weak interaction between $(CH_3)_3PO$ and sulfur dioxide, and the formation of a compound comparable to $(CH_3)_3NOSO_3$ is not realized. The addition product $(C_2H_5)_3NOSO_3$ is stable in the presence of alcohol while $(CH_3)_3POSO_3$ is readily alcoholized.

The comparisons above indicate that in general the molecular addition compounds of trimethylamine oxide are more stable than the corresponding trimethyl phosphine oxides. The presence of alkyl groups on the nitrogen and phosphorus atoms might be expected to increase the donor powers of the oxygen atom in each case because of the base-strengthening effect of such groups. Furthermore, Burg has said that one might expect $(CH_3)_3PO$ to be a far weaker electron-donor than $(CH_3)_3NO$ since the latter has a strictly single-bonded oxygen atom with a considerable negative formal charge, whereas the PO bond could have appreciable double bond character through the use of hybridized 3d orleitals in the phosphorus atom[6] This assumption seems reasonable, and could conceivably be substantiated by a determination of the PO bond distance in $(CH_3)_3PO$ to see if it compares with that observed for the PO double bond distance in molecules where such a double bond is known to exist.

A further factor not considered by Burg would help to account for the fairly strong electron donor ability of $(Ch_3)_3PO$. Since phosphorus is considerably less electronegative than nitrogen the electrons of the oxygen attached to the former would be more available for bonding. This effect would work in opposition to that discussed by Burg and might account for the fact that $(CH_3)_3PO$ is a somewhat better Lewis base than would be expected solely on the basis of Burg's explanation, although still a weaker Lewis base than $(CH_3)_3NO$.

V. References

1. G. Lewis, J. Am. Chem. Soc, 38, 762 (1916)
2. G. Phillips, J. Hunter and L. Sutton, J. Chem. Soc., 1945, 146
3. Dunstan and Goulding, ibid., 75, 1005 (1899)
4. Meisenheimer and Bratring, Ann. 397, 286 (1913)
5. R. Pickard and J. Kenyon, J. Chem. Soc., 1945, 146
6. A. Burg and W. McKee, J. Am. Chem. Soc., 73, 4590 (1951
7. A. Burg, ibid, 65, 1629 (1943)
8. A. Burg and J. Bickerton, ibid., 67, 2261 (1945)
9. H. Lecher and W. Hardy, ibid, 70, 3789 (1948)

SOLVENT EXTRACTION AND ITS APPLICATIONS TO INORGANIC ANALYSIS

Lewis I. Krimen April 8, 1952

INTRODUCTION

Although the partitioning of various inorganic materials between organic and inorganic phases has been reported from time to time, it is only during the past few years that a real interest has developed in the techniques of solvent extraction. This interest can be attributed to the Manhattan Project due to the selective extraction of Uranium compounds by certain organic solvents, also to the pronounced interest in the separation of the less familiar elements.

This discussion will be limited to the solvent extraction of nitrates, chlorides, bromides, and fluorides, and consists of a general survey of conditions and possible explanations for the observed phenomena. Methods involving use of thiocyanates and of inner complexes which are formed with acetylacetone, 1,3-diketones, 8-hydroxy quinoline, etc. are not discussed.

THE SOLVENT EXTRACTION OF NITRATES

The extraction of uranium in the form of uranyl nitrate, $UO_2(NO_3)_2$ (UN) with ether has been known since 1842, when Peligot first employed this procedure for separating and purifying uranium from pitchblende (1). This process has attracted a great deal of attention in the past few years in connection with problems incidental to the atomic energy projects.

It has been found that the percentage of uranium extracted by ether is increased by the presence of nitric acid (2)(3) Fig. 1. and by salting-out agents such as ammonium and other soluble nitrates (3)(4). The diethyl ether may be replaced by other organic solvents, notably other ethers, and ketones, alcohols, and esters, i.e., solvents containing oxygen atoms capable of serving as electron pair donors (5). The insolubility of UN in solvents such as benzene and carbon tetrachloride has been reported (6).

The hexahydrate formula $[UO_2(H_2O)_6](NO_3)_2$ suggests 8-fold coordination around the central uranium atom; when organic solvent molecules replace one or more water molecules in the hydration shell there is a marked tendency to preserve the structure. Mathieson (7) has obtained compounds of the general formula UN, $3H_2O$, S and UN, $2H_2O$, 2S (S = solvent molecule) which favors the original suggestion.

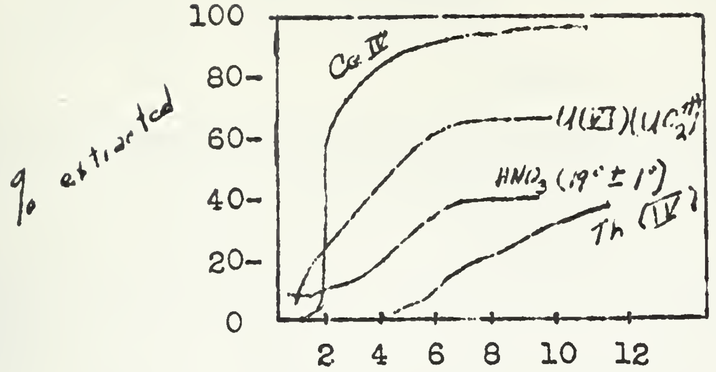


Fig. 1 Conc. of nitric acid, moles/1.

The effect of concentration on the extractability of nitrates by diethyl ether (2).

The increased solubility of water in ether in the presence of UN has been reported; since the resulting solution has a low electrical conductivity it is assumed to contain undissociated particles. The predominant species could be uncharged $[UO_2(NO_3)_2(H_2O)_4]$ which is assciated by "secondary solvation" (hydrogen bonding) with up to four organic solvent molecules (6). The possible formation of covalent bonds between uranyl and nitrate ions is consistent with the existence of the ion $[UO_2(NO_3)_3]^-$ and the formation of the double nitrates $UO_2M(NO_3)$ (where M=K, NH_4, NMe_4, Rb, (S), $UO_2M_2(NO_3)_4$ (where M=K, NMe_4, NEt_4, Rb), and $(NH_4)_2UO_2(NO_3)_4$, $2H_2O$.

Although UN is a strong electrolyte in dilute solution, changes in the visual absorption spectrum of the UO_2^{++} ion on the addition of nitrate ions (8) supports the hypothesis of covalent bonding rather than that of ion pair association.

Neptunyl and plutonyl nitrates behave similarly to UN. After persulphate oxidation of Am^{+3} with subsequent removal of sulphate ions with barium ions and salting out with nitric acid and NH_4NO_3, the amercium is solvent-extracted as a yellow solution (9), indicating by analogy to uranium the existence of hexavalent amercium and the AmO_2^{++} ion.

Although only hydrates of cobalt nitrate (denoted CN) containing 6,4,3, and 2 molecules of water appear in the system CN-water - acetone, when tert-butyl alcohol (B) replaces the acetone, CN, $6H_2O$; CN, $4H_2O$, 2β; CN, $3H_2O$, 3β; and CN, $2H_2O$, 4β represent the solid phases (5). The distribution ratios, under comparable conditions (6) for the bivalent nitrates of Mn^{++}, Co^{++}, Cu^{++}, and UO_2^{++} are 0.1:1:2:10⁷. The disproportionately large ether solubility of uranyl nitrate is clearly related to the high coordination number and valency of its central atom and its greater tendency to coordinate to water, to oxygen-containing molecules, and to the nitrate ion.

Table I lists elements which show a tendency to form nitrate complexes resembling uranium. The values for gold, cerium, and thorium are outstanding (2).

Table I

The percentage of metals extracted by ether from solutions in 8N Nitric acid at room temperature (2).

HNO_3 42%

Be 1.4	β										B	C	N	O
Mg	Al 0.1										Al 0.1	Si	P 20.4	S
Ca	Sc 0.1	Ti $\ll 0.5$	V^{V} 2	Cr^{VI} >15	Mn^{VII} <0.2	Fe^{III} 0.1	Co 0.2	N 0.1	Cu^{II} 0.5	Zn 0.1	Ga <0.2	Ge 2.2	As^{V} 14.4	Se
Sr	Y 0.1	Zr 8	Nb	Mo 0.6	Tc	Ru	Rh	Pd	Ag 2.4	Cd 0.3	In 0.1	Sn	Sb^{V} <1	Te
Ba	La 0.1	Hf	Ta	W	Re	Os	Ir	Pt	Au^{+3} 97	Hg^{II} 4.7	Tl^{+3} 7.7	Pb 0.5	Bi^{III} 6.8	Po
Ra	Ac	Ce^{IV} 96.8	Pr	Nd	rare earths									
		Th 34.6	Pa	U^{III} 65										

Table II illustrates the specific effect of different salting-out agents on the extraction of thorium nitrate.

Table II (2)

Percentage of thorium extracted by ether from 0.1 M Th (IV) in 1.0 M nitric acid saturated with various nitrates, $M^{+n}(NO_3)_{\bar{n}}$

M^{+n}	Li^{+}	Na^{+}	K^{+}	NH_4^{+}	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}	Zn^{++}	Al^{+3}	Fe^{+3}
Percentage extracted	56.5	0.67	0.15	0.36	43.8	56.9	0.8	0.08	80.9	54.1	73.6

Definite evidence is lacking for postulating such complexes to be solvated $H_2Ce(NO_3)_6$, $HAu(NO_3)_4 \cdot H_2Th(NO_3)_6$. There is no certainty that the extracted species remains the same in a particular metal nitrate-solvent-water system, except over a limited range of composition.

Templeton and his coworkers (10) have studied the partition of thorium nitrate between water and a variety of alcohols and methyl ketones. They showed (11) that the extraction of rare earth nitrates by n-hexyl alcohol increased in the order Ce < La < Pr < Nd < Sm and demonstrated practically the feasibility of separating neodynium and lanthanum by solvent extraction (12). Asselin, Audrieth, and Comings (13) have shown that thorium nitrate is extracted preferentially by n-amyl alcohol from an aqueous solution of neodynium nitrate in the presence of ammonium thiocyanate.

It is evident from Figure 1 that efficient extraction of ceric nitrate requires a high concentration of nitric acid; as a result the solvent enters into an exothermic reaction with concurrent reduction of the metal to a state in which it is no longer extractable. Nitromethane and tri-n-butyl phosphate, both non-oxidizable substances, have been tried. The latter proved to have exceptional solvent properties for the nitrates of cerium, thorium and uranium (14).

Typical procedures which depend upon the solvent extraction of nitrates include:

(1) the preparation of pure thorium, cerium, and uranium (2) compounds
(2) the determination of uranium in ores and minerals (4)
(3) the isolation and determination of uranium in microgram quantities by paper chromatography (15)
(4) the removal of the bulk of uranium from a sample prior to the spectrographic determination of rare earths (16)
(5) the preparation of carrier free U-X (17)
(6) the isolation of traces of protactinium after the deuteron bombardment of a 10-gram thorium target (18)
(7) the separation of the first 20 grams of plutonium from 90 kilograms of neutron irradiated UN hexahydrate (19)

THE SOLVENT EXTRACTION OF CHLORIDES

The number of extractable chlorides is greater than the limited number of extractable metal nitrates. Table III gives the figures regarding chloride solubility at the actual conditions specified. As with the nitrates the acid concentration (Fig. II) and the addition of the salting-out agent produce a striking effect on the extractability of the metals. The extractability of arsenic and of tin decreases upon oxidation, while the solubility of iron, antimony, and thallium increases.

Table III (27)

Ether extraction of various elements from 6N HCl Solutions

Element	% Extracted	Element	% Extracted
Ga	97	Ge	40-60
Au	95	In	trace
Mo (MoO)	80-90	Ir	5
Be	0	Os	0
Pd	0	Pt	trace
Rare earths	0	Rh	0
Se	trace	Te	34
Th	0	Tl(TlCl)	90-95
Ti	0	W(with PO)	0
U	0	V(VO)	trace
Zr	0		

The extractability of Thallium (III) is so well defined in dilute hydrochloric acid solutions that very little iron or gallium accompanies it; Hg(II) is the principal contaminant. If thallium is extracted under reducing conditions it will be transferred to the aqueous phase (21).

