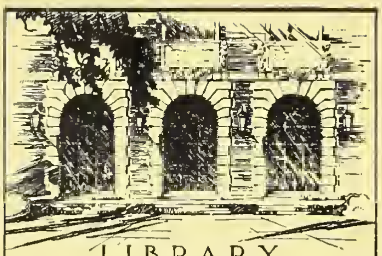

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ALKOXIDES OF SILICON, TITANIUM, AND ZIRCONIUM

October 6, 1953

S. F. West

While investigating the preparation of the alkoxides of silicon, titanium, zirconium and hafnium Bradley and Wardlaw[1] found that zirconium ethoxide could be prepared readily by reacting zirconium tetrachloride with ethanol in the presence of ammonia, as shown by the following equation:

$$ZrCl_4 + 4ROH + 4NH_3 \rightarrow Zr(OR)_4 + 4NH_4Cl.$$

Other zirconium and titanium alkoxides were prepared by this method but the products were appreciably hydrolysed when secondary alcohols were used. The method failed with tertiary alcohols.

Most of the alkoxides of zirconium, titanium, and silicon described herein were prepared by the method of ester interchange from either the tetra-ethoxide or the tetra-isopropoxide produced by the direct ammonia method. The tetra-tert.-butoxides of zirconium and titanium were prepared with some difficulty. Alcohol interchange involving either the tetramethoxide or tetraethoxide of zirconium or titanium with tertiary butanol gave only mixed alkoxides but the tetra-tert.-butoxide was obtained by thermal disproportionation of the mixed alkoxide, followed by fractionation of the products[2]. Hafnium tetraethoxide and tetraisopropoxide were obtained[3] by the action of ammonia on pyridinium hafnium hexachloride in a benzene solution of the appropriate alcohol, as shown in the following equation:

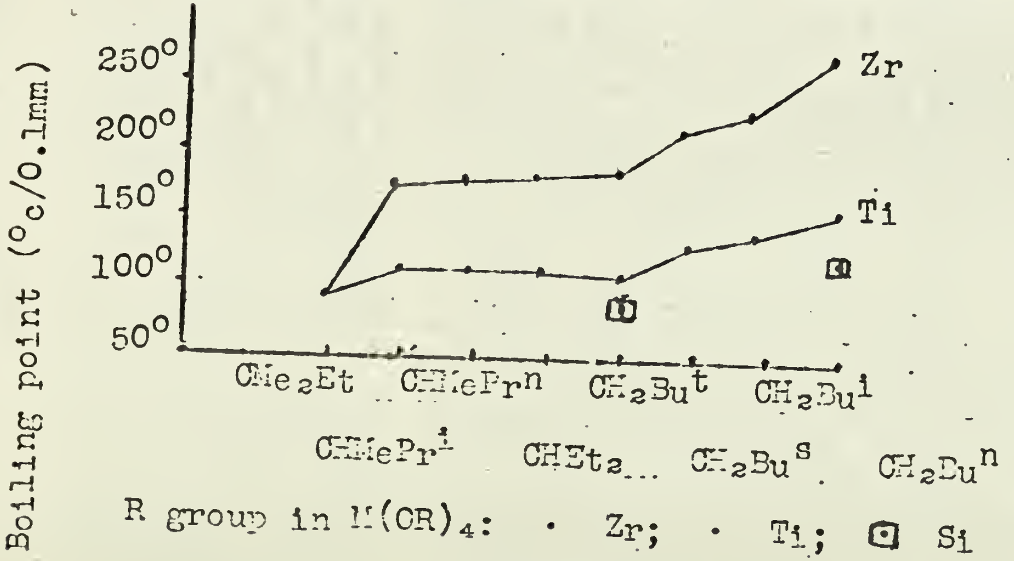
$$(C_5H_6N)_2HfCl_6 + 4ROH + 6NH_3 \rightarrow Hf(OR)_4 + 6NH_4Cl + 2C_5H_5N.$$

The outstanding feature of the isomeric alkoxides of zirconium, titanium and silicon is the increase in volatility as the alkyl group is changed from primary to secondary to tertiary. This led Bradley and coworkers to undertake a study of a series of primary[4], secondary[5], and tertiary[3] alkoxides of silicon, titanium, and zirconium in an effort to account for their properties from a structural viewpoint. The data obtained for the isomeric amyloxides of titanium and zirconium are summarized in Table[6] I. In addition, it was found that the n-amyloxide of silicon (B.p. 154°/0.1mm.), although monomeric, was much less volatile than the isomeric neopentyl orthosilicate (B.p. 85°/0.1mm.). Molecular weights were determined with a conventional Menzies-Wright ebulliometer containing benzene. Boiling points of the alkoxides were obtained at low pressures due to their low volatility.

From the data of Table I, it is quite apparent that branching of the amyl group leads to increased volatility of titanium and zirconium but the effect is most pronounced with the zirconium derivatives. It is further established that volatility is directly related to molecular complexity (determined ebullioscopically in benzene) in the amyloxides of zirconium as portrayed in Figure 2. A similar trend in molecular complexity occurs with the titanium derivatives but the alkoxides of silicon are undoubtedly all monomeric.

Table I[6] (Molecular Complexity = M/formula weight)

Alcohol	Titanium alkoxide B.p.1mm	Titanium alkoxide M	Titanium alkoxide Molecular Complexity	Zirconium alkoxide B.p.1mm	Zirconium alkoxide M	Zirconium alkoxide Molecular Complexity
$CH_2Me\cdot CH_2\cdot CH_2\cdot CH_2OH$	175°/0.8	565	1.4	256°/0.01	1428	3.2
$CHMe_2\cdot CH_2\cdot CH_2\cdot OH$	148°/0.1	490	1.2	247°/0.1	1462	3.3
$CHMeEt\cdot CH_2\cdot OH$	154°/0.5	422	1.1	238°/0.1	1615	3.7
$CMe_3\cdot CH_2\cdot OH$	105°/0.05	500	1.3	188°/0.2	1051	2.4
$CHEt_2\cdot OH$	112°/0.05	399	1.0	178°/0.05	868	2.0
$CHMePr^n\cdot OH$	135°/1.0	410	1.0	175°/0.05	860	2.0
$CHMePr^i\cdot OH$	131°/0.5	415	1.0	156°/0.01	870	2.0
$CMe_2Et\cdot OH$	98°/0.1	405	1.0	95°/0.01	455	1.0



R group in $M(OR)_4$: · Zr; · Ti; ▢ Si

Figure 1.[6]

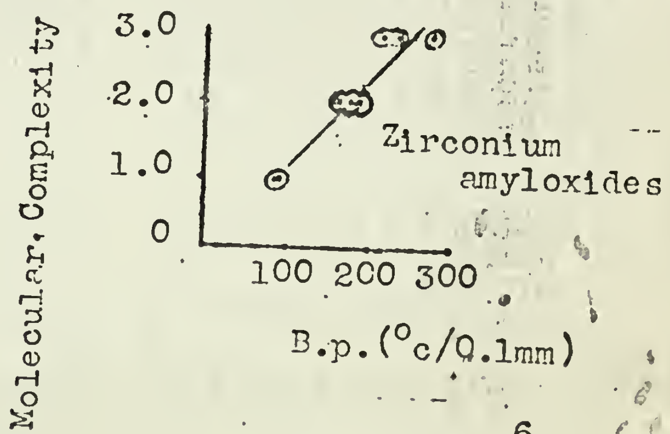
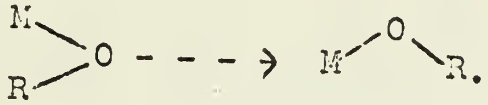


Figure 2.[6]

Intermolecular bonding apparently accounts for the abnormally high boiling points of the less branched alkoxides due to formation of bonds of the type:



This type of molecular association would be strongly opposed when the central atom is shielded by branched alkoxide groups. In the monomeric alkoxides of titanium and zirconium, it is evident that shielding is complete. In contrasting the properties of the alkoxides of zirconium with those of titanium and silicon, the behavior is undoubtedly connected with the radius of the central atom. Zirconium, which is the largest atom of the three, should require more effective shielding than the smaller titanium or silicon and this is indeed borne out by experimental data.

On the basis of molecular weights, one would expect that the order of volatilities for the tetra-tert.-alkoxides of silicon and the group IVB elements would be $Si(OR)_4 > Ti(OR)_4 > Zr(OR)_4 > Hf(OR)_4$. However the actual order appears to be the reverse with the position of silicon somewhat in doubt since the preparation of a tetra-tert.-alkoxide of silicon has not yet been reported, probably due to the small size of the silicon atom. A comparison of the boiling points of the tertiary alkoxides of zirconium and titanium reveals that there is little difference in the boiling points of the titanium and zirconium derivative for a given alkoxide. In fact, the titanium analogue often has the higher boiling point. Moreover, fractional distillation of a mixture of the tetra-tert.-amyloxides of zirconium and hafnium revealed that the hafnium derivative is slightly more volatile. A study of a series of isomeric tertiary alkoxides of zirconium and hafnium confirmed the order of volatility Hf > Zr and in no case was the hafnium alkoxide less volatile than its zirconium analogue[5]. These facts suggest a promising means of separation of zirconium and hafnium, since, by operating in non aqueous solutions, alkoxides of zirconium and hafnium can be isolated and their properties afford a method of separation.

Coughlan et al[7] suggest that each titanium atom in the trimeric alkoxides is surrounded octahedrally by oxygen atoms from alkoxide groups and thatthe trimeric unit comprises three octahedra bound by common faces. A similar arrangement seems reasonable for trimeric zirconium alkoxides but the molecular complexity in zirconium normal alkoxides is significantly greater than three. The fractional value suggests that a species of higher molecular complexity is present and a possible structure for a pentameric complex would be one where octahedra share edges or faces. Additional information concerning the nature of the intermolecular bonding in complex alkoxides has been obtained from molecular weight determinations on zirconium ethoxide and zirconium isopropoxide in ethyl and isopropyl alcohol respectively. Molecular complexity values are less than those obtained in benzene presumably because bonds of the type ${}^{R}_{H}\!\!>O \rightarrow Zr$ replace those of the type ${}^{R}_{Zr}\!\!>O \rightarrow Zr$.

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PRECISE DETERMINATION OF HYDROXIDE AND NITRITE IN A SINGLE SAMPLE

R. A. Reinhardt and F. Mc Collough, Jr. October 13, 1953

INTRODUCTION

Red and white fuming nitric acids are used as oxidants in rocket motors. Decomposition of the acid during storage leads to a ballooning of the storage containers and also to a dilution of the acid, which results in a reduced efficiency in the reaction motors. Ways and means of eliminating or suppressing such decomposition would be of great interest to the armed services. The present work was undertaken as part of an overall investigation of the decomposition of fuming nitric acid.

THEORETICAL

The oxidation of nitrous acid by permanganate ion in acid solution is sufficiently rapid that the addition of excess acid following the addition of excess permanganate to the nitrite solution brings about quantitative oxidation of the nitrite withou loss due to the decomposition of the nitrous acid. The excess permangante can then be determined iodometrically. The excess acid cannot be determined with standard base because of the rapid oxidation of locally formed manganous oxide by dissolved oxygen. The reaction of hydrogen ion with excess iodide and iodate followed by a second thio titration serves as a satisfactory method for determination of the acid. In calculating the original hydroxide ion concentration, account must be taken of the acid required by the stoichiometry of the permanganate-nitrite and the permanganate-iodide reactions, and also the small amount of free base present in the $KMnO_4$ (from decomposition).

EXPERIMENTAL

Weight burets were used for all reagents, except for the dilute thiosulfate solution, a few drops of which sufficed for the end point determination. The weighings were carried out to the nearest milligram. No indicator was used for the end point; one drop of 0.01M thiosulfate was observed to give a clear change at the end point in 150 ml of solution. A split-drop type technique was used in as much as the titration was started with 0.1M thiosulfate to about one drop from the end and then finished with 0.01M thiosulfate. With this procedure, precisions of about 0.02% have been obtained, using 50 gm. samples of 0.1 molal reagents.

The Structure of B_4Cl_4

Stanley Kirschner

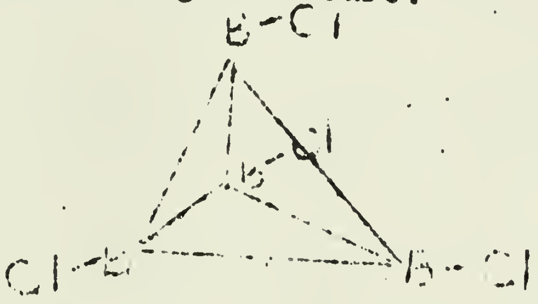
October 13, 1953

After Schlesinger and his coworkers (4,3) had prepared some tetrachlorodiborine (B_2Cl_4) by passing gaseous BCl_3 under reduced pressure through a glow discharge tube, they noticed the formation of a small quantity of yellow crystals while the compound was being decomposed at 0°C.

They established the formula of these crystals as B_4Cl_4 by analysis, and determined that it was a monomer by vapor density measurements. Additional evidence that the material is not a mixture of B_2Cl_4 and boron is found in the fact that B_2Cl_4 decomposes at 0°C. while the yellow crystals undergo no appreciable decomposition up to 70°C. Methanol converts B_2Cl_4 to $B_2(OCH_3)_4$ with the liberation of HCl but no hydrogen, while methanol liberates six gram equivalent weights of hydrogen per mole of B_4Cl_4.

On the basis of the latter observation, the authors (3) suggested that the compound contains six equivalent boron-boron bonds, and that the boron atoms are probably situated at the corners of a tetrahedron - each boron having one chlorine atom associated with it. They also pointed out that an x-ray study performed by Lipscomb (1) gave more than ample support to those ideas on the structure of the material.

However, a question immediately comes to mind which these authors have not considered in their papers - namely the lack of sufficient electrons to form six B-B bonds and four B-Cl bonds of the usual covalent type. This would require a total of twenty electrons in the following structure:



whereas B_4Cl_4 provides only sixteen electrons which are available for the usual type of bonding.

G.H. Duffey (2) has recently put forth a proposal for the structure of B_4Cl_4. He says that there are no single B-B bonds as such, but that three equivalent bond orbitals overlap above the center of each face of an imaginary tetrahedron, and that two electrons occupy each set of three overlapping orbitals, resulting, effectively, in the sharing of two electrons by three atoms rather than by two. Each B-Cl bond contains the usual number of two electrons, which seems logical since the chlorine

atoms would not be situated favorably so as to be able to take part in the π-type of bonding of the tetrahedron containing the boron atoms.

These ideas concerning the structure of B_4Cl_4 appear to be quite reasonable, especially in view of the fact that the sharing of electrons by more than two atoms has already achieved some acceptance in the Molecular Orbital Theory, and also that this structure utilizes only the sixteen available electrons. In addition, these ideas are consistent with the x-ray diffraction evidence which indicates that the boron atoms lie at the corners of a tetrahedron, as well as with the fact that the molecule does not possess a charge, so Duffey (2) has presented what seems to be a credible explanation for the proposed tetrahedral structure of B_4Cl_4.

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GEOCHEMISTRY

B.W. Nelson
(Geology Department)

October 27, 1953

It is the aim of Geochemistry to study the distribution of the elements in the earth and to establish the laws that control that distribution. In order to accomplish this objective it is necessary for chemists and geologists to work together to make use of the special skills and points of view of each of the parent sciences.

The general nature of the laws that control the geochemical distribution of the elements in the earth's crust are discussed, and some of the geological problems of element distribution are pointed out.

In the bibliography there are listed some of the more important publications which will serve as an introduction to the literature of geochemistry. Mason's text (1) is recommended as a survey for the reader untrained in geology, while Rankama and Sahama's book (2) is an excellent source of detailed information. The latter includes a bibliography of over 500 references up to 1948.

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ROLL CALL

Recent Work in Bis-Cyclopentadienyl Complex Chemistry

William C. Smith

October 20, 1953

Some interesting references to the preparation and properties of Bio-cyclopentadienyl complexes have appeared in the literature since the seminar report given by Victor Aftandilian on substances of this type[1]. An interesting method for the preparation of complexes of the type $M^{II}(C_5H_5)_2$, where $M = Co^{++}$, Cr^{++} and Ni^{++} has been described by Fischer et. al. in a series of papers[2,3,4]. This involves the preparation of an alkali metal salt of cyclopentadiene and its subsequent reaction with ammine complexes of the transition elements listed above, in liquid ammonia solution, to give a complex ammine salt containing cyclopentadiene as the anion. Equations to illustrate this method are given below:

$$2\ C_5H_6 + 2K(Li, Na) \rightarrow 2\ C_3H_5K(Li, Na) + H_2$$

$$Co(NH_3)_4(SCN)_2 + 2KC_5H_5 \xrightarrow{NH_3(l)} [Co(NH_3)_6](C_5H_5)_2 + 2\ KSCN$$

The desired cyclopentadienyl complex is then obtained by heating the metal salt containing cyclopentadiene under vacuum at 80° - 120°C to remove the coordinated ammonia.

$$Co(NH_3)_6](C_5H_5)_2 \xrightarrow[\text{vacuum}]{\Delta} Co(C_5H_5)_2 + 6\ NH_3$$

The product may be purified readily by vacuum sublimation.

The high stability of these materials compares to that found for the corresponding Bis-cyclopentadienyl iron(II) compound and they show similar solubilities in non-polar solvents. It is interesting that each of these materials has a melting point of 173-174°C. The cobalt and iron compounds in particular are readily oxidized to the $M(C_5H_5)_2^+$ cation, and a series of salts of the form $[Co(C_5H_5)_2]X$ where $X = F^-$, CN^-, $CO_3^=$, NO_3^-, OH^-, $SO_4^=$ etc. has been reported[5].

Jaffe'[6] has employed the molecular orbital theory in arriving at an electronic structure for Bis-cyclopentadienyl iron(II) ("Ferrocene") which assumes the existence of eight bonding molecular orbitals, so that the iron may be said to be bound to each of the organic radicals by four covalent bonds. This factor, and the rare gas configuration of the iron atom as assumed by Jaffe', are advanced as the principal reasons for the great stability of the iron complex. Such an interpretation is in agreement with magnetic susceptibility data but does not agree with arguments advanced by Woodward et. al.[7] based on the study of the ionization constants of ferrocene dicarboxylic acid. It is apparent that additional experimental studies will be required before a complete understanding of the bonding within this peculiar but very interesting class of substances can be attained.

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Bromine Trifluoride As a Fluorinating Agent

Debabrata Choudhury

November 10, 1953

[Introduction]

Bromine trifluoride was first prepared in 1905, but not until recently have any details of its reactions with inorganic compounds been published. It has been shown that bromine trifluoride is extremely reactive as a fluorinating agent. It has been used for the preparation of the noble metal fluorides, nitrosyl complex fluorides, fluoro sulphonates and numerous other organic and inorganic fluoro compounds. The most important reactions and properties of bromine trifluoride are described in this report.

[Preparation]

Bromine trifluoride is prepared by a method similar to that of Ruff and Barida(1,2). The reaction between bromine vapour, diluted with a stream of nitrogen, and fluorine is carried out in a copper T tube cooled by immersion in water. The crude bromine tri fluoride is purified by distillation in a Steel retort. It also can be prepared by passage of ClF_3 into bromine in a cooled nickel vessel(3).

[Physical Properties]

The physical properties of Bromine trifluoride are summarized in Table I.

Table I

Density	2.843 at 8.8°C
Boiling Point	127°C
Melting Point	281.8°K
Specific Conductivity	8.1×10^{-3} ohm^{-1} cm^{-1}
Heat of fusion	2874.6 ± 3 Cal mole
Heat of Vaporization	10.2 K Cal mole

The specific conductivity of bromine trifluoride(4) decreases with rise in temperature. This is explained by postulating the existence in liquid bromine trifluoride of the ions BrF_2^+ and BrF_4^-, the negative temperature effect being then due to a decrease in stability of one or both of these ionic species with increasing temperature.

[Reactions of Bromine trifluoride]

By treating the halides of elements of constant valency with excess of bromine trifluoride the corresponding fluorides are obtained, whereas the halides of elements of variable valency give mixtures

of the lower and higher fluorides(1). Uranium tetrafluoride goes to hexafluoride when treated with bromine trifluoride. The chlorides of potassium , silver and barium reacts with bromine trifluoride in the normal manner free chlorine and bromine being formed.

$$3KCl + BrF_3 = 3KF + 1/2Br_2 + 3/_2Cl_2$$

The reaction of bromine trifluoride with carbon tetrachloride(5) yields the partly fluorinated products, tri chloro fluoro methane and di chloro di fluoro methane. With carbon tetra bromide and carbon tetraiodide the reaction occurs more smoothly, but no iodo fluoro methanes can be isolated in the case of carbon tetraiodide.

With CuO, B_2O_3, Tl_2O_3, SiO_2, GeO_2, TiO_2, AS_2O_3, Sb_2O_3, ScO_2, VO_3 and I_2O_5 Oxygen evolution is quantitative(6).

$$3SiO_2 + 4BrF_3 \rightarrow 3SiF_4 + 3O_2 + 2Br_2$$

Potassium metaphosphate yields the hexafluoro phosphate in which the coordination number of phosphorus is increased from four to six. Potassium persulfate and pyrosulfate give potassium fluoro sulfonate. Niobium and Tantalum(7) or their pentoxides react with bromine trifluoride to give the fluoro bromium hexa fluoro niobate and hexa fluoro tantalate $(BrF_2)NbF_6$ and $(BrF_2)TaF_6$ which act as acids in bromine trifluoride and are neutralized by bromo fluorides to give hexafluoro niobates.

$$BrF_2^+\ NbF_6^- + K^+BrF_4^- \rightleftharpoons KNbF_6 + 2BrF_3$$

In the similar way by the use of sodium carbonate, rubidium bromide and caesium bromide anhydrous sodium, lithium and rubidium salts are prepared.

There are two methods available for the preparation of complex fluoro acid salts and salts of nitronium ion(8). In the first case the equivalent amounts of substances which produce the acid and base in bromine trifluoride are mixed in that solvent and the excess is removed in vacuo after the reaction has been completed. If silver and phosphorus penta bromide are mixed with excess of bromine trifluoride the salt silver hexafluoro phosphate results. The reaction mechanism is believed to involve an ionic reaction between the base $AgBrF_4$ and the unstable acid $(BrF_2)PF_6$. The second method which is less general involves the reaction between BrF_3 and a suitable oxyacid salt in which the elements need be present in the correct proportions only when the component fluorides produced are non volatile. Borax, for example, yields sodium tetrafluoro borate, the excess of boron being removed as boron trifluoride.

Dinitrogen tetroxide and acid forming substances were mixed and treated with BrF_3 to give the following compounds. $(NO)_2BF_4$, nitronium tetrafluoro borate; $(NO)_2SnF_6$, netronium hexa fluorostannate; $(NO_2)PF_6$ netronium hexafluoro phosphate; etc. With nitrosyl chlorides(9) and substances capable of functioning as acids in bromine trifluoride solution the following complex nitrosyl fluorides are produced: $(NO)BF_4$, $(NO)SbF_6$, $(NO)\ \ F_6$, $(NO)_2GeF_6$ etc. Metallic

platinum(10) is not attacked by bromine trifluoride at room temperature but if the metal is converted into its tetra chloride vigorous reaction takes place on the addition of the reagent. A product of empirical formula Pt Br_2F_{10} results. In bromine trifluoride rhodium tetrafluoride and palladium trifluoride also yield complex fluorides, but these are unstable towards water and have not been obtained pure. When potassium tetra chloro palladate(II) or hexachloro palladate(IV) are treated with bromine trifluoride, a compound of composition $K_2PdF_6 \cdot 0.1BrF_3$ results(11). Rubidium and Caesiumchloro palladates under the similar condition yield the pure Rb_2PdF_6 and CS_2PdF_6 respectively. Gold dissolves readily in bromine trifluoride with evolution of bromine when gently warmed. A compound of empirical formula $AuBrF_6$ results on evaporation.

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POLYMERIZATION OF THE PHOSPHONITRILIC CHLORIDES

E. W. Flynn

November 17, 1953

Stokes[1] in 1897 was the first to show that heat converts the phosphonitrilic chlorides, shown in Figure I, into a rubber-like mixture of the chlorides of high molecular weight, the so-called 'Inorganic Rubber'.

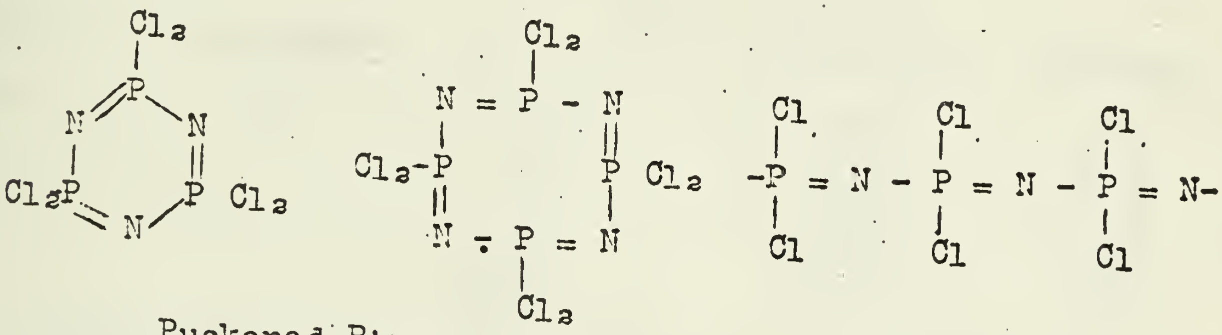
Puckered Rings

FIGURE I

The trimer and tetramer are both white crystalline solids. The method of preparation is that of Schenk and Römer[2] in which NH_4Cl and PCl_5 in a solvent such as $Cl_2CHCHCl_2$ are heated at 135° for 20 hours. They are interesting substances because they are converted by heat into an elastic polymer which resembles rubber. This conversion occurs slowly at 250° and rapidly at 350°. An excellent review by Audrieth, Steinman and Toy[3] covers the work up to 1943.

Since that time the polymerization of the trimer and tetramer of phosphonitrilic chloride at temperatures around 300° has been investigated extensively by Patat and Kollinsky[4]. They studied the course of the polymerization in bulk and in various solvents. Their experiments show that the presence of oxygen is necessary throughout the entire course of the polymerization reaction. The molecular weight of the polymers obtained ranged up to 130,000.

The trimer and tetramer employed by Patat and Kollinsky were prepared essentially according to the method of Schenk and Römer[2]. The yield of trimer obtained was 52.6% and of tetramer 13.6%. Schenk and Römer[2] reported 29.8% and 8.9%, respectively.

In the bulk polymerization the reaction velocity increases with rising temperature, while the soluble fraction of the polymer decreases, as shown in Table I.

TABLE I

Reference	Starting Material	t°C	Time (hours)	Yield grams	Yield %	Soluble % of yield
I-2	$(PNCl_2)_3$	290	3	0.528	26.14	62
K-2		320	3	1.008	50.4	18.7
L-2		350	3	1.416	70.8	14.1
M-2	$(PNCl_2)_4$	300	3	0.864	43.2	38

It will be noticed in the above table that yields of polymer

and of soluble fraction are not influenced appreciably by using the tetramer in place of the trimer as the starting material. The molecular weights of the products obtained from the bulk polymerization ranged from 1120 to 2850.

The influence of oxygen on the bulk polymerization is shown in Table II.

Table II

Starting Material	Time (hours)	N_2-O_2 Mixture (% O_2)	(Mole O_2)	% Yield
$(PNCl_2)_3$	36	10^{-4}	10^{-9}	0.0
		0.01	10^{-7}	23.1
		0.1	10^{-6}	40.9
		1.0	10^{-5}	41.7
		2.0	2×10^{-5}	43.1
		100.0	10^{-3}	36.3

From Table II it can be seen that the velocity increases rapidly with the introduction of a small amount of oxygen, and soon approaches a maximum decreasing slightly in pure oxygen. Due to the low molecular weights of the products obtained in the bulk polymerization Patat and Kollinsky turned to solvent polymerization in an attempt to obtain polymers of higher molecular weight.

The first series of experiments involving solvent polymerization were carried out in solvents which contain hydrogen. These included benzene, toluene, xylene and hexane. The temperature range extended from 280 to 340°, the reaction time from 4 to 84 hours and the concentration from 15 to 45% of the trimer or tetramer respectively. A qualitatively similar discoloration of the solution from clear to dark brown was apparent in each case with the formation of a brown, gelatinous to resinous-like precipitate which increased with increasing time and temperature of reaction. On opening the reaction vessel a noticeable excess of HCl was detected. Since the substances obtained after fractionation showed essentially no viscosity increase, it may be assumed that the $(PNCl_2)$ trimer or tetramer react with the solvent according to the following expression:

$$n\,RH + (PNCl_2)_m \overset{300^\circ}{=} P_m N_m Cl_{2m-n} R_n + n\,HCl$$

Several experiments using a 30% $(PNCl_2)_3$ solution in toluene carried out at 300° for 36 hours, afforded after removal of the solvent various fractions of colorless liquids distillable in vacuum. The residue consisted of gelatinous and resinous products. Analysis of the various fractions gave %C and %H corresponding to the formulae for the following: $PNCl$-C_7H_8, $P_2N_2Cl_3$-C_7H_8, $P_3N_3Cl_5$-C_7H_8, and $P_3N_3Cl_4$-$(C_7H_8)_2$. These substances upon exposure to the air became hard and brittle and evolved HCl. The polymerization in hydrogen containing solvents is catalytically influenced by oxygen. Under a pure N_2 atmosphere neither reaction with the solvent nor polymerization was observed.

To exclude the possibility of reaction between $PNCl_2$ and the solvent, polymerization was carried out in solvents which did not

contain hydrogen. Those investigated $Cl_2C=CCl_2$, Cl_3CCCl_3, $Br_2C=CBr_2$, Br_3CCBr_3, C_6Cl_6, C_6Br_6, PCl_3, $POCl$ and CCl_4. The most satisfactory of these seemed to be CCl_4 even though some of the high polymers were insoluble in this solvent and were always precipitated. The polymer product and solution were colorless throughout, although the former was obtained in a transparent gelatinous gummy condition. Polymerization was carried out in all these cases in air. The experimental results showed that solvent polymerization produces soluble high polymers of molecular weights up to 130,000 in upwards of 50% of the total yield. Yields were found to increase with rise in temperature; and, at a given temperature, with increasing concentration. The reaction velocity was found to follow second order kinetics. In a reaction 30% $(PNCl_2)_3$ solution in toluene at 300° for 3 hours the catalytic influence of oxygen was found to be the same as in the bulk polymerization, with the yield increasing quickly to a maximum and then decreasing slightly. In addition the molecular weight in pure oxygen was found to decrease to half of the former value.

Consideration of the polymerization in inert solvents leads to the conclusion that the reaction is dependent upon the presence of oxygen for its initiation. Thus the oxygen must in some manner cause rupture of the $(PNCl_2)_3$ ring, enabling the $(PNCl_2)_3$ to cause rupture of a second trimer ring and thereby initiate a chain reaction which results in the formation of a linear polymer. The oxygen-trimer addition product originally formed must continue to exist throughout the chain formation in order to prevent any tendency of the polymer to cyclize. Oxygen may also add to the free end of the growing polymer chain and thus become instrumental in the chain termination. Finally another effect of the oxygen can be noticed. If the high polymer $(PNCl_2)_x$ is heated in air it darkens around 400°, becomes brittle and changes to an extraordinarily hard resin which appears to be completely cross-linked. On the other hand in a high vacuum at temperatures above 365°, the polymer decomposes to give oily and waxy products along with minor portions of the trimer and tetramer. After heating in air the polymer is no longer soluble. This reaction with the oxygen of the air may be likened to the vulcanization process for rubber in which oxygen takes the place of the sulfur in linking the atoms together. Thus the effect of oxygen on the polymerization of $PNCl_2$ may be considered to be three-fold:

1. Initiation of the polymerization.
2. Termination of the polymer chain.
3. Vulcanization of the polymer.

In contrast to solvent polymerization bulk polymerization apparently follows third order kinetics. It has been determined that the inert solvent does not intervene in the reaction but only lends a certain homogeneity to the polymerization process. Therefore, it would be expected that the solvent and bulk polymerizations should be similar. As mentioned the oxygen relationship appears to be similar in both cases, and the same course--initiation, propagation, termination-- should describe both reactions. Inasmuch as the three reactions showed no higher than second order kinetics, the observed third order kinetics for the overall reaction may be

caused by another effect. The authors believe the observed third order kinetics to be due to a restriction of the reaction as a result of stratification of polymer layers in the bulk polymerizatio They believe the higher polymers separate near the bottom of the reaction vessel to give a thick network of matted material which hunders further polymerization.

Specker[5] has recently investigated the mechanical deformation of high polymer $(PNCl_2)_x$ in order to determine if observations can be correlated with the modern theory of high elasticity according to Kuhn. This theory predicts a high relaxation time and an increase of the elastic modulus proportional to the absolute temperature. By a series of experiments Specker[6] found the deformation of $PNCl_2$ polymer to be reversible at long reaction times and over the large temperature range from 50° to 160°. At 160° after 1000 seconds the reversible deformation amounts to over 90% whereas at room temperature the reaction is completely reversible only after many hours. This, he concluded, corresponds to the Kuhn demand for an extremely large relaxation time as an elasticity modulus basis in ideal highly elastic materials. Carefully prepared high polymer $(PNCl_2)_x$ is similar to natural rubber with respect to this mechanical property. In other experiments Specker obtained a relationship between the deformation of an elastic high polymer and the absolute temperature which shows that with increasing temperature the deformation decreases, or in other words that the elastic modulus increases. It is interesting that he also found a difference in the elastic modulus of samples aged in air and those from which air was excluded. While the test compound aged with the exclusion of air, showed no change after months, the elastic modulus of the test compound exposed to the air increased. This is explained by a partial hydrolysis due to the moist air, which links two chains with the elimination of HCl. Thereby a decrease of the net deformation weight occurs and consequently an increase in the elastic modulus takes place.

In summary it may be said that polymerization of phosphonitrili chloride trimer or tetramer occurs readily to a rubber-like polymer, and that this polymerization is influenced by the presence of oxygen. The polymer so formed has elastic properties which conform to the modern theory of high elasticity.

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THE TRIFLUOROMETHYL GROUP

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J. E. Dunbar

The trifluoromethyl group has attracted interest because of its abnormally high electronegative character. The extensive study of this group by Emeleus, Haszeldine, and associates has resulted in the synthesis of trifluoromethyl metallic and metalloidal compounds, many of which exhibit anomalous properties.

The gas trifluoroiodomethane is a key intermediate in these studies and is now prepared by two relatively convenient methods:

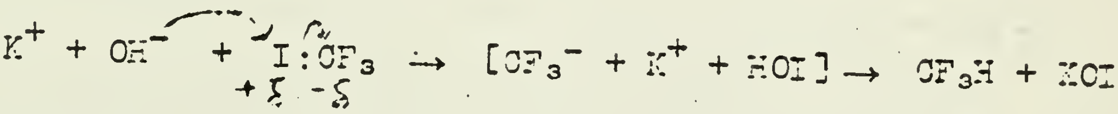
$$CI_4 \xrightarrow{IF_5} CF_3I + \text{other fluoroiodomethanes}^{2}$$

$$CF_3CO_2[Pb,\ Ag,\ Na,\ \text{or}\ K] + I_2 \xrightarrow{\Delta} CF_3I + CO_2{}^{3}$$

The trifluoromethyl group can in some respects be regarded as a halogenoid. It adds to olefinic double bonds:

$$CF_3I + CH_2{=}CH_2 \rightarrow CF_3CH_2CH_2I^{21}$$

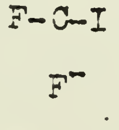
Reaction of alkali with trifluoroiodomethane takes place by the "positive iodine" mechanism, fluoroform resulting instead of the desired alcohol. The postulated mechanism involves heterolytic cleavage of the carbon-iodine bond.[3, 21]



$$K^+ + OH^- + \overset{+\delta}{I}{:}\overset{-\delta}{CF_3} \rightarrow [CF_3^- + K^+ + HOI] \rightarrow CF_3H + KOI$$

Nucleophilic substitution of I^- by OH^-, CN^-, NH_2^-, and NO_2^- has proved impossible. The majority of reactions investigated involve homolytic rather than heterolytic cleavage of the carbon-iodine bond with formation of $CF_3\cdot$ free radicals.[21]

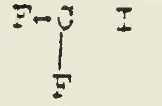
Evidence is given to indicate that resonance forms (A), (B), and (D) contribute to a lesser degree than does form (C), tending to make the carbon-iodine bond weaker.[8]



(A)

(B)

(C)



(D)

Trifluoromethyl Compounds of Sulfur

Although trifluoroiodomethane has been used to prepare bistrifluoromethyldisulfide,[1]

$$CF_3I \xrightarrow{\overset{S}{260^\circ}} (CF_3)_2S_2 + (CF_3)_2S_3 + (CF_3)_2S_4 + CSF_2,$$

a more convenient method involves the fluorination of carbon disulfide with iodine pentafluoride.[5] The structure of the disulfide has been proven by chemical and ultra-violet data.[1,9]

Bistrifluoromethyldisulfide is converted to bistrifluoromethylsulfide in the presence of ultraviolet light *via* the formation of a viscous liquid, which upon further irradiation turns into rhombic sulfur. The mechanism of the photolysis has been postulated as a homolytic cleavage of the sulfur-sulfur bond to give two $CF_3S\cdot$ radicals. This view is supported by smooth formation of CF_3-S-Hg-S-CF_3 in the presence of mercury.[1] A tentative reaction mechanism is

$$CF_3S_2CF_3 \xrightarrow{\text{light}} 2CF_3S\cdot$$
$$CF_3S\cdot + CF_3S_2CF_3 \rightarrow CF_3SCF_3 + CF_3SS\cdot$$
$$CF_3SS\cdot \rightarrow CF_3S\cdot + S, \text{ etc.}$$
$$2CF_3SS\cdot \rightarrow CF_3SSSSCF_3$$
$$CF_3S\cdot + CF_3SSSSCF_3 \rightarrow CF_3SCF_3 + CF_3SSSS\cdot$$
$$2CF_3SSSS\cdot \rightarrow CF_3S_8CF_3, \text{ etc.}$$

A new route to the trifluoromethyl sulfur compounds, in which sulfur is at its highest oxidation state, was recently demonstrated by Clifford, El-Shamy, Emeleus and Haszeldine[15] by the electrolysis of dimethyl thioether in anhydrous hydrogen fluoride to give CF_3SF_5 and $(CF_3)_2SF_4$. Carbon disulfide is similarly fluorinated to give CF_3SF_5 among other products.

Trifluoromethyl Compounds of Arsenic

High yields of trifluoromethyl arsines are obtained when trifluoroiodomethane is heated with arsenic at temperatures above 200°.[12]

$$CF_3I + As \underset{\longleftarrow}{\xrightarrow{220-240^\circ}} As(CF_3)_3 + AsI(CF_3)_2 + AsI_2CF_3 + AsI_3$$

The appearance of tristrifluoromethylarsine as the main product is attributed to disproportionation reactions.[13] The yields of iodotrifluoromethylarsines are increased by addition of arsenic triiodide to the reaction mixture.

The major difference between methyl and trifluoromethyl arsines lies in their behavior on hydrolysis. The methyl group is stable to dilute alkali at room temperature, whereas the trifluoromethyl group is liberated quantitatively as fluoroform.[12] This formation of fluoroform is characteristic of compounds of the type $M(CF_3)_n$ and $M(CF_3)_yX_{(n-y)}$, where M = As, P, Sb, Hg and X = halogen. Unlike $(CH_3)_3As$ the fluoro compound fails to form quaternary compounds.

The more negative the group attached to arsenic, the more easily does alkaline or aqueous hydrolysis occur, and the more resistant is the compound to oxidation. Trimethylarsine and other alkyl arsines are stable to alkali but are easily oxidized. Tetrakistrifluoromethyldiarsine, which is prepared by the action of mercury on bistrifluoromethyliodoarsine,[12] is stable to water but with alkali at room temperature gives about 75% theoretical fluoroform, the remainder of the trifluoromethyl groups being converted into fluoride and carbonate ions. Tetrakistrifluoromethyldiphosphine and tetrakistrifluoro-

methyldisulfide react similarly.

The iodine in trifluoromethyliodo arsines can be replaced with hydrogen by reaction with reducing agents such as lithium aluminum hydride and zinc and hydrochloric acid.[13] Trifluoromethylalkyl arsines can be prepared by the reaction of the iodo compounds with alkyl magnesium iodides.[13]

Trifluoromethyl Compounds of Phosphorus

Trifluoroiodomethane reacts with white phosphorus to give tristrifluoromethylphosphine in 80% yield.[14]

$$CF_3I + P(\text{white}) \overset{220^{\circ}}{\rightleftarrows} (CF_3)_3P + (CF_3)_2PI + CF_3PI_2 + I_2PPI_2 + PI_3.$$

Tristrifluoromethylphosphine is a colorless, spontaneously flammable liquid (b.p. 17°). The iodotrifluoromethylphosphines are of greater chemical interest because of the reactivity of the iodine atoms. These iodo compounds undergo disproportionation as do their arsenic analogues, and the yield of the iodo derivatives is increased by recycling the tristrifluoromethylphosphine and unreacted trifluoroiodomethane with phosphorus and phosphorus triiodide. Quaternary phosphonium compounds were not isolated.

Because of the presence of the strongly electronegative trifluoromethyl groups, tristrifluoromethylphosphine does not undergo compound formation with CS_2, S, AgI, and other metallic compounds as do the unsubstituted alkyl phosphines. Chlorine reacts violently with trialkyl phosphines, but tristrifluoromethylphosphine reacts smoothly at low temperature.[14]

$$(CF_3)_3P + Cl_2 \xrightarrow{-40^{\circ}} (CF_3)_3PCl_2$$

Oxidative hydrolysis of trifluoromethylphosphonium iodide and chloride yields trifluoromethylphosphonic acid, $CF_3PO(OH)_2$. It is one of the strongest known acids ($k_1 = 6.8 \times 10^{-2}$, $k_2 = 1.8 \times 10^{-4}$).[4]

Attachment of the strongly electronegative trifluoromethyl groups to metalloidal atoms M(=P, As, Sb, S, Se) stabilizes the M-M bond. Thus, the stable compound tetrakistrifluoromethyldiphosphine (b.p. 84°) has been prepared by the action of mercury on bistrifluoromethyliodophosphine at room temperature.[14] Few compounds containing the P-P bond are known.

Trifluoromethyl Mercurials

Trifluoromethylmercuric iodide was prepared in 80% yield by treating trifluoroiodomethane with mercury at 110° in the presence of ultraviolet light.[10] The product resembles its hydrocarbon analogue except that it is soluble in water and can be converted in aqueous solution to the corresponding hydroxide, chloride, bromide, and nitrate by treatment with the appropriate reagents.

Bistrifluoromethylmercury has been prepared by treatment of trifluoromethylmercuric iodide with Ag, Cu, Cd, Zn, Mg or Cd-amalgam. Unlike dimethylmercury, it is a crystalline solid, soluble in water and organic solvents, and is a weak electrolyte in aqueous solution.[14]

In aqueous solution it resembles mercuric cyanide, since both compounds exhibit normal molecular weights, and neither gives a precipitate with dilute solutions of potassium iodide, silver nitrate or alkali hydroxides. This indicates the absence of mercuric ions, but may be due to complex formation.[11]

Trifluoromethyl Compounds of Nitrogen

Haszeldine[16] obtained pure trifluoronitrosomethane by irradiation of a mixture of trifluoroiodomethane and nitric oxide in the presence of mercury,

$$CF_3I \xrightarrow{\text{light}} CF_3\cdot \xrightarrow{NO} CF_3NO$$

The product can be oxidized to the nitro derivative with chromic oxide.[7,16]

Tristrifluoromethylamine (b.p. -6 to -7°) has been prepared by the action of cobalt(III) fluoride on trimethylamine at 250°.[17]

Other Trifluoromethyl Compounds

Attempts to prepare trifluoromethyl derivatives of zinc, cadmium, gallium, lead, and lithium have failed.[10] However, Haszeldine succeeded in causing trifluoroiodomethane to form a Grignard reagent by carrying out the reaction at low temperature with spectroscopically pure magnesium.[18,19,20] Trifluoromethylmagnesium iodide has been prepared only for use as an intermediate and has not been purified, as it is unstable at ordinary temperatures.

Table I. Bond Lenths.

Compound	C-F Bond (Å)	C-X Bond (Å)	Reference
CH_3F	1.38	——	22
CH_3Cl	——	1.77	23
CF_3Cl	1.32	1.75	24
CH_3Br	——	1.95	6
CF_3Br	1.32	1.93	3
CH_3I	——	2.13	6
CF_3I	1.32*	2.16	3

*Assumed.

Table II. Boiling and Melting Points of Some Trifluoromethyl Compounds.

Compound	M.p.(°C)	B.p.(°C)	Ref.	Compound	M.p.(°C)	B.p.(°C)	Ref.
CF_3I		-22.5	8	$(CF_3)_3P$		17	14
$(CF_3)_2S_2$		35	1	$(CF_3)_2PI$		73	14
CF_3SF_5	-86.9	-20.4	9	CF_3PI_2		69/29mm	14
$(CF_3)_2S$		-22	1	$(CF_3)_4P_2$		84	14
$(CF_3S)_2Hg$	37.5		1	$(CF_3)_2Hg$	163		11
$(CF_3)_3As$		33.3*	12	CF_3HgI	112.5		10
$(CF_3)_2AsI$		92	12	CF_3HgCl	76		10
$(CF_3)_4As_2$		106-7	12	CF_3NO		-84	16
$(CF_3)_2AsH$		19	13	CF_3NO_2		-30	16

*Calculated from vapor pressure data.

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MONOMERIC ALUMINUM HYDRIDE

Elsie Gulyas

December 1, 1953

In 1939 Wiberg and Stecher[7] became interested in whether aluminum, like boron and the elements in the main groups IV, V, VI, and VII of the periodic table, is able to form volatile hydrogen compounds. Paneth and coworkers had shown that the formation of volatile metal hydrides from the elements in the glow discharge takes place only in the presence of hydrocarbons. Wiberg and Stecher took this as evidence that metal alkyls are formed as intermediates in such reactions[4]. Hence for the attempted preparation of aluminum hydride they chose the method of subjecting a mixture of aluminum trimethyl and hydrogen to a glow discharge. A variety of products were formed, including a viscous, colorless fluid from which the compound $Al_2H_2(CH_3)_4$ could be obtained by distillation in vacuo. This compound corresponded in its composition and properties to the already known tetramethyl diborane, $B_2H_2(CH_3)_4$. On heating to temperatures above 160°, the $Al_2H_2(CH_3)_4$ disproportionates according to the equation:

$$3\ Al_2H_2(CH_3)_4 \xrightleftharpoons{160^\circ} Al_2H_6 + 4\ Al(CH_3)_3.$$

Attempts to obtain aluminum hydride by this reaction were unsuccessful because at the temperature required for the disproportionation the hydride decomposes into the elements. Similarly, attempts to displace the equilibrium to increase the yield of the hydride were unsuccessful.

At the same time Schlesinger and coworkers[2] were investigating a volatile compound of aluminum, boron, and hydrogen (aluminum borohydride) which they had prepared by the reaction of aluminum trimethyl with excess diborane at temperatures up to 80°:

$$Al_2(CH_3)_6 + 4\ B_2H_6 \xrightarrow{t < 80^\circ} 2\ AlB_3H_{12} + 2\ B(CH_3)_3.$$

They found that the aluminum borohydride reacts with trimethylamine at room temperature to give a mixture of solids from which they were able to obtain $BH_3 \cdot N(CH_3)_3$. They attempted, therefore, to prepare aluminum hydride or its trimethylamine complex by extracting BH_3 groups from aluminum borohydride with excess trimethylamine[3]. They were unable to obtain the desired products.

Although Wiberg and Stecher had achieved only partial success n the preparation of aluminum hydride they found that they could repare a volatile hydrogen compound of gallium $(GaH_3)_2$ with relative ase[4]. This discovery strengthened their conviction that an aluminum ydride could exist and they continued their efforts to find experiental conditions under which the preparation would succeed. By assing a glow discharge through a mixture of aluminum trimethyl and ydrogen using a 9 milliampere, 500 cycle alternating current at 0,000 volts and gas pressures from 10 mm. to 15 mm. they obtained a ixture of products including small amounts of hydrocarbons, difficulty volatile substances, and non-volatile substances. On treatment of he non-volatile material with excess trimethylamine a mixture of

compounds was obtained which could be separated into a crystalline and a liquid portion. The crystals were found after purification to have the composition $AlH_3 \cdot nN(CH_3)_3$ where the value of n lay between 1 and 2.

The monoammine which can be obtained from the diammine can be made to give off additional trimethylamine according to the equation:

$$n\ AlH_3 \cdot N(CH_3)_3 \xrightarrow[t\ =\ 85^\circ]{\text{distillation}\ p\ =\ 110\text{-}48\text{mm.}} \underset{(n\ =\ 3\text{-}5)}{(AlH_3)_n \cdot N(CH_3)_3} + (n-1)\ N(CH_3)_3.$$

The residual trimethylamine was entirely removed together with appreciable amounts of aluminum hydride by heating to 100°-135°. The residue, a polymeric aluminum hydride $(AlH_3)_x$, was a non-volatile, white, non-crystalline solid thermally stable up to 105° which became gray above that temperature due to decomposition into the elements. (It should be noted, however, that formation of this polymer accompanies dissociation of the ammine by heating above this temperature. The statements are somewhat inconsistent!)

In 1947 Finholt, Bond, and Schlesinger[1] prepared an ether solution of aluminum hydride as well as the insoluble polymer by the following reactions:

$$3\ LiAlH_4 + AlCl_3 \xrightarrow{\text{ether}} \underset{(92\%\ \text{yield})}{4\ AlH_3} + 3\ LiCl \quad \text{and}$$

$$3\ LiH + AlCl_3 \xrightarrow{\text{ether}} \underset{(85\%\ \text{yield})}{AlH_3} + LiCl.$$

The ethereal solution of the hydride is not stable and polymeric aluminum hydride separates as a white solid soon after the preparation. The solid products contain ether which cannot be completely removed without decomposition of the hydride.

Wiberg, Graf, and Usón[3] then became interested in determining the molecular state of the aluminum hydride formed in ethereal solution by the method just described. They postulated two possible structures for lithium aluminum hydride from which two different molecular forms of aluminum hydride would be expected, i.e.,

$$AlCl_3 + 3\ LiH \cdot AlH_3 \rightarrow 4\ AlH_3 + 3\ LiCl \quad \text{and}$$

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

To resolve this problem molecular weight determinations by the boiling point method were made with ethereal solutions of aluminum hydride. The average molecular weight based upon five determinations was found to be 30.4; this indicates that monomeric aluminum hydride exists in ether solution.

Monomeric aluminum hydride in the free state would be coordinately unsaturated; hence it is assumed that the monomeric form is stabilized in the ethereal solutions by formation of $AlH_3 \cdot nOR_2$. Attempts to isolate the monomeric etherate by evaporation of the solution in vacuo resulted in the formation of polymeric aluminum hydride $(AlH_3)_x$. As already mentioned, ether-containing, solid, polymeric aluminum hydride separates from ethereal solutions merely on standing.

It was expected that the readily polymerizable monomeric aluminum hydride could be stabilized in ether solution by the addition of a tertiary amine to form an aminate since it is well known that the amines form more stable complexes than do the ethers.

Accordingly, a freshly prepared ethereal solution of monomeric aluminum hydride was mixed with an ethereal solution of trimethylamine in the molar ratio $N(CH_3)_3 : AlH_3 = 2:1$. A stable water-clear, colorless solution resulted which on the removal in vacuo of ether and excess trimethylamine left a white, powdery residue having the empirical composition $AlH_3 \cdot 2N(CH_3)_3$. On sublimation at 1 mm. pressure and 40° the compound subliming in the temperature range 30° - 40° has the exact composition $AlH_3 \cdot 2N(CH_3)_3$. The substance is obtained in the form of transparent, colorless, refracting crystals which can be sublimed readily in vacuo even by heat of the hand. It melts without decomposition at 95° and begins to decompose above 100° apparently with the splitting out of trimethylamine and the formation of polymeric aluminum hydride. The crystals fume in air and react vigorously with water with the evolution of hydrogen according to the equation:

$$AlH_3 \cdot 2N(CH_3)_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3H_2 + 2N(CH_3)_3.$$

The aminate is readily soluble in ether, tetrahydrofuran, and benzene. On treatment with dilute acids spontaneous decomposition occurs:

$$AlH_3 \cdot 2N(CH_3)_3 + 5H^+ \rightarrow Al^{+++} + 3\ H_2 + 2\ N(CH_3)_3H^+.$$

The molecular weight of the compound in both ether and benzene solutions, as determined by the boiling point method, showed that the compound is monomeric and undissociated in these solutions.

If ethereal solutions of freshly prepared monomeric aluminum hydride and trimethylamine are mixed in the molar ratio $AlH_3 : N(CH_3)_3 = 1:1$ a white solid may be obtained which sublimes at 50°-60°. The resublimed, transparent, colorless, refracting crystals melt at 76° and, according to analysis, have the composition $AlH_3 \cdot N(CH_3)_3$. The compound can be heated briefly to temperatures above its melting point without decomposition. On rapid heating at 100° the clear crystals become cloudy; this is related to the formation of polymeric aluminum hydride:

$$AlH_3 \cdot N(CH_3)_3 \xrightarrow{100^\circ} 1/x\ (AlH_3)_x + N(CH_3)_3.$$

Heating with a free flame results in the formation of an aluminum mirror:

$$AlH_3 \cdot N(CH_3)_3 \underset{\Delta}{\rightarrow} Al + 1\ 1/2\ H_2 + N(CH_3)_3.$$

The crystals fume in air and decompose explosively with water in accordance with the equation:

$$AlH_3 \cdot N(CH_3)_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3H_2 + N(CH_3)_3$$

Spontaneous decomposition occurs when the compound dissolved in ether, tetrahydrofuran, or benzene, is treated with dilute acid:

$$AlH_3 \cdot N(CH_3)_3 + 4\ H^+ \rightarrow Al^{+++} + 3\ H_2 + N(CH_3)_3H^+.$$

Molecular weight determinations of the compound by the boiling point method were made with both ether and benzene solutions. The values obtained indicate that the compound is monomeric in ether solutions whereas a partial dimerization is indicated in benzene solutions.

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* Review Article

RECOVERY OF SULFUR FROM HYDROGEN SULFIDE

Robert L. Rau December 15, 1953

I. Introduction:

Sulfur, the chemical industries' most versatile and economical raw material has numerous and diversified uses. The increase in demand for this raw material during the past 5 years, and even since the end of World War I comes as a direct result of the tremendous growth of chemical industry since that time,

At the turn of the century the total consumption in this country of sulfur in all forms amounted to not more than half a million tons a year. Today this is about a six weeks supply for American industry. At the beginning of the 20th century the United States imported about 170,000 tons of brimstone a year. Today it exports more than eight times this tonnage. In 1900 the infant sulfur industry produced slightly more than 3,000 tons of sulfur. Today the industry produces nearly 5 times this much in a single day.

In 1950 it was predicted that the native sulfur deposits of the United States would be exhausted within 25 years.

The subject matter of this paper will deal, first with those aspects of our economy and of the world that brought about this shortage and what plans are being made to offset any future shortage that may arise; and second, to review the literature dealing with the commercial recovery of sulfur from hydrogen sulfide and show how the chemical engineer has attempted to ease the sulfur situation.

II. The Economics of Sulfur:

There are a number of ways to guage the shortage of sulfur; one is by price changes and the other is by the condition of the above ground stocks of elemental sulfur.

In the last quarter of 1950 the price of crude sulfur obtainable from the mines increased from $18 per ton, at which level it had remained for many years, to $22 per ton for domestic sale. This represented a 26% increase over the 1935-39 price. During the same interval the average wholesale prices increased 118%. The current price of cure sulfur ranges from $25.50 to $27.50 per ton in car load lots.

In years past the above ground reserves of elemental sulfur represented an 18 month supply. By the end of 1950 this reserve had fallen to the irreducible minimum of a 6 months' supply.

This dangerous decrease in the sulfur supply brought immediate government action. The National Product Authority (NPA), the governments supply guardian, put sulfur under export allocation, limited certain western states in their production of sulfuric acid and restricted the users of sulfur to 90% of their average monthly consumption in 1950 and limited their inventories to a 25 day supply.

Despite all of these danger signals there is no world shortange of sulfur, at least not in the absolute sense. The problem is one of economic production rather than supply. The low cost of sulfur produced from the salt domes of the Gulf States by the Frasch process has made it uneconomical to work the higher cost resources.

What caused the sulfur shortage? Shortly after World War II the chemical industry experienced an unprecidented expansion in every conceivable direction. The tremendous variety of new products, plus an increased demand for those that were difficult to obtain during the war placed an ever increasing demand upon the industry. Sulfur, being a basic constituent of so many important industrial chemicals, especially sulfuric acid, likewise experienced an unprecidented demand.

This increase in home consumption, plus increased demands from abroad rapidly depleted existing reserves and soon led us to the place where consumption was exceeding production.

By the spring of 1952 the shortage was over. The chief factors in the improvement have been:

1. Stepped up production from Frasch mines and other sources.
2. Allocation and controls - first by industry and then by the NPA.
3. Conservation of sulfur and improved processing and recovery.

Although the current sulfur situation is no longer considered to be critical, the recent shortage has, however, made the United States, and the world as well aware of the fact that the sulfur resources made available by the Frasch process will not supply the demand indefinitely. The United States and the world have six basic alternatives. Sulfur can conceivably be obtained from: pyrites, H_2S from natural and refinery gases, smelter gases, calcium sulfate, cool and low grade sulfur deposits.

1. Recovery from Pyrites:
   At present, there is in the United States no large scale use of pyrites as a source of sulfur due to the prohibitive cost.

2. Recovery from Natural and Refinery Gases:
   This source of sulfur is being put into increasing use largely due to the fact that producers are finding it safer to provide their own supply of sulfur and sulfuric acid.

3. Recovery from Smelter Gases:
   Although this source is potentially capable of supplying 75% of our total sulfur needs, it is not extensively used because:

   a) smelter production is at a prohibitive distance from existing markets
   b) much of the SO_2 given off is of uneconomically low strength.

4. Recovery from Calcium Sulfate:
   Except for adverse economics, calcium sulfate, by virtue of its large quantity and wide distribution, could supply a large share of the world's sulfur and SO_4 radical.

5. Recovery from Coal:
   This potential source of sulfur has been little used because of technical and economic disadvantages.

6. Recovery from Low Grade Deposits:

Such deposits have been found in the western states and are largely used in fertilizer production. To date this has not provided an abundant source.

American Markets for Sulfur:

The principal markets for sulfur are the sulfuric acid plants which are concentrated in the Atlantic seaboard states, in Illinois and Ohio and in the southern states.

The sulfur market has been favored by two low cost items.

1. production by the Frasch process
2. low-cost water transportation for a large portion of the Gulf Coast sulfur.

III. Commercial Recovery of Sulfur:

Processes for the recovery of sulfur from H_2S occur in variety as well as volume in the literature of the past 25 years. Most of these methods depend upon the oxidation of the H_2S, either directly or indirectly according to the equation:

$$H_2S + [O] \rightarrow H_2O + S$$

Commercially the most successful of these methods depends upon the vapor phase oxidation of H_2S with either air or SO_2. These oxidations are essentially high temperature reactions and may occur at lower temperatures only on surface or in solution. It was kinetically confirmed that oxidations occur only by contact catalysis below 730°C. Numerous proposals have been made for catalysts. Of those proposed, bauxite seems to be the best. It combines low cost, durability and high activity.

The earliest commerciallization of the vapor phase oxidation was the Claus process. The process consists of the oxidation of H_2S with air over a bauxite catalyst in a single reactor. It was recognized that the lower the operating temperature the greater the yield. Since the oxidation of H_2S is an exothermic reaction the greatest process design problem stems from the highly exothermic nature of the reaction.

The first significant advance in the process was made in 1937 by the I.G. Farbenindustrie. Instead of burning the H_2S directly over a catalyst, one third of the H_2S was burned completely to SO_2 under a waste heat boiler. The SO_2 was then reacted with the remaining two thirds of the H_2S over bauxite at 700-750°F. The improvement in this modification may be seen by comparing the heats of the reactions involved.

Waste heat boiler:

$$H_2S + 3/2\ O_2 \rightarrow H_2O + SO_2$$

$$\Delta H = 124\text{-}138 \text{ K cal.}$$

Catalytic Converter:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3/e\ S_e$$

$$\Delta H = 21\text{-}35 \text{ K cal}$$

Over-all combustion Single Reactor:

$$3H_2S + 3/2\ O_2 \rightarrow 3H_2O + 3/e\ S_e$$

$$\Delta H = 145\text{-}173\ K\ cal$$

Thus only about 1/5 of the total heat of reaction is evolved in the catalytic converter, so that the operating temperature can be maintained at sufficiently low levels.

A third development basic to many modern processes was also introduced by the I.G. Farbenindustrie. This process consists of high temperature (up to 1000° C) non-catalytic combustion of H_2S with air in stoichiometric or greater proportions to produce sulfur directly in yields as high as 60-90 %. The high temperature combustion may be followed by one or more Claus catalytic converters.

By using several simplifying assumptions and applying a general method of calculation used by the chemical engineer a series of curves were developed which describe the yield of sulfur as a function of temperature and pressure. This graph indicates that the conversion to elemental sulfur passes through a minimum value in the region of 800-900°K for the pressure range of 1/2 - 2 atmospheres which effectively covers the conditions encountered in modern industrial practice. By the use of this graph the conditions conducive to maximum yields of elemental sulfur may be determined.

High Temperature Combustion:

The use of a free flame has been found to be a desirable method for obtaining sulfur from H_2S from the following view point.

The presence of a small portion of aromatic or aliphatic hydrocarbons in the H_2S stream was found to cause a continuous deactivation of the bauxite catalysts by coke deposition. Attempts to add the stoichiometric proportion of air necessary for complete combustion of hydrocarbons as well as the conversion of H_2S to sulfur at temperatures up to 460°C were unsuccessful. The result was an increased rate of catalyst deactivation as well as an increased formation of SO_2 at the expense of sulfur.

Thus by effecting the complete combustion of hydrocarbons, the free flame combustion also serves to protect the catalyst from deactivation.

Catalytic Studies:

Most commercial H_2S streams contain appreciable quantities of CO_2 and light hydrocarbons. It has been established that the high combustion temperature of such a gas results in the conversion of part of these carbon compounds to carbonyl sulfide. If the combustion is carried out with the proper proportion of air the gas will contain the stoichiometric quantity of SO_2 necessary to convert all of the COS and H_2S to sulfur according to the following equations:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

$$2COS + SO_2 \rightarrow 3S + 2CO_2$$

The catalyst used in the final stage of the recover process must, therefore, promote both of these reactions efficiently. Bauxite has been shown to do the job.

Commercial Processes:

Theoretical analysis has shown that the reaction must be carried out, at least in its final stages, at temperatures below 300°C in order to achieve yields of 95% or better. In achieving this in a practical process design, two important factors must be taken into account. These are:

1. The exothermic heat of reaction. The greater the amount of reaction taking place in a single unit, the more difficult it is to balance reaction heat with heat removal at a sufficiently low temperature. It is therefore necessary that the recovery process be carried out in at least two stages, the last of which must be catalytic in nature to achieve conversion at temperatures below 300°C.

2. The sulfur dew point of the reaction product. The catalytic reaction must be carried out at a temperature greater than that at which sulfur begins to condense out in liquid form, since the latter effectively poisons the activity of the catalyst.

The Claus process and the various modifications and additions introduced by the I.G. Farbenindustrie have been an attempt to obtain the optimum conditions for sulfur formation. Each modification has added to the overall procedure with the net result that a process has been established which will give 95-98% recovery.

Thus we have seen how sulfur has risen from a position of insignificance in our production economy to one of unparalleled importance. We have seen how the demand has gone beyond the supply and how certain economic conditions have placed limitations on various alternatives which could have conceivably increased our supply.

What has been done to alleviate this dangerous sulfur shortage ? Considering all possible solutions from an economic as well as from a technical view point the chemical engineer has given us a process which will do much in the way of conserving what has often been called "our dwindling sulfur supply."

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THESIS REPORT

STUDIES ON SOME RARE EARTH METAL CHELATE COMPOUNDS

Robert H. Marshall January 5, 1954

Introduction

The rare earth metal ions do not easily form complex compounds because of their relatively large sizes and because they have electronic configurations which possess little tendency to undergo the orbital hybridization accompanying covalent bond formation. However complexes are formed with several powerful coordinating groups, in which cases the tripositive rare earth metal ions display a coordination number of six. Spectrophotometric studies indicate that the 4f level remains unaffected during complex formation, suggesting that 5d, 6s, and 6p orbitals must be involved.

The geometry of these complexes has not been determined. In structural formulas the compounds are usually assigned an octahedral configuration chiefly because this one is most common for hexacoordinated compounds. If the arrangement is actually octahedral and if the bonds between the metal and coordinating groups actually possess sufficient covalency to permit retention of a configuration, then it should be possible to resolve certain of these complexes into their optical isomers. The objective of this research has been to prepare such rare earth metal chelate compounds and to study their properties with particular reference to resolving them into their possible optical isomers.

Ethylenediaminetetraacetic Acid (H_4 enta) Complexes with Neodymium and Yttrium

Preparation. -- These compounds were prepared in the manner described by Moss[1]. The sodium salt of the neodymium complex is prepared by heating an aqueous suspension of Nd_2O_3, H_4 enta, and NaOH in a 0.5:1 mole ratio. Evaporation of the resulting solution gives pink crystals of Na[Nd(enta)]. The free acid, H[Nd(enta)], is insoluble in water and may be obtained by acidifying a solution of the sodium salt. The acid is hygroscopic but can be obtained anhydrous by heating in an oven at 110°.

The preparation of Na[Y(enta)] is comparable to that of Na[Nd(enta)], but the yttrium salt is more soluble. The free acid H[Y(enta)] may be prepared by a direct reaction in aqueous suspension of Y_2O_3 and H_4enta in a 0.5:1 mole ratio. Some $Y[Y(enta)]_3$ is produced in the reaction, and it may be easily extracted from the product by washing. Both the free acid and yttrium salt are very hygroscopic but become anhydrous at 110°.

Structure. -- H[Nd(enta)] shows two distinct absorption bands in the infrared appearing strongly at 1673 cm.$^{-1}$ and very strongly at

1605 cm.$^{-1}$ The latter is due to complexed carboxyl groups, whereas the former indicates a partially associated - COOH group. With H[Y(enta)] the very strong band is present at about 1605 cm.$^{-1}$ and faint absorption occurs at 1720 cm.$^{-1}$ and 1650 cm.$^{-1}$ The 1720 cm.$^{-1}$ band is characteristic of a free - COOH group and the 1650 cm.$^{-1}$ may indicate a carboxyl group with characteristics intermediate to the others. Pure H_4 enta has partially associated -COOH groups absorbing 1690 cm.$^{-1}$ It appears then that in both acids the enta acts as a pentadentate group, leaving open for speculation the manner in which the sixth position in the coordination sphere of the metal ion is satisfied. Perhaps this is accomplished through an adjacent oxygen at in the crystal lattice.

The salts Na[Nd(enta)] and Na[Y(enta)] have broad bands at 1610 cm.$^{-1}$ and 1620 cm.$^{-1}$ respectively. In a salt the -COO$^-$ group has absorption slightly below this area, so without better resolutio one cannot determine whether the enta is penta- or hexadentate in these complexes.

Attempted resolution. -- Strychnine, brucine, quinine, and cinchonin salts were obtained by boiling aqueous suspensions of the free alkaloids and complex acids in a 1:1 mole ratio, With H[Nd(enta)] pink solutions were obtained from which small amounts of unreacted alkaloid or acid were removed by filtration. The solutions were then evaporated by passing a stream of compressed air over the surfaces. The salts of strychnine, quinine, and cinchonine produced heavy sirup, and further drying gave glasses. However, the brucine salt did yield crystals upon evaporation. The crystals were filtered from the mother liquor and fractionally dissolved into three portions by stirring them with small quantities of water. The brucine was quantitatively precipitated from the solutions as the polyiodide by adding an excess of an I_2 and KI solution, then adding crystals of Na_2SO_3 to reduce the excess I_2 to colorless iodide ions. All solutions gave a levo rotation of up to 0.030° with respect to a water blank. It was found that $Nd(NO_3)_3$ solutions also gave apparent levo rotations which increased with increasing neodymium concentration. This behavior is due to using a polarimeter light source which is in the region of the sodium D-line but is not completely monochromatic.

Fractional crystallization of the strychnine and brucine salts of H[Y(enta)] was effected by evaporating the solution down to a small volume and adding increments of absolute ethanol while agitating on a shaking machine. Subsequent dissolution of these crystals and precipitation of the alkaloid left no optical activity. Similar trea ment of the quinine and cinchonine salts yielded gels instead of crystals.

A selective adsorption technique was tried by stirring an aqueous solution of Na[Y(enta)] with d-quartz. No resolution was effected.

Pyramidone with Neodymium and Yttrium Ions

Ryabchikov and Terent'eva[2] have reported the isolation of rare earth complexes with pyramidone of the type $[M(pd)_3]X_3$ but attempts to duplicate their work using neodymium and yttrium were unsuccessful. The visible absorption bands of the neodymium ion in the presence of pyramidone were then examined using the Cary recording spectrophotometer.

and no shifts were found to take place. Shifts in absorption peaks would have indicated that complex species were being formed. Similarly antipyrene causes no shift in the absorption spectrum of neodymium although it does form compounds of the type $[M(ap)_6]X_3$ with rare earth metals. It was decided that even if such species do exist in the crystalline form they must at best be only weakly associated in solution, and resolution of such cations would be impossible.

Inner Complexes of Neodymium and Yttrium

Preparation. -- These materials were prepared by the method described by Ulrich in which the β-diketones are reacted with rare earth metal ions in a 3:1 ratio[3]. This involved dissolving acetylacetone (Hacac or thenoyltrifluoroacetone (HTTA) in a water-dioxane solution, adding an aqueous $NdCl_3$ or YCl_3 solution, and then adding dilute NH_4OH dropwise while stirring vigorously. The pH was kept below 6.5 at all t to prevent precipitation of the metal hydroxides. The products separated out as the reaction proceeded, and they were then recrystallized from benzene.

Attempted resolution. -- Attempts were made to resolve partially these inner complexes into their possible d l-forms by stirring d-quartz with their chloroform solutions for a 15 minute period. With $Nd(acac)_3$ and $Nd(TTA)_3$ there was no significant change in the polarimeter readings after treatment with the optically active quartz, but all readings were levo with respect to pure chloroform. As previously mentioned, this was due to using a non-homogeneous light source on a colored solution. The $Y(acac)_3$ and $Nd(TTA)_3$ form colorless solutions which did not give a significant change in polarimeter readings upon treatment with d-quartz and compared well with those on pure chloroform.

An attempt was also made to resolve $Y(acac)_3$ partially into optical isomers through adsorption on a lactose hydrate column. The column was developed using ethanol-free chloroform under 5 p.s.i. pressure. Eight ml. samples were collected using an automatic fraction collector. Difficulty was experienced in obtaining good polarimeter readings partially because the solutions contained suspended lactose which was not removed by filtration through fluted filter paper. Although the first fractions after break-through were approximately 0.015° levo with respect to the average of the others, the readings lacked precision and cannot be considered conclusive.

Conclusions

During this research previously unreported alkaloid salts have been prepared and studied as well as the inner complex $Y(TTA)_3$. Attempted resolutions of rare earth metal inner complexes and $Na[Y(enta)]$ using d-quartz have given negative results as have the attempts involving alkaloid salts of the anionic "enta" complexes. Work using the lactose hydrate column gave inconclusive results and should be repeated in the future possibly using a different optically active adsorbing agent. Failures to effect resolution so far would suggest that the complexing groups are labile enough to make resolution into optical isomers very difficult or impossible.

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COMPOUNDS OF HIGH NITROGEN CONTENT

Paul G. Gordon

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INTRODUCTION

The existence of the versatile chemical, hydrazine, was first postulated by Emil Fischer[1] in 1875; the compound was later isolated by Curtius and his co-workers[2]. Hydrazine probably would have remained a laboratory chemical had it not been for the extensive research program initiated by the Germans during World War II in an effort to utilize hydrazine as a superior fuel for rocket and submarine engines. Hydrazine is now being prepared in the United States on a substantial commercial scale by a modification of the Raschig process[3]. The ready availability of hydrazine has served to stimulate its uses in various phases of synthetic chemistry, and particularly for the manufacture of a wide variety of biologically active chemicals.

The solvent system theory developed by Franklin[4] has been applied advantageously for the preparation of compounds of high nitrogen content. It has been the purpose of this study to develop methods for preparing in good yields two cyclic hydrazino ammono carbonic acids, urazole and guanazole, from readily available starting materials, and to study some of their physical, chemical, and biological properties. While investigating the synthesis of urazole, allophanyl hydrazide was isolated for the first time; it was subjected to a complete study.