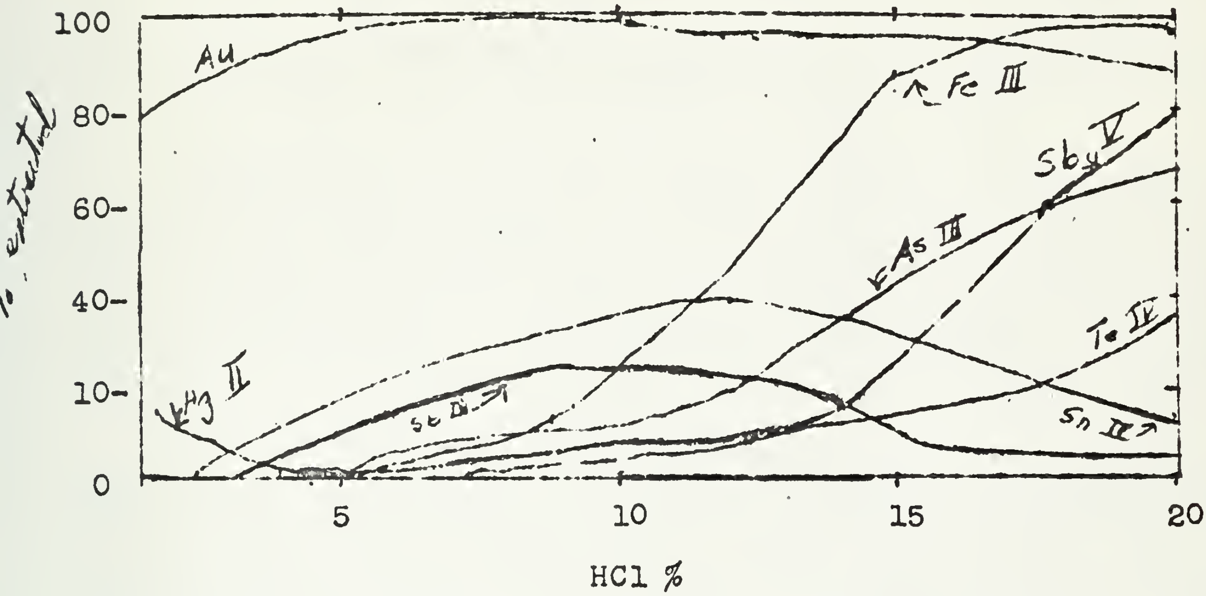


Fig. II

The influence of hydrochloric acid concentration upon the extractability of chlorides.

Rothe first proposed the ether extraction of ferric chloride from hydrochloric acid solution in 1892; this method has received very careful attention (20).

The following tabulation demonstrates that % extractability is a function of concentration; with diethyl ether the maximum is allowed at approximately 7 N.HCl.

Ether used	Percentage of 250 mg. of iron extracted from hydrochloric acid of normality:								
	2.	3.	4.	5.	6.	7.	8.	8.5	9.
Diethyl (26)	1	17.8	81.5	96	99	97.8	87	73	45
Diisopropyl(13)	0	0.4	12.1	80.9	98.1	99.5	99.8	99.6	94
Dichlorodiethyl (23)	0	2	6	25	61	88	97	98	99

This procedure is well suited for the removal of large quantities of iron but with a decrease in iron content the percentage of metal extracted decreases fairly rapidly as shown by the following data: (26)

Iron taken originally, mg.	500	243	203	102	41	22
Percentage extracted by isopropyl ether from 5 M. HCl	90.2	82.4	79.5	67.5	39	36

Several theories have been advanced to account for this behavior. It appears that ferric chloride partitions into isopropyl and dichlorodiethyl ethers along with one equivalent of hydrochloric acid, presumably as solvated $HFeCl_4$, (22)(23). Although the ratio $HCl:FeCl_3$ rises above unity when ether is used in a solution of high acidity, the absorption spectrum of the ether layer does not change, suggesting that the additional acid is loosely associated with the $HFeCl_4$ complex (23).

Nachtrieb and Conway (22), after observing the increased efficiency of the extraction of ferric chloride in the presence of aluminum chloride suggested that this is due to an increase in the acidity of Fe(III). Therefore they concluded that ferric chloride should produce a similar increase in activity which would decrease as the concentration of iron decreases thus causing a drop in the extraction efficiency. Other workers have interpreted the data in terms of a polymerized ferric complex in the organic phase (24).

The extraction of gallium chloride by ether and isopropyl ether is well known and is an important method for concentrating this element and separating it from impurities. Many organic solvents have been investigated. It has been found that ethyl acetate and other aliphatic esters are the most effective and that introduction of chlorine atoms into the oxygenated solvent impairs the extraction (6).

The following table summarizes data with respect to the various elements extracted, conditions, and the efficiency of the extraction.

Element	% removed	Reagents and Conditions	Amount of coextraction
Pt as H_2PtCl_4		Red solns. in HCl produced by reduction with SnCl	(18)(20)
Protactinium	90	Dichlorodiethyl ether, 6 N hydrochloric acid, 8M Mg Cl	2%, U, Mn, Zr, or Ti (18)
Polonium		6 N HCl, 20% tributylphosphate in diethyl ether	separation from Pb and Bi (18)

Anhydrous cobalt chloride has been found to be soluble in aliphatic alcohols, esters, ketones, and acids, and relatively insoluble in aromatic aldehydes and ketones and almost insoluble (0.05%) in aliphatic or aromatic hydrocarbons. The solubilities of anhydrous cobalt and nickel chlorides in commercial 2-octanol were found to be 21.3% and 0.26% respectively but no separation or extraction could be effected (25).

THE EXTRACTION OF BROMIDES AND FLUORIDES

Other than chloride extraction relatively little has been published concerning the other halides. From the following table it can be seen a) that the efficiency of extraction of iron is reduced by replacing hydrochloric by hydrobromic acid, and b) that maximum extraction is attained at a lower acidity. Indium is extracted with difficulty from hydrochlmic acid, but can be completely removed from hydrobromic acid; the extraction of copper (21) and thallic thallium is also facilitated.

THE EXTRACTABILITY OF METAL BROMIDES (28)

Percentage of metal extracted from 20 ml. of aqueous phase by 30 ml. of diethyl ether pre-saturated with hydrogen bromide. Comparative data for chlorides ex hydrochloric acid in parentheses.

Metal	Normality of hydrobromic acid:							
	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0
Tl(III)	99	99	99.2	99.7	99.7	99.8	99.6	92(92-95)
Fe(III)	-	0	0	2 (1)	9.5 (17.8)	69.5 (81.5)	72.5 (96)	60.4 (99)
Ga	-	0	0	0	0.3	3.6	50	57(40-60)
In	-	1	3.2	19.2	89.3	99	-	99 (trace)
Au	-	99	99	-	-	99	-	73(95)
Te	-	0.3	2	3	-	3	-	3(34)
Hg(II)	-	3	1	0.2	-	0.3	-	0,3 (0.2)

McBryde and Yoe (29) have made a thorough study of the solvent extraction of gold as bromoauric acid and found it to be more satisfactory than extraction from hydrochloric acid. When isopropyl ether is used at a low acidity (2.5-3M) relatively little iron, and only osmium (43% as tetroxide) of the platinum metals is extracted. With 2.9 M hydrobromic acid, hexone extracts 54% of iron, 56% of osmium, 21% of palladium, and 13.5% of platinum.

The determination of tantalum and niobium in minerals and ores and their separation from titanium, zirconium, iron, and tin by solvent extraction has been studied using ethyl methyl ketone containing some hydrogen fluoride in conjunction with a column of activated cellulose (30).

Kitahara (31) reported the following data on the ether extraction of fluorides: Sn(II) and Sn(IV) are extracted completely and As, 62.2%; Mo, 9.7%; Sc, 3.1%; Sb, 0.4% from HF solutions of fluorides. Under the same conditions no extraction was observed in the case of Ni, Cr, Co, Mn, K, Ti, Zr, Ga, Ag, U, Bi, Te, Cd, and Os as fluorides or of Pt, Pd, Ir, and Ru chlorides or $NaVO_3$ from hydrofluoric acid solutions.

BIBLIOGRAPHY

1. Ann. Chim. Phys. 5, 7, 42, (1842).
2. Block and Block, Z. Anorg. Chem. 263, 146, (1950).
3. Norstrom and Sillen, Svensk Kem. Tidskr., 60, 277 (1948).
4. Hecht and Grunwald, Mickrochemie Acta, 30, 279-96 (1943).
5. Katzen and Sullivan, AECD 2537.
6. Gluekauf and McKay, Nature, 165, 594 (1950).
7. Mathieson, J. Chem. Soc. S, 294 (1949).
8. Betts and Michels, ibid., S, 286 (1949).
9. Asprey, Stephanou, and Penneman, J. Am. Chem. Soc., 72, 1425 (1950).
10. Templeton, J. Phys. Colloid Chem., 51, 1441 (1947).
    52, 1006 (1948).
    53, 838 (1949).
11. Templeton, J. Am. Chem. Soc., 71, 2187 (1949).
12. Templeton, ibid., 70, 3967 (1948).
13. Asselin and Comings, Ind. Eng. Chem., 42, 1021-1230 (1950); Asselin, Audrieth and Comings, J. Phys. Chem. 54, 640 (1950).
14. Warf, J. Am. Chem. Soc., 71, 3257 (1949).
15. Arden, Burstall, and Linstead, J. Chem. Soc., S, 311 (1949).
16. Hirt and Nachtrieb, MDDC, 903.
17. Erbacher, Herr, and Wiedemann, Z. Anorg. Chem. 252, 282 (1949).
18. Chemical Procedures Used at Berkeley, AECD, 2738.
19. Cunningham and Werner, J. Am. Chem. Soc., 71, 1521 (1949).
20. Sandell, "Colormetric Determination of Traces of Metals", 2nd Edn. New York, 1950.
21. Irving, et. al. unpublished observations, Quarterly Reviews, V, 2, 213, (1951).
22. Nachtrieb and Conway, J. Am. Chem. Soc.,70, 3547, 3552 (1948).
23. Axelrod and Swift, ibid., 62, 33 (1940).
24. Meyers and Metzler, ibid.,72, 3772, 3767 (1950).
25. Garwin and Hixson, Ind. Eng. Chem., 41, 2298, 2303, (1949).
26. Dodson, Forney, and Swift, J. Am. Chem. Soc., 58, 2573 (1936).
27. Swift, J. Am. Chem. Soc., 46, 2375 (1924).
28. Wada and Ishii, Bull. Inst. Phys. Chem. Res., Tokyo 13, 264 (1934).
29. McBryde and Yoe, Anal. Chem. 20, 1094 (1948).
30. Work at the Chem. Res. Lab., D.S.I.R., Teddington; Chem. Res. 46, (1949); Quarterly Rev. V, 2, 217 (1951).
31. Ketahara, Reports to Sci. Res. Inst. (Japan) 25, 165 (1949); Chem. Abs. 45, 3743 (1951).

ALKALI METAL PHOSPHIDES

Paul G. Gordon April 22, 1952

I. INTRODUCTION

Although the literature contains numerous articles concerning the preparation and properties of alkali metal phosphides, the products obtained have not been well characterized. Because of the uncertain nature of these phosphides, Evers and coworker (7,8) reinvestigated methods of preparation, chemical, and physical properties. Other metal phosphides are better characterized; many resemble alloys.

II. CLASSIFICATION

Metal phosphides can be divided into two general classes based on ease of hydrolysis. Alkali metal, alkaline earth, and aluminum phosphides hydrolyze readily; the other metal phosphides resist hydrolysis. Phosphine is usually produced on hydrolysis. The unstable phosphides are non-metallic in appearance, whereas the stable phosphides have metallic luster. A summary of reported phosphides is compiled in the table on page 155.

III. USES

Besides being of academic interest, phosphides have many applications. Peacock (20) and McCanley (18) prepared protective phosphide coatings for iron and steel. Hebler (12) used the unstable phosphides coated with a water soluble covering to mark the path of torpedos. Haun (11) and Freyberg (9) used phosphides in rodent bait. Kah (15) also used phosphides as a source of phosphine for fumigation of grain. Woods (25) is at present investigating possible use of transition metal phosphides as oxidation resistant anodes for fused salt electrolysis. Phosphides present in metals or alloys can alter their properties favorably or unfavorably. For example, phosphides must be removed from iron by oxidation to P_4O_{10}; the latter reacts with the basic lining in the Bessemer converter. Removal of phosphorous prevents "cold shortening" of the product.

IV. GENERAL METHODS OF PREPARATION

A. Stable Phosphides

(1) $\text{Metal(s)} + \text{phosphorous(s)} \xrightarrow[\Delta]{\text{inert atm.}} \text{metal phosphide}$
metal = K, Fe, Co, Ni, Mn, Pd, Pt, Ir, Au, etc.