I. ALLOPHANYL HYDRAZIDE

HISTORICAL

Allophanyl hydrazide (aminobiuret) was first prepared as the hydrochloride by Thiele and Uhlfelder in 1898 by a Zn-HCl reduction of mononitrobiuret. The compound was further characterized by preparation of the nitrate and picrate salts and the benzaldehyde and acetone derivatives. Diazotization was carried out to produce allophanyl azide. Information concerning allophanyl hydrazide is limited primarily to this early investigation[5].

EXPERIMENTAL AND DISCUSSION

A new and improved synthesis of allophanyl hydrazide has been developed which entails a) the preparation of allophanic acid esters from urea and a chlorocarbonic ester (2:1 mole ratio), and b) hydrazinolysis of the ester in methanolic solution under controlled temperature conditions (3:1 mole ratio of N_2H_4:ester).

a) $2H_2NCONH_2 + ROCOCl \rightarrow H_2NCONHCO_2R + H_2NCONH_2 \cdot HCl$

$(R = CH_3 \text{ and } C_2H_5)$

b) $H_2NCONHCO_2R + N_2H_4 \rightarrow H_2NCONHCON_2H_3 + ROH$

Yields of 84% and 81% have been obtained from the methyl and ethyl esters, respectively.

Allophanyl hydrazide has been isolated as the free base for the first time. It is a white crystalline water soluble compound melting at 166° C. with decomposition. It is non-hygroscopic and thermally unstable when heated at 110° C. for twenty-four hours.

The compound was further characterized by preparing two new aldehyde and two new ketone derivatives. The particular carbonyl compounds were selected because other hydrazones prepared from these materials were shown to bilogically active:

a) salicylaldehyde, b) anisaldehyde, c) cyclohexanone, and
d) p-chloroacetophenone.

Allophanyl hydrazide has been shown to behave as a typical primary hydrazide as evidenced by the fact that it will condense with cyanic acid, thiocyanic acid, and cyanamide to produce 1-allophanyl semicarbazide, 1-allophanyl thiosemicarbizide, and 1-allophanyl aminoguanidine, respectively.

Diazotization of the hydrazide to the azide has been carried out. Allophanyl azide has been found to be a useful acylating agent for introducing the allophanyl group, $H_2NCONHCO-$, onto molecules which normally undergo acylation. The allophanylation reaction was carried out on hydrazine, allophanyl hydrazide, and guanazole. The water solubility of these compounds is greatly reduced by introducing the allophanyl group.

Allophanyl hydrazide has been acylated with methyl chlorocarbonate to produce 1-allophanyl methyl carbazinate. This ester was subsequently subjected to hydrazinolysis to give a product, containing a primary hydrazide function, which may be 1-allophanyl carbohydrazide. Attempts to prepare the latter material by interaction of ethyl allophanate and carbohydrazide were not successful.

Sulfanilamidobiuret has been prepared in the hope that it might exhibit some biological activity.

Allophanyl hydrazide had been shown to behave as a monoacidic base (pKb=~11) in aqueous medium as is evidenced by salt formation with hydrochloric, nitric, picric, and oxalic acid. An attempt to form a salt between urazole and allophanyl hydrazide was unsuccessful.

Allophanyl hydrazide has been cyclized by heating at 120-130°C. over an extended period of time, and by heating in an aqueous medium (100°C.) in the presence of a two mole excess of hydrazine. The latter procedure is preferred for it produces high yields (83%) of relatively pure hydrazine urazolate.

The following new compounds were prepared:

a) Allophany hydrazide
b) Salicylaldehyde derivative of allophanyl hydrazide
c) Anisaldehyde derivative of allophanyl hydrazide
d) Cyclohexanone derivative of allophanyl hydrazide
e) p-Chloroacetophenone derivative of allophanyl hydrazide
f) 1-Allophanyl semicarbazide
g) 1-Allophanyl thiosemicarbazide
h) 1-Allophanyl aminoguanidine hydrochloride
1-Allophanyl aminoguanidine picrate
1,2-Diallophanyl hydrazine
1-Allophanyl methyl carbazinate
1-Allophanyl carbohydrazide (?)
1-Sulfanilamidobiuret
Allophanyl hydrazide oxalate

II. URAZOLE

Although numerous methods have been reported in the literature since 1894 for preparing urazole, a cyclic hydrazino ammono carbonic acid, none of the procedures uses readily available starting materials or gives a good yield of the desired product. Urazole has been prepared by: a) thermal deammonation of biurea[6,7,8] b) hydrazinolysis of biuret[9,10] c) thermal deammonation of allophanyl hydrazide hydrochloride and nitrate[5] and d) dehydrazination of 1,5-diaminobiuret with HCl at 0°C.[11]. Small amounts of urazole have also been obtained by heating carbamyl azide in benzene[12], and by the hydrazinolysis of ethyl carbethoxythiocarbazate. Benzaldehyde has been used to remove hydrazine from hydrazine urazolate for conversion into urazole.

Urazole is a water soluble, crystalline, non-hygroscopic compound which melts at 249-50°C. with decomposition. Aqueous solutions of urazole are acidic to litmus, liberate carbon dioxide from carbonates, and are oxidized by ferric chloride. Urazole acts as a weak monobasic acid and has been shown to form salts with various metallic ions. The study of its chemical reactivity has been essentially limited to the replacement of the three hydrogen atoms present in the molecule by alkyl or aryl groups, and oxidation of the hydrazo linkage to an azo linkage. Numerous compounds related to urazole in which the oxygen atoms are replaced by =NH and =S functions have been described in the literature.

EXPERIMENTAL AND DISCUSSION

Several efforts to bring about the cyclization-deammination of biurea (hydrazidicarbamide) to urazole by a) fusion, b) by the action of acid, base, and thionyl chloride have shown that this synthetic approach is not a feasible one.

A new and superior synthesis of urazole has been developed which entails the following steps: a) preparation of methyl allophanate from urea and methyl chlorocarbonate, b) hydrazinolysis of the ester in aqueous medium to obtain hydrazine urazolate (83% yield), and c) conversion of hydrazine urazolate to free urazole by refluxing with acetone (91% conversion). When a 3:1 mole ratio of N_2H_4:ester is used and the alcohol formed during the reaction is removed as overhead, a 78% over-all yield of urazole is obtained:

$$\mathrm{H_2NCONHCO_2CH_3 + 2N_2H_4 \rightarrow H\underline{NNHCONHC}O\cdot N_2H_4 + CH_3OH}$$

$$\mathrm{\underline{HNNHCONHCO}\cdot N_2H_4 + (CH_3)_2CO \rightarrow H\underline{NNHCONHC}O + (CH_3)_2C{:}NN{:}C(CH_3)_2}$$

The acid dissociation constant of urazole was found to be 1.6 X 10^{-6} by a pH titration (pKa = 5.78).

III. GUANAZOLE

HISTORICAL

Guanazole may be regarded as a cyclic hydrazino ammono carbonic acid. This compound has been prepared from dicyandiamide and a) hydrazine hydrate at 100°C.[14], b) hydrazine hydrochloride at 100°C.[15], c) hydrazine hydrate at 70°C.[10]. Two procedures developed

by the American Cyanamid Company were made available to the author involving interaction a) of sodium dicyanamide with hydrazine sulfate in the presence of sodium hydroxide at 100°C. (75% yield), and b) dicyanamide and hydrazine dihydrochloride at 45-50°C. The latter procedure is preferred, since it gives almost quantitative yields.

$$H_2NC(NH)NHCN + N_2H_4 \rightarrow HN\underline{NHC(NH)NHC}(NH) + NH_3$$

Guanazole is a water soluble crystalline compound which decomposes at 206°C. It gives an alkaline reaction to litmus in aqueous solutions, is oxidized by ferric chloride, and forms salts readily with acids. Guanazole may be represented by five tautomeric structures which may be cited as evidence for aromatic character, especially since the 3-and 5-amino groups are readily diazotized.

EXPERIMENTAL

Quantitative solubility data for guanazole in methanol, ethanol, and water were determined; it is also soluble in liquid ammonia. The pure substance was found to be thermally stable at 100°C. and slightly hygroscopic at 90% relative humidity.

Guanazole was found to behave as a monoacidic base (pKb=~9) in aqueous solution. The following normal salts were prepared: a) hydrochloride, b) nitrate, c) sulfate, d) picrate, and e) oxalate.

Numerous attempts to prepare mononitrosoamino and dinitrosoamino derivatives of guanazole lead to the formation of yellow and red-orange powders, respectively, which could not be recrystallized from solvents without decomposition. The compounds do not give the Liebermann nitroso test, and are probably coupling products.

Guanazole was found to react with allophanyl azide to produce 3-allophanamido-5-amino-1,2,4-triazole. Reaction with p-acetamidobenzenesulfonyl chloride and subsequent hydrolysis gave 3-sulfanilamido-5-amino-1,2,4-triazole. The compound undergoes a cyanate condensation to produce 3-ureido-5-amino-1,2,4-triazole.

1-Phenyl guanazole was prepared[16] and its pKb value found to be ~10.

BIOLOGICAL TESTS

The compounds prepared in this study are being evaluated for possible usefulness as bactericides, insecticides, herbicides, fungicides, plant growth regulators, hypnotics, and anticonvulsants. Preliminary screening tests have shown allophanyl hydrazide and several of its derivatives to be effective tuberculostatic agents "in vitro".

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The Oxygen Electrode in Molten Salts

January 19, 1954

R. N. Hammer
(Roll Call)

The Lux-Flood concept of acid-base character in fused salts containing oxygen is useful in the rationalization of reactions in such media. Recent work by Flood and his students represents an attempt to establish an experimental technique for the quantitative measurement of acid strength in oxide systems.

The measurement of the acidity of a melt may be regarded as an examination of oxide ion activity analogous to the determination of hydrogen ion activity in water. Theoretically it should be possible to determine oxide ion activities by means of an electrode at which the potential is determined by the reaction $O^{--} \rightleftharpoons 1/2O_2 + 2e$.

In order to determine whether or not a reversible oxygen electrode could be built, Flood[1] measured the e.m.f's of a series of concentration cells $Pt,O_2/Na_2SO_4-Na_2CO_3-CO_2/Na_2SO_4-Na_2CO_3-CO_2/O_2,Pt$. The two half cells were maintained at constant temperatures ranging from 950 to 1150°C with a porous MgO "salt bridge" connection. The e.m.f. is expressed by the equation $E = RT/2F \ln N_2/N_1$, where N_1 and N_2 are the mole per cents of Na_2CO_3 as determined by analysis. From this fact it may be inferred that such an electrode behaves as a reversible O_2--O^{--} electrode, that Na_2SO_4 and Na_2CO_3 form an ideal solution, and that the liquid junction potential is negligible.

In the more acidic system $K_2CrO_4--K_2Cr_2O_7$ the observed e.m.f. was 15% lower than calculated. This could be due to a junction potential or to partial electronic conduction and does not necessarily indicate deviation from ideality of the solution.

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PYROSULFAMIDE AND SOME RELATED COMPOUNDS

Milton K. Snyder　　　　January 19, 1954

In 1838 Rose(4) attempted to make pyrosulfamide by the reaction of pyrosulfuryl chloride with ammonia as follows:

$$Cl-SO_2-O-SO_2-Cl + 4NH_3 = NH_2-SO_2-O-SO_2-NH_2 + 2NH_4Cl$$

The analysis of the entire product revealed a sulfur to nitrogen ratio of 1:3 instead of the expected 1:2.

Hayek, Engelbrecht and Wagner recently solved this puzzle(1). The reaction actually proceeds as follows:

$$Cl-SO_2-O-SO_2-Cl + 6NH_3 = NH_4NH-SO_2-O-SO_2-NHNH_4 + 2NH_4Cl$$

Pyrosulfamide is an acid, which might have been suspected on the basis that it is an aquo-ammono derivative of pyrosulfuric acid.

In this connection it is interesting to note that Kirsanov and Zolotov have prepared imidodisulfamide(2):

$$NH_2-SO_2-NH-SO_2-NH_2$$

This compound is acidic and can be titrated with sodium hydroxide.

The electron withdrawing power of the sulfuryl group has been demonstrated in hydrolysis reactions. Hayek and coworkers found that free pyrosulfamide cannot be isolated by the acidification of its salts because complete hydrolysis was immediate. Likewise Kirsanov and Zolotov(3) found that free imidodisulfamide hydrolyzes more rapidly than the sodium salt and less rapidly than the mono-methyl derivative.

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Potassium Fluodisulfate

Harold J. Matsuguma

January 19, 1954
(Roll Call)

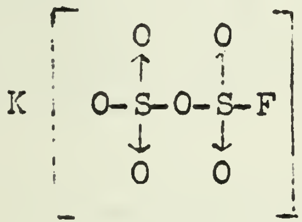
Potassium fluodisulfate has been prepared by the direct reaction of sulfur (VI) oxide and potassium fluoride.

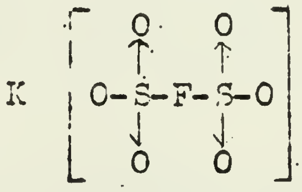
Finely ground, well dried KF is allowed to react with SO_3 under anhydrous conditions at room temperature. The reaction mixture is then liquified by heating it to 35°C. for 12-24 hours, depending upon the amount and surface area of the KF. The excess SO_3 is removed by allowing the reaction mixture to stand over concentrated sulfuric acid at room temperature at 13 mm. Hg. Transparent, prismatic crystals of potassium monofluopolysulfate then precipitate from the reaction liquor.

These crystals effloresce slowly at room temperature (rapidly at 35° C.) to give a white, opaque solid having the empirical composition $KF \cdot 2SO_3$. This compound has an appreciable vapor pressure of SO_3, and the vapor pressure is dependent upon the temperature and duration of heating. Heating at 100° C. will bring about the formation of KSO_3F in four hours.

Proof of the fact that the compound $KF \cdot 2SO_3$ is actually KS_2O_6F is found in the fact that its Debye X-ray diagram is markedly different from that of KSO_3F.

There are two possible configurations for KS_2O_6F:


(I)


(II)

Of these (I) is most probably the correct one. An analogous compound, NaS_2O_6Cl, has been assigned the configuration shown by (I).

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The Problem of Naturally Occurring Technetium(1)

Edward Alperovitch February 16, 1954

The non-existence of technetium in nature, long considered a fact of axiomatic validity, has become subject to considerable doubt in recent years due to the discovery of technetium in the sun(2) and in certain stars(3).

According to Jordan(4), the presence of technetium in stars can be explained in three different ways.

1.) Existence of a hitherto undiscivered stable technetium isotope;

2.) Continuous formation of $2.1\mathrm{x}10^5$yTc^{99} in stars;

3.) Continuous formation of matter in the universe.

The third explanation cannot account for the presence of technetium in the sun, while the second one is incompatible with present ideas about nuclear reactions and energy balance in stars. The first explanation, though rejected by Jordan, deserves serious consideration, since the two "missing" isotopes of technetium, Tc^{97} and Tc^{98}, are presumed to be stable or long-lived.

Technetium 97, with a half-life of $>10^4$ years(5) can either be stable, in which case its isobar, Mo^{97}, will undergo $\beta-$ decay, or unstable, decaying by electron capture. Technetium 98, having an odd number of both protons and neutrons, cannot be stable, but will decay to Ru^{98} and/or Mo^{98}. Due to its high nuclear spin $(\leqslant 7^+)$, a long half-life may be expected; the latest experimentally determined limit is $>10^7$ years(6).

A review(7) of past work shows that the chemical procedures used by the Noddacks(8) in their search for technetium in nature must, by necessity, have led to irreproducible results, since the chemical behaviour of the element was not well enough known. Negative evidence obtained by other authors(9)(10) is of limited significance because these investigators failed to detect rhenium, that was most certainly present in the minerals examined. Under these circumstances, the failure of the Noddacks to produce further evidence in addition to x-ray spectrograms, may not be taken as proof for the non-existence of technetium in nature, and a new search appears justified.

An attempt is made to predict the expected geochemical distribution of technetium based upon the known geochemical behaviour of its congener rhenium(11) as well as other pertinent factors, such as ionic radii, relative stability of lower oxidation states, volatility, and geochemical affinity. An enrichment of technetium is expected in chromite, rutile, and various late stage pegmatitic minerals of columbium, tantalum, and the rare earths.

The original cosmic abundance of Tc^{97} is estimated from the

general abundance trend(12) in that region of the periodic table and the abundance ratios of other isobaric pairs. The values obtained are $2.2x10^{-3}$ and $1.3x10^{-3}$ atoms/10000 atoms of silicon, respectively. Similar calculations, based upon the abundance ratios of other "odd-odd" nuclei (K^{40}, V^{50}, La^{138}, Lu^{176}) and their isobars give values of $3x10^{-4}$ and $9x10^{-5}$ for the original cosmic abundance of Tc^{98}.

The present steady-state concentration of the $2.1x10^{5}$y Tc^{99} in certain minerals is computed in order to preclude interferences from this source. The spontaneous fission of U^{238} gives a concentration of $1.5x10^{-12}$ atoms Tc^{99}/ atoms U^{238} while the capture of cosmic-ray produced neutrons by molybdenum 98, followed by β-decay of Mo^{99} yields $1.5x10^{-14}$ gTc/gMoS_2.

Of four available methods of detection (x-ray spectroscopy, emission spectroscopy, mass spectrometry, and neutron activation), only the last two are found to be of the requisite sensitivity and specificity.

Mass spectrometry can be used to detect Tc^{97} and Tc^{98} directly, by the isotope dilution method (sensitivity - 10^{-10}g)(13); or indirectly, by means of their decay products Mo^{97}, Mo^{98}, and Ru^{98}(14), if the half-lives of Tc^{97} and Tc^{98} are comparable to geological times. A detectable perturbation in the isotopic composition of Mo and Ru is most likely to be found in minerals of high geologic age ($2-3x10^{9}$y). The actual sensitivities obtainable are further dependent on the initial Tc/Mo and Tc/Ru ratios in the mineral at the time of its formation, and the branching ratio for the decay of Tc^{98}. By making certain assumptions, sensitivities of 10^{-8} to 10^{-17}gTc/g of mineral are calculated for several typical minerals.

Another method, neutron activation analysis(15) can be used to detect Tc^{98} directly. Technetium 98 forms two products upon neutron capture: Tc^{99m} and Tc^{99}. The former of these possesses sufficiently unique radiation and decay characteristics (140 kev γ-ray; 6h half-life) to render it suitable for the detection of Tc^{98}. The sensitivity obtainable depends on the neutron flux and the activation cross section (reaction probability). Since the latter quantity is not known, it can only be estimated to lie between two limiting values: 10^{-8}g and 10^{-14}g (at a neutron flux of $2x10^{12}$n $cm^{-2}sec^{-1}$).

Unfortunately, the 6h Tc^{99m} can also be formed from molybdenum by the reaction:

$$Mo^{98} \xrightarrow{(n,\gamma)} Mo^{99} \xrightarrow[67h]{\beta^-} Tc^{99m}$$

As little as 10^{-9}g of Mo will interfere, so that a complete separation of Tc from Mo must be accomplished prior to the irradiation. Rhenium in quantities of 10^{-12}g likewise interferes due to emission of 137 and 152 kev γ-rays by Re^{186} and Re^{188}, formed from Re^{185} and Re^{187} by neutron capture.

An ultimate solution of the technetium problem depends, to a large extent, on a determination of the half-lives of Tc^{97} and Tc^{98}. If they are long compared to geological times, direct detection of Tc in nature should be possible. If they are short ($\leqslant 2-5x10^{8}$y),

they can be determined by cyclotron experiments. If they are intermediate, Tc can be detected and the half-lives determined by both direct and indirect methods.

Five groups of experiments are required to cover the entire range of half-lives:

1.) Stable Tc^{97}. Molybdenum minerals of high geologic age should be examined for Tc^{97} formed by β-decay of Mo^{97},

2.) Intermediate to long-lived Tc^{98}. Concentrates from various minerals of high geologic age should be examined for Tc^{98} by neutron activation analysis.

3.) Intermediate to long-lived Tc^{97} and Tc^{98}. Concentrates from the activation experiments are to be examined mass spectrometrically for Tc^{97} and Tc^{98}.

4.) Intermediate to long-lived Tc^{97} and Tc^{98}. Molybdenum and ruthenium fractions from the same minerals are to be examined mass spectrometrically for radiogenic Mo and Ru.

5.) Short-lived Tc^{97} and Tc^{98}. Cyclotron and pile experiments are to be undertaken to determine the half-life of both species, if all preceding experiments yield negative results.

Four of these five groups of experiments involve the isolation of submicrogram amounts of technetium from macro quantities of other elements. The purity requirements are rather stringent, since both neutron activation and mass spectrometric methods, are quite susceptible to interferences. The decontamination factors to be attained in neutron activations are:

Mo - $4x10^{10}$
Re - 10^{10}
Ru - 10^{6}
59 other elements - 10^{3} to 10^{11}.

A procedure meeting these requirements was developed by a combination of ion-exchange chromatographic and distillation techniques, and experiments begun within the project outlined above.

1.) Stable Tc^{97}. No technetium was found by emission spectroscopy in concentrates from 3 pre-Cambrian molybdenites. A lower limit of $>2.4x10^{16}$y can now be set for the half-life of Mo^{97}.

2.) Tc^{98} - Neutron Activation. Of six minerals examined, three, a columbite and two yttrotantalites, gave positive results indicating a Tc^{98} content of 10^{-10} to 10^{-16} and 10^{-9} to 10^{-15} g/g, respectively.

3.) Tc^{97} and Tc^{98} - Mass Spectrometry (direct).

4.) Tc^{97} and Tc^{98} - Mass Spectrometry (indirect). Technetium and molybdenum concentrates from the above sources have been

sent to Dr. M. G. Inghram at the Argonne National Laboratory for mass spectrometric examination. Results are not available at this date.

5.) Tc^{97} and Tc^{98} - Cyclotron and Pile Experiments. According to Boyd(6), molybdenum x-rays have been observed from pile-produced Tc^{97} samples, indicating a decay by electron capture, with a half-life of $5 \times 10^{5\pm1}$ years.

An irradiated molybdenum target containing Tc^{98} will be examined in approximately 5 years, after the decay of 60d Tc^{95} and 90d Tc^{97m}(6).

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Recent Developments in the Chemistries of Selenium and Tellurium

S. F. West February 23, 1954

A series of publications in recent months dealing with the halides and oxyhalides of selenium and tellurium have served to clarify much of the earlier, contradictory information concerning these species, and to further elucidate the behavior of these two elements, often neglected in favor of their more abundant and more important predecessor, sulfur. The properties of the halides of sulfur have been the subject of more investigation than the halides of the heavier members of the "sulfur group" and are fairly well defined. The behavior of some of the halides of selenium and tellurium, particularly the fluorides, has been re-evaluated in the light of new preparative methods, substantiating trends observed in the transition from the small, nonmetallic sulfur atom to the larger, more metallic tellurium atom.

Table. Physical Properties of the Sulfur-Group Fluorides

	Melting Point (°C)	Boiling or Sublimation Point (°C)	Heat of Vaporization or Sublimation (Cal)	Inter-Atomic Distances (Å)
S_2F_2	-120.5	-38.4		
SF_4	-124	-40	5180	
SF_6	-50.8	-63.8	5460	S-F, 1.58
S_2F_{10}	-92°	29±1°	7000	S-S, 2.3
				S-F, 1.58
SeF_4	-9.5	106	11,240	Se-F, 1.76
SeF_6	-34.6	-46.6	6600	Se-F, 1.70
Se_2F_{10}(?)				
TeF_4	129.6			
TeF_6	-37.8	-38.9	6740	Te-F, 1.84
Te_2F_{10}	-34	54°	9440	

The fluorides of sulfur, selenium, and tellurium are formed in varying proportions, with considerable evolution of heat, when fluorine combines directly with the elements. These substances are gases

or volatile liquids (TeF_4 is a white solid). Sulfur hexafluoride is a remarkably unreactive gas; SeF_6 hydrolyses slowly in water to form HF and H_2SeO_4; TeF_6 also hydrolyses slowly, but at a rate greater than for SeF_6. Ditellurium decafluoride, though fairly stable is more reactive than S_2F_{10}.

Selenium tetrafluoride can be produced by reaction of selenium and fluorine well diluted with nitrogen at 0°.[1] above 100°, or with concentrated fluorine, SeF_6 is mainly produced. By using a shallow bed of selenium on a well cooled surface, a pure product was obtained which melted to a colorless liquid at -9.5° and boiled at 106°. By contrast, $SeCl_4$ melts, under pressure at 305°±3 and sublimes at 196°. The vapor pressure of the product obtained in the above manner was found to obey the relationship $\log p = 9.44-2457/T$ between 20° and 70° giving an extrapolated boiling point of 101.6°. The latent heat of vaporization of the liquid is 11,240 cal., giving a value of 30.0 for Troutons constant[2]. The magnitude of this value along with a wide liquid range are suggestive of good solvent properties and the colorless liquid does indeed exhibit some interesting solvent effects.

Solvent Properties of SeF_4. The fluorides of Na, K, Rb, and Cs are soluble in selenium tetrafluoride to form complexes whose composition approach $MSeF_5$, in contrast with other complex selenium halides, M_2SeX_6 (ibid). These substances possess an appreciable vapor pressure of SeF_4 and dissociate slowly in vacuum, even at room temperature. They are immediately decomposed by water. Thallous fluoride dissolves to form an isolable complex of similar formula, but with silver fluoride, the complex is very unstable altho evidently formed. The fluorides of barium and lithium dissolve, the latter halide being soluble in the cold and insoluble at higher temperatures; both retain some SeF_4 on drying. The behavior of LiF may be explained by the instability of the complex at higher temperatures. Ammonium fluoride is reported to be somewhat soluble in the cold, but on being warmed, the solution turns brown and Se is deposited. Mercury dissolves slowly below 20°, faster at the boiling point, and upon refluxing, a white solid, $HgSeF_4$ is formed[2].

Brown V_2O_5 is readily soluble giving a colorless solution. On cooling, crystalline plates of $VOF_3 \cdot 2SeF_4$ [probably the salt $(SeF_3)_2VOF_5$ (C.f.K_2VOF_5)] separate. TiO_2 and Ta_2O_5 are also soluble.

Sulfur trioxide reacts when heated and on removal of excess SeF_4 in vacuum, an oily liquid $SeF_4 \cdot SO_3$ is obtained which gives colorless crystals on cooling, m. 70°. It is also reported that the liquid can be supercooled readily in the absence of solid, and can be vacuum distilled at 170° without decomposition.

Potassium permanganate reacts vigorously, first forming a green solution which immediately becomes reddish brown, evolving oxygen and depositing a red brown solid, $KMnF_5$. The reaction probably proceeds according to:

$$4KMnO_4 + 10SeF_4 \rightarrow 4KMnF_5 + 10SeOF_2 + 3O_2.$$

Selenium tetrafluoride is decomposed violently by water and attacks glass on standing, even when completely free from HF. The solvent is also reported to be miscible in all proportions with

H_2SO_4, alcohol, ether, and IF_5, and dissolves appreciable quantities of CCl_4, $CHCl_3$, bromine, iodine, sulfur and selenium[1].

Since SeF_4 is the only colorless liquid of Group VI having an "inert pair", the Raman spectrum of the compound was investigated by Rolfe and coworkers[3]. The spectral evidence supports a trigonal, bipyrimidal structure with the lone pair in an equatorial position. This structure was also deduced by Bowen[4] after an electron diffraction study of the compound.

Addition of SeO_2 in excess followed by fractionation gives pure $SeOF_2$, which is the best method reported to date, for the preparation of the oxyfluoride. Two other new methods for the preparation of $SeOF_2$ have been reported[1] recently, which give, after redistillation in vacuum, a purified product boiling at 126° and melting at 15° (approximately 10° higher than previously reported). One method, leading to yields of up to 80% based on the dioxide involves the action of fluorine diluted with nitrogen on SeO_2. The oxyfluoride was also produced by the combustion of selenium in a stream of fluorine containing about 60% oxygen.

Tellurium tetrafluoride. The existence of TeF_4 was recently confirmed when the compound was prepared in a two step process from fluorine and tellurium[5]. Direct combination at 200° in the presence of excess fluorine produced the hexafluoride which was reduced to the tetrafluoride with additional metal at 180°. The white solid melts at 129.6° but above 193.8° is unstable toward TeF_6. TeF_4 was used to prepare the following complexes with pyridine[6]:

$$(C_5H_5N)TeF_4,\ (C_5H_5NH)TeF_5,$$

$$(C_5H_5NH)_2TeF_6,\ \text{and}\ (C_5H_5NH)_2TeX_6(X{=}Cl,\ Br,\ I).$$

Any of the complex halides may be converted into a lower one by treatment with the appropriate halogen acid.

Ditellurium decafluoride (Te_2F_{10}) was recently obtained in yields of up to 20% from the direct fluorination of Te in the presence of CaF_2[7]. The decafluoride is a colorless, heavy liquid of remarkable volatility. Though it has a molecular weight of 445, it boils at 54° (327°K), representing by far the highest ratio of molecular wright to boiling point of any compound known. Te_2F_{10} melts at -34° to -33°, has a latent heat of vaporization of 9440 Cal/mole at the normal boiling point, and the value of Troutons constant is 28.3. The liquid has a density at 25° of 2.88 and is similar to S_2F_{10} in most of its properties.

Tellurium dichloride. Streaming Arcton 6 (dichlorodifluoromethane) over molten tellurium provides a new method of preparing $TeCl_2$. in a pure state and in good yields[8]. The old method of treating hot Te with chlorine gave a mixture of di- and tetrachlorides which were separated by fractional distillation. The product from the new method melts sharply at 208° and boils at 328° (corr), agreeing with Carnelly and Williams (m. 209±5°, b. 327°, J. Chem. Soc., 1879, 563). Contrary to published data[9], the dichloride disproportionates rapidly in ether to give Te and $TeCl_4$. Thus Aynsley points out[8] that much of the reported chemistry of $TeCl_2$ in ether actually represents the behavior of $TeCl_4$ due to disproportionation of the starting material.

An excess of liquid bromine reacts exothermically with $TeCl_2$ forming $TeCl_2Br_2$, a yellow powder which melts at 292° to a ruby red liquid and boils at 415° forming an orange vapor. The following series of complexes with pyridine were prepared from $TeCl_2Br_2$:

$$(C_5H_5N)_2TeCl_2Br_2,\ (C_5H_5NH)_2TeCl_4Br_2,$$
$$\text{and } (C_5H_5NH)_2TeI_6.$$

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$TeCl_4 \cdot AlCl_3$ can be distilled in high vacuum

REDUCTION OF PHOSPHATES BY HYDROGEN
(Preparation of Phosphorus at Low Temperatures)

M. J. Sirotek   March 2, 1954

INTRODUCTION

Several methods for the reduction of phosphates to phosphorus have been reported in the literature. The usual method consists of a high temperature reduction by carbon in the presence of silica. Elemental phosphorus is produced in this way. Calcium orthophosphate can be reduced by silicon monoxide[1] (supposedly formed by vaporization of the mixture of silicon dioxide and silicon) with the formation of phosphorus. Rudakov[2] has reported a bacterial reduction of phosphates. Metaphosphoric acid, hypophosphorous acid, and phosphine were formed. However Liebert[3] has challenged this observation.

Hutter[4] has studied the reduction of phosphates by hydrogen at or near atmospheric pressure and at temperatures below 1000°. This method is believed to have industrial possibilities for the preparation of phosphorus at temperatures ranging from 450-800C°. It can also be used for the preparation of pure metaphosphoric acid. Several authors[5-9] have studied this type of reduction.

EXPERIMENTAL PROCEDURE

The method consists in the circulation of a known quantity of reducing gas G in a closed system while the temperature of the furnace increases linearly with time at the rate of 250° per hour. An absorbent eliminates the gas GO formed during the reaction and thus prevents establishment of an equilibrium. Ordinarily the pressure increases with rising temperature but, when reduction occurs the pressure falls due to absorption of the gaseous product.

A single experiment gives the following information:

1. the temperature at which reduction begins
2. the formation of intermediate compounds
3. the quantity of hydrogen used in the reduction

This experimental apparatus was first devised by Jolibois[10] and later used by Olmer[9] and Dunoyer[11]. This procedure may be compared with "differential thermal analyses" and could possibly be called "differential piezometric analysis".

EXPERIMENTAL RESULTS

Most of the orthophosphates were prepared by precipitation from a solution of disodium orthophosphate and the pyrophosphates from a solution of sodium pyrophosphate. Experimental results are summarized in Table 1.

Table 1

REDUCTION OF PHOSPHATES WITH HYDROGEN

Substance Reduced	Temp. of Reduction	Phosphorus	Reduction Products ($+H_2O$) Metal	Phosphide	Other Product
1. $Pb_3(PO_4)_2$	650°	P	Pb		
$3Pb_3(PO_4)_2PbCl_2$	800°	P	Pb		
2. Sn(IV)phosphate undefined	600°	P	Sn		
3. $SbPO_4$	450°	P	Sb		
4. $BiPO_4$	425°	P	Bi		
5. $Hg_3(PO_4)_2$	200°		Hg		$Hg_3(PO_4)+H_3PO_4+Hg_4P_2O_7+HgPO_3$
Hg_3PO_4	200°		Hg		$Hg_4P_2O_7+HgPO_3$
$HgPO_3$	300°		Hg		HPO_3
HPO_3 (12)	600°	P			
HPO_3 (Au boat)	475°	P			
6. Ag_3PO_4	140°		Ag		H_3PO_4
$Ag+H_3PO_4$	425°	P			
7. $CrPO_4$	600°	P		CrP, Cr_2P	
8. $Mn_3(PO_4)_2$	850°	P		Mn_2P (13)	
9. $FePO_4$ (Calç.)	460°				$Fe_2P_2O_7$
$Fe_2P_2O_7$	620°			FeP (10)	
10. $Co_3(PO_4)_2$	550°			CoP, Co_2P	
$Co_2P_2O_7$	530°			CoP	
$Co(PO_3)_2$	670°	P		Co_2P (14)	
11. $Ni(PO_4)_2$	450°	P		Ni_2P	
$Ni_2P_2O_7$	450°	P		Ni_2P	
$Ni(PO_3)_2$	600°	P		Ni_2P	
12. $Cu(PO_4)_2$ $Cu_2P_2O_7$	300°		Cu	$CuPO_3+HPO_3 \xrightarrow{cool} Cu+Cu(PO_3)_2$	
$CuPO_3 \cdot HPO_3$	350°	P		Cu_3P	
13. $H_3PO_4+SiO_2$	700°	P			
14. $Zn_3(PO_4)_2$	650°			Zn_3P_2 (15,16)	
15. $(UO_2)_3(PO_4)_2$	550°				UP_2O_7
UP_2O_7	750°	P			UO_2

The compositions of the phosphides of Cr, Co, Ni and Cu were verified by means of Debye-Scherrer X-ray patterns.

Several of the phosphides of Co and Ni contain the same proportion of metal to phosphorus as the original phosphates. The composition of these phosphides was determined by reducing the phosphates in the presence of tin(IV) phosphate, which decomposes at 600° into tin and phosphorus and thus allows the reduction of the cobalt and nickel phosphates to take place in the presence of an excess of phosphorus.

CONCLUSIONS

The data summarized in Table 1 can be considered from three different points of view.

1. The process of the reduction
   Reduction occurs in two stages when a phosphate, $P_2O_5 \cdot MO$, is heated in a current of hydrogen. These two stages occur singly or together depending on the nature of the metal ion M.

   a. If the metal can exist in a lower oxidation state than in the original phosphate or if it is slightly electro positive, the group MO is reduced at a low temperature (300°). Either the metal can be reduced partially giving a pyro- or metaphosphate of the metal in a lower oxidation state

   $$2FePO_4 + H_2 \rightarrow 2FePe_3 + H_2O$$

   or it can be reduced completely giving ortho phosphoric acid and the metal

   $$Ag_3PO_4 + \frac{3}{2} H_2 \rightarrow H_3PO_4 + 3Ag.$$

   b. If the oxide is not too basic, P_2O_5 can be reduced at a more elevated temperature (600°) with liberation of phosphorus. Often the two stages occur simultaneously and either phosphorus and the metal are liberated or a phosphide is formed.

   $$Pb_3(PO_4)_2 + 8H_2 \rightarrow 2P + 3Pb + 8H_2O$$
   $$Zn_3(PO_4)_2 + 8H_2 \rightarrow Zn_3P_2 + 8H_2O$$

   If the metal is very electropositive and forms an oxide which is not reducible by hydrogen, only the P_2O_5 is reduced. Phosphorus is liberated and the metallic oxide remains.

   $$UP_2O_7 + 5H_2 \rightarrow 2P + UO_2 + 5H_2O$$

2. Classification of the metals according to products

   a. Ag, Hg, Sn, Pb, Sb and Bi either do not form phosphides or form phosphides which are unstable at high temperatures. Phosphorus and the metal are obtained.

   b. Cr, Mn, Fe, Co, Ni, Cu and Zinc each give at least one phosphide stable at higher temperature. Phosphides of low thermal stability usually will produce phosphorus.

   c. Fe, Hg and U exist in several oxidation states.