(2) $\text{metal(s)} + \text{phosphorous(g)} \xrightarrow[\Delta]{} \text{metal phosphide}$

(3) $\text{Gr. I metal(s)} + \text{Gr. II metal(s)} + \text{P(s)} \xrightarrow[\Delta]{} \text{M(I)M(II)P}$
Metal = Li, Mg and Zn

(4) $\text{metal ion} + PH_3\text{(g)} \xrightarrow{\text{solvent}} \text{metal phosphide}$
metal = Ag, Cu, Hg, Pb and Cd.

(5) metal ion + P(s) $\xrightarrow{\text{solvent}}$ metal phosphide
metal = Hg or Cu

(6) metal oxide or halide + fused phosphate $\xrightarrow{\text{electrolysis}}$ metal phosphide.
metal = Fe, Ni, Co, Mo, W, Mn, Cr and V

(7) metal oxide + phosphorus(s) $\xrightarrow[\Delta]{}$ metal phosphide
metal = Ca

B. Unstable Phosphides

Hackspill and Bossuet (10) have prepared the compounds M_2P_5 where M is an alkali metal, by treating the elements directly and subjecting the products to the action of vacuum at high temperatures. This procedure prevents all possibilities of identifying any phosphides which might be stable only at low temperatures. Normal phosphides were assumed to be formed by union of the elements in various media by Vourasos (23) only on the basis that phosphine was produced when the product was treated with water. This assumption is, of course, erroneous.

Legoux (17) has prepared the same substances as Hackspill and Bossuet by thermally decomposing metal derivatives of phosphine, thus confirming the existance of high temperature stable forms. When heated, the compounds MPH_2 decompose successively evolving phosphine then hydrogen and, finally, free metal as the temperature is raised, leaving the compound M_2P_5 as non-volatile residue. Joannis (14) reported that normal phosphides are formed on pyrolysis of $NaPH_2$ and KPH_2. Schober and Spanutius (21) also reported formation of <u>normal</u> phosphides by passing phosphine over the heated metals. Again the basis of their conclusions was the release of phosphine when the product was treated with water.

Hugot (13) has described the preparation of KP_5 and NaP_3 by using an excess of red phosphorous with alkali metals in liquid ammonia. Brauer and Zintl (4) reported that lithium would not react with red phosphorous in liquid ammonia.

Evers and coworkers (7,8) allowed white phosphorous to react with alkali metals in liquid ammonia at its boilding point. This solvent was chosen because it affords a convenient means for carrying out reactions of the elements in a homogeneous state under controlled conditions. Compounds with the emperical formulas Na_2P, Li_2P and K_3P_2, which are believed to exist as dimers, were prepared. K_6P_4 can be further reduced by lithium and sodium to produce mixed phosphides, K_3LiP_2 and K_3NaP_2 respectively. Normal phosphides were not formed under these experimental conditions.

Albers and Schuler (1) have reported the preparation of Na_3P by the action of triphenyl methyl sodium on phosphine in ether in an atmosphere of nitrogen.

V. PHYSICAL PROPERTIES

Metal phosphides posses either a metallic luster or are obtained as amorphous powders; they are vari-colored (2).

Phosphides can be further classified according to their crystal type (24).

A.	Ionic :	Li_3P, Na_3P - Na_3As structure Be_3P_2, Mg_3P_2 - inti isomorphous to Mn_2O_3 Zn_3P_2, Cd_3P_2 - Zn_3P_2 structure
B.	Covalent:	AlP, GaP - zinc blend
C.	Interstitial :	LaP, PrP, GeP - rock salt Ir_2P, Rh_2P - antifluorite
D.	Miscellaneous:	FeP, CoP - nickel arsenide

Brewer and others (5) have compiled thermodynamic properties of some phosphides. The structures of phosphides have been determined by Stackelberg (22), Passerini (19), Biltz (6), and Brauer (3). Many phosphides of M_3P_2 type were found to be anti-isomorphous with their oxides, M_2O_3.

VI. ALKALI METAL PHOSPHIDES

Evers and coworkers (7,8) used the conventional apparatus for investigating the reaction between alkali metals and white phosphorus in liquid ammonia (16). Lithuim was cut and weighed under oil just before using, and the other metals were prepared in weighed ampules. A standard solution of phosphorous in toluene was also prepared and checked by converting phosphorous to orthophosphate with bromide water and nitric acid and precipitating it as $MgNH_4PO_4$ and ignition to $Mg_2P_2O_7$. The products were analyzed in a similar manner. The composition of the product was also calculated from the amounts of reagents used in their preparation. The products all contained ammonia of crystallization which was removed by heating in a vacuum.

Lithium reacts readily with white phosphorous to give Li_4P_2. Sodium reacts more slowly to give Na_4P_2. Potassium reacts to produce K_6P_4. This compound was bound to be stable in the presence of excess potassium, but was reduced to K_3LiP_2 and K_3NaP_2, by excess lithium and sodium respectively.

By analysis of the products and calculation of the phosphorous to metal ratio, only the empirical formulae could be determined. The reasons for assuming these compounds to be dimers are as follows: (1) from valence considerations. (2) P-P bond is strong and cannot be reduced by the solvated electron either in the case of Li_4P_2 or Na_4P_2. (3) $K_3P_2\text{-}P_2K_3 + 2Na$ or $2Li \xrightarrow{(L)\ NH_3} 2K_3NaP_2$ or $2K_3LiP_2$. (4) The compounds can be considered derivatives of P_2H_4, tetrahydrogen diphosphide.

Further investigation of Na_4P_2 (8) showed that the crude product is obtained with two moles of ammonia for every mole of salt. Tetrasodium disphosphide undergoes reactions in liquid ammonia:

(1) $Na_4P_2 + Na \longrightarrow N.\ R.$

(2) $Na_4P_2 + 2\ Na + 4\ NH_4Br \rightleftharpoons 2\ NaPH_2 + 4\ NaBr + 4\ NH_3$

or $P_2^{-4} + 2e^- + 4\ NH_4^+ \rightleftharpoons 2\ PH_2^- + 4\ NH_3$

(3) $P_2^{-4} + 2\ NH_4^+ \rightleftharpoons HPPH^{-2} + 2\ NH_3$ orange

$\downarrow$

$HPPH^{-2} + 2\ NH_4^{-1} \rightleftharpoons \underset{\hookrightarrow PH_3}{H_4P_2} + 2\ NH_3$ yellow

(4) $H_2P\text{-}PH_2 + 2e^- \rightleftharpoons 2\ PH_2^-$

(5) $P_2^{-4} + 2\ NH_4^+\ 2e^- \rightleftharpoons 2\ PH^{-2} + 2\ NH_3$

The reactions are explained by Evers as follows: Equation (1) shows that the P-P bond is stable to electron reduction in the presence of only sodium in liquid ammonia. (2) is important for it presumably illustrates the first acid catalyzed electron reduction of an inorganic compound. Many acid catalyzed electron reductions of organic compounds are known. A hydrogen reduction would be expected for a reaction such as (2), but it presumably does not occur in this case, because no hydrogen was evolved; the blue color of free metal was observed until exactly four moles of NH_4^+ was added; the presence of PH_2^- was proved rather than PH^{-2} as would be expected if hydrogen reduction had taken place according to equation (5). Note that (5) required only two moles of NH_4^+ to remove the blue color from solution. (3) showed that the NH_4^+ alone could produce P_2H_4 which can be reduced according to (4).

VII. TABULATION OF METAL PHOSPHIDES

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA
Li_3P Li_4P_2 Li_xP_x	Be_3P_2						H_3P H_4P_2 H_2P_5 H_2P_9 H_6P_{12}						
Na_3P Na_2P NaP_3 Na_2P_5 Na_4P_5	M_gP_2 $M_{13}P_2$											AlP Al_3P_7 Al_5P_3 Al_3P Al_2P_2	
K_3P K_2P_5 KP_5 K_6P_4 K_3NaP_2 K_3LiP_2	Ca_3P_2		TiP Ti_2P	VP_2 VP V_2P V_3P_2 V_3P	CrP_2 CrP Cr_2P Cr_3P	MnP_3 MnP Mn_2P Mn_3P MnP_2	FeP FeP_2 Fe_2P Fe_3P Fe_xP_y	CoP_3 CoP Co_2P CoP_2 Co_3P_2 Co_4P_3	NiP_3 NiP_2 Ni_6P_5 Ni_2P Ni_7P_3 Ni_5P_3	CuP_2 Cu_3P Cu_5P_2 Cu_2P Cu_3P_2 CuP	ZnP_2 Zn_3P_2 ZnP Zn_3P_4 ZnP_4	GaP	GeP
Rb_2P_5	Sr_3P_2 SrP_5 Sr_xP_x		ZrP_2 ZrP Zr_3P	NbP_2 NbP	MoP_2 MoP Mo_3P		RuP_2 RuP Ru_2P	RhP_3 RhP_2 Rh_5P_4 Rh_2P	PdP_2 Pd_5P_2 Pd_3P Pd_5P	Ag_3P AgP_3 AgP_2 Ag_2P_3 Ag_2P_5 AgP	CdP_2 Cd_3P_2 Cd_2P	InP	SnP_3 Sn_3P_4 Sn_4P_3 Sn_5P_2 Sn_2P Sn_3P
Cs_2P_5				TaP_2 TaP	WP_2 WP W_4P W_2P W_3P_4	ReP_3 ReP_2 ReP Re_2P	OsP_2	IrP_2 Ir_2P IrP	PtP_2 Pt_2P PtP Pt_3P_5 $Pt_{20}P_7$	Au_2P_3	Hg_3P Hg_3P_2 Hg_3P_4	Tl_3P	PbP_5 Pb_3P_2
		LaP		PrP	NdP								
			Th_3P_4 ThP		UP_2 U_3P_4 UP								

VIII. BIBLIOGRAPHY

(1) Albers, H. and Schuler, W., Ber., 76,23(1943)
(2) Annon., Z. Metalkunde, 10,56(1919)
(3) Brauer, G., FIAT Rev. German Sci., Inorg. Chem., Part II, 71(1948
(4) Brauer, G. and Zintl, E., Z. physik. Chem., 37B,323(1937)
(5) Brewer, L., et. al., "National Nuclear Energy Series", Div. IV, 19B, 40(1950)
(6) Biltz, W., Z. physik. Chem., A189, 10(1941)
(7) Evers, C., J. Am. Chem. Soc., 73,2038(1951)
(8) Evers, C., Street Jr., E. and Jung, S., ibid 5088.
(9) Freyberg, W., Ger. 720,760(1942)
(10) Hackspill, L. and Bossuet, R., Compt. rend., 154,209(1912)
(11) Haun, F., Z. Untersuch. Lebensm., 72,307(1936)
(12) Hebler, P., Ger. 526,766(1927)
(13) Hugot, C., Compt. rend., 121,207(1895)
(14) Joannis,A.,Compt. rend., 119,537(1894);Ann.Chim.phys. [1]7,101(1906
(15) Kah, E., Ger. 698,721(1940)
(16) Kraus, C. and Carney, E., J.Am.Chem.Soc., 56,765(1934)
(17) Legoux, C., Bull. soc. chim. (France) [5] 7,(1940); Compt. rend., 207,634(1938); 209,47(1939)
(18) McCanley, R., U.S. 2,007,978(1935)
(19) Passerini, L., Gazz. chim. ital., 58,655(1928)
(20) Peacock, S., U.S. 1,456,252(1923)
(21) Schober, W. and Spanutius, F., J.Am.Chem. Soc., 16, 229(1894)
(22) Stackelberg, M., Z.physik.Chem., B27,53(1934);B22,305(1933)
(23) Vournasos, A., Z. anorg. allgem. Chem., 81,364(1913)
(24) Wells, A. "Structural Inorganic Chemistry", 476, Oxford at the Claredon Press(1950)
(25) Woods, D., University of Illinois (1952)

PREPARATION AND PROPERTIES OF SOME BRANCHED POLYSILOXANES*

Richard A. Rowe April 29, 1952

INTRODUCTION

In previous work done by J. R. Wright and R. N. Lewis at the University of Delaware, a new method was devised to prepare compounds containing both quadrivalent silicon and the univalent radical $(CH_3)_3Si-$, by the replacement of ethoxy groups in ethyl silicate with trimethylsiloxy groups, which will be designated by the letter M. The compound prepared in that work was $Si(OM)_4$ which is the initial member of a series with the general formula $MO(Si(OM)_2)_xM$.

Some work has been done on the partial hydrolysis products of ethyl and methyl silicates. Of the series $RO(Si(OR)_2O)_xR$ ($X = 2-10$ and $R = Me$ or Et) nothing has been reported other than their boiling point ranges. It was necessary to find a method or preparing these polysiloxanes from the ortho silicate in good yield. Since methyl silicate cannot be purchased, a good procedure for its preparation had to be developed.