Reduction leads to the pyro- and metaphosphates of the metal in a lower valence state.

d. Cu, Ag, and Hg are very weakly electropositive. Reduction gives ortho phosphoric acid and the metal.

e. Al, Si, and U are very electro positive metals whose oxides are not very basic. Phosphorus and a metallic oxide are obtained.

3. Practical Applications

Phosphorus can be prepared at relatively low temperatures by reducing metals of group (a) and (e). The reduction of lead chlorophosphate $3Pb_3(PO_4)_2 \cdot PbCl_2$ to phosphorus has industrial possibilities. This compound exists in the natural state as pyromorphite or can be prepared easily from natural lime phosphate[17,18]. Phosphorus can also be prepared by the reduction of ortho-phosphoric acid in the presence of silica. The silica hinders volatilization of the acid but does not hinder its reduction.

Pure metaphosphoric acid can be prepared by reducing mercury(I) phosphate at 350° in a current of hydrogen.

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SODIUM BOROHYDRIDE

Mark M. Chamberlain March 9, 1954

I. Historical

The first reference to a compound of sodium, boron, and hydrogen formed by reacting sodium amalgams with diborane and thought to be $Na_2(B_2H_6)$ is credited to Stock and Laudenklos (15) in 1936. Subsequent investigation suggests that the compound prepared at that time was actually sodium borohydride, $NaBH_4$. (4)

The first thorough characterization of sodium borohydride was made by Schlesinger and his co-workers (1941-1946) as part of their work on the preparation of a new, highly volatile uranium compound, uranium IV borohydride (10).

II. Preparation

Methods for preparing sodium borohydride may be divided into two groups: those requiring the use of diborane and a second group of procedures employing other starting materials.

A. With Diborane (1) (11)

1. $NaH + B(OCH_3)_3 \longrightarrow NaBH(OCH_3)_3$
   $2NaBH(OCH_3)_3 + B_2H_6 \longrightarrow 2NaBH_4 + 2B(OCH_3)_3$

2. $NaBH(OCH_3) + CH_3OH \longrightarrow NaB(OCH_3)_4 + H_2$
   $3NaB(OCH_3)_4 + 2B_2H_6 \longrightarrow 3NaBH_4 + 4B(OCH_3)_3$

3. $NaOCH_3 + 2B_2H_6 \longrightarrow 3NaBH_4 + B(OCH_3)_3$

B. Without Diborane (12)

1. $4NaBH(OCH_3)_3 \xrightarrow{230^\circ} NaBH_4 + 3NaB(OCH_3)_4$

2. $NaBH(OCH_3)_3 + 4NaH \xrightarrow{225-275} NaBH_4 + 3NaOCH_3$

3. $2Na + H_2 + 2B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$

4. $4NaH + 2B_2O_3 \longrightarrow 3NaBO_2 + NaBH_4$

III. Purification

Sodium borohydride may be separated from its reaction mixture by extraction with isopropylamine or liquid ammonia (11) and may be recrystallized from water as the dihydrate from liquid ammonia as the diammoniate or from isopropylamine with purity greater than 99%. (11)

IV. Physical Properties

1. Thermally stable to 400° C (11)

2. Stable in air or in alkaline solution (3)

IV. Physical Properties (Cont'd)

3. Soluble in water, alcohols, primary amines, and liquid ammonia. Insoluble in ethers, ethyl acetate, and methyl borate (11)

4. Reduction potential (vs standard H_2 electrode)
   -0.43 volts in acid solution (5)
   -1.23 volts in basic solution (8)

V. Reactions

A. Inorganic

1. $NaBH_4 + 2H_2O \xrightarrow[Cat]{} NaBO_2 + 4H_2$ (14)
   liberates 2.37 liters (STP) H_2/gram

2. $3NaBH_4 + 4(C_2H_5)_2O : BF_3 \longrightarrow 3NaBF_4 + 4Et_2O + 2B_2H_6$ (11)

3. $AlBr_3 + 3NaBH_4 \longrightarrow Al(BH_4)_3 + 3NaBr$ (13)

4. Reduction of metallic ions in aqueous medium CeIV, CrVI, FeIII, HgII, HgI give next lower stable oxidation state.
   Iron may be determined analytically by reduction of FeIII to FeII (5)
   AsIII, SbIII, and Bi(III) are also reduced (9)

5. Hydrogenation catalysts as effective as or more effective than Raney nickel are prepared by reduction of a pure aqueous solution of nickel II ion or reduction of aqueous solutions containing Ni II and chromium, molybdenum, or tungsten ion (7)

B. Organic (2) (3)

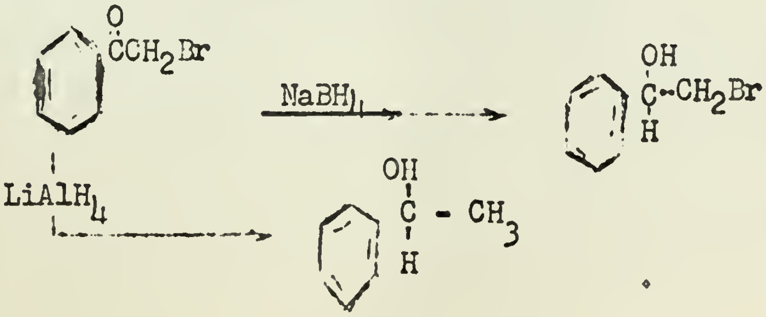
Sodium borohydride is a highly selective reducing agent for carbonyl groups. The carbonyl group is reduced to the corresponding alcohol while esters, acids, anhydrides, olefinic double bonds, nitriles, ring nitro compounds, and ordinary alkyl and aryl halides are not affected. Sugars are reduced, however; acid chlorides are reduced by sodium borohydride suspension in dioxane.

The reduction of carbonyls is thought to proceed through the tetra-alkoxyborohydride:

$$4R_2C = O + NaBH_4 \longrightarrow NaB(OCHR_2)_4$$

$$NaB(OCHR_2) + 2NaOH + H_2O \longrightarrow Na_3BO_3 + 4R_2CH_2OH$$

<u>example</u>:



VI. Comparison with $LiAlH_4$

Both sodium borohydride and lithium aluminum hydride are strong reducing agents. However, sodium borohydride is more selective, may be handled in moist air, and is not decomposed rapidly in aqueous or alcoholic media. Both sodium borohydride and lithium aluminum hydride may be obtained from the Metal Hydrides Company at a cost of 9.7¢ and 8.7¢ per gram respectively (in 100 g. lots). (6)

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THESIS REPORT

NITROGEN COMPOUNDS OF THE PHOSPHORIC AND PHOSPHONIC ACIDS

William C. Smith

March 16, 1954

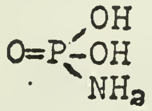
INTRODUCTION

The recent discovery that certain organic derivatives of the phosphoric and polyphosphoric acids possess biological activity has stimulated considerable research in the organophosphorus field since the end of World War II. The preparation and study of phosphoric and phosphonic acid derivatives into which hydrazine was introduced as replacement for the hydroxyl group was begun in this laboratory by Gher (1); such a modification of structure was felt to be worthy of consideration in connection with the enhancement of biological activity, in view of the toxiphoric nature of the analogous C-N-N linkage. The preparation and characterization of amides of phenylphosphonic acid and phenylphosphonothionic acid was also undertaken because it was felt that these substances might constitute useful starting materials for the preparation of the corresponding hydrazides.

Although the synthesis of new chemical compounds of potential biological value was one objective of this study, exploratory work of this nature is also of theoretical interest since it provides information with respect to the degree of similarity of the C-N and P-N linkages in the carbonic and corresponding phosphoric, phosphonic and phosphinic acid derivatives.

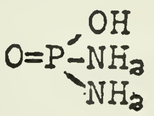
HISTORICAL

The amides of the phosphoric, phosphonic and phosphinic acids, whose formulas are given below, may be looked upon as aquo ammono and ammono derivatives of the parent aquo compounds. An analogous and equally extensive series of thiono compounds, in which the doubly bonded oxygen (oxo) atom is replaced by sulfur, can also be visualized.



Phosphoramidic Acid

(Ia)

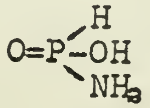


Phosphorodiamidic Acid

(Ib)

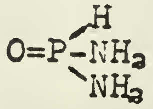
Phosphoric Triamide

(Ic)



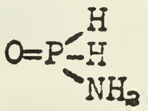
Phosphonamidic Acid

(IIa)



Phosphonic Diamide

(IIb)



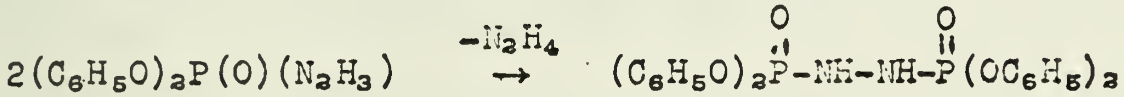
Phosphinic Amide

(III)

The parent substances in the phosphoric acid series have been prepared (2,3,4), but the amides of phosphonic and phosphinic acids represented above are still unknown. Derivatives representative of all but one of these classes have been prepared, however, as have compounds illustrative of many of the thiono analogs.

Replacement of one or more of the $-NH_2$ groups in the ammono compounds cited above by the hydrazide radical leads to another group of compounds for which an equally large number of organic derivatives can be postulated. While significant contributions to the knowledge of organic derivatives containing unsubstituted $-N_2H_3$ groups have been made by Gher, a limited number of such hydrazides have previously been characterized in the form of N-substituted derivatives.

Related to the amides and hydrazides of phosphoric, phosphonic and phosphinic acids and their thiono analogs are a number of compounds which can be regarded as desolvation products of these classes of substances. Ammono derivatives of compounds containing the P-O-P link have in fact been quite well defined, but very little is known about other condensation products. Compounds containing the P-N-N-P linkage have been reported, (1,5,6) however; several such products, together with hypothetical desolvation reactions by which they might form, are illustrated below:

(1) 

$$2(C_6H_5O)_2P(O)(N_2H_3) \xrightarrow{-N_2H_4} (C_6H_5O)_2\overset{O}{\overset{\|}{P}}-NH-NH-\overset{O}{\overset{\|}{P}}(OC_6H_5)_2$$

(2) 

EXPERIMENTAL

A. Phenylphosphonic diamide, $C_6H_5P(O)(NH_2)_2$, was prepared by the reaction of the acid chloride with liquid ammonia. The compound appears to have no basic character and is decomposed in both acidic and basic media with the simultaneous cleavage of the P-N bond.

B. Phenylphosphonothionic diamide, $C_6H_5P(S)(NH_2)_2$, was also prepared by ammonolysis of the acid chloride, using liquid ammonia. The compound melts at 41° C and tends to decompose on standing.

C. Alkyl P-phenylphosphonamidates having the general formula $C_6H_5P(O)(OR)(NH_2)$ can be prepared by partial alcoholysis of phenylphosphonic diamide according to the equation:

$$C_6H_5P(O)(NH_2)_2 + ROH \rightarrow C_6H_5P(O)(OR)(NH_2) + NH_3$$

The ethyl, n-propyl, n-butyl and n-amyl esters were synthesized.

D. Phenylphosphonic dihydrazide, $C_6H_5P(O)(N_2H_3)_2$, was prepared by treating an ether slurry of hydrazine with phenylphosphonic dichloride. This substance behaves as a typical hydrazide since it reacts with carbonyl compounds such as acetone, p-chloroacetophenone and p-methoxybenzaldehyde to yield the corresponding phenylphosphonohydrazones.

E. Phenylphosphonothionic dihydrazide was prepared in good yield by the method of Gher (1); initial indications that this compound could form salts were substantiated by the preparation of the dihydrochloride.

F. Attempts to prepare phenylphosphonic dihydrazide by the hydrazinolysis of phenylphosphonic diamide in alcoholic solution were unsuccessful. It was found, however, that partial hydrazinolysis could be accomplished if the reaction was carried out in n-propanol; under the proper conditions the principal product was phenylphosphonamidic hydrazide, $C_6H_5P(O)(NH_2)(N_2H_3)$, although an appreciable quantity of n-propyl phenylphosphonamidate, was also isolated.

The molecular formula of this unusual hydrazinolysis product was substantiated by molecular weight determination, and by iodate titration to establish the percentage of hydrazine nitrogen in the compound. This "phosphonamidrazide" reacts with acetone and p-methoxybenzaldehyde, thus establishing its character as a hydrazine compound.

The iodate titration method for the determination of hydrazine nitrogen was found to have general application for phosphoric and phosphonic acid derivatives containing the N_2H_3 group; high results are obtained in the titration of thiono compounds, however, presumably because of concomitant oxidation of the phosphorus-sulfur linkage.

BIOLOGICAL TESTS

A variety of biological tests have been initiated to determine the toxiphoric characteristics of various phosphorus-nitrogen compounds prepared in the course of this work. The pharmacological, insecticidal and fungicidal studies are still in progress.

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Thesis Report

STUDIES ON THE SYNTHESIS OF HYDRAZINE

Ervin Colton March 23, 1954

Because of its possibilities as a fuel and because its derivatives have been found useful for numerable purposes, hydrazine has become an important chemical of commerce. Presently, hydrazine is prepared by the Raschig Synthesis[1], which consists in the oxidation of ammonia or urea in alkaline solution in the presence of an inhibitor such as gelatin.

$$NaOCl + NH_3 \rightarrow NH_2Cl + NaOH$$
$$NH_2Cl + NaOH + NH_3 \rightarrow N_2H_4 + NaCl + H_2O$$

One of the major difficulties attending a detailed study of the mechanism of the Raschig Synthesis is that encountered in evaluating the effects due to sodium chloride and sodium hydroxide inevitably present in solutions of sodium hypochlorite. A search was therefore undertaken for an oxidant that could be prepared easily in a concentrated form, free from the impurities usually found in sodium hypochlorite solutions. *t*-Butyl hypochlorite was selected as fulfilling the requirements for such a compound for several reasons: (a) it can be prepared in a high degree of purity; (b) it is stable at room temperature if stored in subdued light; (c) it provides a source for he introduction of high concentrations of the hypochlorite group, nd (d) it was hoped that it would react in a manner similar to odium hypochlorite.

I. The oxidizing agent, t-butyl hypochlorite.

t-Butyl hypochlorite is prepared by the chlorination of -butyl alcohol in strongly basic solution[2].

$$(CH_3)_3COH + Cl_2 + NaOH \rightarrow (CH_3)_3COCl + NaCl + H_2O$$

he product is a yellow liquid which is insoluble in water. Although t has been used previously as a chlorinating agent, this investigation reports for the first time the use of *t*-butyl hypochlorite as N-chlorinating agent toward ammonia and urea.

II. The oxidation of aqueous ammonia with t-butyl hypochlorite[3].

t-Butyl hypochlorite has been shown to react with aqueous monia first to form monochloramine, whose existence was proven ectrophotometrically and by the identification of *p*-chloronzalchlorimine.

$$(CH_3)_3COCl + NH_3 \rightarrow NH_2Cl + (CH_3)_3COH$$

$$p\text{-}ClC_6H_4CHO + NH_2Cl \rightarrow p\text{-}ClC_6H_4CHNCl + H_2O$$

nochloramine then reacts with further quantities of ammonia, as eviously shown, to form hydrazine. The yield of hydrazine from onia and *t*-butyl hypochlorite is dependent upon three factors:

(a) the mole ratio of ammonia to hypochlorite; (b) the presence of a permanent base such as sodium hydroxide, and (c) the use of an inhibitor such as gelatin.

The active intermediate in the Raschig Synthesis is believed to be the chloramide ion, $NHCl^-$.

III. The oxidation of urea with t-butyl hypochlorite[4].

t-Butyl hypochlorite has been shown to react with urea in basic solution to form hydrazine.

$$H_2NCONH_2 + OCl^- + 2OH^- \rightarrow N_2H_4 \cdot H_2O + Cl^- + CO_3^{--}$$

The first product of reaction between urea and t-butyl hypochlorite has been identified as N-chlorourea, $H_2NCONHCl$. The yield of hydrazine from urea is dependent upon the same three factors encountered in the Raschig Synthesis. Larger yields of hydrazine from smaller mole ratios of urea to hypochlorite are obtainable than was the case with ammonia. A typical Hofmann rearrangement is operative in the urea process, the active intermediate being the $[H_2NCONCl]^-$ ion.

IV. The oxidation of liquid ammonia with t-butyl hypochlorite.

Liquid ammonia reacts vigorously with t-butyl hypochlorite irst to form monochloramine, NH_2Cl, which is further ammonolyzed, nder pressure, to form hydrazine. Yields are very small, a maximum f 8% being obtained for a mole ration of ammonia to hypochlorite f 92.

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THESIS REPORT

DERIVATIVES OF HYDRAZINE

Synthesis of N-substituted Hydrazines by Modification of the Raschig Synthesis.

Louis H. Diamond March 23, 1954

Introduction:

The recent commercial availability of hydrazine has lead to an increased interest in the preparation and utilization of a wide variety of hydrazine derivatives. Among such derivatives are the alkyl hydrazines, which have been prepared previously by methods involving the indirect alkylation of hydrazine[1] or the reduction of nitroamines and nitrosoamines[2]. The present investigation was undertaken for two major purposes, (1) to determine if the mechanism of the Raschig synthesis of hydrazine is applicable to systems in which an amine is substituted for ammonia, and (2) to develop a simple method for the preparation of N-substituted hydrazines.

Discussion:

Chloramine, produced by the reaction of equimolar quantities of hypochlorite and ammonia in alkaline solution, was shown by Raschig to be capable of reacting with further quantities of ammonia at elevated temperatures to produce hydrazine[3,4]. It has been postulated that this reaction involves either formation of the $NHCl^-$ ion or the imide molecule, NH, as the active intermediate.[5] The particular reaction leading to the formation of hydrazine from chloramine could involve the imide molecule as an electron deficient structure. If this be the case, one might expect that the reaction with other Lewis bases such as water or amines would lead to the formation of hydroxylamine and the N-substituted hydrazines, respectively.

$$[\ {:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H] + B \rightleftharpoons B \rightarrow [\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H\ ]$$

B= Lewis Base (H_2O, NH_3, RNH_2, R_2NH)

Experimental:

It has been found that chloramine does in fact react with various primary, secondary, and polyamines to produce the corresponding N-substituted hydrazines. Conditions leading to the formation of alkyl hydrazines are similar in many respects to those which apply to the Raschig synthesis. The yield of N-substituted hydrazine has been found to depend upon a) the mole ratio of amine to chloramine, b) addition of an inhibitor, such as gelatin, c) the presence of a permanent base, and d) the temperature. However, significant differences were also observed, a) the molar ratio of amine to chloramine necessary for maximum yields is much smaller than the ammonia to chloramine necessary to obtain maximum yields in the synthesis of hydrazine, and b) the temperature required for the formation of the alkyl hydrazine is considerably lower than that necessary for the formation of hydrazine. In carrying out the reaction of methylamine with chloramine appreciable quantities of methylhydrazine were formed at a temperature of 0°. Yields of methylhydrazine in excess of 60% have been obtained with a 5:1 molar ratio of methylamine to chloramine in the presence of small amounts of gelatin. Methyl hydrazine has been isolated and

quantitatively analyzed as methylhydrazine sulfate. In addition, the method has been extended to the production of a series of N-substituted hydrazines.

TABLE I

Compound	M.P.
$MeNHNH_2.H_2SO_4$	142°
$EtNHNH_2.H_2SO_4$	125
$n\text{-}PrNHNH_2.H_2SO_4$	122
$i\text{-}PrNHNH_2.H_2SO_4$	68
$n\text{-}BuNHNH_2.H_2SO_4$	141
$i\text{-}BuNHNH_2.H_2SO_4$	145
$t\text{-}BuNHNH_2.HCl$	187
Cyclohexyl $NHNH_2.H_2SO_4$	117
$NH_2CH_2CH_2NHNH_2.2H_2C_2O_4$	206

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MECHANISM OF CO-ORDINATION

March 30, 1954 B. Das Sarma

Bjerrum's[1] contribution to the chemistry of co-ordination compounds may be regarded as next in importance to that of Werner. The formation of complexes has been treated on a statistical basis by Bjerrum, involving all the possible intermediate steps in a reversible manner. A very useful survey of this precise and quantitative approach to the mode of formation, nature and stability of chelate compound, the most important type of co-ordination complexes, is presented by Martell and Calvin[2]. It has been observed that much more data are required before a sound theoretical picture of the same can be attained.

The determination of stability of a complex MA_n, where M is the central metal ion and A is the ligand, either uni- or polyfunctional, is defined by the mass action equilibrium constant for the reaction,

$$M + nA \rightleftharpoons MA_n$$

to give

$$K = \frac{[MA_n]}{[M][A]^n} \qquad \text{----------------} \quad ①$$

The equilibrium constant K is related to the individual equilibria involved in the stepwise formation of the co-ordinatively saturated complex MA_n, by

$$K = k_1 \cdot k_2 \cdots k_n \qquad \text{----------------} \quad ②$$

where

$$k_n = \frac{[MA_n]}{[MA_{n-1}][A]} \qquad \text{----------------} \quad ③$$

Bjerrum et al, defines $\bar{n}$ as the average number of donor groups attached to a metal ion,

$$\bar{n} = \frac{\sum_{n=n}^{n=1} n[MA_n]}{[M] + \sum_{n=n}^{n=1} [MA_n]} \qquad \text{----------------} \quad ④$$

From 3 and 4 we derive

$$\bar{n} = \frac{\sum_{n=n}^{n=1} n \cdot k_1 \cdot k_2 - - - k_n[A]^n}{1 + \sum_{n=n}^{n=1} k_1 \cdot k_2 ---- k_n[A]^n} \qquad \text{------------} \quad ⑤$$

Experimentally a method is used whereby the ligand concentration [A] is directly known or can be easily calculated from the data. So $\bar{n}$ may be obtained as

$$\bar{n} = \frac{[C_A] - [A]}{[C_M]}$$

where $[C_A]$ is the total ligand concentration in all state (both free and combined) and $[C_M]$ is the total metal concentration in all forms. Equation (5) then reduces to the solution of n simultaneous equations. k_n is generally obtained by plotting [A] or $-\log[A]$ against $\bar{n}$, and approximating $k_n = \frac{1}{[A]_{\bar{n}=n-\frac{1}{2}}}$

as $[MA_{n-1}]$ and $[MA_n]$ are practically equal at $\bar{n}=n-\frac{1}{2}$. The constants k_n can also be obtained from the nature and slope of this formation curve.

These investigations have generally been carried out as formation reactions [Bjerrum, Calvin, Mellor Schwarzenbach and their co-workers][3], whereas Ray and co-workers[4] have followed such reactions from either direction, for example decomposition of the stable metal biguanidine and amidine complexes in aqueous acid solutions as well as the formation of these same complexes from metal ion and donor molecules.

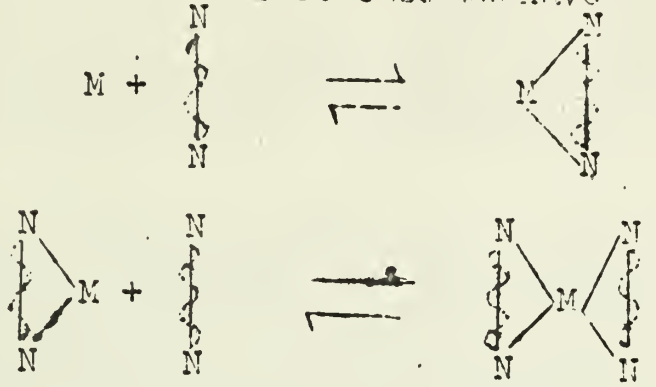
Various methods have been used for the determination of stability of complexes among which the following have been used most successfully:- p_H and potentiometric titrations, methods based on Beer's Law, polarographic measurements, ion exchangers and solubility measurements.

Calvin and Martell have attempted to correlate the stability of the chelate with the size and number of rings formed by chelation, entropy effects, basic strength of the chelating agent, resonance effects, nature of the donor atom and effect of substitution on the ligand. Symmetry in the formation of a chelate also seems to be important.

It was Bjerrum[5] who first pointed out that the association of a metal ion with a ligand actually entails the displacement of water or solvent molecules from the solvated metal ion. More detailed study in mixed solvents will be interesting, especially by varying the proportions in mixed solvents. The correlation of the nature of the metal ions, on the basis of their ionization potentials, number and availability of the 3d electrons, nature, charge and radius of the metal ions, their hydration states etc., and the stability of the chelates formed by them with a particular ligand has been emphasized by Calvin and co-workers.

The bond type of the complexes or chelates formed by them have been studied mainly through magnetic measurements, color, exchange rates with radioactive isotopes. Isolation and stability of optical isomers are taken as evidence for stable covalent bond formation in the complex and some work[6] has been done on the nature of displacement of an optically active ligand in the complex with racemic ones or vice versa.

The mechanism of stepwise formation of a complex presents no difficulty with a simple ion or unidentate molecule. A polydentate ligand, however, presents some more interesting aspects. Let us consider two bidentate ligands with functional N∼∼∼N and N∼∼∼O groups respectively. Where the metal attaches itself to the two nitrogens in the first case we have



This picture may be applicable to symmetrical molecules or at least to those bidentate molecules where the nature of the two nitrogen atoms is the same or very similar. Is it also true when they differ markedly? There is evidence[7] that a polydentate ligand may not be fully utilized. Is it not more natural and logical that in such instances or with the other case where the donor groups are N∼∼∼O, the metal will attach more easily to the nitrogen or oxygen first, depending on the nature of the metal?

There are small number of compounds in the tetra-co-ordinated series where a metal is bonded to only one bidentate ligand or with two different bidentate ones, whereas more is known of compounds of the type $[MA_2B]$, $[MA_2X_2]$, $[ML(A \text{ or } X_2)]$, where M is a hexa-co-ordinated metal ion like Co^{+3} or Cr^{+3} and A and B are bifunctional groups, L a quadridentate one and X is a uni-dentate molecule or ion.

The question is still more pressing with a tri, tetra or hexadentate ligand like O∼∼∼N∼∼∼S∼∼∼S∼∼∼N∼∼∼O


[9]

$$(O)_2N\sim\sim\sim N(O)_2$$

, O∼∼∼N∼∼∼N∼∼∼N∼∼∼N∼∼∼O[10],

N∼∼∼N∼∼∼N∼∼∼N∼∼∼N∼∼∼N[11]. It has been reported by Dwyer[12] that when the resolved K[Cobalt^{III}versinate] is treated with ethylenediamine, there is obtained a pure optical isomer D or L$[Co\ en_3]^{+3}$

This same substance when treated with dl-propylene-diamine[13], permits a 10% resolution of the racemic propylenediamine. These observations point to the fact that polydentate ligands do not dissociate from the metal ion in a single step, otherwise such asymmetric reactions would be impossible to interpret.

It has been reported[14] that the formation or dissociation of complexes with quadridentate ligands may be explained satisfactorily on the basis of a one-step equilibrium.

In the case of decomposition of Co^{+3}, Cr^{+3}, Cu^{+2} and Ni^{+2} complexes of biguanidines, it has been found that the stepwise decompositions with aqueous acids of the first three of these metals

is accompanied by a change of color. This led to the isolation of intermediate compounds, which are more interesting in the case of copper. Beautiful crystalline deep blue complexes with $[\mathrm{Cu}\ \underset{X_2}{\mathrm{Big.}}]$ type were isolated[15] - a direct proof of the stepwise formation theory so far as Cu^{+2} complexes are concerned. Dibiguanidines of Cu^{+2} or biguanidines of Ni^{+2} were found to show no transition of color between those of the normal complexes and that of the hydrated metal ion. No intermediate compounds have been isolated in these cases. The formation of nickel biguanidines may be explained as a continuous one step process, k_1 and k_2 being almost equal in magnitude.

These observations led ultimately to the isolation[15] of heterochelate complexes of copperII with biguanidines and amino acids, where the stability values of the mono-complexes are very similar. These have been found to be definite complexes through their magnetic measurements, absorption spectra and isolation of a number of salts. Their decomposition in aqueous acid media, however, represents a dismutation reaction to the more symmetrical copper bis-biguanidine and bis-amino acid complexes. The attempted resolution was naturally unsuccessful.

Bailar and co-workers[16] have demonstrated that, - when a complex of the type $[MA_2^*B]$ reacts with $2[dl\text{-}C]$ - where M is Co^{+3}, A^* is an active bidentate donor, B is an ordinary bifunctional ligand and C is a racemate of another bidentate molecule, - an asymmetric synthesis of $[MA_2^*C^*]$ and C^* occurs. However, the amount of resolution varies in different cases. Similar reactions have been used with Cu^{+2} and Ni^{+2} d-tartarate and d or l-amino acid complexes with racemic diamines and amino acids. Some resolution of the dl-mixtures (maximum 5%) does occur. Since these complexes are very easy to prepare and the active ligands are very inexpensive these investigations may lead to a useful method of resolution. We are trying to interpret these directive influences in resolution with the stepwise dissociation of the functional groups in a polydentate ligand.

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THE OXIDATION OF FERROUS HYDROXIDE

April 6, 1954

R. J. Moolenaar

Ferrous hydroxide is a white solid which turns green in the presence of a trace of air. The green substance has been shown to contain both iron II and iron III. Upon standing in contact with air for about a week the green solid becomes still darker and finally reaches the composition of gamma ferric oxide. This green intermediate substance has also been prepared by addition of sodium hydroxide to a solution containing small amounts of ferric ion in ferrous sulfate solution. If oxidation takes place rapidly the green intermediate compound is not observed.

Conflicting statements have appeared in the literature concerning the reaction products of the oxidation of iron II in basic and neutral solution. A series of experiments have been carried out recently by Mayne and co-workers[6] in an attempt to clarify the matter. It was found that the film deposited on the iron metal surface which is responsible for the passivity of iron in alkaline solution is mainly a substance with the crystalline structure of gamma ferric oxide or magnetite.

The oxidation of ferrous hydroxide is pH dependent.

1. When $Fe(OH)_2$ is oxidized in a pH range of 4-5 gamma Fe_2O_3 is formed irrespective of the rate at which the oxidation is carried out.

2. When $Fe(OH)_2$ is oxidized in more alkaline solution alpha Fe_2O_3 is obtained if the oxidation is rapid; a material having a composition intermediate between Fe_3O_4 and gamma Fe_2O_3 forms if the oxidation is slow.

Clearly, gamma Fe_2O_3, which is the major constituent of the oxide coating produced on iron when immersed in water or alkaline medium, could be formed by the oxidation of ferrous hydroxide. These results may now be applied to the inhibition of the corrosion of iron by alkaline solution.

When a thoroughly cleaned iron strip is placed in 0.1N NaOH, the rate of attack is dependent on the oxygen content of the solution. This relationship becomes apparent from the data depicted graphically in Figure 1 in which the potential of the Fe-$Fe(OH)_2$ couple is plotted as a function of time.

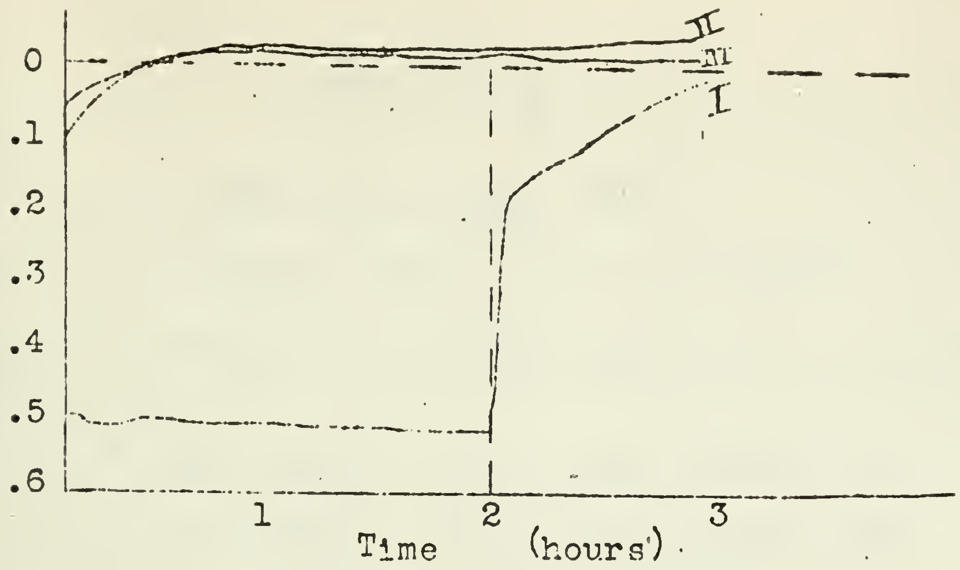

Figure 1. Potential of the Fe-Fe$(OH)_2$ couple.
I. De-areated 0.1N NaOH. Air admitted after 2 hours.
II. 0.1N NaOH in contact with air.
III. De-areated solution containing 0.1M K_2CrO_4 (Air admitted after 2 hours).

Iron is attacked very slowly by de-areated 0.1N NaOH. Since the curve is flat it appears that the electro-chemical attack is mainly under cathodic control and is governed by the slow cathodic discharge of hydrogen ions rather than anodic polarization by $Fe(OH)_2$. When air is admitted the potential rapidly approaches zero to hydrogen. If air or another oxidizing agent is present in the solution the iron becomes passive almost immediately.

Inhibition of corrosion of iron by dissolved oxygen is probably due to three different reactions:

1. Direct reaction of dissolved oxygen with surface iron atoms.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

2. Cathodic reduction of oxygen during electrochemical attack.

$$\begin{array}{ll} \text{cathode:} & 4e^- + O_2 + 2H_2O \rightarrow 4OH^- \\ \text{anode:} & Fe + 2OH^- \rightarrow \underline{Fe(OH)_2} + 2e^- \end{array}$$

3. Oxidation of intermediate products formed by electrochemical attack on Fe.

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O$$

Since the air formed film is quickly strengthened by immersion n sodium hydroxide solution, it is believed that ferrous hydroxide is much more easily oxidized by oxygen to Fe_2O_3 than is free iron. t is concluded, therefore, that the formation of Fe_2O_3 in alkaline solution in the presence of air is mainly a combination of the reactions represented by 2 and 3 above.

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MECHANISM AND STEREOCHEMISTRY OF OCTAHEDRAL SUBSTITUTIONS

April 13, 1954

Robert L. Rau

I Introduction:

More than 40 years ago Werner investigated the stereochemistry of octahedral substitutions; he was mainly concerned with the following type of reaction:

$$Y^- + MR_4AX \rightarrow MR_4AY + X^-$$

He showed that some substitutions involve cis-trans changes while others preserve the original configuration.[1]

Werner suggested that solubility is the factor that determines whether a change in configuration takes place, whereas Jaeger has postulated crystalline structure as being the configuration determining factor; neither of these theories have proven satisfactory.

Werner has observed the following:

$$l\text{-}[Coen_2Cl_2]^+ \xrightarrow{K_2CO_3} d\text{-}[Coen_2CO_3] + 2KCl$$

Using Ag_2CO_3 instead of K_2CO_3 Bailar and his co-workers obtained different results depending on how long the solution of the complex was allowed to stand prior to the addition of Ag_2CO_3.[2]

$$l\text{-}[Coen_2Cl_2]^+ \xrightarrow{Ag_2CO_3} l\text{-}[Coen_2CO_3]^+ + 2AgCl$$

$$l\text{-}[Coen_2Cl_2]^+ \xrightarrow[\text{standing}]{H_2O} [Coen_2Cl(H_2O)]^{++} \xrightarrow{Ag_2CO_3} d\text{-}[Coen_2CO_3]^+$$

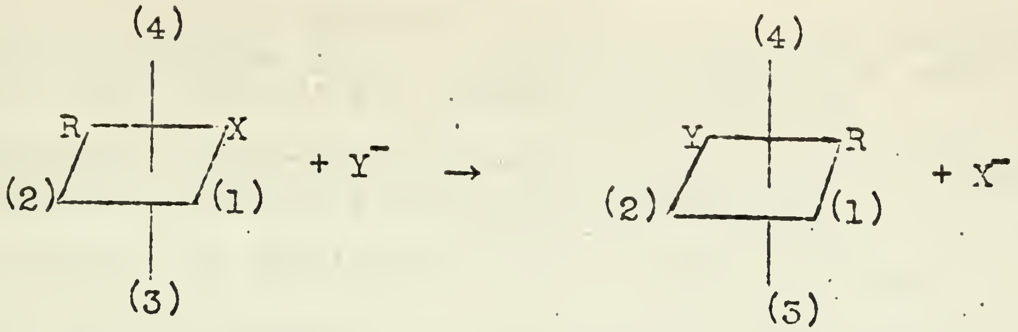
That aquation plays an important part in this process is shown y the fact that the longer the solution of the complex is allowed o stand before the addition of Ag_2CO_3 the more dextrorotary is the roduct.

Mathieu has shown that when $l\text{-}[Coen_2Cl_2]^+$ aquates it gives the - and l- forms of $[Coen_2Cl(H_2O)]^{++}$ with the d isomer in greater uantities.[3]

Bailar et al have described this change in configuration as an xample of a Walden Inversion in inorganic chemistry.

I Edge-Displacement as a Unifying Hypothesis

Brown, Ingold and Nyholm have attempted to explain these arlier observations on the basis of what is termed an edge-displac nt mechanism[4]. Their hypothesis may be briefly stated as follows:



The authors describe this change as not being dependent upon the groups Y, R and X, but on the position of some unaffected group A whose relation to the replaced and replacing groups X and Y is denoted by the prefixes d and l or cis and trans.

The above illustion is given for the general reaction

$$Y^- + MR_4AX \rightarrow MR_4AY + X^-$$

If A is in position (1) the above process may be described as cis → trans. If A is in position (2) the reaction may be described as trans → cis, and if A is in position (3) or (4) the reaction may be described as d → l or l → d.

Although any observed stereo change can be understood as an edge-displacement an observed absence of stereo change in octahedral substitution does not always imply the absence of edge displacement. If, however, the groups in positions 1 and 2, and likewise those in positions 3 and 4 can be superimposed one on the other by a rotation of the molecule, then a cis starting material will yield a cis product. Where a trans starting material yields a trans product it is implied that substitution takes place without edge displacement. Werner has observed several trans → trans substitutions, therefore it is assumed that octahedral substitution can occur with or without edge displacement.

III Kinetics of Octahedral Substitutions[5]

The kinetics of substitution of the anions OCH_3^-, N_3^-, NO_2^-, NCS^-, Br^-, Cl^- and NO_3^- in their displacement of a chloride ion from the cis-dichlorobisethylene diamine cobalt(III) ion has been studied in methyl alcohol as a solvent. The methods of study have been polarimetric, spectroscopic, chemical and radiochemical.

In general the results obtained from these kinetic studies have been as follows: If we arrange the seven anions previously mentioned in order of decreasing coordinating power (OCH_3, N_3^-, NO_2^-, NCS^-, Br^-, Cl^-, NO_3^-) then on passing through the series the reaction remains second order with strongly absolutely diminishing rates (reaction rates of OCH_3^-: N_3: NO_2^- are in the proportion of 30,000:100:1). Starting with the NCS^- ion we enter a transition zone and beyond this a point is reached where the reaction becomes first order, with the reaction rates remaining constant thereafter.

IV Steric Course of Some Unimolecular Substitutions[6]

The mechanism postulated for the unimolecular process involves a rate determining step which consists of the removal of one of the

ttached chlorine atoms; thereby leaving an optically inactive uincuicovalent cobaltium ion. The substituting anion comes in at he final and rapid step of the unimolecular process.

This mechanism presents a stereochemical problem, mainly, where oes the substituting anion enter the cobaltium ion.

A. Steric Course of Substitution by the Chloride Ion.

It was experimentally determined that the dissolved complex maintains the same composition from the beginning of the change to the end. A color change from violet (cis) to the green (trans) has led to the conclusion that the dissolved complex undergoes a stereochemical isomerization apart from its loss of optical activity.

Two things follow from these observations:

1. Thermodynamically, the trans cation is much more stable than the cis cation.

2. Kinetically, while many routes of reversible change may be available to the cis cation, at least one leads to the trans isomer which is the primary product.

The equality of rate between Cl^- exchange and loss of optical activity is consistent with only two routes of molecular change. Either of these might be followed, or both may take place concurrently. The possibilities are as follows:

a. Every l- cis cation which suffers a loss of optical activity directly yields the trans cation.

b. Of any large number of original l- cis cations suffering a loss of optical activity 50% reform the l- cis cation while the other 50% form d- cis cations.

Since we have determined that the trans isomer is the primary product formed as a result of substitution we are forced to the conclusion that process "a" is involved.

The question still to be answered is in what proportion does process "b" accompany process "a". This can be determined by comparing the rate of production of the trans isomer with the loss of optical activity of the original cis isomer.

Evidence has been obtained which indicates that the rate of formation of the trans isomer is not as great as the loss in optical activity of the cis isomer. It is concluded that the rate of change from cis → trans is only 82±2% of the loss in optical activity of the cis form.

In view of the various reactions which have been indicated as possibilities it is concluded that of 100 original l- cis cations once substituted at 35.8°C

82 produce the trans cation
9 give the new l- cis cation
9 give the original d- cis cation

As the temperature increases the per cent conversion to the trans form also increases.

The competing reactions may be pictured as follows:

$$\begin{tikzcd}[column sep=large]
 & & \text{trans- cation} \\
\text{l- cis cation} \arrow[r, "(1)", "\text{slow}"'] & \left\{\begin{matrix}\text{Cobaltium ion}\\ + \\ \text{Chloride ion}\end{matrix}\right\} \arrow[ur, "(2)", "\text{fast}"'] \arrow[dr, "(3)", "\text{slow}"'] & \\
 & & \text{(d+l) cis- cation}
\end{tikzcd}$$

Calculation of the activation energies for the alternative final steps (2) and (3) shows, in a qualitative manner, that E_2 is greater than E_3, thus indicating that a larger energy barrier resists the entry of the Chloride ion into the cobaltium ion to form the trans rather than the cis dichloro cation.

B. Stereochemical Picture of the Course of Unimolecular Substitution of the Chloride Ion.

Two possible pictures can be given for the process previously described which differ with respect to the geometry of the quinquecovalent cobaltium ion.

From the data available, Brown and Nyholm believe that a triangular bipyramid is the most logical structure of the cobaltium ion. This structure requires the least rearrangement to form the cis product and the greatest rearrangement to form the trans product. Such a picture is consistent with the observation that E_2 is greater than E_3.

VI Conclusion.

The mechanism here presented has support from anology. It was shown in 1935, for nucleophylic substitution on a carbon atom, that if the substituting agents were arranged in order of decreasing nucleophylic power with respect to their substitutions on the same alkyl compound, then on passage through the series the reaction remains second order with absolutely diminishing rates until a point is reached where the reaction becomes first order with a constant reaction rate. The present study of nucleophylic substitutions of octahedral complexes has revealed a similar pattern of results.

If we may be permitted to follow this anology a little further, it logically follows that this duplexity of mechanism will undoubtedly have a notable part to play in the future study of inorganic substitutions, just as it has been basic to the growth of our knowledge of organic substitutions.

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DICHLORYL TRISULFATE[1]
$(ClO_2)_2S_3O_{10}$

April 13, 1954 Elsie Gulyas

Introduction: In general, reactions of salts of mineral oxygen acids with sulfur trioxide proceed with the liberation from the salt of the corresponding acid anhydride and the formation of a higher sulfate as in the reaction:

$$K_2CO_3 + nSO_3 \rightarrow CO_2 + K_2(S_nO_{3n+1})^2.$$

The anhydride formed may then react with excess sulfur trioxide as, for example:

$$N_2O_5 + nSO_3 \rightarrow (NO_2)_2(S_nO_{3n+1})^3.$$

The latter type of reaction is possible only when the affinity of sulfur trioxide for oxygen is greater than is that of the reacted anhydride. Recent attempts, for example, to prepare selenyl(V) polysulfate, $(SeO_2)(S_nO_{3n+1})$ were unsuccessful.

In the work reported here, Lehmann and Krüger studied the reaction of potassium salts of chlorine oxyacids with sulfur trioxide from this point of view.

The Reaction of $KClO_4$ with SO_3: The reaction of dry $KClO_4$ with SO_2-free SO_3 at 25°-30°C proceeds according to the equation:

$$2KClO_4 + nSO_3 \rightarrow K_2(S_nO_{3n+1}) + Cl_2O_7.$$

From 75.2 mg. $KClO_4$, 91.5 mg. $K_2S_3O_{10}$ (calculated yield 90.8 mg.) was obtained.

The Reaction of $KClO_3$ with SO_3: The reaction of $KClO_3$ with SO_3 takes place with evolution of heat. With excess SO_3 two liquid phases are obtained; the lower layer is dark red in color while the upper SO_3 layer remains practically colorless provided that care is taken to keep the mixture cool and to distill off the SO_3 slowly. If these precautions are not observed the upper layer also becomes colored due, presumably, to the disproportionation of the chlorine(V) oxide which is formed initially. The reactions are:

$$2KClO_3 + nSO_3 \rightarrow K_2(S_nO_{3n+1}) + Cl_2O_5^{*}$$

$$Cl_2O_5 + 3SO_3 \rightarrow Cl_2O_5 \cdot 3SO_3$$

$$2Cl_2O_5 \rightarrow Cl_2O_6 + 2ClO_2.$$

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* This hypothetical intermediate has not yet been prepared presumably because of its ready dissociation into ClO_3 and ClO_2.

Under mild reaction conditions the latter reaction is largely suppressed.

The dark red, viscous layer of the composition $Cl_2O_5 \cdot nSO_3$, after removal of excess SO_3, solidifies to well-formed, red needles having the composition $Cl_2O_5 \cdot 3SO_3$. The net reaction is given by the equation:

$$2KClO_3 + 6SO_3 \rightarrow K_2S_3O_{10} + Cl_2O_5 \cdot 3SO_3.$$

Properties of the Compound $Cl_2O_5 \cdot 3SO_3$: Pure $Cl_2O_5 \cdot 3SO_3$ may be obtained by high vacuum distillation. It melts without decomposition at 75.5° after first becoming amorphous at 73.5° and solidifies with slight undercooling between 65° and 68° to large, well-formed red, needle-like crystals. On cooling at liquid air temperature the substance becomes light yellow. The melting point is markedly pressure dependent; excess SO_3 likewise has a pronounced effect on the melting point.

The substance begins to decompose into Cl_2, O_2, and SO_3 between 85° and 90°; at 100° the decomposition is vigorous.

The Structure of $Cl_2O_5 \cdot 3SO_3$: The insolubility of $Cl_2O_5 \cdot 3SO_3$ in sulfur trioxide is taken as evidence that it is not an addition compound or homopolar compound. The formal analogy between $Cl_2O_5 \cdot 3SO_3$ and $N_2O_5 \cdot 3SO_3$ which is formulated as nitronium trisulfate $(NO_2^+)_2(S_3O_{10}^{=})$* permits the postulation that the former compound may likewise be regarded as ionic at least to a high degree.

The relatively high melting point, the ease of crystallization, and the fading of color on cooling to low temperatures are taken as additional evidence for the ionic constitution of the compound.

The intense color of the compound at room temperature is, on the other hand, contrary evidence which is, however, offset by the fact that the compound melts without decomposition.

From the evidence cited, the authors formulate the compound as $(ClO_2)_2S_3O_{10}$, dichloryl trisulfate in which the cation is the chloryl ion, ClO_2^+.

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* The structure of nitronium trisulfate has not been specifically determined; the formulation is by analogy with the known struc of the disulfate and from knowledge concerning polysulfuric acids.

THESIS REPORT

Stabilization of Valence Through Coordination

Robert L. Rebertus April 27, 1954

For the more labile complexes a convenient criterion of stability is stability toward oxidation or reduction. The redox potential is then a quantitative measure of the degree of stability. Many labile complexes exhibit reversible electrode behavior, and potential values may be obtained directly. Where irreversible electrode processes occur, it is often possible to determine stability constants by other means; these, in turn, may be related to redox potentials.

I. The Stabilities of Some Complexes of α-Amino Acids With Divalent Metals.

In this part of the investigation, the stabilities of the complexes of glutamic acid, ornithine, norvaline, and valine with copper, nickel, zinc, cobalt, and cadmium ions have been determined by polarographic, pH titrimetric, and spectrophotometric techniques.

Coordination Positions. --- Although all the amino acids used have 5-carbon chains, striking differences in stability constants are observed; the reason for these differences must be assigned to the nature or lack of the ω-functional group.

The anions of norvaline or valine are bidentate toward divalent metal ions with practically no charge associated with the ω-carbon atom. Ornithinate chelates similarly since the ω-amino group remains protonated under the experimental conditions used here. The acid dissociation constant of this group is $10^{-10.7}$, and most data were obtained at pH<8. The preparation of bis-(ornithinato hydrochloride) copper(II) also confirms this contention. Thus a positive charge is associated with the ω-functional group of the coordinated ornithinate ligand, and, therefore, under our experimental conditions ornithinate may only act as a bidentate ligand.

The ω-carboxyl group of glutamic acid is relatively strongly acidic, and, in the case of these more labile complexes, chelation may take place only after this carboxyl group has been neutralized. At lower pH values, the M(II)-α-NH_2 bond is broken, and the complex is decomposed. Thus, a negative charge is associated with the ω-functional group. It is possible that this carboxylate may coordinate to form a seven-membered ring. The glutamate anion, therefore, may be bidentate or tridentate, and the stability constant data provide a means to resolve this problem.

Stability Constant Data. --- A summary of the stability constant data is given in Table 1. The values obtained by the methods of pH titrimetry and polarography show good agreement, the error being ±0.15 log K units. Since the precision of either of these methods was found to be ± 0.03 log K units, it is possible that the slightly higher log K values obtained by pH titrimetry are the result of the lower value of ionic strength, 0.02, as compared with the value, 1.00

used throughout the polarographic determinations.

The spectrophotometric technique was found to be greatly inferior to the other two methods in the case of the glutamate- and ornithinate-copper(II) systems. Exact values of extinction coefficients of the intermediate complex species could not be obtained due to the presence of three mutually-dependent colored species, the spectra of which overlap. The value of log K_2 for bis-(ornithinato hydrochloride) copper(II) was found to be 4.57 by this method, whereas a value of 5.55 was obtained by the method of pH titrimetry.

The order of decreasing stability is Cu, Ni, Zn, Co, and Cd for each series of complexes. This is also the order of decreasing value of the second ionization potential of the metal. It was first observed by Calvin and Melchior[1] that a plot of second ionization potential of the metal against stability constant yields a straight line, and, indeed, this was found to be true. Qualitatively, this correlation arises from the fact that the energy required to lose the two electrons is regained when a coordinate covalent bond is formed.

Correlation of Stability Constants With the Structures of the Complexes. --- The mono-(glutamato) complexes of cadmium(II), cobalt(II), zinc(II), and nickel(II) are more stable than the corresponding mono-(norvalinato), mono-(valinato), or mono-(ornithinato hydrochloride) complexes. Mono-(glutamato) nickel(II) is paramagnetic, non-conducting, and relatively insoluble. Mono-(glutamato) cadmium(II) adds one bromide ion and does not undergo ion-pair formation with tri-positive, non-complexing ions. It is concluded, therefore, that these complexes have the tetrahedral configuration in which three coordination positions are occupied by the glutamate ligand.

Stackelberg[2] has confirmed the planar configuration for a number of copper chelates by means of x-ray crystal analysis, and the mono-(sodium glutamato) copper(II) ion is probably also planar. Consideration of visible and ultraviolet absorption spectra indicates that the chromophor in this complex is the same as that in bis-(glycinato) copper(II). Molecular models indicate that the glutamate ligand cannot be tridentate in a planar structure. The norvalinato complex of copper(II) is more stable than either mono-(sodium glutamato) or mono-(ornithinato hydrochloride) copper(II) . Thus, the result of either a (-) or a (+) charge on the uncoordinated functional group tends to lower the stability of these copper chelates.

The fact that the ornithinato complexes have proven the least stable in every instance suggests that the electrostatic effect exerted by the $-NH_3^+$ group may be effective. This is in accord with the reasoning of Tanford and Shore[3], who observed a difference of 0.98 log K units between log K_1 of the arginine complex of cobalt(II) and the corresponding alanine complex. They maintain that, if the guanidine group were uncharged, the value of log K_1 would be the same for each complex, and the difference observed is attributed to the (+) charge on the guanidine group. We have found that log K_1 for mono-(ornithinato hydrochloride) cobalt(II) has the value 4.08 and that log K_1 for mono-(norvalinato) cobalt(II) has the value 5.06

—a difference of 1.04 log K units.

The decrease in stability caused by the uncoordinated carboxylate group in the copper complex may be the result of a distortion of normal configuration. In other words, the carboxylate group may compete with the chelate part of the glutamate without actually forming a seven-membered ring.

A comparison of log K_2 values (Table 1) shows that it is more difficult to add the second ornithinate group or the second glutamate group than to add the second norvalinate. In the case of ornithinate this may again arise from an electrostatic effect. In the case of the glutamato complexes, however, when the second ligand coordinates, the mono-(glutamato) cobalt(II), nickel(II), zinc(II), or cadmium(II) complex must change to the octahedral configuration or the incoming ligand must replace water in addition to the ω-carboxylate in the tetrahedral configuration.. The second norvalinate group must only replace two molecules of water.

Table 1

Formation Constants of the Glutamato, Norvalinato, and Ornithinato Complexes With Some Divalent Metals.

M^{++}	Method*	Values of pK_1 and pK_2 for the various ligands**					
		Glutamate		Norvalinate		Ornithinate	
		log K_1	log K_2	log K_1	log K_2	log K_2	log K_2
Cd^{++}	1	4.78	2.78	4.29	3.20	3.70	2.70
	2	4.72	2.72	4.58	2.66	3.41	2.41
	3	(colorless)		(colorless, insol.)		(colorless)	
Co^{++}	1	5.06	3.40	4.80	3.58	4.02	2.90
	2	(irreversible)		(irreversible)		(irreversible)	
Zn^{++}	1	5.45	4.01	5.09	4.10	4.10	3.20
	3	(colorless)		(colorless, insol.)		(colorless)	
Ni^{++}	1	5.90	4.44	5.68	4.42	4.85	3.86
	2	(irreversible)		(irreversible)		(irreversible)	
Cu^{++}	1	7.85	6.55	8.68	7.10	6.90	5.55
	2	(14.80 log K_1K_2)		----	----	----	----
	3	----	4.24	(insoluble)		----	4.57

* Methods: 1, pH titrimetry; 2, polarography; 3, spectrophotometry.
** Values for norvalinates and valinates are identical.

II. A Polarographic Study of the Complexes of Hydrazine With Zinc and Cadmium.

Formation Constants of Zinc-Hydrazine Species. --- The polarographic behavior of zinc ion in hydrazine media at various pH values has been investigated[4]. The reduction processes are diffusion controlled and reversible. At pH 9 or below the half-wave potentials are dependent only on hydrazine concentration. The aquated zinc

ion reacts with hydrazine to form the complex species, $[Zn(N_2H_4)(H_2O)_3]^{++}$, $[Zn(N_2H_4)_2(H_2O)_2]^{++}$, $[Zn(N_2H_4)_3(H_2O)]^{++}$, and $[Zn(N_2H_4)_4]^{++}$. The overall formation constants are 2.5×10^3, 5.0×10^3, 6.0×10^3, and 7.5×10^3 respectively. Above pH 9 the half-wave potentials are dependent upon both pH and hydrazine concentration, and zinc hydroxide is in equilibrium with soluble hydroxy-hydrazine complexes.

Formation Constants of Cadmium-Hydrazine Species. --- The reduction of cadmium ion in hydrazine media is reversible, and the half-wave potentials are dependent only upon the concentration of free hydrazine. The species, $[Cd(N_2H_4)(H_2O)_3]^{++}$, $[Cd(N_2H_4)_2(H_2O)_2]^{++}$, $[Cd(N_2H_4)_3(H_2O)]^{++}$, and $[Cd(N_2H_4)_4]^{++}$, are formed successively in solution, and the overall formation constants are 1.78×10^2, 2.50×10^2, 6.00×10^2, and 7.83×10^3, respectively. At low hydrazine concentrations, cadmium hydroxide is in equilibrium with hydrazine cadmium complexes.

Discussion. --- Both the zinc-hydrazine and cadmium-hydrazine complexes are less stable than the corresponding ammonia complexes. It is surmised that the coordination of the hydrazine molecule is monodentate. The isolation of the many complexes of zinc and cadmium containing only two molecules of hydrazine is facilitated by the low solubility of these compounds, whereas the complexes containing three and four molecules of hydrazine are highly soluble.

The existence of hydroxy-hydrazine complexes with zinc ion is probably a manifestation of the tendency for this ion to be amphoteric. Cadmium ion, on the other hand, is very weakly amphoteric, and no evidence for hydroxy-hydrazine cadmium complexes was found.

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SOLVOLYTIC BEHAVIOR IN LIQUID SULFUR DIOXIDE

April 27, 1954 E. C. Gohrbandt

I. Introduction

The properties of liquid sulfur dioxide as a solvent were first recognized by Walden[8] at the beginning of the 20th century. The solubilities, conductances, and reactions of inorganic and organic compounds in this solvent have been studied during recent years principally by Jander and his coworkers.[2-7]

Jander and Wickert[7] developed the sulfito system of compounds based upon the presumed autoionization of the solvent in a manner analogous to that of water and liquid ammonia.

$$\begin{array}{l} 2H_2O = H_3O^+ + OH^- \\ 2NH_3 = NH_4^+ + NH_2^- \\ 2SO_2 = SO^{++} + SO_3^{=} \end{array}$$

On the basis of this "sulfito" system, sources of thionyl ions can be regarded as acid analogs, whereas sources of sulfite ions can be regarded as base analogs in liquid sulfur dioxide.

"When the dissolved solute reacts with the solvent in such a way that the normal anion and cation concentrations of the solvent are changed, the solvent is said to have undergone solvolysis[1]".

The extent of solvolysis must be determined by analyses of reaction products; dissociation constants in liquid sulfur dioxide are not known, and the ionic concentrations of the ions present have not been measured.

On the basis of thermodynamic data it is possible to predict whether a solvolylic reaction will take place[3]. Solvolysis will occur if the heat of formation for the net reaction is negative.

$$\begin{array}{ll} P(s) + 1/2\ O_2\ (g) + 3/2\ Cl_2(g) - POCl_3(l) & -146.78\ \text{Kcal.} \\ P\ Cl_5\ (s) = P(s) + 5/2\ Cl_2(g) & +104.5\ \text{"} \\ SO_2\ (l) = S(s)_{rh} + O_2\ (g) & +76.86\ \text{"} \\ S(s)_{rh} + 1/2\ O_2(g) + Cl_2(g) = SOCl_2\ (l) & -42.7\ \text{"} \\ \hline PCl_5(s) + SO_2(l) = POCl_3\ (l) + SOCl_2\ (s) & -6.12\ \text{"} \end{array}$$

Sulfur tetra chloride does not react with liquid sulfur dioxide.

$$\begin{array}{ll} SCl_4\ (l) = S(s) + 2Cl_2(g) & +13.7\ \text{Kcal.} \\ SO_2(l) = S(s) + O_2(g) & +76.86\ \text{"} \\ 2\ Cl_2 + 2S(s) + O_2(g) = 2SOCl_2\ (l) & -85.4\ \text{"} \\ \hline S\ Cl_4\ (l) + SO_2(l) = 2SOCl_2\ (l) & +5.16\ \text{"} \end{array}$$

The extent of solvolysis also depends upon

1. The conditions under which the reaction is carried out.

2. The solubility of the halide in sulfur dioxide.
3. The stability toward decomposition of the reaction products[6].
4. The metallic character of the element with which the halide is combined.

II. Solvolytic Reactions of the Alkali Metal Halides[2].

The alkali metal iodides solvolyze readily, because

1. they are very soluble in liquid sulfur dioxide
2. the reaction product, thionyl iodide, decomposes readily.

The reactivity of the bromides is less, that of the chlorides hardly perceptible. The acetates are solvolyzed slowly even at -50°C.

Potassium iodide undergoes complete solvolysis according to the following reactions:

$$\begin{array}{l} 8\ KI + 8\ SO_2 \rightleftarrows 4\ K_2SO_3 + 4\ SOI_2 \\ 4\ SOI_2 \rightleftharpoons 2\ S + 4I_2 + 2\ SO_2 \\ \underline{4\ K_2SO_3 + 2I_2 \rightleftarrows 2\ K_2SO_4 + 4\ KI + 2SO_2} \\ 4\ KI + 4SO_2 \rightleftarrows 2\ K_2SO_4 + 2S + 2I_2 \end{array}$$

The reactions of potassium bromide and potassium chloride with sulfur dioxide are similar, except for the fact that the resulting sulfur dihalide does not decompose.

III. Solvolytic Reactions of the Halides of Groups III, IV, V, VI[2,3]

In spite of the fact that the solubilities of the halides in these groups are in reverse order from those of the alkali metal halides (i.e., $Cl^- > Br^- > I$); the bromides and chlorides do not react. The chlorides and bromides exhibit a tendency toward solvate formation; the iodides solvolyze readily due to the decomposition of the thionyliodide. In general, solvolysis of the compound decreases with an increase in the metallic character of the element combined with the halide.

Solvolytic Reactions of the Halides of Groups III, IV, V, VI.

Group III

Compounds Investigated	Experimental Conditions	Type of Reaction	Reaction Product
BCl_3	stand for 10 yrs.	solvolysis	B_2O_3, $SOCl_2$
BBr_3	-70°C	solvolysis	$B2O_3$; $SOBr_2$
BI_3	70-80°C	solvolysis	B_2O_3, I_2, S
$AlCl_3$	(presence of ($[(CH_3)_4N]_2SO_3$?.(70-80°	solvolysis solvation	$(Al_2(SO_3)_3$ $(AlCl_3)_2 \cdot SO_2$ $(AlCl_3)_2 \cdot 2SO_2$
$AlBr_3$	-	solvation	$AlBr_3 \cdot 2SO_2$
AlI_3	70-80°C	solvolysis	$Al_2(SO_3)_3$; I_2, S

Group IV

Compounds Investigated	Experimental Conditions	Type of Reaction	Reaction Products
CCl_4, $SiCl_4$	70-80°C	no reaction	-
$ZrCl_4$, $SnCl_4$, $TiCl_4$	70-80°C	solvation	($ZrCl_4\cdot 1/2SO_2$ ($SnCl_4\cdot 1/2SO_2$, ($TiCl_4\cdot 1/2SO_2$
CI_4	25°C	solvolysis	CO, I_2, S
$COCl_2$	200-400°C	solvolysis	CO_2, SCl_4
ZrI_4	70-80°C	solvolysis	$Zr(SO_3)_2$, I_2, S

Group V

Compounds Investigated	Experimental Conditions	Type of Reaction	Reaction Products
VCl_4, $TaCl_5$, $TaBr_5$, $SbCl_5$, $SbCl_3$, $AsBr_3$	70-80°C	no reaction	
PCl_5	-50°C-80°C	solvolysis	$POCl_3$, $SOCl_2$
$NbBr_5$	60-70°C	solvolysis	$NbOBr_3$, $SOBr_2$

Group VI

Compounds Investigated	Experimental Conditions	Type of Reaction	Reaction Products
SCl_2, SCl_4, $MoCl_5$	-	no reaction	
WCl_6	60°C	solvolysis	$WOCl_4$, $SOCl_2$
WBr_6	60°C	solvolysis	WO_2Br_2, $SOBr_2$
UCl_5	80-90°C	solvolysis	UO_2Cl_2, $SOCl_2$

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Dithiocyanogen

G. W. Bailey May 4, 1954

Introduction

There are numerous inorganic radicals which in the free state have properties similar to the halogens. As anions they resemble the halide ions. These substances have been called halogenoids and pseudo-halogens. Walden and Audrieth (1) have defined the term halogenoid: "to designate any univalent chemical aggregate composed of two or more electronegative atoms, which shows in the free state certain characteristics of the halogens, and which combines with hydrogen to form an acid, and with silver to form a salt insoluble in water." The halogen and halogenoid ions have been arranged in the following order of activity: F^-, ONC^-, OCN^-, Cl^-, N_3^-, Br^-, CN^-, SCN^-, $SCSN_3^-$, I^-, $SeCN^-$, $TeCN^-$. A summary of similarities among the halogens and halogenoids has also been presented by Walden and Audrieth.

Various methods of preparation of dithiocyanogen, often called thiocyanogen, have been described in the literature. All methods for the preparation of thiocyanogen solutions make use of anhydrous solvents (2) because moisture causes rapid hydrolysis and subsequent decomposition. Söderbäck (3) first prepared thiocyanogen by the action of iodine on an ethereal suspension of silver thiocyanate. Thiocyanogen is also obtained by the oxidation of a hydrogen thiocyanate solution in ether with manganese dioxide (4), and by electrolyses of thiocyanate solutions in alcohol (5). The method described in "Inorganic Syntheses" involves the displacement of thiocyanogen by bromine from the lead salt in an acetic acid-acetic anhydride solution (2).

A new method (6) leads to the preparation of pure solid thiocyanogen by a double decomposition reaction between potassium thiocyanate and nitrosyl chloride in liquid sulfur dioxide. Nitrosyl thiocyanate first forms and then decomposes into nitric oxide and thiocyanogen.

Experimental

The starting materials for this synthesis include chlorine- and nitric oxide-free nitrosyl chloride, water free potassium thiocyanate, and liquid sulfur dioxide which has been dried over phosphorus pentoxide. The reactions are carried out in the special apparatus in which contact with the atmosphere is avoided. The KSCN is placed in the lower bulb of the reaction vessel; enough SO_2 is then condensed on the solid to more than cover it. The suspension is solidified in a liquid air bath; nitrosyl chloride is then introduced and finally an additional quantity of sulfur dioxide. The reaction proceeds as the solid mass is allowed to melt; the temperature being held at about -30° C. After one hour the deep red suspension is cooled to -50° C. The solvent is removed by evaporation by immersing the condensation vessel which originally contained the solvent in liquid air. The NOSCN decomposes at the same time with the evolution of nitric oxide. After the red color has almost completely disappeared, the originally used solvent is condensed again into the reaction vessel and the solution thus formed is filtered. By again

removing solvent by evaporation completely colorless $(SCN)_2$ is obtained in practically 100 percent yield. The precipitated KCl remains behind on the ground glass plug between the two vessels. The reactions in the order of occurence are:

$$(1)\ NCCl + KSCN \longrightarrow NOSCN + KCl$$

$$(2)\ 2NOSCN \longrightarrow 2NO + (SCN)_2$$

The melting point of thiocyanogen prepared in this manner was found to lie between 15 and 16° C. as compared with -2 to -3°, a previously recorded determination by Söderbäck (3). An analysis of the product gave the following results:

Calculated:			Found:		
	C	20.68		C	21.02
	N	24.12		N	24.16
	S	55.20		S	54.93

Conclusion

Thiocyanogen may be used as a titrimetric oxidizing agent (like iodine) and for determining unsaturation in organic materials (7). Free thiocyanogen is placed between bromine and iodine as an oxidizing agent (8), having a standard potential of -0.77 volts. It has been reported that a partial dissociation of the $(SCN)_2$ into SCN radicals occurs (9) in dilute solutions of $(SCN)_2$ in hexane or carbon disulfide. X-ray data (10) supports the following structure:

$$\begin{array}{l} :\ddot{S}:C:::N: \\ :\underset{\cdot\cdot}{S}:C:::N: \end{array}$$

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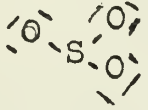
REACTIONS OF SULFUR TRIOXIDE

May 4, 1954 H. Ruus

The sulfur trioxide molecule may be represented as a planar, equilateral triangle with the sulfur atom in the centre. The electronic formula can be drawn as follows:



The sulfur atom has six electrons around it and has the tendency to accept a pair of electrons to form an octet acting as a Lewis acid. The simplest example of this is the formation of α, β and γ sulfur trioxide where sulfur in one sulfur trioxide molecule accepts a pair of electrons from the oxygen of another sulfur trioxide molecule.

Sulfuric acid is formed when sulfur trioxide accepts a pair of electrons from the oxygen of water followed by the migratoon of hydrogen.[1]

Sulfur trioxide can add to organic ethers and alcohols, but the simplest addition products are usually unstable and re-arrange to derivatives of sulfuric acid. Dioxane sulfo-trioxide is known to be stable in carbon tetrachloride solution.[2]

When sulfates, phosphates, carbonates, perchlorates, and salts of other oxygen acids react with sulfur trioxide the other acid anhydride is usually liberated. Oxides of metals [illegible] give the sulfate ion.

$$O^{-2} + SO_3 \rightarrow SO_4^{-2}$$

But not only oxygen but also halogen and nitrogen can act as donors of electrons. Iodine can add sulfur trioxide and forms the compounds $I_2 \cdot 6SO_3$, $I_2 \cdot 2SO_3$ and $I_2 \cdot SO_3$.[3] Hydrogen fluoride and hydrogen chloride add each only one molecule of sulfur trioxide.

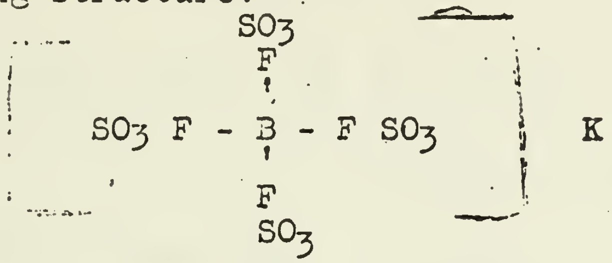
$$SO_3 + HF \rightarrow HF\text{-}SO_3 \rightleftharpoons FSO_3H$$

The primary addition product rearranges by the migration of a hydrogen from halogen to the oxygen atom.[1] The fluorides and chlorides can add more than one molecule of sulfur trioxide.

With hydrogen bromide and hydrogen iodide and their salts sulfur trioxide reacts as an oxidizing agent liberating free halogen.[4]

$$2HBr + SO_3 \rightarrow Br_2 + H_2SO_3$$

Potassium bero fluoride reacts with sulfur trioxide to give a compound that has the composition $KBF_4 \cdot 4SO_3$. For this Baumgarten[5] suggests the following structure:



$$\left[\begin{array}{c} SO_3 \\ F \\ SO_3F - B - FSO_3 \\ F \\ SO_3 \end{array}\right] K$$

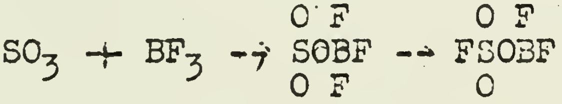
Lehmann and Kolditz [6] found the products of thermal decomposition of $KBF_4 \cdot 4SO_3$ to be potassium fluorosulfate, trisulfurylfluoride, sulfur trioxide, and a residue having the composition $S_{10}\ F_8\ B_6\ O_{35}$. According to these results they propose the following structure for $KBF_4 \cdot 4SO_3$

$$K\ (F\ SO_3\ SO_3\ BF_2\ SO_3\ SO_3\ F)$$

The best method for the preparation of trisulfurylfluroide is by saturating liquid sulfur trioxide with boron trifluoride at room temperature. The mixture is treated with concentrated sulfuric acid under cooling and trisulfurylfluoride layer is separated.[7]

$$BF_3 + SO_3 \rightarrow S_3\ O_8\ F_2$$

In this reaction the authors present sulfur trioxide as an electron donor.