NOMENCLATURE

A committee was organized by the American Chemical Society in 1946 to set up rules for the naming of silicon compounds. A brief summary of the more applicable rules follows.

(1) Silane rather than Silicane will be used for SiH_4.
(2) Disilane, trisilane, etc. will be used for the higher homologs.
(3) Compounds of the general formula $H_3SI(OSiH_2)_xOSiH_3$ will be called disiloxane, trisiloxane, etc.
(4) Compounds of the general formula $H_3Si(NHSiH_2)_xNHSiH_3$ will be called disilazane, trisilazane, etc.
(6) Cyclic compounds will be named cyclotrisiloxane, cyclotrisilazanes, etc.
(10) Names for common silicon containing radicals are: H_3Si-silyl, H_2Si silylene, $H_3Si-SiH_2$-disilanyl, H_3SiO-siloxy, H_3SiNH-silylamino.
(11) Hydroxy derivatives in which -OH is attached to silicon will be named by adding suffixes ol, diol, triol, etc. Ex. $H_2Si(OH)_2$ is silanediol.
(12) Compounds such as $H_2Si(OEt)_2$; $H_2Si=O$; $H_2Si=NH$ are called diethoxysilane, oxosilane, and iminosilane respectively.
(13) Chains are numbered from one terminal Si atom to another according to practice. Ex. $H_2SiOSiH_2OH$.

---

*Work done in partial fulfillment of the requirements for the Master of Science degree at the University of Delaware.

GENERAL

Silicon is an electropositive element with some of the properties of the metals. It usually exhibits a covalency of 4, but can combine to form a maximum covalency of 6 in compounds such as the fluosilicate ion and the acetylacetonate where the atoms are relatively small with high nuclear charge.

Hydrides: The simplest covalent compounds of silicon are the hydrides. Since chain lengths of seven Si atoms or more are unstable only those up to and including the hexamer have been separated. The best methods for their preparation are:

(1) Action of mineral acid on crude magnesium silicide that results from the reduction of silica by magnesium.

$$xMg_2Si + 2x + 2H^+ \rightarrow Si_xH_{2x+2} + 2xMg^{++}$$

(2) Action of lithium tetrahydroaluminate on the corresponding chlorides. $LiAlH_4 + SiCl_4 \rightarrow SiH_4 + AlCl_3 + LiCl$ All the hydrides will react with oxygen and are ignited spontaneously in air. The Si-Si bond is attacked by aqueous alkali and is oxidized by the water with the liberation of hydrogen.

Halides: Silanes react directly with halogens and halogen acids in the presence of an aluminum halide catalyst to form the halogenated silanes. Chloroform or Carbontetrachloride can be used in the presence of $AlCl_3$ as chlorinating agents. Trichlorosilane can be prepared much more easily by the direct action of hydrogen chloride on silicon, ferrosilicon or calcium silicide.

The halides have been the building blocks for the construction of most of the simple and complicated molecules known in modern silicone chemistry. Some of the more important reactions used in the synthesis of compounds are as follows:

Ethers: $SiCl_4 + 4EtOH \rightarrow Si(OEt)_4 + 4HCl$

$$Si(OEt)_4 + 2H_2O \rightarrow SiO_2 + 4EtOH$$

$$Si(OR)_4 + R'MgX \rightarrow R'Si(OR)_3 + MgORX$$

Silylamines: $3SiH_3Cl + 4NH_3 \rightarrow (SiH_3)_3N + 3NH_4Cl$

$$SiCl_4 + 8NH_3 \rightarrow Si(NH_2)_4 + 4NH_4Cl$$

$$Si(NH_2)_4 \rightarrow Si(NH)_2 \rightarrow Si_3N_4$$

Ortho Silicic Acid: $SiCl_4 + H_2O \rightarrow Si(OH)_4 + 4HCl$

Organosilicon Compounds: Many reactions employing the alkyls of zinc, mercury, and aluminum are used.

$$Zn(CH_3)_2 + 2(CH_3)_2SiCl_2 \rightarrow 2(CH_3)_3SiCl + ZnCl_2$$

Wurtz type reactions can be employed using sodium or lithium.

$$SiCl_4 + 4RCl + 8Na \rightarrow SiR_4 + 8NaCl$$

The researches of Kipping made the use of the Grignard reagent the most popular method for preparing these compounds.

$$SiCl_4 + 4RMgX \rightarrow SiR_4 + 4RMgXCl$$

Direct methods have been developed to synthesize organosilicon halides from elemental silicon. These reactions can be carried out with the organo halogen in either the vapor or liquid state. (Copper is used as catalyst)

$$Si + 2RX \rightarrow R_2SiX_2$$

Unsaturated hydrocarbons can be made to add directly to halosilanes.

Silicones: By hydrolysis of dichlorosilanes or dihaloalkylsilanes a siloxane network of long chains is formed. The hydrolysis of the alkyl monomers leads to the formation of a group of polymers called "silicones". Branched anc crossed-linked polymers can be made by hydrolyzing appropriate mixtures of the dichloro, trichloro, and tetrachloro compounds. A step-wise example of a simple case would be the hydrolysis of dimethyldichlorosilane.

(1) $Me_2SiCl_2 + 2H_2O \rightarrow Me_2Si(OH)_2 + 2HCl$

(2) $2Me_2Si(OH)_2 \rightarrow HOSiMe_2\text{-}O\text{-}SiMe_2OH + H_2O$

Steps 1 and 2 can be repeated over and over until cyclic or long chains are formed. If trichloromethylsilane had been added, crossed-linking would take place.

THEORETICAL

It has been shown that ethyl silicate when hydrolyzed in the presence of sulfuric acid and hexamethyldisiloxane (M_2O), gives yields of 80 percent or more of $Si(OM)_4$.

$$Si(OEt)_4 + M_2O + 2H_2O \xrightarrow{H_2SO_4} Si(OM)_4 + 4EtOH$$

A reaction time of a week showed little evidence of a reshuffling of M groups to form an infinite number of cyclic or branched polysiloxanes in the series $MO(Si(OM)_2)_xM$. The fact that the dimer was found on initial runs was attributed to the existence of $(EtO)_6Si_2O$ as an impurity in the ethyl silicate. This reaction can be represented by the equation:

$$(EtO)_6Si_2O + 3M_2O + 3H_2O \xrightarrow{H_2SO_4} (MO)_6Si_2O + 6EtOH$$

This conclusion suggested the possibility of preparing the higher homologs of the series with the general formula $Si_nO_{n-1}(MO)_{2n+2}$ by reactions similar to the preparation of $Si(OM)_4$. Instead of using the alkylsilicate, its hydrolysis products could be used.

The polyester polysiloxanes are not yet commercially available, but can easily be obtained in fair yields by hydrolyzing orthosilicate. The reaction for the non-cyclic polymers complies with the general equation:

$$n(RO)_4Si + (n-1)H_2O \xrightarrow{H^+} Si_nO_{n-1}(OR)_{2n+2} + 2(n-1)ROH$$

The ethyl and methyl esters of the compounds where $n = 2, 3, 4$ are of particular interest. Since a mixture of these compounds would be formed from any one run, the individual polysiloxane esters must be separated by distillation. Experiments were run to find the ratios of H_2O to the orthoester needed to give maximum yields of each individual ester.

From these esters and the stoichiometric amount of hexamethyldisiloxane the desired dimer, trimer, or tetramer will result. Theoretically these reactions should produce good yields of stable trimethylsiloxy compounds.

In order to compare the reactions of the methyl polysilicates with the ethyl polysilicates, the methyl orthosilicate had to be prepared. Quite a problem was involved in preparing the methyl silicate in good yield since it is not commercially available and no good procedure could be found in the literature. Three methods of preparation were investigated.

The hydrolysis products of methyl silicate would be easier to separate because of their lower molecular weights.

EXPERIMENTAL

Preparation of Methyl Silicate:

Method (1) $SiCl_4 + 4MeOH \rightarrow Si(OMe)_4 + 4HCl$

Several attempts to prepare ethylsilicate by adding silicon tetrachloride to cooled methyl alcohol failed to produce a yield better than 50 percent. When the reaction mixture was cooled to -70°C no reaction took place. Yields of 90 percent and better are obtained, however, if the reaction is run by adding the methyl alcohol to the silicon tetrachloride at room temperature. No agitation is needed since the reaction runs smoothly with the evolution of HCl at the interface of the two layers. The reaction probably goes to completion since the HCl evolved is much less soluble in the mixture when it is run in this way.

Method (2) $SiCl_4 + 4NaOMe \rightarrow Si(OMe)_4 + 4NaCl$

The above method produced a yield of 52 percent. This method proved to be a poor one since it necessitated filtration to separate the silicate which exposed it to the atmosphere and possible chance for hydrolysis.

Method (3) $(EtO)_4Si + (excess)MeOH \xrightarrow{NaOMe} 4EtOH + Si(OMe)_4$

This transesterification method produced a yield of 66 percent after several distillations to remove the ethyl alcohol formed in the shift in equilibrium. The method proved lengthy and cumbersome. It may have some use in industrial preparation where constant redistillation would be no problem.

Hydrolysis of Ethyl Silicate:

Attempts were made to hydrolyze ethyl silicate without using a solvent. These experiments proved unsatisfactory since too great a percentage of the monomer was converted to the higher molecular weight polymers. Thirteen-percent hydrochloric acid was used as the source of water in all hydrolysis reactions. Before distillation the acid was neutralized with anhydrous ammonia. However, when ethyl alcohol was used as a solvent satisfactory results could be obtained when different mole ratios of $H_2O/Si(OEt)_4$ were used. It was found that the greatest yield of $(EtO)_6Si_2O$ was obtained when a mole ratio of 0.65 was used, $(EtO)_8Si_3O_2$ when a ratio of 0.85 was used, and $(EtO)_{10}Si_4O_3$ when a ratio of 0.88 was used. Of course, a great percentage of the silicate was converted to the higher polymers at these higher ratios. A reflux period of 24 hours was used for each run before distillation.

Hydrolysis of Methyl Silicate:

Due to its higher polarity, methyl silicate reacts with greater speed than ethyl silicate. If an acid catalyst is used in the hydrolysis a gel is formed. Since water is very soluble in methyl silicate, no solvent has to be used. In fact methyl silicate and its hydrolysis products are so susceptible to moisture that they are rather hard to keep. On the other hand, they are more volatile than the corresponding ethyl polysilicates and much easier to separate.

Replacement of Ethoxy Groups by Trimethylsiloxy in Polysiloxanes:

A direct replacement of ethoxy groups by trimethylsiloxy groups was affected by adding water to a strongly acidified mixture of hexamethyldisiloxane and the esters obtained from the hydrolysis of ethyl silicate. The following compounds were made by this method.

Compound	B.P.	M.P.	Mol. Weight
$Si(OM)_4$	215	-57	384
$Si_2O(OM)_6$	300	249	606
$Si_3O_2(OM)_8$	275	-	828
$Si_4O_3(OM)_{10}$	320	-	1050

$M = -Si(CH_3)_3$

Replacement of Methoxy Groups by Trimethylsiloxy Groups;

A modification of this method was required with the methyl silicates, because of the rapidity of their hydrolysis. In order to increase the rate of attack by "siliconium" ions the hexamethyldisiloxane was dissolved in an excess of sulfuric acid before adding the silicate and water. The results show that even methoxy groups can be replaced readily by the trimethylsiloxy groups.

The last member of the series, $Si_4O_3(OM)_{10}$ is a new compound. It is unusual in that it is probably the only compound with a molecular weight over a thousand which can be distilled at atmospheric pressure. It is reasonable to expect that still higher homologs can be prepared as the corresponding alkoxysilanes become available.

BIBLIOGRAPHY

1. Rochow, E. G. "Chemistry of the Silicones", John Wiley and Sons, Inc., 1946, pp. 1-57.
2. Chemical and Engineering News, 1233, May 10, (1946).
3. Wakeman, R. L. "The Chemistry of Commercial Plastics".
4. Kipping, F. S., J. Chem. Soc., 101, 2106, (1912).
5. Hellström, N., Svenk Kem. Tid 60, 223-7, (1948); C.A. 43, 2573, (1949).
6. Stock, A. and Sanieski, C., Ber., 52, 695, (1949).
7. Rochow, E. G. and Gilliam, W. F., J. Am. Chem. Soc., 63, 798, (1941).
8. Wright, N. and Hunter, M. J., J. Am. Chem. Soc., 69, 803, (1947).
9. Wright, J. R., Masters Thesis, University of Delaware (1949).

THE REDUCTION OF COMPLEX CYANIDES WITH ALKALI METALS IN LIQUID AMMONIA

Robert N. Hammer

April 29, 1952

I. INTRODUCTION

1. Choice of medium. Two outstanding factors make liquid ammonia an excellent medium for the study of lower oxidation states (1). First, the stability of compounds containing elements in lower oxidation states is undoubtedly associated with the reducing character of this solvent. Secondly, the solubility of the alkali metals in ammonia makes possible the use of the most powerful of all chemical reducing agents in an easily handled form.

2. Reduction of cyanide complexes. In aqueous solution it is fairly well established that reduction of cyanide complexes of nickel, palladium, and manganese with a strong reducing agent such as potassium amalgam results in the formation of products in which the metal exists in the +1 oxidation state (2). The formation of these reduction products quite naturally suggests the study of cyanide complexes in liquid ammonia.

3. Experimental techniques. Although preparative problems in the study of unusual oxidation states are often difficult, studies of the reduction of cyanides in liquid ammonia have been concerned primarily with the development of apparatus and of methods for the characterization of the reduction product. In most cases the design of apparatus (3,4,5,6,7) must include provision for:

(a) accurate determination of amounts of reacting substances
(b) collection and measurement of gases liberated
(c) repeated washing of precipitates with liquid ammonia
(d) analysis of compounds out of contact with air.

Among the many methods available for the characterization of a reduction product, the following have been applied to cyanides:

(a) quantitative analysis to determine the empirical formula
(b) determination of the reacting ratio of starting material and reducing metal
(c) measurement of the reducing power of the product
(d) magnetic susceptibility measurements

4. Compounds studied. Reduction of the following compounds has been attempted in liquid ammonia (8).

$K_2Ni(CN)_4$
$K_2Pd(CN)_4$
$K_3Mn(CN)_6$
$K_2Pt(CN)_4$
$K_3Cr(CN)_6$
$K_3Co(CN)_6$
$K_2Cd(CN)_4$
$K_3Cu(CN)_4$
$K_2Zn(CN)_4$
$K_4Fe(CN)_6$
$KAg(CN)_2$

In all compounds except those of Ni, Pd, Mn, and Pt, the complex was decomposed, usually with the liberation of the free metal. Preliminary study (9) indicates the existence of a reduction product of $K_2Pt(CN)_4$, but a detailed investigation has not been carried out because of the slight solubility of the starting material in liquid ammonia and because of the excessive evolution of hydrogen. In the case of Ni, Pd, and Mn, there is excellent experimental evidence for the existence of cyanide complexes in which the metal exhibits an oxidation number of zero.

II. Lower oxidation states of nickel (9,10).

1. Reaction of excess $K_2NI(CN)_4$ with reducing metal. Treatment of a solution of potassium tetracyanonickelate(II) with a limited amount of alkali metal in liquid ammonia results in the precipitation of a red compound having the empirical formula $K_2Ni(CN)_3$. This substance dissolves in water to form a strongly reducing solution with properties corresponding to those of aqueous cyanonickelate(I) solutions. Even though the compound is completely stable in ammonia, it shows signs of decomposition after an hour's exposure to air.

2. Reaction of $K_2Ni(CN)_4$ with excess reducing metal. Potassium tetracyanonickelate(II) reacts with potassium in a molar ratio of 1 to 2 when an excess of reducing metal is present. The product is quite stable in ammonia but is extremely unstable in air and turns black on momentary exposure. It is a powerful reducing agent which will liberate hydrogen from water and instantly reduces AgI or HgI_2 to the free metal. Analysis indicates the formula to be $K_4Ni(CN)_4$.

III. Lower oxidation state of palladium (9).

A solution of $K_2Pd(CN)_4$ reacts with potassium in a molar ratio of 1 to 2 to form a light yellow precipitate as the sole reaction product. Analysis indicates the Pd to K ratio is 1 to 4 and substantiates the formula $K_4Pd(CN)_4$. When treated with NH_4Br, a suspension of $K_4Pd(CN)_4$ dissolves until two to three equivalents of NH_4Br have been added. Precipitation of KBr then begins and continues until four equivalents of NH_4Br have been used up. Concentration of the resulting $(NH_4)_4Pd(CN)_4$ solution results in decomposition into metallic palladium. Cyanopalladate (0) compounds have great reducing power and react in a manner similar to $K_4Ni(CN)_4$.

IV. Lower oxidation states of manganese.

Although the exact nature of the material has been disputed, there is substantial evidence for the preparation in water of a manganese cyanide in which the metal exists in the +1 oxidation state (11,12,13,14). As a result, a rather detailed study of the manganese cyanides has been carried out by Dr. Jacob Kleinberg and his students* at the University of Kansas. This work is as yet unpublished.

---

*R. N. Hammer, 1947-1949; V. J. Christensen, 1949-1952. The writer would like to express his appreciation to Mr. Christensen for supplying the latest data report here. All of the quantitative measurements are Mr. Christensen's work.

1. Reduction of $K_3Mn(CN)_6$. Because of difficulties in preparing cyanomanganate(II) salts which are rather unstable, $K_3Mn(CN)_6$ was used as the starting material in all reduction reactions. The very slight solubility of this compound in liquid ammonia required the development of new techniques for the reduction of solid material. Finely ground $K_3Mn(CN)_6$ was added slowly to a large excess of potassium dissolved in liquid ammonia. As reduction occurred, the blue and green colors associated with Mn(II) compounds were observed, but eventually the entire material was converted to a creamy yellow solid insoluble in liquid ammonia. This material is completely stable in an ammonia atmosphere, but is instantly oxidized by contact with air.

2. Characterization of the product. The following approaches have been used to demonstrate that the reduction product is a solvated double cyanide of Mn(0) and Mn(I) having the formula $K_5Mn(CN)_6 . K_6Mn(CN)_6 . 2NH_3$:

(a) Analytical data. Average values for several determinations are as follows:

K = 48.29%   Mn = 12.51%   CN = 35.11% NH_3 = 4.29%

This corresponds to an empirical formula $K_{10.9}Mn_2(CN)_{11.9} \cdot 2.2NH_3$, or in round numbers, $K_{11}Mn_2(CN)_{12} . 2NH_3$. This corresponds to an average oxidation number for manganese of $+\frac{1}{2}$ and can be interpreted as a compound of the type $K_5Mn(CN)_6 . K_6Mn(CN)_6 . 2NH_3$ containing Mn(I) and Mn(0) in equal proportions.

(b) Reacting ratios. In a series of experiments using varying ratios of K to $K_3Mn(CN)_6$ it was found that excess potassium was present at the end of several hours for all ratios above 2.7 to 1, while for ratios below 2.3 to 1 all of the potassium was used up in about 15 minutes. Between 2.3 and 2.7 the line was not clear cut, probably because the design of the apparatus did not permit rapid mixing. These results are in keeping with the postulated formula which would require a reacting ratio of 2.5 to 1 as indicated by the equation

$$K_3Mn(CN)_6 + 2\frac{1}{2}\ K \rightarrow K_{5\frac{1}{2}}Mn(CN)_6$$

(c) Reducing power. Direct quantitative measure of the reducing power of the reaction product was obtained by treating the material with a liquid ammonia solution of $AgNO_3$ and determining the amount of metallic silver formed. To oxidize Mn($\frac{1}{2}$) to Mn(II) would require 1.50 gram-equivalents of Ag per gram-atom of Mn; experimental values were 1.50, 1.51, and 1.53.

(d) Magnetic measurements. Magnetic susceptibility measurements have not been completed, but the best value in preliminary work indicates a moment of 1.29 Bohr magnetons, as compared with a value of 1.73 for the one unpaired electron which might be expected to be associated with $K_5Mn(CN)_6 . K_6Mn(CN)_6 . 2NH_3$. Although this discrepancy is considerable, it could be accounted for by the oxidation of a small portion of the material. Detailed consideration of the magnetic susceptibility must be postponed until the completed data are available.

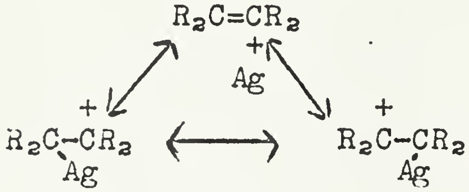
V. Bibliography

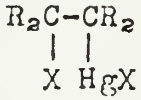
1. Jacob Kleinberg, J. Chem. Ed., 27, 32-6 (1950).
2. Jacob Kleinberg, "Unfamiliar Oxidation States and Their Stabilization", University of Kansas Press, Lawrence, 1950, pp. 90-2, 118, 82-3.
3. W. C. Fernelius and W. C. Johnson, J. Chem. Ed., 6, 441-50 (1929).
4. G. W. Watt and T. E. Moore, J. Am. Chem. Soc., 70, 1197-1200 (1948).
5. G. W. Watt and C. W. Keenan, J. Am. Chem. Soc., 71, 3833-5 (1949)'
6. G. W. Watt and J. B. Otto, Jr., J. Electrochem. Soc., 98, 1-8 (1951).
7. W. M. Burgess and E. H. Smoker, Chem. Rev., 8, 265-72 (1931).
8. G. W. Watt, Chem. Rev., 46, 289-315 (1950).
9. J. T. Burbage and W. C. Fernelius, J. Am. Chem. Soc., 65, 1484-6 (1943).
10. J. W. Eastes and W. M. Burgess, J. Am. Chem. Soc., 64, 1187-1189, 2715-6 (1942).
11. W. Manchot and H. Gall, Ber., 60B, 191-4 (1927).
12. G. Grube and W. Brause, Ber., 60B, 2273-8 (1927).
13. W. Manchot and H. Gall, Ber., 61B, 1135-40 (1928).
14. W. D. Treadwell, O. Gübeli, and Dora Huber, Helv. Chim. Acta, 24, 152-7 (1941).

STRUCTURE OF THE PLATINUM-OLEFIN COMPLEXES

James W. Currier April 29, 1952

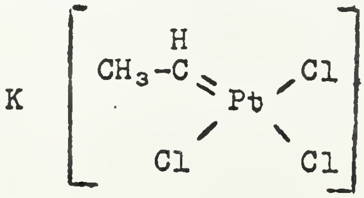
The ability to combine with olefins is quite widely distributed among the metals. Considerable attention has been focused upon these metal-olefin complexes, primarily because of the challenging problems centering around their structures (8). Seemingly satisfactory structures have been proposed to explain such phenomena as "protonated double bonds," silver-olefin complexes, and the addition of mercuric salts to olefinic linkages. The concept of the protonated double bond is well established; The differences between silver and mercury addition compounds with olefins have been resolved by depicting the silver-olefin compounds as ionic complexes represented by several resonance structures (12) and the mercury-olefin compounds as being true molecular addition compounds (8).





$$\begin{matrix} R_2C-CR_2 \\ | \quad\;\; | \\ X \quad HgX \end{matrix}$$

The platinum metals form a series of interesting extremely stable olefin complexes which have defied structural representation by any of the above or the classical electron pair co-ordination theory. The ability to combine with olefins is most strongly exhibited by platinum compounds. A considerable quantity of experimental data concerning these platinum complexes has accumulated in the literature. Recently Chatt (5) has correlated these data and proposed a structure which appears to be in accord with most of the experimental phenomena. There are two essential features to this proposed structure as pictured by Chatt. The first of these involves an electron pair donation by the olefin and in turn a donation (as it may be pictured) of d electrons from the platinum (II) compound to form a double bond between the olefin and the platinum atom. The second feature is depicted as a shift of one of the hydrogens adjacent to the olefinic bond to the neighboring carbon thus forming an ethylidene structure containing a platinum-olefin double bond as shown below for Ziese's salt.



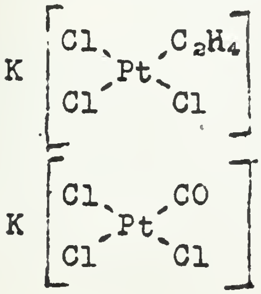
Actually Hel'man (7) was the first to suggest that d electrons of the platinum atom were involved in platinum-olefin bonds. She carried out potentiometric titrations of $NH_4[Pt(C_2H_4)Cl_3]$,

$K_2[PtCl_3(C_4H_6)PtCl_3]$, $NH_4[Pt(NH_3)Cl_5]$, and $K[Pt(NH_3)Cl_3]$ with permanganate. Only $K[Pt(NH_3)Cl_3]$ was oxidized. In addition the observed starting potentials for the ethylene and butadiene platinum (II) complexes were of the order of that found for the platinum (IV) rather than the platinum (II) complex. Hel'man interpreted these results to mean that d electrons of platinum were tied up in the olefin complexes in a manner equivalent to the platinic state.