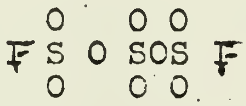


$$SO_3 + BF_3 \rightarrow \begin{matrix} O\ F \\ SOBF \\ O\ F \end{matrix} \rightarrow \begin{matrix} O\ F \\ FSOBF \\ O \end{matrix}$$

The second step would entail rearrangement of a fluoride from boron to sulfur. It is postulated that not one molecule of sulfur trioxide but several react at once with boron trifluoride to form a structure:

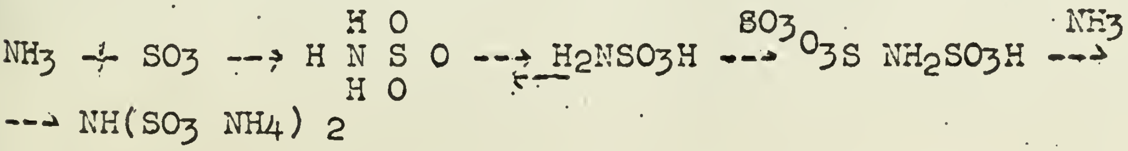
$$FSO_3{-}{-}{-}SO_3\ BFSO_3{-}{-}{-}SO_3\ SO_3F \rightarrow FSO_3SO_3\ SO_3{-}{-}{-}OBFSO_3{-}{-}SO_3F$$

From this trisulfurylfluoride would be removed leaving a body of high molecular weight. The structure of trisulfurylfluoride is postulated by the authors to be



$$\begin{matrix} & O & & O\,O & \\ F & S & O & SOS & F \\ & O & & O\,O & \end{matrix}$$

With ammonia sulfur trioxide should add to the electron pair of nitrogen, and give sulfamic acid in the form of the ammonium salt. Sulfamic acid is only isolated in a very small yield. The main reaction product is the ammonium salt of the imidodisulfuric acid.



$$NH_3 + SO_3 \rightarrow H\begin{matrix} H \\ N \\ H \end{matrix}\begin{matrix} O \\ S \\ O \end{matrix}O \rightarrow H_2NSO_3H \xrightarrow{SO_3} O_3S\ NH_2SO_3H \xrightarrow{NH_3}$$

$$\rightarrow NH(SO_3\ NH_4)_2$$

Sulfamic acid is prepared technically from urea and sulphur trioxide.[8]

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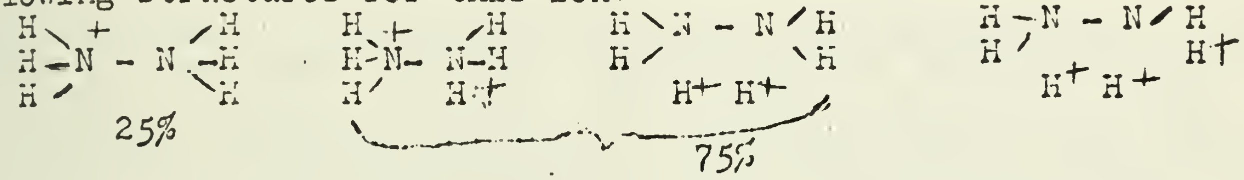
COORDINATION OF HYDRAZINE

May 11, 1954 Frank Hersman

The hydrazinium ion $N_2H_6^{++}$ has the geometrical form of the ethane molecule with which it is isoelectronic. Schwarzenbach states that the hydrogen atoms in the $N_2H_6^{+2}$ ion point in different directions. This would make it unlikely that a 3- membered chelate ring is formed due to steric requirements. Wells,[2] however gives the following structures for this ion:



The structures postulated by Wells appear more likely since ordinary formulation with single bonds gives both the N atoms formal charges of +1. If the hydrogen atoms do point in different directions it is possible that a bridged polynuclear structure would be formed instead of a 3- membered ring. Such a polynuclear complex would explain the low solubility which is characteristic of many hydrazine complexes. This is in striking contrast to the solubilities of other ammine and diamine complexes.

Schwarzenbach studied metal ion-hydrazine complexes in the presence of the fluoborate ion, where the products remain in solution, and calculated the number of hydrazine molecules which are bound per metal ion. This is given by the following equation:

$$g = \frac{\Sigma [M(N2H4)i]}{[M]\ \text{total}}$$

where g is the average number of ligands attached to the central metal ion. By plotting g as a function of the concentration of free hydrazine a neutralization curve may be obtained.

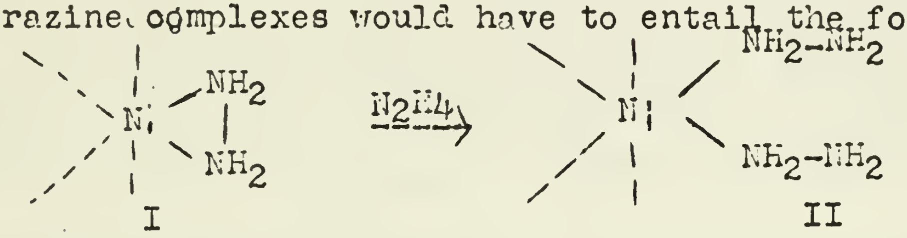
FORMATION OF NICKEL HYDRAZINE COMPLEXES

Nickel - hydrazine complex formation occurs over a range of hydrazine concentrations from 10^{-3} to 0.5 molar. The logarithms of the formation constants may be calculated from the hydrogen concentration and are recorded below:

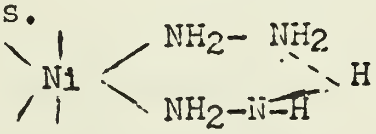
$$Ni^{+2} \xrightarrow{2.76} Ni(N_2H_4)^{+2} \xrightarrow{2.44} Ni(N_2H_4)_2^{+2} \xrightarrow{2.15} Ni(N_2H_4)_3^{+2}$$

$$\xrightarrow{1.85} Ni(N_2H_4)_4^{+2} \xrightarrow{1.55} Ni(N_2H_4)_5^{+2} \xrightarrow{1.24} Ni(N_2H_4)_6^{+2}$$

The first three species $[Ni(N_2H_4)]^{+2}$, $[Ni(N_2H_4)_2]^{+2}$, and $[Ni(N_2H_4)_3]^{+2}$ cannot be chelate complexes since the addition of suceeding hydrazine complexes would have to entail the following process:

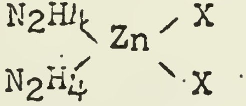


The logarithms of the formation constants are proportional to the free energies: hence, the free energies for the addition of the first three hydrazine molecules (I) should be larger than those involving the subsequent addition of more hydrazine to form (II). Such a difference is not observed. This is also evident from the values of q for the consecutive formation constants according to the expression: $q_i = \frac{K_{Ni(N_2H_4)i}}{K_{Ni(N_2H_4)i+1}}$, etc. Of these quotients q_3 would possess an especially large value should a chelate ring be formed. This is observed with ethylene diammine, where q_3 is infinite since a fourth molecule cannot coordinate. Consequently, there would appear to be no evidence for the formation of chelate structures among the nickel-hydrazine complexes. The formation constants in the nickel-hydrazine system are analogous to those calculated for the nickel ammonia system. It is interesting to note that complexes of nickel with hydroxylamine, such as $[Ni(NH_2OH)_6]SO_4$, reveal that hydroxylamine serves as a monodentate ligand.[5] The fact, however, that the formation constants are larger for the nickel-hydrazino complexes than with the nickel-ammonia complexes is incompatible with the known observation that hydrazine is a weaker base. Schwarzenbach explains this finding on the basis that the hydrazine molecules in the complex are not held together solely through the metal cation, but are bound further through hydrogen bridges between the distant amino groups.



ZINC AND HYDRAZINE

In the titration of zinc ion with hydrazine in the presence of fluborate ion at an overall pH of 6.7 a precipitate begins to form which contains both BF_4^- and OH^- in addition to ZN^{++} and N_2H_4. The hydrazine which is used in the complex formation at the point of precipitation corresponds to more than that necessary for the composition of the solid zinc hydrazine complex $[Zn(N_2H_4)_2]XZ$.

Apparently the zinc ion can coordinate a maximum of four hydrazine molecules. In this case a larger overall formation constant is observed in the Zn^{++}--NH_3 system than in the hydrazine system as one would expect. In the tetrahedral configuration the distance between the amino groups are greater than in the octahedral configuration, thus reducing markedly the hydrogen bonding. Since the complex forms before the addition of hydrazine necessary to give it bidentate character it may be that there is formed a neutral complex species of the type  forms, analogous to the complex tetrachlorate zincate structure. However the hydrazine complex is insoluble in organic solvents contray to what one would expect.

It is to be noted that there may be precipitated from solution a hydroxylamine complex $[Zn(NH_2OH)_2]Cl_2$ in which the hydroxylamine primarily functions as a bidentate ligand.

In summary no precipitation occurs if hydrazine is added to solutions of the fluoborate of Ni and Zn. The amount of hydrazine coordinated by the metal cation in such solutions would indicate that this substance functions as a monodentate ligand.

These data are in accord with the polargraphic investigations carried out by Rebertus, Laitinen and Bailar.[4] These studies involved 20-600 fold excesses of free hydrazine whereas the studies of Schwarzenbach involved only a 2.5 fold excess, under which condition the percentage of lower complexes should be greater. They found evidence for the existence of the cationic complexes $[ZN(N_2H_4)_3\,OH]^-$ and $[Zn(N_2H_4)\,(H_2O)\,(OH)]^+$ thereby concluding that hydrazine functions only as a monodentate ligand.

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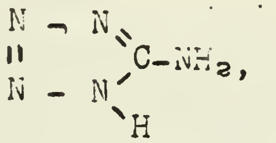
COMPOUNDS OF HIGH NITROGEN CONTENT
DERIVATIVES OF 5-AMINOTETRAZOLE

James V. Currier

May 11, 1954

5-Aminotetrazole,  is an unusually stable high nitrogen content compound which may be regarded from the Franklin solvent system point of view as a cyclic, condensed nitrous acid, ammono carbonic acid hydrazide (1,2). As an extention of the previous studies carried out in this laboratory on the synthesis of condensed solvo carbonic acids, the present investigation has dealt with the preparation and characterization of some condensed solvo carbonic acids derived from 5-aminotetrazole.

An improved synthesis of N-(5-tetrazolyl) urethane was developed based upon a Schotten-Baumann modification of the original synthesis by Stolle which involved the acylation of 5-aminotetrazole with ethyl chlorocarbonate (3). Attempts to ammonolize this urethane derivative in aqueous and anhydrous liquid ammonia failed to produce the corresponding amide. Hydrazinolysis of the ester, however, was readily accomplished in boiling 85 per cent hydrazine hydrate. The product, the hydrazine salt of 4-(5-tetrazolyl) semicarbazide, was converted by acidification to the free 4-(5-tetrazolyl) semicarbazide. This substance gives reactions typical of a hydrazide forming hydrazones with aldehydes and ketones and 1-benzoyl-4-(5-tetrazolyl) semicarbazide on treatment with benzoyl chloride. In addition, this substance like other 5-monosubstituted tetrazoles forms amine and metal salts. The ammonium, hydrazinium, lithium, sodium, potassium, and barium as well as some transition and heavy metal salts of this substance were prepared. Diazotization of the free 4-(5-tetrazolyl) semicarbazide produced the sensitive compound, N-(5-tetrazolyl) carbamyl azide, which due to the extremely reactive azide group readily undergoes solvolysis with nitrogen bases to produce N-(5--tetrazolyl) ureas. Thus ammonolysis of this compound produced the ammonium salt of N-(5-tetrazolyl) urea. By acidification of this salt pure N-(5-tetrazolyl) urea was first produced. Characterization of this urea derivative aided in the development of other methods for the synthesis of this compound.

Pure samples of N-(5-tetrazolyl) urea have also been prepared in good yield by the thermal rearrangement of its isomer, 5-tetrazolylammonium cyanate, in a xylene or di-n-butyl ether suspension. Purification of the crude product was accomplished by washing the solid residue with boiling water. 5-Tetrazolylammonium cyanate was prepared from a relatively concentrated solution of 5-aminotetrazole and cyanic acid according to a procedure used by Thiele and Ingle (4). This salt was further identified by a comparison of its solvolytic reactions with those of its isomer, N-(5-tetrazolyl) urea.

Impure samples of N-(5-tetrazolyl) urea have also been prepared in rather poor yield from dilute aqueous solutions of 5-aminotetrazo. and cyanic acid by Smith (5). This product could not be purified, but the presence of N-(5-tetrazolyl) urea was established by its x-ray diffraction pattern.

Since the above synthesis was not satisfactory, the analogous reaction of 5-hydrazinotetrazole and cyanic acid reported by Thiele and Ingle was repeated (4). This synthesis gives 1-(5-tetrazolyl) semicarbazide in good yield. The difference in the two syntheses apparently lies in the difference between the basicity of the 5-hydrazino and 5-aminotetrazoles.

For the purpose of comparing their properties with those of N-(5-tetrazolyl) urea and compounds of related structure, N-ethyl, N,N-dimethyl, and N,N-diethyl-N'-(5-tetrazolyl) ureas were prepared by the respective reactions of 5-aminotetrazole with ethyl cyanate, N,N-dimethyl carbamyl chloride, and N,N-diethyl carbamyl chloride.

In addition to these carbonic acid derivatives, the synthesis of 1-octadecyl-5-octadecylaminotetrazole was accomplished by the following steps: N,N'-dioctadecyl-S-methyl-thiouronium hydrochloride was hydrazinolized effecting the replacement of the S-methyl group with a hydrazide group to form N-amino-N',N''-dioctadecyl guanidine. The subsequent diazotization of this product in glacyl acetic acid produced 1-octadecyl-5-octadecylaminotetrazole.

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THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

May 18, 1954

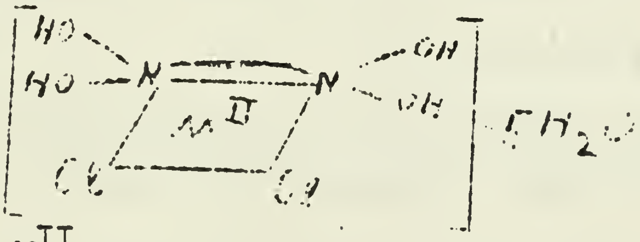
Daryle H. Busch

In view of the apparent tendency of additional chelate rings to enhance the stability of complex ions,[1] the maximum number of chelate rings would normally be expected to form. With this principle in mind it has been possible to design suitable complexes and study the stereochemistry of hexadentate, tetradentate, pentadentate, and bidentate complexes of ethylenediaminetetracetic acid (EDTA). An attempt has also been made to add additional chelate rings to coordinately saturated amine complexes, without replacement of the coordinated atoms.

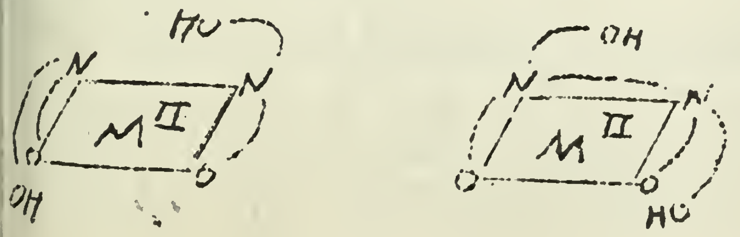
I. The stereochemistry of Ethylenediaminetetraacetic Acid Complexes.

In spite of the vast literature on the complexes of this chelating agent, very little has been proven with regard to the stereochemistry of the complex ions it forms. Schwarzenbach[2] has demonstrated that it can act as a pentadentate or a hexadentate donor in cobalt (III) complexes, although there is still some question as to the ability of EDTA to occupy six positions in a coordination sphere. Comparison of the infrared spectra of the pentadentate and hexadentate complexes confirms these structures. Partial resolution of the hexadentate complex was attained through the strychnine salt and by absorption on optically-active quartz. The pentadentate complexes are not sufficiently stable to allow a thorough study of their stereochemistry. Partial resolution of the complex $[Co(EDTA)Br]^-$ was accomplished. Its conversion to the hexadentate species is not accompanied by complete racemization.

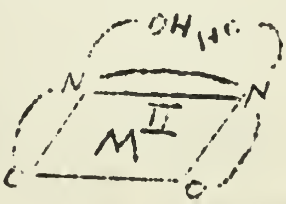
Platinum (II) and palladium (II) were employed to study complexes containing three or fewer chelate rings. The reaction of K_2PdCl_4, K_2PtCl_4, $PdCl_2$, $PtCl_2$ with Na_2H_2Y (Y is $EDTA^{4-}$) produces crystalline compounds of the empirical formula, $H_4M^{II}YCl_2 \cdot 5H_2O$. These compounds are assigned the structure



These were converted to $H_2M^{II}Y$, in which the EDTA is tetradentate as shown by the existence of two equally intense carbonyl bands. These complexes contain two asymmetric nitrogens, so they may be racemic or meso:



racemic



meso

Fractional crystallization of the strychine salt of the palladium(II) complex provides evidence for all three forms. The order of solubilities is

meso $<$ dextro $<$ racemic $<$ levo.

II. Reactions of Coördinated Amines and Hydrazines.

The reactivity of coordinated metal amines toward carbonyl compounds has been demonstrated by early workers.[3] These reactions are often attended by formation of additional chelate rings, although the introduction of a more powerful donor atom is sometimes sufficient for Shiff base formation. It should be possible to design a system such that two or three bidentate groups could be joined into a cyclic molecule completely surrounding a complexed metal ion, by reaction of adjacent donor atoms with a bifunctional carbonyl compound.

Investigations based on the reaction of two moles of diacetyl with two moles of coordinated diamine have produced a variety of results.

System	Major Product
t-[Co en_2 Cl_2] Cl+2 diacetyl	[Co en_2 $diac_3$]Cl_2
[Co(trimethylenediamine)$_2$]Cl_2+2 diacetyl	[Co $trim_2$ $diac_3$]Cl_3
[Co(o-phenylenediamine)$_2$]Cl_2+2 diacetyl	[Co $ophyn_3$ diac]Cl_2
[Cu en_2]Cl_2+2 diacetyl	[Cu en $diac_2$]
[Cu(triethylenetetramine)]Cl_2+ diacetyl	[Cu_2 trien $diac_2$ Cl_2]
[Pd en_2]Cl_2+2 diacetyl	[Pd en Cl_2]
[Pd(triethylenetetramine)]Cl_2+ diacetyl	[Pd trien] [Pd Cl_4]
$FeCl_2$+3 diacetyl +3 en	[Fe en_2 $diac_5$]Cl_2

Some of these products are unstable and are probably only average compositions as written. Several factors may be operative in preventing the formation of expected compounds. These investigations are being extended.

Bis(oxalyldihydrazide) nickle(II) reacts with diacetyl yielding a product having the composition, Na_2[Ni $dihy_2$ $diac_2$]. The cobalt derivative is similar.

III. The Iron(II)-methine Chromophore.

Krumholtz[4] showed that the chromophoric group in the diacetylbis-(methylimine) complex of iron(II) is essentially the same as that present in the complexes of iron(II) with o-phenanthroline and dipyridyl. In view of the importance of the group -N=C-C=N- to the

work discussed in the preceding section, a study of this chromophoric system was undertaken.

The ultraviolet, visible, and infrared spectra were obtained for the compounds (a) tris(o-phenanthroline)Iron(II) chloride, (b) tris (dipyridyl)iron(II) perchlorate, (c) tris(pyridinalmethylamine) iron(II) iodide, (d) tris diacetylbis(methylimine) iron(II) iodide, (e) dipyridinalethylenediamineiron(II) chloride, (f) o-phenanthroline, (g) dipyridyl, and (h) dipyridinalethylenediamine. The visible spectra for the iron(II) compounds are all quite similar, indicating the presence of a common chromophoric group. This similarity carries over to ultraviolet, indicating that the unsaturated grouping linked to the iron(II) ion is present in a similar electronic state in all the metal-containing species. Comparison of the infrared spectra of the complex compounds with those of the free ligands indicates that the diamagnetic species ((a), (b), (c), (d)) all involve bonds fundamentally dependent on the participation of the iron(II) atom in a conjugated chelate ring. The anomalous behavior of compound (e) indicates that six equivalent bonds to the iron(II) are necessary to obtain the characteristic diamagnetic type.

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THESIS REPORT

Some Electrochemical Properties of Hydrazine and Chloramine

R. N. Hemmer

May 18, 1954

The attempted anodic formation of hydrazine in liquid ammonia

It has been claimed[1] that hydrazine can be prepared by the anodic oxidation of amide ions in liquid ammonia according to the equation

$$2\ NH_2^- \rightarrow N_2H_4 + 2\ e.$$

Although it is reasonable to believe that this reaction might occur under suitable conditions in liquid ammonia, all attempts to carry out such a synthesis have been unsuccessful. In studying the possibility of forming hydrazine at an anode in liquid ammonia, solutions of a suitable electrolyte were electrolyzed at -50°C in an H-cell constructed with a fritted glass diaphragm separating the electrode compartments. After each electrolysis a few milliliters of the anolyte were withdrawn, added to water, and the resulting aqueous solution was tested for the presence of hydrazine. Electrolytic solutions ranging in composition from saturated potassium amide (strongly basic solution) to saturated ammonium chloride (strongly acidic solution) were electrolyzed using bright platinum, platinum black, and graphite anodes with current densities ranging from 4 x 10^{-4} to 4 amperes per square centimeter. In no case was a positive test for hydrazine obtained.

Voltammetry in liquid ammonia

In order to support the claim that hydrazine cannot be obtained by anodic oxidation in liquid ammonia as well as to determine whether or not hydrazine is stable at an anode in this solvent, a technique was developed for determining current-voltage curves at a platinum micro electrode in liquid ammonia. For this purpose a suitable three-compartment cell was constructed so that a rotating electrode assembly could be operated in one of the outer compartments and so that a reference electrode could be placed in the other. The middle compartment served as a salt bridge. An electron electrode[2] was used s a reference and consisted of a large platinum sheet in contact vith a solution of sodium metal. At such an electrode the reaction s the reversible passage of electrons from the platinum into the olution, or vice verse.

Although sodium acetate was used as the supporting electrolyte n early work, sodium perchlorate was later found to be more satisactory. At first current-voltage curves were plotted manually, ut when the technique proved successful, a recording polarograph as used.

Current-voltage curves of basic and neutral solutions in liquid mmonia show a region of about three volts over which there is virually complete polarization of the micro electrode. This region xtends from about +3.0 volts, at which nitrogen evolution occurs, o about 0.0 volt, at which electron dissolution begins. In acidic

solutions, however, the range is restricted by the discharge of ammonium ions at $E_{1/2} \simeq 0.6$ volt.

The fact that neither basic nor acidic solutions show an oxidation wave before nitrogen evolution confirms the belief that hydrazine cannot be obtained by anodic oxidation in liquid ammonia. In addition, it was found that solutions of hydrazine are neither oxidizable nor reducible.

The cathodic reduction of chloramine in liquid ammonia

Chloramine reacts slowly in liquid ammonia to form hydrazine[3] according to the equation

$$NH_2Cl + 2\ NH_3 \longrightarrow NH_4Cl + N_2H_4.$$

In order to determine whether this reduction also can be carried out electrochemically, a study of the behavior of chloramine in liquid ammonia was undertaken using the rotating platinum micro electrode technique.

Under these conditions chloramine gives a symmetrical S-shaped reduction wave with a well-defined diffusion plateau. Its half-wave potential is about +1.7 volts versus the electron electrode, although both the rate and direction of polarization of the rotating electrode cause some variation in this value. In solutions containing ammonium salts, the chloramine wave is followed by a second wave at $E_{1/2} \simeq +0.5$ volt representing the reduction of ammonium ions.

At -78°C the chloramine diffusion current changes very little over a period of 24 hours, indicating that under these conditions the solution is quite stable. At -35°C, however, the wave height decreases at a measurable rate. If hydrazine is added to the solution, it reacts with chloramine so rapidly at -78°C that the latter is completely consumed in an hour or less.

At a micro electrode only indirect methods can be used to determine <u>n</u>, the number of electrons involved in the electrode reaction. Although it seems likely that $n = 2$, this has not yet been established with certainty. Polarographic data show that the reduction of chloramine in aqueous solution is a two-electron process. If this is also the case at a platinum electrode in liquid ammonia, the reduction product is not hydrazine but the amide ion, as shown by the equation

$$NH_2Cl + 2\ e \longrightarrow NH_2^- + Cl^-$$

Polarography of chloramine in aqueous solution

In aqueous solution, chloramine was found to be reducible at the dropping mercury electrode. Its polarographic behavior was studied in basic solutions varying from a buffer of pH 8.85 to 0.8 <u>N</u> KOH. Polarograms were run using chloramine concentrations from 42 millimolar down to 0.1 millimolar, and in all cases the diffusion current--concentration plot was linear, indicating that chloramine may be determined quantitatively by polarographic or amperometric methods. Since $i_d/C\ m^{2/3}\ t^{1/6}$ is essentially constant and independent of pH, careful control of the pH is unnecessary for analytical

purposes. The value of the half-wave potential lies in the range -0.35 to -0.40 volts versus the saturated calomel electrode.

Alkaline solutions of chloramine are unstable and decompose according to the equation

$$3\ NH_2Cl + 3\ OH^- \rightarrow 3\ Cl^- + NH_3 + N_2 + 3\ H_2O$$

The rate of decomposition of chloramine in an 0.8 N KOH solution at 25° C was followed by measuring the diffusion current at constant potential over a period of 600 minutes. A plot of log i_d versus time showed the decomposition to be first order, although at higher chloramine concentrations the plot showed a slight curvature in a direction indicating that initially the rate of decomposition is several times slower than during the remainder of the decomposition. A second order plot of $1/i_d$ versus time was decidedly non-linear. Analysis of the gaseous decomposition product of chloramine using the mass spectrometer showed it to be pure nitrogen.

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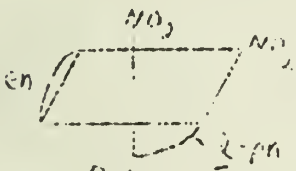
THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

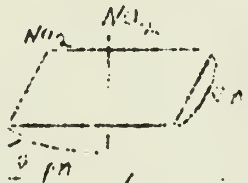
OPTICAL-GEOMETRIC ISOMERISM OF THE DINITRO-ETHYLENEDIAMINE-ISOBUTYLENEDIAMINE-COBALT (III) ION

William E. Cooley May 18, 1954

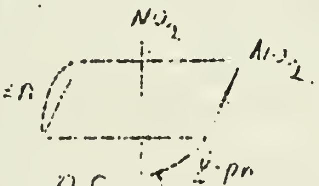
In 1918 Werner and Smirnoff (1) reported the resolution of the cis-dinitro-ethylenediamine-propylenediamine-cobalt (III) ion into all eight of the theoretically possible isomers. Four of these isomers are shown below for levo-propylenediamine (l-pn); four corresponding forms exist for dextro-propylenediamine. The Methyl group on the propylenediamine molecule is indicated by a short line.



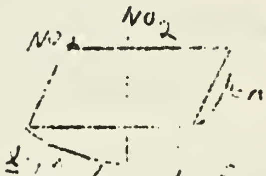
D, α



L, α



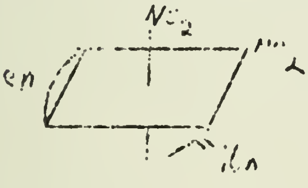
D, β



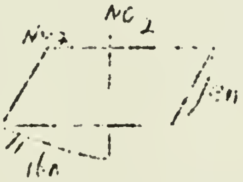
L, β

The α and β forms are geometric isomers, forming different crystal types, while the D and L forms are optical isomers. The rotations of polarizes light produced by the isomers illustrated above are all different. Each of these forms has an optical antipode among the four forms containing dextro-propylenediamine. These characteristics of the eight isomers are described by the term optical-geometric isomerism.

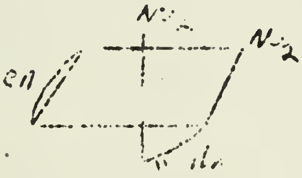
This study has shown that the cis-dinitro-ethylenediamine-isobutylenediamine-cobalt (III) ion, which contains no optically active ligand, also exhibits optical-geometric isomerism. The four theoretically possible isomers of cis-$[\text{Co en ibn}(NO_2)_2]^+$ have been isolated.



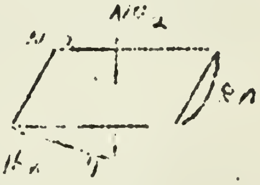
D, α



L, α



D, β



L, β

Because of its geometric isomerism the compound cis-$[\text{Co en ibn}(NO_2)_2]Cl$ crystallizes as rhombic prisms (α form) and needles (β form). These designations have not been correlated with the molecular structures as labeled above. Each of the geometric isomers has been resolved into optical antipodes.

To prepare the *cis*-$[Co\ en\ ibn(NO_2)_2]^+$ ion, $[Co(NH_3)_3(NO_2)_3]$ was treated with ethylenediamine to form $[Co\ en\ NH_3(NO_2)_3]$. This was converted to $[Co\ en\ ibn(NO_2)_2]NO_2$ by reaction with isobutylenediamine. The *cis* and *trans* forms of $[Co\ en\ ibn(NO_2)_2]NO_2$ were separated by concentrating the solution and precipitating with alcohol the less soluble *cis* form. The nitrate salts were converted to the bromides with sodium bromide and then to the *d*-α-bromocamphor-π-sulfonates with silver *d*-α-bromocamphor-π-sulfonate. These salts were fractionally crystallized to separate the four isomers, which were re-converted to the bromides with hydrobromic acid.

An improved method has been developed for the preparation of $[Co(NH_3)_3(NO_2)_3]$. This method yields the complex in large laboratory quantities in a highly pure state.

The ultraviolet absorption spectra of *cis* and *trans*-$[Co\ en\ ibn(NO_2)_2]^+$ have been determined. The absorption maxima of the *trans* form are nearer the visible band, respectively, than those of the *cis* form. These findings agree with those of Basolo (2) for analogous complexes.

Extension of the study to includedemonstration of the optical-geometric isomerism for the ion *cis*-$[Pt\ en\ ibn\ Cl_2]^{++}$ was attempted unsuccessfully. The ion could not be prepared in any of the methods tried.

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THESIS REPORT

THE STEREOCHEMISTRY OF ORGANOSILICON AND COMPLEX INORGANIC COMPOUNDS

I. A STUDY OF THE MECHANISM OF A NUCLEOPHILIC SUBSTITUTION REACTION ON AN ORGANOSILICON COMPOUND

II. THE PARTIAL RESOLUTION OF RACEMIC PROPYLENEDIAMINE THROUGH AN OPTICALLY ACTIVE COMPLEX INORGANIC COMPOUND

Stanley Kirschner May 25, 1954

I. A Study of the Mechanism of a Nucleophilic Substitution Reaction on an Organosilicon Compound

The mechanism which is operative during a nucleophilic substitution reaction on an organosilicon compound should be distinguishable among four possible mechanisms (1, 2, 3, 4), (a) The "Walden Inversion" or S_N2, (b) The "Front-Side Attack", (c) The "Ionic", S_N1, or "Siliconium Ion", or (d) The "Pentacovalent (or Hexacovalent) Intermediate", by a study of (1) the rate of racemization of an optically active organosilicon compound when it is attacked by a nucleophilic agent, (2) the rate of exchange of a radioactive nucleophilic attacking agent with the organosilicon compound, and (3) the kinetics of the reaction.

An optically active organosilicon compound containing a displaceable group, $(CH_3)(n\text{-}C_3H_7)(CH_2CH_2CH_2N[C_2H_5]_2)Si(OCH_3)$, was prepared from CH_3SiCl_3 by a series of Grignard and methanolysis reactions (5). It was resolved by preparing and fractionally crystallizing the dibenzoyl-d-hydrogen tartrate salt in an acetone-ether mixture. This procedure gave the diastereoisomer containing the levo enantiomer of the organosilicon compound in the least soluble fraction, from which the resolving agent could be removed by treatment with piperidine or N-ethylpiperidine to give the free, resolved organosilicon compound.

However, the rate of racemization is extremely rapid in piperidine or N-ethylpiperidine as the solvent, so the remainder of the study was carried out in methanol solution. The stoichiometric quantity of sodium methoxide was added to the diastereoisomeric salt to effect the removal of the resolving agent, and two equivalents of methoxide were then added as the attacking agent. Under these conditions the racemization of the organosilicon compound was extremely slow. It was concluded, therefore, that since the organosilicon compound racemizes, and since the rate of racemization is sensitive to the concentration of the attacking agent, neither the "Front-Side Attack" mechanism nor the "Ionic" (or S_N1) mechanism holds for the reaction. In addition, it appears more probable that the "Pentacovalent (or Hexacovalent) Intermediate" mechanism is the operative one than the S_N2 mechanism, since the reaction is so rapid in very high concentrations of attacking agent, but is extremely slow in

moderate concentrations of the agent. This behavior is similar to reactions of silicon compounds which form hexacovalent molecules (6), which lends support to the "Pentacovalent (or Hexacovalent) Intermediate" mechanism. Furthermore, S_N2 reactions rarely occur in ionizing solvents such as amines and alcohols (1, 2), lending additional support to the conclusion that the "Pentacovalent (or Hexacovalent) Intermediate" is probably the operating mechanism in this reaction.

II. The Partial Resolution of Racemic Propylenediamine Through an Optically Active Complex Inorganic Compound

Of the eight isomers of $[Co(pn)_3]Cl_3$ (pn = propylenediamine) which are theoretically capable of existence, only two, the D-$[Co(d\text{-}pn)_3]Cl_3$ and the L-$[Co(l\text{-}pn)_3]Cl_3$ salts, have ever been isolated (7). In addition, Dwyer (8) reports that if D-K[Co(enta)] (enta = ethylenediaminetetraacetate anion) is treated with ethylenediamine (en), the partially resolved complex compound, D-$[Co(en)_3]$Kenta, is obtained. Hence, treatment of D-K[Co(enta)] with racemic propylenediamine should lead to at least a partial resolution of the material, since one would expect the dextro enantiomer of it to react preferentially with the D-K[Co(enta)] to give D-$[Co(d\text{-}pn)_3]$Kenta, leaving the levo isomer in solution.

The compound DL-$Ba[Co(enta)]_2$ was prepared by a variation of the method of Schwarzenbach (9), and resolution was effected through the use of levo strychnine sulfate (10). The strychnine cation was removed with potassium iodide, leaving L-K[Co(enta)] in aqueous solution. Treatment with racemic propylenediamine resulted in the formation of L-$[Co(l\text{-}pn)_3]$Kenta and in a partial resolution of the propylenediamine, indicating that the original premise was correct - a partial resolution of racemic propylenediamine can be obtained in this manner.

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THESIS REPORT

THE SYNTHESIS OF HYDRAZINE

Harold J. Matsuguma May 25, 1954

Hydroxylamine-O-sulfonic acid, H_2NOSO_3H, like chloramine, will react with ammonia to give hydrazine and with amines to give substituted hydrazines. Both HOS and chloramine liberate iodine from acid solutions of KI. Both are acids although chloramine is extremely weak whereas HOS is strong. Formally they may also be considered as analogues, i.e., as agents which may be regarded as potential imide donors in the reactions which they undergo with many inorganic and organic compounds.

$$\begin{aligned} NH_2Cl &\rightarrow NH\cdot HCl \\ H_2NOSO_3H &\rightarrow HN\cdot H_2SO_4 \\ H_2NOH &\rightarrow HN\cdot H_2O \\ HN_3 &\rightarrow HN\cdot N_2 \end{aligned}$$

With chloramine the velocity of its reactions with ammonia or amines depends upon the basicity of the latter. The same is true for HOS. Chloramine also reacts with water in hot, strongly alkaline solutions to give NH_2OH(1), but no such reaction has been noted for HOS except in acid solution.

Two methods for the preparation of HOS have been reported (2,3). One method involves the reaction of HN_3(g) with fuming H_2SO_4 at elevated temperatures, and the second, the reaction of $NH_2OH\cdot HCl$ or $(NH_2OH)_2\cdot H_2SO_4$ with $ClSO_3H$. The latter procedure is best adapted for preparation on a laboratory scale.

It has been found that the hydroxylamine salt should be added to a 200 - 300% excess of $ClSO_3H$ then heated for at least five hours. If $NH_2OH\cdot HCl$ is used the reaction seems to entail two separate steps. The first is a desolvation reaction during which HCl is evolved, yielding a clear solution; the second is one which leads to the formation of HOS with the evolution of more HCl. The second step is brought about by heating to 100° for at least five hours.

The white, solid product is then washed with anhydrous, ice-cold ether and analyzed iodometrically. The purest product obtained by this method assayed 97% HOS. The impurity seems to be $NH_2OH\cdot HCl$ or $(NH_2OH)_2\cdot H_2SO_4$. Further purification from methanol, as recommended in the earlier literature, gives no appreciable increase in purity, but lowers yields by 60 - 80%.

HOS as prepared by this method is a white, microcrystalline solid. It is quite hygroscopic, but may be handled without difficulty if exposure to moist air is minimized.

HOS reacts with NH_3 in aqueous solution to give hydrazine which was identified by the isolation of the salicylalazine, m. pt. 214°. The yields of N_2H_4 were noted to increase with the increasing molar ratio NH_3:HOS and were also seen to rise when

gelatine was added; the presence of base (NaOH) caused a decrease in yield.

Addition of Cu(II) ion to the reaction mixture caused complete disappearance of N_2H_4; the Co(II) ion was also found to have a slight inhibitory effect. Thus it was concluded that the reaction of HOS and NH_3 resembles that of chloramine and NH_3 and may be represented by;

$$H_2NOSO_3H + NH_3 \rightarrow N_2H_4 + H_2SO_4$$

The yields of hydrazine were found to increase with an increase in concentration of reactants at any given molar ratio. This point will be investigated more fully, since it seems to indicate some ionic character in the reaction - and in this respect differs from the NH_2Cl - NH_3 reaction.

The reaction of HOS and methylamine was found to be much more rapid than that of NH_3 with HOS. The yields at comparable molar ratios were higher; gelatine and permanent base were also found to effect favorably yields of methylhydrazine.

Yields of $CH_3N_2H_3$ increased 50 - 60% with the addition of 100 mg of gelatine, and yields also increased 70 - 80% with molar ratios of OH^-:HOS of 9 - 13. The base effect was not pronounced at a high molar ratio of CH_3NH_2:HOS. Yields up to 94% were obtained in solutions havimg molar ratios of CH_3NH_2: HOS of 20 (0.06 mole of HOS/200 ml of solution), molar ratios of NaOH:HOS of 9 and containing 100 mg of gelatine per 200 ml of solution.