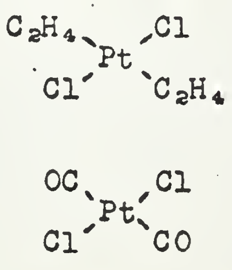
By way of disproving this view, Chatt (3) attempted to prepare a complex between ethylene and trimethyl boron. Since the boron compound is a Lewis acid yet contains no d electrons, it was assumed that the co-ordination between the olefin and the boron compound would disprove the proposal that d electrons of the metal are necessary to stabilize the platinum olefin co-ordination bond. Chatt found no evidence, however, for co-ordination between trimethyl boron and the olefin and thus concluded that olefins cannot co-ordinate to the platinum metals by a simple electron pair donation to the metal.

The relative stabilities of the platinum complexes of substituted olefins further substantiates the theory that d electrons of platinum are involved in the bond formation. Anderson (2) undertook to determine why electron withdrawing groups on the olefins stabilized the resulting metal-olefin complexes while the opposite appeared to be true if electron donating groups are substituted on the olefin. Thus styrene formed a more stable platinum (II) complex than propylene. Although the relative volatilities of the olefins undoubtedly govern the stability of these complexes to some extent, the complete reversal of stabilities that would be predicted by the electron pair co-ordination theory indicates that the electron withdrawing power of the olefins governs the stability of the platinum-olefin complexes.

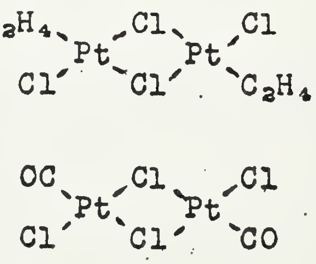
Finally the formal analogy between platinum (II) carbonyl and olefin complexes offers an insight into the true nature of these metal olefin complexes. Recently Chatt (4) prepared the bis-ethylene platinum (II) chloride complex to complete the ethylene-platinum chloride series. It is noted that ethylene and carbon monoxide form platinum (II) complexes with neutral molecules or negative ions in contrast to the positive ion complexes of olefins with silver. Likewise steric considerations show that these platinum complexes could not be true addition compounds like the olefin-mercury compounds.



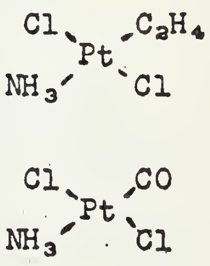
I



II



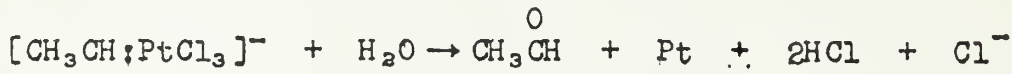
III



IV

Actually the above analogy is not merely a formal relationship. Both olefins and carbon monoxide exhibit strong trans influence in their platinum complexes as opposed to the cis influence of most complexing groups. As a consequence of this trans influence groups entering the co-ordination sphere of such complexes co-ordinate in a trans position and are held by a weakened trans co-ordination bond. This causes monomeric forms such as II and IV to change to the dimeric complex III. This trend in stability is just the opposite of that in the analogous amine complexes which form more stable monomers than dimers. Since the carbonyl and olefin complexes of platinum are alike, yet so different from normal complexes of the platinum (II) state, it is only natural to assume that they might have similar structures. Pauling (10) has shown that certain metal carbonyls have partial double bond character between the metal and carbon atoms. Therefore by inference it would appear that the olefin complexes of platinum also have some double bond character. However, this is not the only clue to be gained by the olefin-carbonyl analogy. Pauling also states that the partial double bonds of the carbonyl complexes do not alter the spacial arrangement of co-ordination groups about the central atom. The platinum (II) olefin complexes would therefore be expected to retain the planer configuration which they have been shown to possess.

The evidence supporting Chatt's contention of a hydrogen shift within the olefin is not as decisive as that supporting a platinum olefin double bond. However, some of this evidence certainly supports the idea of an unsymmetrical linkage of the olefin to the metal. Chatt cites the fact that hydrogen migrates from one carbon to the other when ethylene is brought into contact with a nickel catalyst at room temperature (6). Actually it is probable that no analogy exists between this observation and the olefin complex since it appears that this phenomenon on a nickel catalyst is due to atomic hydrogen and may take place through a free radical mechanism. However, it cannot be discounted entirely. A more conclusive bit of evidence supporting unsymmetrical coupling between the olefin and metal is brought to light by the hydrolysis of a platinum ethylene complex in which acetaldehyde is formed (1).



$$[CH_3CH;PtCl_3]^- + H_2O \rightarrow CH_3\overset{O}{CH} + Pt + 2HCl + Cl^-$$

A similar reaction takes place with the analogous carbonyl compound to produce carbon dioxide (11).

$$[OC:PtCl_3]^- + H_2O \rightarrow CO_2 + Pt + 2HCl + Cl^-$$

Acetaldehyde might not be expected on hydrolysis if the olefin were bound symmetrically. As a further proof of the proposed unsymmetrical binding of the olefin, Chatt has attempted to prepare another compound, $[Pt(NH_3)_4][(Ph)_2C{=}PtCl_3]$ (4). Although the method of preparation is not discussed Chatt reports that a compound of this composition has been prepared. He suggested this as a possible proof for both the double bond character and unsymmetrical binding of the olefin complex.

Chatt also suggests that cis and trans olefins should be allowed free rotation when complexed in the manner in which he pictures their structures. Evidence concerning this was lacking, however, at the time of his last publication. Unpublished work by Oppengard (9) has shown that such free rotation cannot be permitted since cis or trans isomers can be recovered from the platinum complex unchanged.

In conclusion it can be stated that the double bond character of the platinum-olefin complexes seems to be well established. However, the ethylidene structure still remains doubtful. It would appear that further evidence is necessary to prove or disprove this latter contention.

Bibliography

1. Anderson, J. Chem. Soc., 1934 971.
2. Anderson, J. Chem. Soc., 1936 1042-7.
3. Chatt, J. Chem. Soc., 1949 3340-8.
4. Chatt, Nature, 165 859-60 (1950).
5. Chatt, Research, 4 180-3 (1951).
6. Farkas and Farkas, Proc. Roy. Soc., A165 630 (1934).
7. Hel'man, Compt. rend. acad. sci. U.R.S.S., 16 29 (1936).
8. Keller, Chem. Revs. 28 229-67 (1941).
9. Oppengard, Thesis, University of Illinois (1949).
10. Pauling, "Nature of the Chemical Bond," Cornell University press, 1948, New York, 2 Ed., p. 250.
11. Schültzenberger, Bull. Soc., Chim. 14 17 (1870).
12. Winstein and Lucas, J. Am. Chem. Soc., 60 836 (1938).

THESIS REPORT

Robert F. Vance May 6, 1952

I. SYNTHESIS AND CHEMISTRY OF GUANAZINE

For many years it has been known that compounds containing hydrazine linkages possess interesting physiological properties. But only recently, however, has a concerted attempt been made to correlate such observations with similarities in structure. Many important and valuable discoveries in this field have now been made, highlighted, perhaps, by the recent report of phenomenal antitubercular activity exhibited by a hydrazide of isonicotinic acid (1). Discoveries of this nature have stimulated a more intensive characterization of many classes of hydrazine derivatives.

The object of this investigation was, first, to improve the synthesis of guanazine, systemmatically named 3,4,5-triamino-1,2,4-triazole, and second, to characterize a number of its derivatives. Guanazine was first isolated in 1905 by Pellizzari (2) as a by-product in the synthesis of diaminoguanidine from cyanogen bromide and hydrazine. At that time its chemical behavior was investigated to some extent, then interest was dropped.

A useful starting point in the characterization of such a compound is to compare its chemical behavior with that of structurally related compounds. Guanazine may be considered as a cyclic mixed hydrazino ammono derivative of carbonic acid. Its relation to acyclic compounds of high nitrogen content, for example, diaminoguanadine, is readily apparent. The consideration of cyclic congeners, such as guanazole (of similar structure but without an N-amino group), urazine, and urazole is also useful in the characterization of guanazine.

A number of different approaches to the synthesis of guanazine were attempted; the only one possessing preparative value, however, was the method already mentioned, i.e., the cyanation of hydrazine. It was thought that the isolation of cyanogen bromide might be eliminated by dropping hydrazine directly into an aqueous solution of sodium bromide and cyanogen bromide; difficulty in purification of the product was encountered. The procedure finally selected involved the addition of hydrazine hydrate to an aqueous solution of cyanogen bromide at temperatures not exceeding 25°. The product was isolated as the hydrobromide salt upon addition of isopropyl alcohol, yields of 54% being obtained. Order of addition made no difference in yield or purity of guanazine hydrobromide.

Guanazine has previously been isolated as the free base only by reaction of the hydrobromide with freshly prepared lead hydroxide (3); the procedure is inconvenient and yields are poor. The free base, like many amines of very high nitrogen content, is so soluble in water than no extraction whatsoever is obtained with organic solvents. Guanazine was freed from its hydrobromide salt by treatment with sodium hydroxide in methanol, a crude yield of

86% being obtained. This procedure appears to be of general preparative value for basic nitrogen compounds of high water-solubility. A combination of sodium or potassium hydroxide with either methanol or ethanol, depending upon the solubility of the amine in these solvents, may be used. A pH titration of guanazine with hydrochloric acid was carried out and the basic dissociation constant calculated to be 2.5×10^{-8}. This value indicates that guanazine is a much weaker base than ammonia and hydrazine but stronger than guanazole and pyridine. A number of guanazine salts were prepared by reaction of the free base with the acid. Guanazine usually shows the characteristics of a monoacidic base, but the dihydrobromide was prepared by recrystallization from the concentrated acid. Dibasic acids, such as sulfuric and oxalic acids, form normal salts.

Reaction with potassium cyanate yielded a monoureido derivative as the hydrobromide, but it was too susceptible to hydrolysis to warrant further study. The monobenzal derivative was prepared in acidic solution; the dibenzal compound, in basic medium. A reaction analogous to quinoxaline formation occurred with 1,2-diketones. The product obtained using benzil is a 2,3,5,8,9-pentaazaindene; this ring nucleus had never before been reported.

An investigation of the complexing ability of guanazine was made. Copper (II) ion, a powerful nitrogen-coordinating agent, gave a noticeable color change in solution. A polarogram showed positive evidence of a copper(I) complex, which is reversibly reduced to copper(0); the presence of a copper(II) complex was obscured by an uncharacterized oxidation process taking place at the same potential. The copper(II) complex was studied with a Cary spectrophotometer and evidence of a complex containing two copper(II) ions to one guanazine molecule obtained. A structure has been postulated.

II. BASICITY STUDIES ON ORGANIC SULFIDES

The unsubstituted three- to six-membered cyclic imines were reported by Brown and Gerstein (4) to exhibit basicity toward trimethylboron in the order, $4 > 5 > 6 > 3$-membered rings. This behavior was ascribed to F- and I-strain. F-strain, as proposed by Brown (5), is essentially a steric hindrance caused by groups adjacent to the basic atom. This theory predicts the highest degree of basicity to be exhibited by the smallest ring. I-strain was proposed to account for the anomolous basicity of the three-membered ring; it may be defined as the change in internal strain of a ring compound which results from a change in the coordination number of a ring atom involved in a chemical reaction. It is believed in some quarters, however, that these theories are too dependent upon interaction with other molecules and ignore the possibility that these effects may be due to an alteration of electron distribution with ring size (6). Searles and Tamres (6), in investigating the basicity of both unsubstituted and substituted ethers using spectroscopic and heat-of-mixing techniques to

measure degree of hydrogen bonding, found that substitution in the alpha position invariably increased the basicity of cyclic ethers. These facts indicate that electron distribution around the basic atom is more important than F- and I-strain.

The present work extends the study of basicity as a function of ring size to the sulfide series. Hydrogen bonding interaction was too weak to be measured spectroscopically or by heats of mixing; another measure of basicity (in the Lewis sense) was employed. Equimolar quantities of the sulfide and boron trifluoride were introduced into a vacuum system and the vapor pressure of the mixture measured. If no interaction occurred, the observed pressure of the mixture should be the sum of the pressures of the components. The depression from this sum is a direct measure of interaction between the sulfide and boron trifluoride, assuming that the molecular addition compound exerts negligible vapor pressure. Results of the unsubstituted series showed basicity of the order, $4 > 5 > 6 \gg 3$ atoms in the ring, exactly the same order as that of the cyclic ethers. Indeed, a plot of the ether data as ordinate against data for the sulfides of identical ring size as abscissa gave a straight line, indicative of similar degree of reaction as a function of ring size for each series. Since the same order of basicity is observed in each series, although the basic atom has been greatly increased in size, it appears that factors other than F- and I-strain must also be considered.

Bibliography

1. Chem. Eng. News 30, 902 (1952).
2. Pellizzari, G. and Cantoni, C., Gazz. chim. ital. 35 I, 291 (1905).
3. Pellizzari, G. and Repetto, A., Gazz. chim. ital. 37 II, 317 (1907).
4. Brown, H. C. and Gerstein, M., J. Am. Chem. Soc. 72, 2926 (1950).
5. Brown, H. C., Bartholomay, H. Jr., and Taylor, M. D., J. Am. Chem. Soc. 66, 435 (1944).
6. Searles, S. and Tamres, M., J. Am. Chem. Soc.. 73, 3704 (1951).

Thesis Report

Fred L. Pundeack May 6, 1952

Investigations on 8-Quinolinol and Substituted 8-Quinolinol Chelates of the Group III B Elements

8-Quinolinol, or "oxine" as it is more familiarly known, forms a number of more or less intensively colored compounds with various metal ions. This property has led to the extensive use of oxine as an analytical reagent since it was first introduced by Hahn (3) and by Berg(1). Since its introduction, oxine has been used first as a quanititative precipitating agent, then as a colorimetric reagent, and more recently as a chromatographic agent (4) (7). In addition to its uses in analytical chemistry, oxine and certain of its metal derivatives have found application as fungicides, and even as urinary antiseptics.

In the formation of metal chelates an equivalent of a metal ion replaces the acidic hydrogen on oxine, and at the same time a coordinate covalent bond is formed between the metal ion and the amine nitrogen of oxine. In general, the number of oxine "ions" attached to a metal "ion" in a metal oxinate is the same as the valence number of the metal in question. Such chelates are true inner complexes, and as such are essentially non-ionic and insoluble in water, but they do dissolve in less polar solvents such as benzene and chloroform.

On the whole the investigations of the chelate compounds of oxine have been made from an analytical approach. With the exception of the recent work by Moeller and Cohen (2) (6) and by Maley and Mellor (5), no systematic studies of metal oxinates in order to determine the effects of size, charge, basicity, etc. of the central metal "ion" upon the chelate appear to have been made. In addition, the possibility of employing dihalogenated oxines instead of oxine in order to achieve a greater degree of selectivity in precipitation of metal ions does not appear to have been fully investigated. These considerations made it appear that a systematic study of oxine and dihalogenated oxine derivatives of a family of elements would prove worthwhile.

In the present investigation, attention has been devoted to the preparation and study of the 5,7-dihalogenated oxinates of gallium and induim. Data on certain aluminum and thallium oxinates have been considered for purposes of comparison. The absorption spectra of the dihalogenated oxine derivatives of gallium and induim in chloroform solutions have been evaluated in order to observe the effect of substituents on the oxine nucleus. The adherence of the absorption bands to Beer's Law has been determined and the applicability of the compounds to analytical procedures has been considered. In view of the conflicting data in the literature concerning the optimum conditions for the extraction of metal oxinates into chloroform, a study of the extraction of gallium oxinate and dihalogenated oxinates into chloroform was made. In conjunction with these studies, the distribution of oxine between water and chloroform also was determined.

The similarity of the absorption spectra of metal oxinates in organic solvents and the absorption spectrum of oxine in acidic aqueous solution was noted, and an investigation of this phenomenon was instituted.

In the course of evaluating the effect which changes in the size and weight of the metal "ion" had on the absorption spectra of metal oxinates, it became apparent that an investigation of the important but ill-defined effect which the solvent exerted on the absorption spectra would be worthwhile. Therefore, the absorption spectra of gallium oxinate in a variety of solvents were evaluated, and an attempt to relate absorption band shifts to physical properties of the solvents was undertaken.

In general, the method employed for preparation of all of the gallium and induim dihalogenated oxinates involved the addition of acetone solutions of the reagents to hot aqueous solutions of gallium (III) and induim (III) salts at a pH of less than 1. The yellow chelates which were precipitated were dried at ca. 110°C. Under these conditions all of the dihalogenated oxines quantitatively precipitated gallium (III) and induim (III).

The absorption spectra of all of the gallium and induim oxinates and dihalogenated oxinates in chloroform solutions are characterized by three absorption peaks in the wavelength region 3000-9000 A. These peaks are located in the general regions of 3300Å, 3450Å, and 4000Å respectively. It was found that increasing the size and weight of the central metal "ion" shifted the absorption peaks to longer wavelengths (i.e., a bathochromic shift), but did not alter the shape of the absorption spectra. In general, the effect of substituting halogens in the 5,7- positions on the oxine nucleus is to bring about a bathochromic shift coupled with an increase in the extinction value (e.e., a hyperchromic shift) of the absorption peaks. The magnitude of the bathochromic and hyperchromic shifts appeared to be directly related to the weight of the substituted halogens, although the major shift resulted when halogens were introduced in the 5,7- position. The specific nature of the halogens introduced was of somewhat lesser importance.

The chloroform solutions of all of the metal oxinate and dihalogenated oxinates investigated were found to be subject to photochemical decomposition, which resulted in hypsochromic (i.e., shift of absorption band towards shorter wavelengths) and hypochromic (i.e., decrease in extinction value) shifts of the absorption bands. However, with suitable precautions the solutions were stable for periods of one week or longer.

In all of the absorption spectra evaluated, the three absorption peaks of the dihalogenated oxinates were found to adhere to Beer's Law. However, since all of the reagents have an absorption peak in the vicinity of 3300Å, the metal oxinate peak at 4000Å is the only peak of analytical importance. This absorption peak may be used for the spectrophotometric determination of concentrations of gallium as low as 0.2 mg. of gallium per liter of solvent, and concentrations of induim as low as 0.4 mg. of induim per liter of solvent.

Extraction experiments showed that gallium oxinate, dichloroxinate, and chloroiodoxinate can be quantitatively extracted from an aqueous phase into chloroform over definite pH limits. It was shown that the lower pH limit for the quantitative extraction of gallium oxinate and aluminum oxinate differ by at least one pH unit, and consequently gallium oxinate could be selectively extracted from aluminum oxinate, and the gallium concentration determined spectrophotometrically.

The distribution of oxine between chloroform and water was found to be dependent upon the pH of the aqueous phase. Maximum distribution of oxine into the chloroform phase occurred over a pH range of 6 - 8.

During the course of these investigations it was noted that the absorption spectrum of oxine in acid aqueous solution was similar to the absorption spectra of metal oxinates in organic solvents. This phenomenon is believed to be due to the hydrogen bonding in the acidic species of oxine which results in a structure very similar to the inner complex structures of metal oxinates.

The absorption spectra of gallium oxinate in a variety of solvents were determined. It was shown that the absorption peak underwent a hypsochromic shift as the dielectric constant of the solvent increased and that this shift could be expressed and predicted as a function of the dielectric constant of the solvent.

Bibliography

1. Berg, R., J. prakt. Chem. 115, 178 (1927)
2. Cohen, A. J., Doctorial Dissertation, Univ. of Illinois, 1949
3. Hahn, F. L., Z. angew. Chem. 39, 1198 (1926)
4. Laskowski, D.E., and McCrone, W.C., Anal. Chem. 23, 1579 (1951)
5. Maley, L.E., and Mellov, D.P., Australian J. Sci. Research 2A, 92 (1949)
6. Moeller, T., and Cohen, A.J., J. Am. Chem. Soc. 72, 3546 (1950)
7. Robinson, G., Discussions Faraday Soc. 1949 [7], 195

THESIS REPORT

Earle Scott May 13, 1952

INTRODUCTION

Expanded production of hydrazine on a commercial scale, coupled with an intensive effort to develop new synthetic procedures - brought about by the discovery of certain military applications during World War II - make it appear that hydrazine hydrate and the highly concentrated base will someday be available for wide scale industrial use. The relatively recent discovery that a variety of organic hydrazine derivatives display marked biological activity has stimulated greatly the study of the chemistry of hydrazine and of its derivatives. The present investigation was undertaken in order to organize and clarify the chemistry of the hydrazine derivatives of the carbonic and the thiocarbonic acids and to synthesize compounds to be tested for a variety of biological effects.

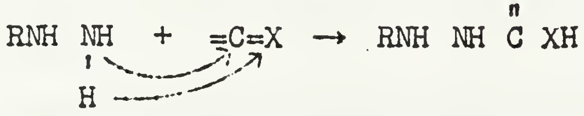
HISTORICAL

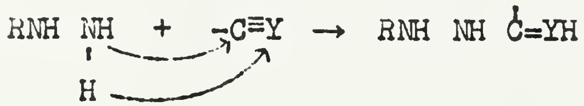
The solvent system theory developed by Franklin (1) may be employed to elucidate the relationships existing between the thiocarbonic acid derivatives, considered as members of a series of compounds derived from hydrogen sulfide as the parent solvent, and the analagous aquo, ammono, and hydrazino compounds. Conversions of carbonic acid derivatives of any one system to those of any other system may be accomplished experimentally by processes of solvation and solvolysis.

All methods which have been developed for the preparation of hydrazine derivatives of carbonic acid may be placed in one of three classes: (2)

a) Reduction of compounds containing an N-N linkage e.g. nitroamino, nitrosoamino and diazonium compounds.

b) Hydrazination reactions - defined as involving the addition of hydrazine or substituted hydrazine to a multiple bond according to the generalized equations (1) and (2),

(1)

$$RNH\ \underset{H}{\underset{|}{NH}} + {=}C{=}X \rightarrow RNH\ NH\ \overset{\|}{C}\ XH$$

(2)

$$RNH\ \underset{H}{\underset{|}{NH}} + {-}C{\equiv}Y \rightarrow RNH\ NH\ \overset{|}{C}{=}YH$$

c) Hydrazinolysis reactions defined as involving the displacement of a functional group characteristic of another solvent system by hydrazine or a substituted hydrazine to form a hydrazine derivative.

$$(3)\ RNH\ NH_2 + \equiv C{-}X \rightarrow RNH\ NH\ C\equiv + HX$$

$$(4)\ RNH\ NH_2 + {=}C{=}Y \rightarrow RNH\ N{=}C{=} + H_2Y$$

Cyclization reactions which the hydrazine derivatives of carbonic acid undergo are classified into two groups.

a) Solvation cyclization reactions - In which one terminal functional group of a chain compound adds to an unsaturated function on the other end of the molecule to form a ring.

b) Desolvation cyclization reactions (3)(4) - In which a hydrogen atom and one terminal functional group are eliminated from the chain compound (as a solvent molecule) in the process of cyclization. Ring closures involving the elimination of water, alcohols, hydrogen halides, hydrogen sulfide, mercaptans, ammonia, amines, and hydrazine are placed in this category.

EXPERIMENTAL

The type reactions outlined above were used to synthesize derivatives of thiocarbohydrazide and thiosemicarbazide. The specific experimental procedures included the following:

a) Hydrazination of cyanic acid, thiocyanic acid and carbon disulfide to give carbamyl, thiocarbamyl and dithiocarbonic acid derivatives respectively.

b) S-methylation of derivatives of the thiocarbonic acids by the reaction of these compounds or their alkali metal salts with methyl iodide.

c) Hydrazinolysis of S-methyl compounds to effect the replacement of the mercapto group by a hydrazide function.

Aldehyde and ketone derivatives of compounds containing a free hydrazide function were prepared both as characterizing derivatives and for biological evaluation.

The following new derivatives of thiocarbohydrazide(I) were prepared:

a) The anisaldehyde, p-hydroxybenzaldehyde, and p-chloroacetophenone derivatives.

b) S-methyl thiocarbohydrazide hydroiodide was prepared by direct combination of (I) and methyl iodide. It was characterized by the formation of the picrate and the benzaldehyde derivative, and conversion into triaminoguanidine hydroiodide by hydrazinolysis.

c) Carbamylthiocarbohydrazide(II) was prepared by the reaction of (I) with cyanic acid and by the hydrazinolysis of methyl semicarbazidodithiocarbonate. It was characterized by the formation of the benzaldehyde, anisaldehyde, p-hydroxybenzaldehyde, and p-chloroacetophenone derivatives.

d) S-methyl carbamylthiocarbohydrazide hydroiodide(III) was prepared by allowing (II) to react with methyl iodide.

e) Carbamyltriaminoguanidine hydroiodide (IV) was prepared by hydrazinolysis of both (III) and carbamyldiaminoguanidine hydroiodide and was identified by conversion to the picrate.

f) Thiocarbamylthiocarbohydrazide(V) was prepared by hydrazinolysis of methyl thiosemicarbazidodithiocarbonate and by the reaction of thiocyanic acid with (I). The acetone derivative was prepared for the purpose of characterization.

g) S-methyl thiocarbamylthiocarbohydrazide was prepared by the addition of methyliodide to a basic solution of (V).

h) The anisaldehyde and p-chloroacetophenone derivatives of 1-phenylthiocarbohydrazide have been prepared.