From the results obtained to date, it would appear that the reaction between HOS and CH_3NH_2 proceeds as follows in accordance with one of the following mechanisms;

(1) $$H_2NOSO_3H + 2\ OH^- \rightarrow [HNOSO_3]^= + 2\ H_2O$$

$$[HNOSO_3]^= + CH_3NH_2 \rightarrow CH_3N_2H_3 + SO_4^=$$

(2) $$HN \cdot H_2SO_4 + 2\ NaOH \rightarrow [HN] + Na_2SO_4 + 2\ H_2O$$

$$[HN] + CH_3NH_2 \rightarrow CH_3N_2H_3$$

The latter mechanism seems the more reasonable, since HOS in alkaline solution has been postulated by Sommer, Schulz and Nassau(4) to decompose in the following manner;

$$H_2NOSO_3H + 2\ OH^- \rightarrow 2\ H_2O + SO_4^= + [HN]$$

$$3\ [HN] \rightarrow NH_3 + N_2$$

Such a mechanism is consistent with the experimental facts and emphasizes the similarity of the HOS-NH_3 reaction with the processes occurring in the Raschig Synthesis of hydrazine.

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Place in the Periodic System of the Heaviest Elements

Ervin Colton March 10, 1953

The heaviest elements refer to elements of atomic numbers 89-98, inclusive, i.e., actinium through californium. The suggested electronic configurations (beyond radon and xenon) for gaseous atoms of the actinide and lanthanide series are shown below for reference:

At. No.	Element	Configuration	At. No.	Element	Configuration
89	Ac	$6d^1 7s^2$	57	La	$5d^1 6s^2$
90	Th	$6d^2 7s^2$ (or $5f^1 6d^1 7s^2$)	58	Ce	$4f^2 6s^2$
91	Pa	$5f^2 6d^1 7s^2$ (or $5f^1 6d^2 7s^2$)	59	Pr	$4f^3 6s^2$
92	U	$5f^3 6d^1 7s^2$	60	Nd	$4f^4 6s^2$
93	Np	$5f^5 7s^2$ (or $5f^4 6d^1 7s^2$)	61	Pm	$4f^5 6s^2$
94	Pu	$5f^6 7s^2$ (or $5f^5 6d^1 7s^2$)	62	Sm	$4f^6 6s^2$
95	Am	$5f^7 7s^2$ (or $5f^6 6d^1 7s^2$)	63	Eu	$4f^7 6s^2$
96	Cm	$5f^7 6d^1 7s^2$	64	Gd	$4f^7 5d^1 6s^2$
97	Bk	$5f^8 6d^1 7s^2$	65	Tb	$4f^9 6s^2$
98	Cf	$5f^9 6d^1 7s^2$	66	Dy	$4f^{10} 6s^2$

Arguments according to Seaborg (1,2):

Present evidence points to the conclusion that it is the 5f electron shell that is being filled in these heaviest elements. Further, the evidence seems to suggest a second rare-earth like series, beginning with actinium in the same sense that the "lanthanide" series begins with lanthanum. Such an "actinide" series is suggested on the basis of the following observations: (A) chemical properties, (B) absorption spectra in aqueous solution and crystals,

(C) crystallographic structure data, (D) magnetic susceptibility and (E) spectroscopic data.

A. Chemical properties: A table of oxidation states of the lanthanide and actinide elements is shown below. Values in parentheses have been reported but are unstable:

atomic no.	89	90	91	92	93	94	95	96	97	98
element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
oxid. state		(+2)					(+2)			
	+3	(+3)	(+3)	+3	+3	+3	+3	+3	+3	+3
		+4	+4	+4	+4	+4	+4		+4	
			+5	+5	+5	+5	+5			
				+6	+6	+6	+6			

atomic no.	57	58	59	60	61	62	63	64	65	66
element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
oxid. state						+2	+2			
	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
		+4	+4						+4	

The regularity of the +3 state in the lanthanide series is not so well pronounced in the actinide series. The +4 oxidation state, as well as the +3 state, seems to characterize the actanides. It becomes increasingly difficult to effect oxidation to higher valence states with increasing atomic number among heavier elements. The following table shows some oxidation potentials of the actinides in 1M aqueous solution:

element	III to IV	IV to VI
U	+0.63 v.	-0.60 v.
Np	-0.14	-0.94
Pu	-0.95	-1.11
Am	~ -2.6	

The metals of the elements Th to Am bear striking resemblance to those of the rare earth metals. A marked similarity is also noted in that americium ($5f^77s^2$) and europium ($4f^76s^2$) both have densities much lower than those of their neighbors.

B. Absorption spectra in aqueous solution and crystals:

Sharp absorption bands, to a large degree in the visible region, are characteristic of the lanthanide series - a series whose properties are ascribed largely to the 4f electrons. The absorption spectra of aqueous tripositive actinide elements are strikingly similar to the spectra of the tripositive lanthanide elements; thus lending support to the concept that 5f electrons are involved in the building up of the actinide group. It has also been observed that the absorption spectra become greatly simplified as the middle of each of the two series is approached. The spectra for gadolinium and curium, each with seven f electrons, show only one sharp peak between 2000 and 11,000 A°, whereas for the other elements of both series the spectra are more complex. Absorption spectra with crystals, especially those of americium halides, reveal sharp lines with widths comparable to the sharpest rare earth spectra.

C. Crystallographic structure data: Zachariasen has observed the isomorphism of the compounds ThO_2, PaO_2, UO_2, NpO_2, PuO_2 and AmO_2, and a regular decrease in radius of the metallic ion in these oxides. He has also used x-ray diffraction studies to determine the structure of a large number of compounds of Th, U, and the transuranium elements. The fluorides ThF_4, UF_4, NpF_4 and PuF_4 are of identical structure types as are the chlorides UCl_3, $NpCl_3$, $PuCl_3$ and $AmCl_3$. Calculations of ionic radii show a progressive decrease in size with increasing atomic number, analogous to the well-known lanthanide contraction. The compounds of the rare-earth elements are in turn isomorphous with the corresponding compounds of the actinide elements. The following table illustrates these considerations:

crepancies between chemical properties and electronic structure come about because of the slight difference in energy between the 5f and 6d levels. Coryell (5) suggests that these discrepancies may be resolved by recognition of a delay in the filling of the 5f subshell.

Conclusion: On the basis of the present evidence, both chemical and electronic, and the opinions of various qualified workers, the views of Coryell seem to be more rational. The heavier elements constitute a "uranide" series rather than an "actinide" series. The periodic classification, in part, would appear thusly:

La				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
	Hf	Ta	W									
	Th	Pa	U				Np	Pu	Am	Cm	Bk	Cf
Ac												

Note: As a tool in remembering the elements in the two series, the following mnemonics may prove useful:

Lancer prince needs 61 small European gods to be dyed wholly early tomorrow. Why be ludicrous?

Actual thoughts pass under Neptune's public amnesty, calming balky coffles.

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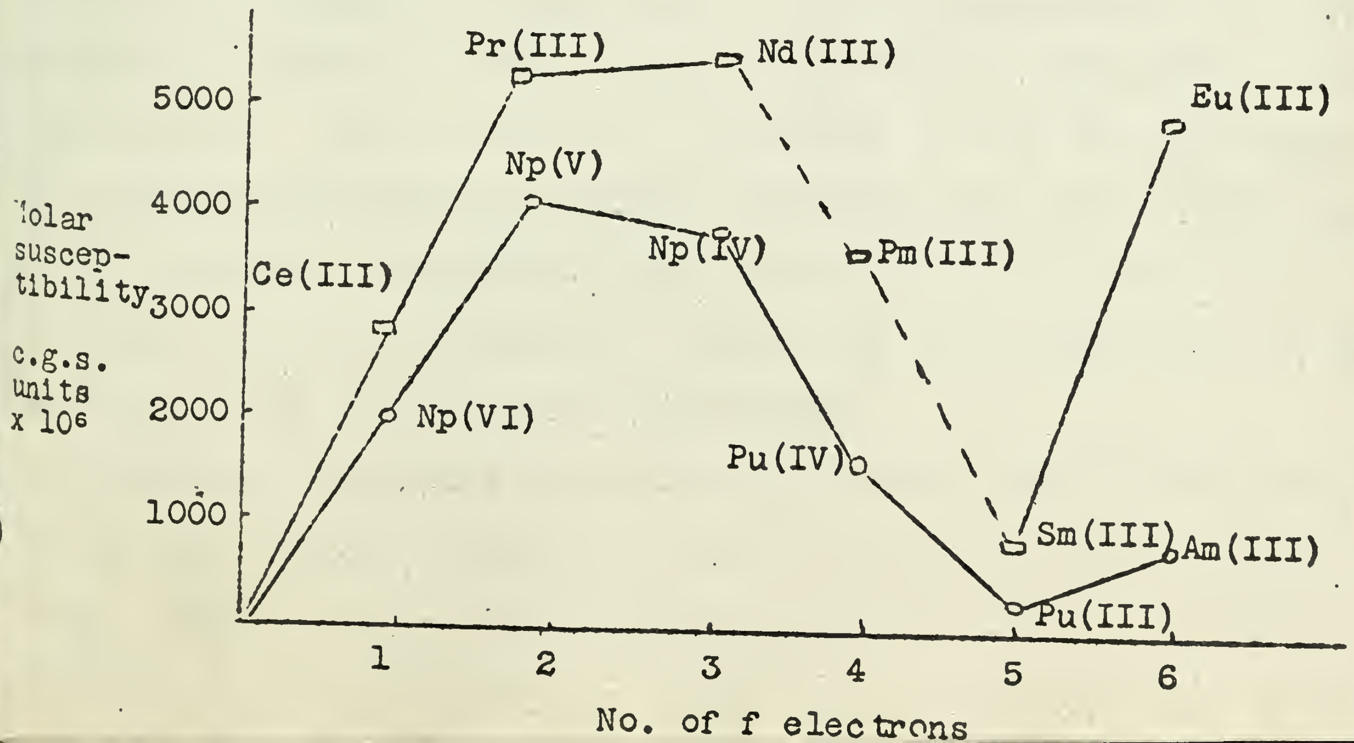
Ionic radii of actinide and lanthanide elements

No. of 4f or 5f elns.	Actinide series III state		Actinide series IV state		Lanthanide series	
0	Ac^{+3}	1.11 A°	Th^{+4}	0.95 A°	La^{+3}	1.04 A°
1	(Th^{+3})	(1.08)	Pa^{+4}	0.91	Ce^{+3}	1.02
2	(Pa^{+3})	(1.06)	U^{+4}	0.89	Pr^{+3}	1.00
3	U^{+3}	1.04	Np^{+4}	0.88	Nd^{+3}	0.99
4	Np^{+3}	1.02	Pu^{+4}	0.86	Pm^{+3}	(0.98)
5	Pu^{+3}	1.01	Am^{+4}	0.85	Sm^{+3}	0.97
6	Am^{+3}	1.00			Eu^{+3}	0.97

D. Magnetic susceptibility: One would expect magnetic measurements on compounds of the heaviest elements to give information on the quantum states of the responsible electrons. However, the situation is complex, and the exact behavior of the heaviest elements on the basis of either 5f or 6d electrons has not yet been worked out. Yet, qualitatively speaking, observed paramagnetic behaviors of a number of ions in various oxidation states are similar to those of the lanthanide group. The following figure brings out these qualitative similarities:



E. Spectroscopic data: Information in this field is still rather scarce as far as the heaviest elements are concerned. Investigation of the spectrum of uranium atoms gave the lowest state of neutral uranium as $5f^3 6d^1 7s^2$, a consistent configuration since uranium is the third element in the series. Observations on gaseous Th^+ indicate that the 5f and 6d electrons are very close in the neutral, free thorium. Qualitative comparisons of the emission spectra of americium and europium show a strong analogy between the intensity of the lines, thus suggesting strongly that the configuration for gaseous Am in the ground state should be $5f^7 7s^2$.

Arguments against the "actinide" series (3,4,5):

On the basis of observations that the heavier elements exhibit both +3 and +4 oxidation states, Zachariasen prefers to speak of a "thoride" series for the tetravalent states and of an "actinide" series for the trivalent states.

Thorium has been shown to be a true homologue of zirconium and hafnium. The great instability in aqueous solution of the triidides of thorium, zirconium and hafnium is in marked contrast to the stability of cerium triiodide. Protactinium is similarly a homologue of niobium and tantalum. Ease of oxidation of uranium to the +6 state brings out its strong resemblance to tungsten and emphasizes its lack of similarity to neodymium. Uranium is most stable in the +6 state; if it were to be regarded as an "actinide", similar to the lanthanides, it should exist primarily in the +3 oxidation state.

Seaborg's arguments leading to the designation of the series as the actinide series, insofar as they are based on direct chemical evidence, would involve an extrapolation backward from the proposed $5f^6$ configuration for americium +3 and $5f^7$ for curium +3. Some of the di

Complex Anion Determination by Ion Exchange

H. K. Snyder March 10, 1953

While measuring the potential of cadmium amalgam electrodes, Leden (3) found evidence for the formation of an anionic cadmium sulfate complex. Fronaeus (2) calculated that the copper in a 0.01 $\underline{M}$ copper sulfate solution made 0.5 $\underline{M}$ with respect to sodium sulfate is present as an anionic complex, to the extent of eighty per cent. In order to clarify this situation, Leden (4) studied these complexes with ion exchangers.

For the study, Amberlite IRA 400 was used. In the first experiments, solutions of cadmium perchlorate, sulfate, chloride, and iodide were put through a column containing the resin in the perchlorate, sulfate, chloride or iodide form. Then the resin was washed with 10 ml. of water followed by successive 25 ml. portions of water. The number of 25 ml. portions necessary to remove all of the cadmium from the resin was used as an indication for the formation of anionic complexes. The results are shown in Table 1.

Table 1

Expt. No.	Resin was Saturated by:	Conc. of 10 ml. of Cd solution influent	No. of Portions
1.	$3\underline{M}$ $NaClO_4$	$0.01\underline{M}$ $Cd(ClO_4)2$	1
2.	$2\underline{M}$ Na_2SO_4	$0.01\underline{M}$ $CdSO_4$	1
3.	$2\underline{M}$ Na_2SO_4	$0.01\underline{M}$ $CdSO_4$ and $0.5\underline{M}$ Na_2SO_4	1
4.	$3\underline{M}$ NaCl	$0.01\underline{M}$ $CdCl_2$	6
5.	$3\underline{M}$ NaCl	$0.01\underline{M}$ $CdCl_2$ and $0.5\underline{M}$ NaCl	8
6.	$3\underline{M}$ NaI (?)	$0.01\underline{M}$ CdI_2	-

In experiment six of this series, the cadmium could not be removed at all. It was also shown that cadmium is entirely removed from a solution of cadmium iodide when it is shaken with the resin. Since these data indicate that cadmium sulfate forms an anionic complex to no greater extent than cadmium perchlorate, it seems likely that previous indications for the formation of such a species were erroneous.

Similar experiments were carried out with copper perchlorate, sulfate, chloride, and acetate, with the exception that the washing was done with successive 10 ml. portions of water. The results are given in Table 2.

Table 2

Expt. No.	Resin was Saturated by:	Conc. of 10 ml. of Cu solution influent	% Cu in successive 10 ml. portions of effluent						
			1	2	3	4	5	6	7
1.	5M $NaClO_4$	0.01M $Cu(ClO_4)2$	5	75	20				
2.	0.7M Na_2SO_4	0.01M $CuSO_4$	15	60	25	1			
3.	0.7M Na_2SO_4	0.01M $CuSO_4$ and 0.5M Na_2SO_4	35	40	20	3	0.3		
4.	5M NaCl	0.01M $CuCl_2$	10	80	10				
5.	5M NaCl	0.01M $CuCl_2$ and 0.5M NaCl	15	60	25	1			
6.	3M NaAc	0.01M $CuAc_2$	5	65	25	5	1	0.1	
7.	3M NaAc	0.01M $CuAc_2$ and 0.5M NaAc	0	55	30	10	3	1	0.3

For the influent in experiments 2, 3, 6, 7, Fronaeus (2) has calculated that the per cent of copper in an anionic complex is 0.1%, 80%, 0.5%, 50% respectively. Similarly for the influent in experiment 5, Bjerrum (1) has calculated that 0.02% of the copper is present as an anion. Apparently there is little formation of an anionic complex of copper sulfate, at least not as much as Fronaeus had previously assumed.

Salmon (5) used ion exchange methods to study the complexes which are formed between ferric ion and orthophosphate. Since both cationic and anionic complexes have been reported in the literature, both types of exchangers were tried. However, Permutit Zeo-Karb 225, the cation exchanger, removed nearly all of the iron from solution, but no phosphate. Either no cationic species were present, or if they were present, they were very unstable. In further preliminary studies, unsaturated solutions of iron in phosphoric acid were put through columns with the Zeo-Karb and then through the chloride form of the IRA 400. The process was then reversed. Results are summarized in Table 3. These data seem to indicate an easily displaced equilibrium between ferric ion or a cationic complex and an anionic complex.

Table 3

SOLUTION			COLUMNS		% Fe in		
$\underline{M}P_2O_5$	$\underline{M}Fe_2O_3$	Ml. Used	1st	2nd	Z.K.	IRA	Effluent
0.16	0.001	25.00	ZKH	---	100	---	---
0.16	0.001	50.00	ZKH	---	97	---	---
1.13	0.066	5.85	ZKH	ZKH	100	---	---
0.7	0.015	10.20	ZKH	IRACl	98	2	nil
1.8	0.067	5.10	ZKH	IRACl	96.5	3.5	nil
1.5	0.046	5.00	IRACl	ZKH	82	18	nil
1.13	0.066	5.01	IRACl	ZKH	79.6	18.4	2
1.8	0.067	5.00	IRACl	ZKH	82	17	1
1.13	0.066	6.00	$IRAPO_4$	ZKH	30	70	---
1.13	0.066	6.65	$IRAPO_4$	$IRAPO_4$	---	99	1
1.13	0.066	55.00	$IRAPO_4$	$IRAPO_4$	---	100	---

Further anion exchange was carried out with the phosphate form of IRA 400 which was left in contact with saturated ferric phosphate for 1-8 weeks. After filtering, the resin was washed in a column with water and then eluted with 2N HCl. The eluate was analyzed for iron and phosphate. Table 4 shows the results.

Table 4

SOLUTION				ADSORBED ON RESIN		
% P_2O_5	% Fe_2O_3	$\frac{P_2O_5}{Fe_2O_3}$	Ml. Used	mg. P_2O_5	mg. Fe_2O_3	$\frac{P_2O_5}{Fe_2O_3}$
31.3	4.77	7.37	6.00	548	181	3.4
29.1	4.95	6.60	7.25	708	238	3.4
26.6	5.31	5.65	6.70	645	260	2.8
18.0	2.25	9.01	6.00	563	179	3.5
9.08	0.59	17.3	6.01	575	143	4.5
6.07	0.11	60.5	6.00	598	76	8.8

The minimum value approached by the P_2O_5/Fe_2O_3 ratio at approximately 25% P_2O_5 was interpreted as an indication that the anionic complex under these conditions contains three phosphate groups for each iron atom. The increase beyond 25% P_2O_5 may be due to one of two things, viz., the increase in concentration of H_3PO_4 results in increasing competition of the phosphate for the resin or complexes with increasing numbers of phosphate groups may be formed.

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THE NATURE OF THE FRIEDEL-CRAFTS COMPLEX

Clayton T. Elston   March 17, 1953

Since the original publications of Friedel and Crafts (1) the literature dealing with the reaction has grown to quite extensive proportions and has been the subject of numerous reviews (2). Early investigators assumed that the reaction involved an intermediate organo-aluminum compound, followed by coupling of this material with the alkyl halide. This and related theories were later shown to be untenable. Further studies also revealed that many other compounds are capable of catalyzing the reaction between alkyl halides and aromatic compounds. Examples are: $FeCl_3$, $SnCl_4$, $TiCl_4$, $BiCl_3$, $ZnCl_2$, BF_3, and H_2SO_4. In general, any compound whic has strong acid character (Lewis Definition) exhibits catalytic activity. In an attempt to explain this activity the binary syste aluminum halide-alkyl halide and aluminum halide-aromatic hydrocarbon and the ternary system aluminum halide-alkyl halide-aromatic hydrocarbon, will be discussed.

Carefully purified ethyl bromide is practically nonconducting ($k = 3 \times 10^{-9}$ mhos). On the addition of $AlBr_3$ the conductivity increases with increasing concentration to about $k = 1.21 \times 10^{-4}$ mhos for a 20% solution of $AlBr_3$. Plotinkoff (3) was the first to study the electrolysis of solutions of $AlBr_3$ in ethyl bromide. Using aluminum electodes he found that metallic aluminum deposited on the cathode. Similar results were obtained by other investigators. Wertyporoch (5) studied the same system using platinum electrodes but his results were inconclusive. He found that the aluminum concentrations in the neighborhood of the cathode and anode were almost equal. He also reported that a noticeable separation of aluminum occurred at the anode. A recent study on this system has given somewhat different results (6). It was found that the principal electrode reactions are the deposition of metallic alumi at the cathode and liberation of bromine at the anode. The alumin concentration in the anode compartment remains almost constant; a reduction in the aluminum concentration occurs in the cathode compartment. On the basis of these data it would appear that the aluminum is present in solution in both the anionic and cationic form. The simplest explanation would involve equilibria such as t following.

$$AlBr_3 \rightleftharpoons [AlBr_2]^+ + Br^-$$

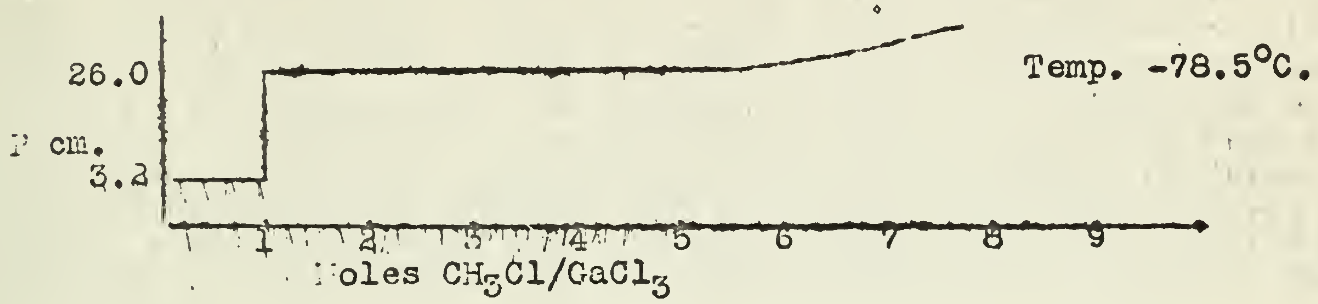
$$2AlBr_3 \rightleftharpoons [AlBr_2]^+ + [AlBr_4]^-$$

$$R\text{-}Br + AlBr_3 \rightleftharpoons R\,Br\cdot AlBr_3 \rightleftharpoons R^+ \quad [AlBr_4]^-$$

Vapor pressure studies on the system metal halide-alkyl hal have given evidence for complex formation of the type.

$$CH_3Cl + GaCl_3 \rightleftharpoons CH_3ClGaCl_3$$

Brown (7) reports the following vapor pressure-composition diagram for the system $GaCl_3$-CH_3Cl. Van Dyke (6) obtained no evidence for such complex formation with the system $AlBr_3$-C_2H_5Br but his results are inconclusive.



Positive evidence for the equilibrium, $R_3CCl + AlCl_3$ $R_3CCl \cdot AlCl_3$ is furnished by the rapid racemization of optically active alkyl halides in the presence of $AlCl_3$. Similarly when $AlCl_3$ containing labelled chlorine was used as a catalyst for the reaction of benzene with t-butyl chloride it was found that complete interchange of chlorine atoms had occurred (8).

Although several workers (6)(9) have reported the formation of complexes between aluminum halides and aromatic hydrocarbons the existence of stable complexes is still questionable. Such complexes if formed, would appear to involve only weak attractive forces. Their role in the Friedel-Crafts reaction is uncertain but is probably a very minor one.

Benzene has a very small specific conductance ($k = 1 \times 10^{-13}$ mhos at 25°C.) and upon addition of aluminum halide there is no noticeable increase in conductivity. However, addition of alkyl halide or halogen acid to such a solution produces a very marked change (10). The solution becomes colored and as the concentration of the alkyl halide (or halogen acid) is increased a second liquid phase separates. The lower phase is highly colored and strongly conducting ($k = 1 \times 10^{-2}$ mhos) while the upper phase is only slightly colored and weakly conducting ($k = 1.9 \times 10^{-5}$ mhos). The reactions involved were found to be reversible since removal of the halogen acid yielded a homogeneous system which could be further separated into pure aluminum halide and hydrocarbon.

In studying the system aluminum chloride-toluene-hydrochloric acid, Brown (11), found that $AlCl_3$ dissolves in toluene in the presence of HCl to give a brilliant green solution. Relating solubility of $AlCl_3$ to the pressure of HCl above the solution at -80°C. they found that as a limiting case approximately one mole of HCl is taken up for each mole of $AlCl_3$ which goes into solution. At -45°C. one mole of HCl is taken up for every two moles of $AlCl_3$. They suggest that the Friedel-Crafts complexes are organic salts of the hypothetical acids $HAlCl_4$ and HAl_2Cl_7. The high solubility

$$Ar + HCl + AlCl_3 \rightleftharpoons ArH^+ \; AlCl_4^-$$

of $AlCl_3$ in such complexes would tend to indicate that complexes of

a higher order are also possible. The general formula would be $ArH^+ [Al_nX_{3n+1}]^-$. It should be noted that results of various workers (7)(8) have shown that there is no evidence for an acid of the type $HAlCl_4$ or $HAlBr_4$. Studies of the system AlX_3-HX over a wide range of temperatures (-120° to 300°C.) revealed that the pressure of HX is not affected by the presence of AlX_3. It would thus be extremely improbable if a detectable concentration of the free acid could exist under the conditions of the Friedel-Crafts reaction. The exchange between labelled $AlCl_3$ and HCl at low temperatures offers a means of estimating the equilibrium concentration of $HAlCl_4$ and such an investigation is now being conducted by Professor Benson

$$AlCl_3^* + HCl \rightleftharpoons AlCl_3 + HCl^*$$

at the University of Southern California.

The electrolysis of the ternary complex aluminum bromide-ethyl bromide-benzene using an aluminum anode has been shown to be an efficient method for aluminum plating (12). The overall electrode reaction is the solution of aluminum at the anode and the deposition of aluminum at the cathode. It seems reasonable to assume that $AlBr_3$ could behave as a 1:3 electrolyte when dissolved in the highly polar complex phase. Wertyporoch (5) studied electrical transference in the system aluminum bromide-ethyl bromide-hexaethylbenzene and found that aluminum concentrates in the anode compartment, while bromine and hexaethylbenzene concentrate in the cathode compartment. Such data substantiate the formulas proposed by Brown.

Brown (11) assumes that the formation of the ternary complex is involved in the rate-controlling step of the Friedel-Crafts reaction. The highly polar complex phase, which is capable of dissolving an excess of any of its three components would presumably furnish an excellent medium for the ionic reactions involved.

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ACID-BASE BEHAVIOR IN INERT SOLVENTS

March 24, 1953 Daryle H. Busch

Introduction. At the turn of the century, the ionization theory of acids and bases was commonly believed to apply to all solvent systems. Substances such as hydrogen chloride were not considered to be acids in solvents which produced no ions. In 1902, Kahlenberg (31) reported several ionic type reactions in benzene. Shortly thereafter, Vorlander (43) carried out the titration of aniline with hydrogen chloride in benzene using methyl yellow as an indicator. These and similar developments led a number of investigators to suspect that ionization is not a necessary condition for acid character.

Methods Employed in the Study of Acids and Bases in Aprotic Media.

Hantzsch was of the opinion that a more broadly valid criterion for acid strength than "hydrogen ion concentration" could be found in the relative tendencies of acids to form salts with indicator bases. A technique was developed for describing the relative strengths of acids in terms of the stabilities of such salts. (21)(22)(29) Hantzsch and his co-workers also measured the catalytic effects of different acids on the rate of inversion of succrose and the rate of decomposition of diazoacetic ester and related these rates to the intrinsic strengths of the acids. (21)(22)(26) They found that the acids were commonly stronger in this respect in inert solvents such as benzene and chloroform than in basic media like water.

The investigations carried out by LaMer and Downes (36)(37)(38) are especially significant in demonstrating the use of indicator methods in determining the relative strengths of acids and bases in aprotic media. In the ideal case, HA is considered to react with a base B to produce a much weaker acid HB in the presence of an indicator I. The indicator is partially converted to its acid form HI. From a consideration of the acidity constants for the acids HA, HB, and HI the following expression is derived:

$$\log [A]/[HA] = \log [I]/[HI] - pK_{HA} + pK_{HI}$$

A plot of log [A]/[HA] against log [I]/[HI] then gives a family of parallel straight lines with unit slopes whose intercepts on the log [I]/[HI] axis give a measure of the strengths of the acids as compared to the indicator HI.

An extensive investigation of the reaction of various organic bases with indicator acids in inert media has been undertaken by Davis and her associates. The technique employed is best characterized as a spectro-photometric titration of an indicator acid with a basic material. The relative strengths of a series of bases have been determined and association constants corresponding to the reaction shown below were measured.

$$B + HA \rightleftharpoons BH^{+}\ldots A^{-}$$

Two indicators were synthesized during the early phases of these studies (9); bromphthalein magenta E (tetrabromophenolphthalein

ethyl ester) and bromphthalein magenta B (tetrabromophenolpthalein n-butyl ester). These indicators are more soluble in aprotic media and often give simpler color changes (10) than the more familiar indicators.

A parameter representing the true strengths of bases in combination with a standard indicator acid is found in the association constant, K_a, for the reaction mentioned above.

$$K_a = \frac{[BHA]}{[B][HA]}$$

From this expression the equation below is obtained.

$$\log [BHA]/[HA] - \log [B] = \log K_a$$

The association constant may be evaluated by plotting log [BHA]/[HA] against - log [B]. In order for K_a to be valid, the plot should be a straight line with a negative slope equal to unity. The validity of the results may be judged from Table 1 below. (9)

Table 1

Organic Base	Log K_a	K_a	Slope of Curve
di-n-butylamine	4.19	$1.5x10^4$	-1.17
triethylamine	4.36	$2.3x10^4$	-1.03
piperidine	5.08	$1.2x10^5$	-1.08
diphenylguanidine	5.35	$2.2x10^5$	-1.03
ditolylguanidine	5.80	$6.3x10^5$	-1.23

Another type of information which has been obtained by Davis et al stems from the nature of the color changes which the indicator undergoes upon addition of a base. These color changes provide some insight into the nature of the chemical reactions which are taking place. All of the changes observed may be explained on the basis of three assumptions:
1. The yellow color of solutions of bromphthalein magents (BPM) in aprotic media is characteristic of the neutral, unsolvated, and non-ionized acid form of the indicator. 2. The blue color of solutions of tetraalkylammonium salts of BPM in aprotic solvents is characteristic of the BPM anion when it is associated with the positive constituent of the salt only through coulombic attraction. 3. The magenta color of solutions of BPM containing an excess of a tertiary amine is characteristic of a highly polar addition compound formed by incomplete removal of the proton from the indicator anion (a hydrogen bridge exists between the amine and the anion).

The shift in color from that represented by the primary addition compound formed by a primary, secondary, or tertiary amine with the acid indicator to the color characteristic of the coulombically bonded tetraalkylammonium salt in basic solvents or upon the addition of a small amount of a basic solvent to a solution in an inert medium may be explained similarly with the generalized mechanism.

$$B + HA \rightleftharpoons BH^{+}\ldots A^{-} + B' \rightleftharpoons (BH^{+}\ldots B')\ A^{-}$$

It also follows that the stability of the color characteristic of the primary reaction, when an indicator acid is dissolved in a basic solvent of very large steric requirements, stems from the reaction of one molecule of base to form a highly polar addition compound whose hydrogen bridge is so shielded by the large solvent molecule that the secondary reaction, breaking of the hydrogen bond between the anion of the acid and the cation by the action, of the second solvent molecule, cannot be accomplished. This sort of phenomenon finds support in the studies of Brown and his co-workers who showed that when the steric requirements of an acid and base pair are too large no reaction can occur. (9)(18)

Theoretical Significance of Studies in Aprotic Solvents. Although it is probable that no solvent of practical value is completely devoid of acidic or basic character, solvents such as hydrocarbon halogenated and partially halogenated hydrocarbons may be considered to have neither acidic nor basic properties since their relative tendencies to behave either as acids or as bases are much smaller than is the case with the substances which are under study.

The factor which would be most significant in its effect on the measurable properties of acids and bases and their salts in aprotic media is the dielectric constant of the solvent. The effect of dielectric constant on the behavior of acids and bases and their salts has been studied by Bronsted,(7) by Hammett,(20) and by Kraus and Fuoss.(32) Kraus (34) reported that the properties of an acid in an inert solvent are largely dependent on the quantum forces between the proton and the anion. The role played by the dielectric properties of the solvent was found to be relatively slight. Other investigators (1)(2)(16) report that a solvent of higher dielectric constant than is known would be required to dissociate an acid without the formation of a new chemical bond. Kraus (34) and Hammett (20) have shown that the degree of dissociation of a salt depends on the dielectric constant of the medium. In benzene, ion pairs would be expected to form.(4)(33) The interionic attraction theory relates the dielectric constant of the medium to activity coefficients.(3)

The Mechanism of Acid-Base Reactions. Bronsted (7) envisions the combination of two hypothetical half reactions to produce neutralization. No mechanism for the exchange of the proton is offered.

The Lewis theory arrives at the same final result by presuming that the reaction involves contact of the Base A with the acid HB. The intermediate compound is supposed to have only a transient existence since it is considered unrealistic to suppose that a proton can share two pairs of electrons simultaneously.(39)

Demonstration of the formation of the hydrogen-bonded addition compound as the first product of the reaction of a hydrogen acid with an amine provides a link between the Lewis and Bronsted theories In fact, this scheme presents a unique case of neutralization in the Lewis concept only because of the high polarity of the compound formed. The evidence cited in support of the existence of this addition

compound is: (13) (a) Ionization is unimportant in the reaction; (b) It is possible to calculate an equilibrium constant for the reaction assumed; (c) Spectrophotometric evidence makes it possible to identify the species with the conditions under which it exists; (d) The "salts" formed in these reactions have dipoles quite similar to those found for the more obvious products of Lewis acid-base reactions.

The two-stage mechanism proposed by Davis and co-workers is represented by the scheme below. (13)

$$\underset{\text{yellow}}{R_3N + HI} \rightleftharpoons \underset{\text{magenta}}{R_3NH^+ \ldots I^-}$$

$$\underset{\text{magenta}}{R_3NH^+ \ldots I^-} + R_3N \rightleftharpoons \underset{\text{blue}}{(R_3NH^+ \ldots NR_3)I^-}$$

The first equation represents the formation of a hydrogen bond. The second equation represents rupture of the old hydrogen bond, which joined equal and opposite charges, and the formation of a new hydrogen bond with the incidental effect that ion pairs are produced.

From less thorough investigations, the effect of acid molecules on the process of neutralization may be inferred. Maryott (40) observed that an excess of acid increases the conductance of solutions of salts of carboxylic acids and sulfonic acids in inert media. The effect is too sensitive to be attributed to the change in dielectric constant of the solution accompanying salt formation. Since cryoscopic data(42) obtained for a related system indicates complex formation between carboxylic acids and their salts in inert solvents, it was proposed that the anion, $RCOO^-$, of the salt forms a dimer with a molecule of acid. The species formed would be somewhat analogous to the ordinary dimeric structure of the free acid in an inert solvent.

Inasmuch as no solvent has been found which possesses acidic but not basic properties and since autoprotolysis of such strong acid solvents as sulfuric acid and hydrofluoric acid has been demonstrated (3) the scheme appears to be quite reasonable. This leads to the conclusion that the dissolution of a base in an acidic solvent follows a two step equilibrium.

<u>The Relative Strengths of Acids and Bases</u>. The recognition that water and other basic solvents exert a leveling effect(18)(25) on the strengths of acids in solution has been instrumental in causing various investigators to study acid strengths in aprotic solvent The leveling effect may be demonstrated by the addition of water to solutions of various acids (29) in aprotic media. Such an experiment would reveal that the relative acidities of the weaker acids are increased while those of the stronger acids are decreased. In gener the restriction posed by the leveling effect is that no acid may exist in a basic solvent whose proton donating tendency exceeds that of the onium ion of the solvent. It is obvious in view of this limitation that the strengths of the stronger acids must be measured in solvents of very slight basic character.