Two new compounds derived from thiosemicarbazide have been synthesized.

a) S-methyl carbamylthiosemicarbazidehydroiodide(VI) was prepared by the reaction of methyl iodide with carbamylthiosemicarbazide and characterized by the formation of the picrate.

b) Carbamyldiaminoguanidine hydroiodide was synthesized by the hydrazinolysis of (VI). It was characterized by the formation of the picrate and the benzaldehyde derivative and by hydrazinolysis to (IV).

A new synthesis of thiosemicarbazide was developed which involves refluxing a very concentrated solution of ammonium thiocyanate and hydrazine, present in a mole ratio of 3:1 for a period of two hours. Thiosemicarbazide may be isolated directly from the reaction mixture.

The known methods of synthesis of thiocarbohydrazide were modified and a new synthic procedure developed which entails hydrazinolysis of methyl dithiocarbazinate.

The possible use of polyphosphoric acid as a deammonating agent to effect ring closure of hydrazine derivatives of carbonic acid was investigated. This reagent effects the transformation of bisthiocarbamyl hydrazine to 2-amino-5-thiol-1,3,4-thiodiazole in good yields.

The hydrogen peroxide oxidation of hydrazine derivatives containing 1,4-sulfhydryl groups to form thiadiazoles (5) was applied to the formation of 2-amino-5-thiol-1,3,4-thiadiazole and 2-amino-5-methylmercapto-1,3,4-thiadiazole from potassium and methyl thiosemicarbazidodithiocarbonate, respectively.

Preliminary experiments indicate that many of the hydrazine derivatives of the thiocarbonic acids form complexes with a number of metal cations. Some of these complexes can be extracted into organic solvents and may have application in the field of analytical chemistry.

BIOLOGICAL TESTS

A variety of biological tests have been carried out to determine the toxiphoric characteristics of various hydrazine derivatives.

a) Compounds were tested for fungicidal activity and for their effect on plant growth by Dr. Harold W. Gausmann of the Department of Agronomy of the University of Illinois.

The fungicidal properties of the compounds were compared to those of a good commercial fungicide Thiocarbohydrazide, 1-phenylthiocarbohydrazide, carbamylthiocarbohydrazide, carbamylcarbohydrazide and triaminoguanidine display activity roughly comparable to that of the control.

Albinism has been produced in several species of plants by application of bisthiocarbamylhydrazine and its cylation product either to the soil or directly to the plant. Inhibition of growth has been observed when relatively high dosages of some of these compounds were applied.

b) Compounds were tested as tuberculostatic agents and for their effects on hypertension under the direction of Dr. T. Carney and Dr. E. C. Rohrmann of the Eli Lilly Company.

c) Preliminary tests, carried out under the direction of Professor C. W. Kearns in the Department of Entomology of the University of Illinois indicate that thiocarbohydrazide, 1-phenylthiocarbohydrazides and some of their derivatives display insecticidal properties.

BIBLIOGRAPHY

1. Franklin: "The Nitrogen System of Compounds," Reinhold Publishing Corporation, New York, N.Y., 1935!

2. Lieber and Smith: Chem. Rev., 25, 213 (1939).

3. Guha and Mehta: J. Indian Inst. Sci., 21A, 41-56 (1938).

4. Arndt and Bielich: Ber., 56, 2276 (1923).

5. Fromm: Ann., 433, 1-17 (1923).

THESIS REPORT

Ralph Gher

May 13, 1952

I. SODIUM TETRAMETAPHOSPHATE

INTRODUCTION

The modern method for the preparation of tetrametaphosphate is based upon the work of Bell, Audrieth, and Hill (1) who prepared tetrametaphosphoric acid by the low temperature hydration of phosphorus (V) oxide. However, sodium tetrametaphosphate prepared in this manner had not been proven to be identical with that obtained by earlier workers. Discrepancies in x-ray data reported by various investigators (2)(3) made comparison impossible. It was therefore considered desirable to prepare the tetrametaphosphate both by the above procedure and by the older thermal dehydration method so that positive identification might be achieved by direct comparison.

EXPERIMENTAL

Sodium tetrametaphosphate was prepared by the high temperature dehydration procedure representing a modification of the older Warschauer (4) method by Andress (5), in accordance with the following equation:

$$Cu(NO_3)_2 \cdot 3H_2O + 2H_3PO_4 \rightarrow Cu(H_2PO_4)_2 + 2HNO_3 + 3H_2O$$

$$2Cu(H_2PO_4)_2 \xrightarrow{420^\circ} Cu_2(PO_3)_4 + 4H_2O$$

$$Cu_2(PO_3)_4 + 2Na_2S \rightarrow Na_4(PO_3)_4 + 2CuS$$

Sodium tetrametaphosphate, prepared by neutralization of the low temperature hydration product of phosphorus (V) oxide, was obtained from the Victor Chemical Works.

Both materials, when subjected to crystallization from aqueous solutions under appropriate conditions were found to give the low and high temperature modifications of the 4-hydrate. Dehydration of the 4-hydrates resulted in the formation of identical anhydrous salts. Positive identification was made possible by a complete study of the x-ray diffraction patterns of all samples, demonstrating that the tetrametaphosphate prepared by the more convenient low temperature hydration procedure is the same as the products prepared heretofore by less efficient methods.

Attempts were made to define more precisely the relationships between the two crystalline modifications of the 4-hydrate. The high temperature form is easily prepared by crystallization from warm aqueous or alcoholic solutions or by allowing the so-called low temperature form to stand in contact with a saturated solution of the compound at room temperature or above.

The so-called low temperature modification appears to be meta-stable with respect to the high temperature form. The low temperature 4-hydrate is easily converted to the high temperature form, but the reverse process has not been shown to take place. Crystallization even at low temperatures (0 to -7°C) usually results in the formation of the high temperature form or, at best, in a mixture of the two forms. It is significant, however, that crystallization by the addition of acetone to an aqueous solution of the salt results in the formation of the almost pure low temperature form.

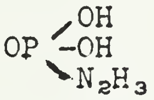
II. THE HYDRAZIDES OF THE ARYL PHOSPHORIC AND PHOSPHONIC ACIDS

INTRODUCTION

The surprising biological activity of certain organic derivatives of the phosphoric and polyphosphoric acids has stimulated a tremendous amount of research in the field of organo-phosphorus compounds designed not only to develop new and useful economic poisons, but also to correlate biological activity with chemical structure. The introduction of hydrazine into the phosphoric acid molecule as replacement for the hydroxyl group would seem to represent a modification of structure not yet considered in connection with enhancement of biological activity. The similarity in structure of the resulting P-N-N group to the known toxiphoric groups, S-N-N and C-N-N, suggested that the hydrazides and hydrazones of the alkyl and aryl phosphoric and phosphonic acids should be toxiphoric.

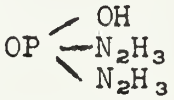
HISTORICAL

Theoretically, it should be possible to prepare compounds derived from the mon-, di-, and trihydrazides of phosphoric acid whose formulas are given below:



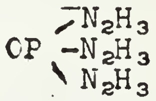
$$OP\begin{cases}OH\\OH\\N_2H_3\end{cases}$$

Phosphoric Acid
Monohydrazide



$$OP\begin{cases}OH\\N_2H_3\\N_2H_3\end{cases}$$

Phosphoric Acid
Dihydrazide

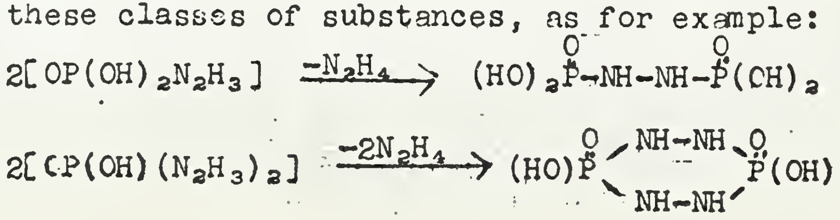


$$CP\begin{cases}N_2H_3\\N_2H_3\\N_2H_3\end{cases}$$

Phosphoric Acid
Trihydrazide

Derivatives of monohydrazido and dihydrazido phosphoric acid, as well as the N-substitution derivatives of phosphoryl trihydrazide have been prepared, although the parent substances have not been isolated.

Related to the mono- and dihydrazido phosphoric acids are a number of compounds which can be regarded as desolvation products of each of these classes of substances, as for example:



$$2[OP(OH)_2N_2H_3] \xrightarrow{-N_2H_4} (HO)_2\overset{O}{P}\text{-NH-NH-}\overset{O}{P}(CH)_2$$

$$2[CP(OH)(N_2H_3)_2] \xrightarrow{-2N_2H_4} (HO)\overset{O}{P}\begin{matrix}\text{NH-NH}\\ \\ \text{NH-NH}\end{matrix}\overset{O}{P}(OH)$$

EXPERIMENTAL

The compounds listed below have been synthesized:

A. Diphenyl phosphoric acid hydrazide, $(C_6H_5O)_2PON_2H_3$, was prepared by hydrazinolysis of the chloride in alcoholic solution, [equation (1)].

$$(1)\ (C_6H_5O)_2POCl + 2N_2H_4 \rightarrow (C_6H_5O)_2PON_2H_3 + N_2H_4.HCl$$

A number of aldehyde and ketone derivatives were synthesized, a) to verify the existence of the parent compound, and b) to determine the effect of these substituents on the biological activity of the hydrazide. Derivatives of the following were prepared: benzaldehyde, p-hydroxybenzaldehyde, salicylaldehyde, anisaldehyde, acetone, p-chloroacetophenone, cylcohexanone, and acetylacetone.

The hydrazi derivative, $(C_6H_5O)_2OPNHNHPO(OC_6H_5)_2$, was prepared by the condensation reaction between the hydrazide and the chloride according to equation (2).

$$(2)\ (C_6H_5O)_2PON_2H_3 + ClPO(C_6H_5O)_2 \rightarrow (C_6H_5O)_2OPNHNHPO(OC_6H_5)_2 + HCl$$

B. Phenyl thionophosphonic acid dihydrazide, $C_6H_5PS(N_2H_3)_2$ was prepared by hydrazinolysis of the chloride in anhydrous chloroform, [equation (3)].

$$(3)\ C_6H_5PSCl_2 + 4N_2H_4 \rightarrow C_6H_5PS(N_2H_3)_2 + 2N_2H_4.HCl$$

Derivatives of the following ketones were also prepared: acetone, p-chloroacetophenone, and cyclohexanone.

The dihydrazide gives indication of weakly basic character. The mono-picrate and a hydrochloride were prepared but analytical results for the latter were not too satisfactory. A di-N-carbethoxy derivative, $C_6H_5PS[NHNHCO(OC_2H_5)\ ]$, was prepared by treatment of the dihydrazide with ethylchlorocarbonate.

C. Phenyl phosphoric acid dihydrazide, $(C_6H_5O)PO(N_2H_3)_2$, was prepared by hydrazinolysis of the chloride in anhydrous ether followed by repeated recrystallizations from absolute ethanol, [equation (4)].

$$(4)\ (C_6H_5O)POCl_2 + 4N_2H_4 \rightarrow (C_6H_5O)PO(N_2H_3)_2 + 2N_2H_4.HCl$$

The identity of the dihydrazide was verified by conversion to the di-benzylidene derivative.

Biological Tests

Preliminary tests have shown that some of these compounds possess biological activity. Diphenyl phosphoric acid hydrazide and its p-hydroxybenzaldehyde derivative possess tuberculostatic activity. These compounds also possess some fungicidal activity. The phenyl thionophosphonyl dihydrazide is also toxic and has been shown to possess some hormonal activity on plants.

BIBLIOGRAPHY

1. Bell, R.N., Audrieth, L.F., and Hill, O.F., Ind. Eng. Chem. 44 568-72 (1952).

2. Thilo, E. and Rätz, R., Z. anorg. Chem. 260 255 (1949).

3. Bonneman, P., Compt. rend. 204 865 (1937).

4. Warschauer, F., Z. anorg. Chem. 36 137 (1903).

5. Andress, K.R., Gehring, W., and Fischer, K., Z. anorg. Chem. 260 331 (1949).