The most common method of measurement of the strengths of acids in aqueous solutions is by determining the electromotive force with an electrode reversible to hydrogen. The electrode potential as a criterion for acidity is independent of the interpretation given to it by the Bronsted theory. It is the activity of hydrogen which is measured in this manner, and this activity is not necessarily parallel with the concentration of hydrogen or hydronium ions. It is, to the contrary, a measure of the reversible work required to transfer a proton from one given base to another. In the ideal case, (5)(20)(38) the hydrogen electrode potential would provide the means for extending the precise measurement of acid and base strengths to all solvents. This is not feasible at the present because of such complicating factors as liquid junction potentials (22)(23) and individual ion activities.(24)

In attempting to measure the relative strengths of acids in aprotic media, methods based on colorimetric or spectrophotometric techniques have proven most fruitful.(6)(17)(21)(28)(38) The formulation most often used is essentially that given by LaMer and Downes; this analysis follows the Bronsted theory. Table 2 lists series of acids in the order of their decreasing strengths as observed by several investigators. The values of pK are given for two of the series. These parameters differ in their numerical values primarily because different arbitrary standards were chosen by the respective investigators. The general trends are the same.

LaMer and Downes(37)(38) have demonstrated an ingenious technique for setting up a series of relative acid strengths based on indicator studies in inert solvents. This method also involves the Bronsted scheme for the acid-base reaction. These investigators found that their indicator method was limited, for any given indicator, to those acids whose pK values differed by plus or minus one unit, or less, from the pK value of the indicator. They then pointed out that, if the relative acidities of two indicator systems could be established, the acid systems studied with these two indicators could then be compared. For example, dichloroacetic acid is weaker than dimethyl yellow but stronger than bromphenol blue. The experimental curves for these two indicators can then be displaced along the log [I]/[HI] axis of a graph of log [A]/[HA] against log [I]/[HI] until they become continuous. By a stepwise correlation of indicators in this manner it is possible to establish a complete numerical scale for all the acids.

A number of investigators (4)(14)(15)(27)(28)(30)(35) have concluded that the primary reaction which takes place between a base and a proton acid culminates in the formation of a highly polar addition compound. The extent to which this reaction proceeds may be measured and an equilibrium constant may be calculated. Table 3 lists the systems which have been studied and gives the association constants for this primary reaction.

Table 2

Relative Acid Strengths

Investigator	Bronsted(6)	Hall(19)	Hantzsch(21)(22)	Hantzsch(26
Method	Indicator	pKd	Indicator	Inversion of Sugar
Solvent	Benzene	Water	Chloroform	Water
	hydrochloric	-7.4	perchloric	hydroiodic
	methyl red	4.9	sulfonic acids	perchloric
	dimethyl yellow (ion)	3.5	hydrobromic	bydrobromic
	trichloroacetic	0.7	hydrochloric	benzene-sulfonic
	dichloroacetic	1.3	nitric	hydrochlori
	picric	0.3	trichloroacetic	nitric
	o-nitrobenzoic	2.3	tribromoacetic	trichloro-acetic
	chloroacetic	2.9	maleic	sulfuric
	salicylic	3.0	malonic	chloroaceti
	bromphenol blue	4.1	chloroacetic	formic
	b-dinitrophenol	3.7	a-bromopropionic	acetic
	o-chlorobenzoic	2.9	bromoacetic	
	neutral red (ion)	6.9	formic	
	m-chlorobenzoic	3.8	b-iodopropionic	
	bromcresol green	4.7	acetic	
	benzylammonium ion	9.4		
	formic	3.7		
	phenylacetic	4.3		
	benzoic	4.2		
	acetic	4.7		
	isoamylammonium ion	10.6		
	bromcresol purple	6.3		
	piperidinium ion	11.1		
	bromthymol blue	7.0		

Investigator	LaMer and Downes(38)		Griffiths(17)	
Method	Indicator		Indicator	
Solvent	Benzene		Chlorobenzene	
	Acid	pK	Acid	pK
	methyl red	0.55	bromphenol blue	3.46
	trichloroacetic	0.55	trichloroacetic	3.37
	propyl red	0.7	dichloroacetic	2.52
	dimethyl yellow	0.8	chloroacetic	0.77
	dichloroacetic	1.7	salicylic	0.74
	salicylic	2.6	dinitrophenol	0.00
	chloroacetic	2.8	benzoic	-0.58
	bromphenol blue	3.2	acetic	-1.00
	bromcresol green	3.4	propionic	-1.08
	formic	3.7		
	benzoic	4.5		
	neutral red	4.6		
	acetic	5.2		
	diethylammonium ion	5.5		

Table 3

Association Constants, K_a, and Dissociation Constants, K_d, for Primary Acid-Base Reactions in Inert Solvents.

ase	Acid	Solvent	K_a	K_d
ribenzylamine (11)	trinitro-m-cresol	benzene	450	--
riphenylguanidine (13)	bromphthalein magenta E	benzene	525	--
ribenzylamine (11)	picric acid	benzene	1,600	--
i-n-butylamine (9)	bromphthalein magenta E	benzene	15,500	--
riethylamine (9)	bromphthalein magenta E	benzene	23,000	--
riethylamine (9)	bromphthalein magenta B	benzene	23,000	--
iperidine (9)	bromphthalein magenta E	benzene	120,000	--
iphenylguanidine (13)	bromphthalein magenta E	benzene	220,000	--
iphenylguanidine (9)	bromphthalein magenta B	benzene	220,000	--
i-o-tolylguanidine (9)	bromphthalein magenta E	benzene	860,000	--
i-o-tolylguanidine (9)	bromphthalein magenta B	benzene	860,000	--
,N-dimethylaniline (12)	hydrogen chloride	$CHCl_3$	67,000,000	--
niline (35)	picric acid	$C_6H_5NO_2$	125	2×10^{-5}
imethylaniline (35)	picric acid	$C_6H_5NO_2$	4,000	4.1×10^{-5}
yridine (35)	picric acid	$C_6H_5NO_2$	61,300	5.54×10^{-5}
rimethylamine (41)	sulfur dioxide	benzene or $CHCl_3$	525	--

Equilibrium Constants, K_2, for the Secondary Reaction of Acids and Bases

Base	Acid	Solvent	K_2
iphenylguanidine (14)	bromphthalein magenta	benzene	15.5
riphenylguanidine (14)	bromphthalein magenta	benzene	22.5

A second measurable equilibrium has been demonstrated by Davis and Hetzer.(13)(14) This equilibrium measures the extent to which the addition compound $BH^+...A^-$ is solvated and dissociated into ion pairs by one mole of base B', which may be the same as or different from the base B. The values of the equilibrium constants reported for the two secondary reactions studied by Davis and Hetzer are listed in Table 3.

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METAL-DIAMINE CHELATE COMPOUNDS CONTAINING HIGHER-MEMBERED RINGS

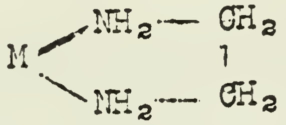
William E. Cooley March 31, 1953

I. Introduction

It is well known that nitrogen atoms in amines readily act as electron pair donors in coordinating with certain metal ions. Many stable complex compounds contain coordinated ammonia or amine molecules. Even greater stability results from coordination of ethylenediamine or its homologs, since formation of a chelate ring takes place. Chelate rings having five or six members appear to be much more stable than larger rings, with respect to their resistance to hydrolysis in water solution and decomposition by heat.

II. Five-membered Rings

Ethylenediamine (en) and substituted ethylenediamines form five-membered chelate rings with metal ions.



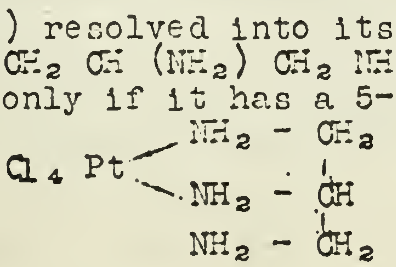
M= Co, Cr, Pt, Ni, Cu, Fe, etc.

Substituted groups on the carbon atoms of ethylenediamine usually have little effect on the color, stability, or method of preparation of these complexes. Solubility in water is sometimes increased by the addition of such groups; the propylenediamine (pn) and 2, 3-butylenediamine (bn) complexes of cobalt are more soluble than their ethylenediamine homologs. (1) Cyclopentanediamine (1), cyclohexanediamine (5), iso-butylenediamine (ibn) (9), and meso-stilbenediamine (1) have also been used as chelating ligands.

III. Six-membered Rings

Increasing to three the number of carbon atoms between the amine groups lowers the stability of diamine chelates. Pfeiffer and Haimann (10) were unable to prepare chromium complexes with trimethylenediamine (tn) by the same reaction which they found to give good yields of ethylenediamine and propylenediamine chelates. Bailar, Rollinson, and Work (1, 15) likewise found that anhydrous ethylenediamine and anhydrous chromium (III) sulfate react to form $[Cr\ en_3]_2-(SO_4)_3$, but that anhydrous trimethylenediamine does not undergo a parallel reaction.

Mann and Pope (7) resolved into its optical antipodes the chelate compound $[Cl_4\ Pt\ NH_2\ CH_2\ CH\ (NH_2)\ CH_2\ NH_2]$. Resolution of this compound is possible only if it has a 5-ring structure.



Coordination in the 1 and 3 positions would yield a symmetrical 6-ring.

It is possible, however, to produce six-membered chelate rings. Tschugaeff (17) reported that addition of trimethylenediamine to nickel disuccinimide 8-hydrate resulted in the formation of a violet, water-soluble complex compound, $[\mathrm{Nitn_3}]$ (succinimide)$_2 \cdot 2H_2O$. Also prepared by Tschugaeff (19) were the blue-violet crystalline compound $[\mathrm{Ni\ tn_2}]SO_4$ and the unstable red-violet $[\mathrm{Nitn_3}]SO_4$. The chloroplatinite salt of $[\mathrm{Nitn_3}]^{++}$ is more stable and may be formed from nickel (II) chloride in water solution, trimethylenediamine, and potassium chloroplatinite.

Werner(21) prepared bis-trimethylenediamine complexes of cobalt (III) by the same methods used for bis-ethylenediamine complexes.

Tschugaeff(19) and Drew and Tress(4) found that addition of trimethylenediamine to a water solution of potassium chloroplatinite at room temperature produces yellow $[\mathrm{Pttn\ Cl_2}]$. At higher temperatures $[\mathrm{Pttn_2}][\mathrm{Pt\ Cl_4}]$ is formed.

Breuil(2) added trimethylenediamine to ferrous chloride, ferrous bromide, and ferrous iodide in anhydrous methyl alcohol. With the work carried out in a hydrogen atmosphere, the corresponding tris-diamine complexes, $[\mathrm{Fetn_3}]X_2$, were formed. These compounds decompose in air.

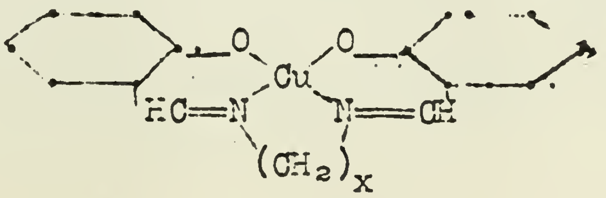
Bailar and Work(1) have prepared trimethylenediamine complexes of cobalt, noting that $[\mathrm{Cotn_3}]^{+++}$ may be prepared only in the presence of a catalyst, such as activated charcoal. Otherwise carbon dioxide from the air forms carbonate ions, which coordinate more readily than the diamine, yielding $[\mathrm{Cotn_2\ CO_3}]^+$.

Chelates containing six-membered rings have also been prepared with 2, 2-dimethyltrimethylenediamine(1), 2-methyltrimethylenediamine (6), and 2, 4-diaminopentane.(3,19)

IV. Rings of More Than Six Members.

Tschugaeff (17,18), Werner(21), Drew and Tress(4) and Pfeiffer and Haimann(10) attempted to form chelates containing tetramethylenediamine and pentamethylenediamine. Their efforts resulted in the formation of insoluble residues, products without fixed compositions, or metal hydroxides. In some instances no reactions at all took place. Pfeiffer and Lübbe(12) also were unable to form chelates of seven and eight-membered rings. These investigators studied decamethylenediamine and octadecamethylenediamine as well, but no chelates were obtained. McReynolds(8) found that coordination takes place between decamethylenediamine and cupric ions, but there is no indication of the presence of chelates.

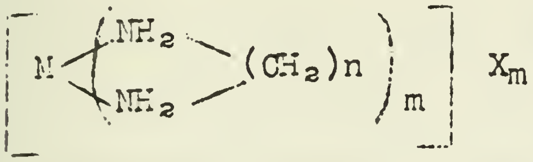
Pfeiffer(11) succeeded in forming such complexes as



x=4, 5, 10

in which a large ring is stabilized by the presence of two six-membered rings.

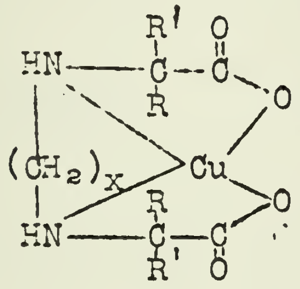
Pfeiffer, Schmitz, and Böhm(14) have recently reported success in stabilizing diamine chelate rings of more than six members. Using alcohol and ether solutions as reaction media, these workers have isolated crystalline compounds whose composotions correspond to


$$\left[M \left(\begin{matrix} NH_2 \\ NH_2 \end{matrix} \right\rangle (CH_2)_n \right)_m \right] X_m$$

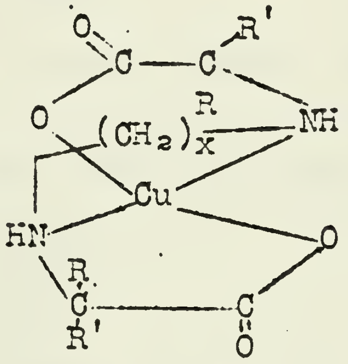
$M = Cu^{++}, Ni^{++}, Zn^{++}, Hg^{++}, Cd^{++}$ (m=2) and Ag^{+}(m=1).
$n = 4, 5, 6.$
$x = ClO_4^-$, $\beta\text{-}OSO_2C_{10}H_7^-$, NO_3^-

The mercury and silver compounds are usually colorless and in some cases may be recrystallized from hot water. The copper and nickel compounds are blue and blue-violet; in general they decompose rapidly in water. The authors state that these compounds form upon merely mixing the metal salts and diamines in alcohol or ether, then evaporating the solvent. The absence of water molecules appears to lessen competition with the amine groups for coordination positions.

The work of Schlesinger(16) suggests another possible structure for the compounds prepared by Pfeiffer and his associates. Schlesinger found that the inner complexes of copper with bis-imino acids, $[Cu(CH_2)_x\text{-}(NHCRR'COO)_2]$, have the blue color, general solubility in water, and characteristic conductivity of copper-amino acid complexes if x is 2 or 3. If x is 10, the bis-imino acid complexes are violet and only slightly soluble. For intermediate values of x, both forms appear. Schlesinger assumed that cis-trans isomerism is present, with the longer molecular chains spanning the trans positions and the shorter chains being confined to the cis positions, as in the amino acid complexes.



cis Form



trans Form

V. Diamines as Metal Deactivators

Small amounts of metals, especially copper, have been found to be powerful catalysts for autoxidation of petroleum products and many other organic compounds. Complexing agents function as metal deactivators, reducing the catalytic effect by forming stable complexes with the metals present. In the case of diamines, deactivation ability falls off rapidly as the number of carbon atoms separating the amine groups increases beyond three. This tendency reflects the greater stability of five-and six-membered chelate rings.(20)

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Cyclopentadienyl Complexes

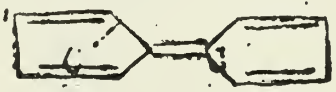
Victor D. Aftandilian April 7, 1953

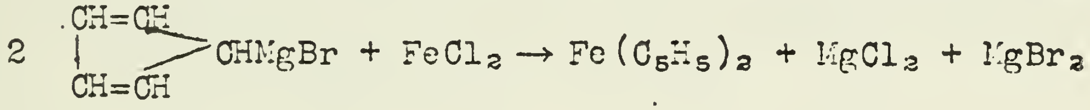
Gringnard reagents have been shown (1) to form hydrocarbons by the coupling reaction:

$$2RMgX + MX_2 \rightarrow R\text{-}R + 2MgX_2 + M$$

Brown and Lichtenwalter (2) obtained an almost quantitative yield of biphenyl from phenylmagnesium bromide and ferric chloride. Ferric chloride is initially reduced to ferrous chloride by the Grignard reagent, which in turn reacts with the excess of the reagent to form biphenyl. Several mechanisms have been proposed for this reaction, the most feasible one being that offered by Krizewski and Turner(10). They postulated that probably unstable organometallic intermediate compounds are formed, which decompose giving hydrocarbons and the free metal as shown below:

$$2RMgX + MX_2 \rightarrow R\text{-}M\text{-}R + 2MgX_2$$
$$R\text{-}M\text{-}R \rightarrow R\text{-}R + M$$

As a possible route to fulvalene () synthesis, Keally and Pauson (9) applied this reaction to cyclopentadienylmagnesium bromide, but instead obtained bis-cyclopentadienyliron(II).



$$2\ \begin{matrix}CH{=}CH\\ |\\ CH{=}CH\end{matrix}\!\!>\!CHMgBr + FeCl_2 \rightarrow Fe(C_5H_5)_2 + MgCl_2 + MgBr_2$$

Less than a month before this discovery was reported, Miller and co-workers (11) prepared $Fe(C_5H_5)_2$ by passing gaseous cyclopentadiene over reduced iron in nitrogen atmosphere at 300° and atmospheric pressure. The formation of bis-cyclopentadienyliron(II) proceeds only for 10-15 minutes, after which further reaction is only effected after careful oxidation and re-reduction of iron at 450° C and in an atmosphere of nitrogen containing steadily increasing proportions of oxygen, and finally air. Kaplan and co-workers (8) modified the Keally and Pauson procedure by the addition of one-third of a molar equivalent of ferric chloride to cyclopentadienylmagnesium bromide, both in tetrahydrofuran, and obtained 51% yield.

Some of the physical properties of bis-cyclopentadienyliron(II) are listed in Table I.

Table I.

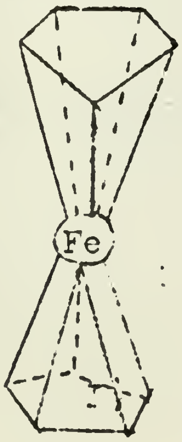
Physical Properties of Bis-cyclopentadienyliron(II) or "Ferrocene" *

Formula	$Fe(Cp)_2$**		
Formula weight	186		
Melting point, °C	173-174		(9)
	172.5-173		(10)
Boiling point, °C	249		(8)
Triple point, °C	183		(8)
Vapor pressure of the solid	$\log P_{mm} = 7.615 - \frac{2470}{T}$		(8)
Vapor pressure of the liquid	$\log P_{mm} = 10.27 - \frac{3680}{T}$		(8)
Heat of sublimation of the solid	16.81	kcal/mole	(8)
Heat of vaporization of the liquid	11.3	kcal/mole	(8)
Heat of fusion	5.5	kcal/mole	(8)
Heat of formation	25.6	kcal/mole	(8)
Trouton's constant	21.2		(8)
E^0_{298} $Fe(Cp)_2 \rightleftharpoons [Fe(Cp)_2]^+ + \bar{e}$	-0.56***		(12)
(in acidic solution)	-0.59***		(16)
Bond distance, A°			
C-C	1.41		(5)
Fe-C	2.0		(5)

---

* Woodword and co-workers (17) proposed this name.
** The symbol Cp, representing cyclopentadienyl unit, will be used in this abstract.
*** Latimer convention.

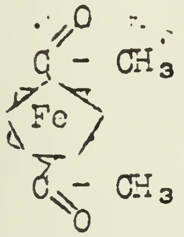
The infrared absorption spectrum of ferrocene shows a single band at 325 mμ which indicates the presence of only one type of C-H bond in this compound. Wilkinson etal (16) proposed structure (I) for ferrocene based upon the above observation.



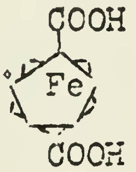
(I)

This structure, in which the iron atom is symmetrically placed between two cyclopentadienyl rings, making a "sandwich" type molecule, has been confirmed by x-ray crystal measurements. (5 and 6). In spite

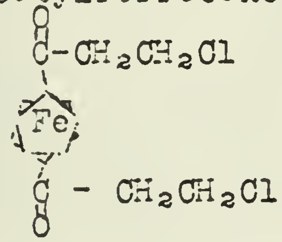
of its high degree of formal unsaturation, ferrocene does not possess properties typical of polyolefinic substances. For example, it does not react with maleic anhydride in boiling benzene; it is not hydrogenated under normal conditions over reduced platinum(II) oxide; it is resistant to the action of acidic reagents, and has high thermal stability. Woodward and co-workers(17) carried out several typical aromatic reactions with ferrocene and reported the following organic derivatives:



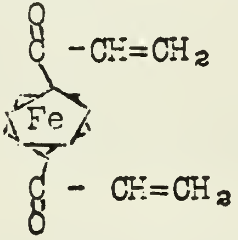
diacetylferrocene



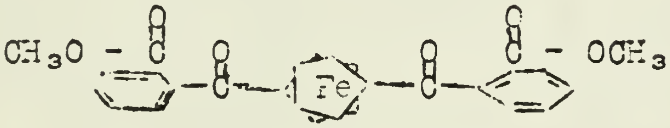
ferrocenedicarboxylic acid



bis-β-chloropropionylferrocene



bis-acryloylferrocene



dimethyl ester of bis-o-carboxybenzoylferrocene

Perhaps a more convincing proof for the aromaticity of ferrocence is the striking resemblance of the infrared absorption spectra of its derivatives to those of benzene. (See Table II).

Table II Infrared Band Positions for Opposite Cases

	R=ferrocenyl	R=phenyl
	μ	μ
H-R	3.26	3.27
CH_3CO-R	5.97	5.93
$CH_3O\overset{O}{C}-R$	5.82	5.81
$o-CH_3OOC-C_6H_4-\overset{O}{C}-R$	6.02	5.97

Even greater interests are the ionization constants for the carbaxylic acids, measured in two-to-one ethanol to water solutions.

Ferrocene dicarboxylic acid	pK_1	$3.1x10^{-7}$
	pK_2	$2.7x10^{-8}$
Benzoic acid	pK_1	$2.7x10^{-7}$

Woodword etal (17) postulated that "the very small differences between the two dissociation constants of ferrocene dicarboxylic acid indicates that the carboxyl groups interact very little, and must be very far apart, while the near identity of the first constant with benzoic acid demonstrates that the ring carbon atoms of ferrocene, and thence, necessarily the central iron atom as well, are subsequently neutral." This observation is of importance with respect to the detailed electronic structure of ferrocene, since it excludes any form of hybridization which leads to charge separation within the molecule. For example, the possibility of coordination of iron with 18 electrons (five from each cyclopentadienyl unit, plus 8 from the iron) to have effective number of 36, krypton structure, as in the case of ferrocyanide, is ruled out. In addition to the objection that the aromatic properties of ferrocene make it seem most unlikely that all the electrons of the cyclopentadienyl rings can be involved in the filling of the orbitals of the metal atom, it seems that a high negative charge would also be placed on the central metal atom and this was shown not to be the case in the determination of the ionization constants of ferrocence dicarboxylic acid. At present there is not sufficient evidence to predict the actual electronic structure of ferrocene. Eiland and Pepinsky (5) are investigating the nature of the bonding and the electronic configuration of the iron atom in ferrocene by a method of three-dimensional analysis.

Ferrocene is readily oxidized to the blue $[Fe(Cp)_2]^+$ cation. Oxidation may be effected anodically, by air in presence of acids or by halogens, by ferric chloride or ceric sulfate. Especially convenient are aqueous silver sulfate or p-bezoquinone in organic solvents in the presence of acids. The ferricinium ion is reduced by stannous chloride. Ferricinium ion has been isolated in the form of crystalline salts: $[Fe(Cp)_2]GaCl_4$, $[Fe(Cp)_2]$picrate, and $[Fe(Cp)_2]ClO_4$ [illegible]

In view of the above postulations concerning ferrocene, it was to have been expected that ruthenium (II) and cobalt (III), both of which are isoelectronic with iron(II), and also other transition elements, which have available d orbitals, would form similar complexes. Table III lists the cyclopentadienyl complexes which have been reported in literature to date.

Table III
List of Cyclopentadienyl Complexes.

Complex	Special Name	References
$Fe(Cp)_2$	Ferrocene	8, 9, 11
$[Fe(Cp)_2]^+$	Ferricinium ion	16
$Ru(Cp)_2$	Ruthenocene	13
$[Ru(Cp)_2]^+$	Ruthenicinum ion	13
$[Co(Cp)_2]^+$	Cobalticinium ion	14
$Ni(Cp)_2$		15
$[Ti(Cp)_2]^{++}$		15
$[Ti(Cp)_2]^+$		15
$[Zr(Cp)_2]^{++}$		15
$[V(Cp)_2]^{++}$		15

Cyclopentadienyl complexes have opened an interesting field of study in inorganic chemistry; intensive investigations are being conducted to determine their structures, to study their properties, and to find uses for these compounds.

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Disulfur Heptoxide

April 14, 1953 A. B. Galun

M. Berthelot(1,2,3) was the first to describe a material which he called "acide persulfurique". It was obtained by passing either sulfur dioxide or sulfur trioxide mixed with oxygen through an electric discharge. The product was considered to be a compound of heptavalent sulfur. However, Mendelejeff(4) pointed out that this compound must be a peroxide. H. Giram(5) calculated the heat of formation:

$$S_2O_7 \rightarrow 2SO_3 + 1/2\ O_2 + 9.7\ \text{cal.}$$

A. Moser(6) found later (1910) that S_2O_7 could be prepared in a discharge tube even at 70°C (Berthelot claimed it decomposed at room temperature). F. Meyer et al(7) repeated Berthelot's experiments in 1922 and obtained products corresponding to the formula S_3O_{11}. They assumed the material to consist of a mixture of SO_3 and SO_4 and claimed that Berthelot's compound was of the same composition. This point of view was supported by T. Maisin(8) who obtained the same compound in 1928.

Pure SO_4 was prepared by R. Schwarz and H. Aschenbach(9) in 1934; mixtures of SO_3 and SO_4 were also characterized(10). V. Wannagat and G. Mennichen(11) prepared pure S_2O_7 and have characterized it chemically. The results of their investigations are summarized in the discussion which follows.

<u>Method of Preparation:</u> A discharge tube was evacuated and filled up to a certain pressure with SO_2. The tube was immersed in liquid air to freeze out the SO_2, and then filled with oxygen gas. The gases were allowed to mix overnight at 20°C, and a discharge of about 1mA and 11KV was passed through the tube. A solution of $CaCl_2$ was used as "coating liquid". A solid separated as a film on the walls of the discharge tube.

Berthelot assumed that nitrogen prevents the crystallization of S_2O_7 but does not interfere with its formation. The authors repeated the experiments in presence of nitrogen and obtained a product which proved to be $(NO)_2\ S_2O_7$ (12). A. Moser(6) also carried out his experiments in presence of nitrogen.

If equal volumes of SO_2 and O_2 are employed, and S_2O_7 is formed according to the equation: $4SO_2 + 3O_2 \rightarrow 2S_3O_7$ (solid), the gas volu should decrease to 1/3 that of the original. It was found that th pressure does drop as shown in figure 1, but never to Po/8.

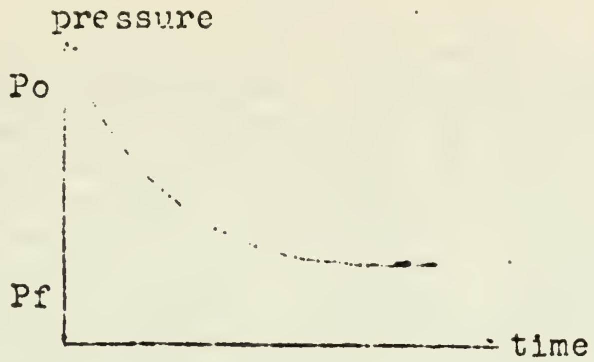


Figure 1

The residual gas was found to contain SO_3 and SO_2 but no S_2O_7. It was concluded that several equillibria established under discharge conditions: $S_2O_7 \rightleftarrows 2SO_3 + 1/2\ O_2$ and $SO_3 \rightleftarrows SO_2 + 1/2\ O_2$. This postulate was confirmed by subjecting S_2O_7 (which is quite stable up to 40°C) to a discharge in a closed system and measuring the pressure. It was found that under discharge conditions S_2O_7 always assumes the same final pressure irrespective whether the starting materials are S_2O_7 or SO_2 and O_2 (fig. 2).

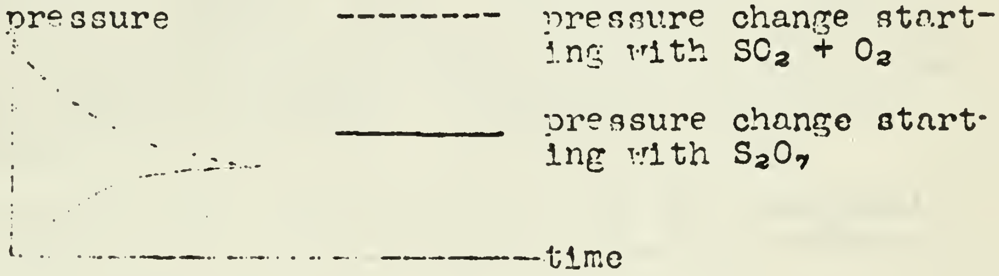


Figure 2

Analysis: This was carried out by titrating free iodine and H^+ after treatment of the substance with a KI solution:

$$(SO_3)_X O_{active} + 2I^- + (X-1)H_2O \rightarrow I_2 + XSO_4^= + 2(X-1)H^+$$

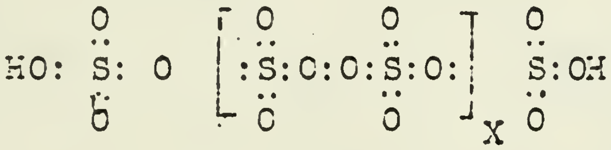
where X is the ratio between SO_3 and active oxygen. (For all peroxides the ratio $\frac{I+H^+}{S}$ should be 2). $SO_4^=$ was determined as $BaSO_4$.

In hydrolytic experiments the ratio $H_2SO_5:H_2S_2O_8:H_2SO_4$ was determined in presence of each other according to a special method devised by K. Gleu(12): Caro's acid is reduced by HBr and the bromine is absorbed in excess standard arsenite. Excess arsenite is determined by titration with standard potassium bromate. H_2O_2 is then titrated in the same solution with $KMnO_4$, the endpoint being determined by appearance of free bromine. Finally, $H_2S_2O_8$ is hydrolized by strong acid and Caro's acid and hydrogen peroxide determined as before.

Reactions of $(S_2O_7)_x$ 1) Concentrated H_2SO_4: Disulfur heptoxide does not dissolve in concentrated H_2SO_4, whereas SO_3, SO_4 and their mixtures(10) as well as the products prepared by Berthelot and Meyer dissolved readily. 2) Titanyl ions: Addition of an acid solution of titanyl sulfate to $(S_2O_7)_x$ gives an intensive orange colored ring(H SO_4 does not give a titanyl peroxide reaction.(9)

3) Aniline: Aniline is completely oxidized to a tar by $(S_2O_7)_x$. SO_4 oxidizes aniline to nitrobenzene. 4) Mn(II): $MnSO_4$ is attacked only very slowly in presence of silver ions by $(S_2O_7)_x$ (at about the same rate as the slow conversion of $(S_2O_7)_x$ to Caro's acid). SO_4 oxidizes Mn^{++} instantaneously to MnO_4^- 5) Cu(II): $(S_2O_7)_x$ does not oxidize Cu(II) in alkaline solution to the alkali cuprate(III). It is claimed (9) that SO_4 brings about this oxidation. 6) $Cr_2O_7^=$: The dichromate ion is not oxidized by $(S_2O_7)_x$ 7) Water: $(S_2O_7)_x$ dissolves readily in cold water with some gas evolution (probably ozone) and formation of $H_2S_2O_8$, H_2SO_5 and a minor quantity of H_2SO_4 in solution.

Structural considerations: The proposed structure for $(S_2O_7)_x$ is:



$$\mathrm{HO{:}}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}{:}\,\mathrm{O}\left[{:}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}{:}\mathrm{O}{:}\mathrm{O}{:}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}{:}\mathrm{O}{:}\right]_x\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}{:}\mathrm{OH}$$

This linear structure is supported by the following facts:
1) Hydrolysis gives $H_2S_2O_8$, H_2SO_5 and a little H_2SO_4. $(S_2O_7)_x$ is essentially the anhydride of $H_2S_2O_8$. 2) By increasing the amount of oxygen in the preparation of disulfur heptoxide a product containing a higher percentage of active oxygen (and consequently yielding upon hydrolysis a higher percentage of $H_2S_2O_8$) is obtained. It may be assumed that more S:O:O:S and fewer S:O:S bridges are formed.

A two dimensional sheet-like structure may also be considered ("This is consistent with the film-like nature of $(S_2O_7)_x$"-authors).

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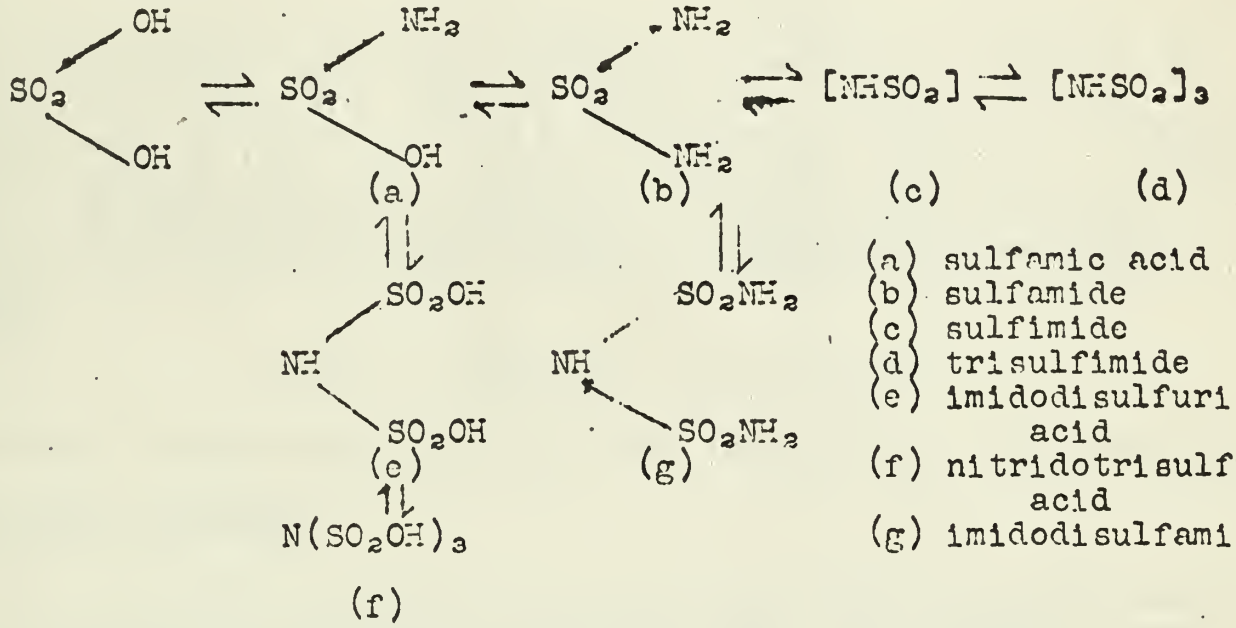
SULFANURIC CHLORIDE

L. H. Diamond

April 21, 1953

INTRODUCTION:

Franklin[1] in his development of the nitrogen system of compounds set up the following tabulation of the nitrogen derivatives of sulfuric acid, or the aquo-ammono sulfuric acids:



(a) sulfamic acid
(b) sulfamide
(c) sulfimide
(d) trisulfimide
(e) imidodisulfuric acid
(f) nitridotrisulfuric acid
(g) imidodisulfamide

These relationships are somewhat formal and do not imply that the compounds are necessarily preparable from each other by the scheme outlined. Various aspects of the chemistry of the aquo-ammono sulfuric acids have been reviewed previously.[2,3] This report will consider the chemistry of trisulfimide, specifically the acid chloride of trisulfimide.

HISTORICAL:

Traube[4] isolated a number of salts from the reaction of sulfuryl chloride with ammonia. Analysis of the silver, sodium, potassium, and barium salts led him to believe that they were derived from sulfimide. Hantzsch and Holl[5] established that sulfimide did not exist as the simple momer, $[NHSO_2]$, but as the trimer $(NHSO_2)_3$. A ring structure was assigned to the compound based on its resemblance to cyanuric acid; the name sulfanuric acid has been suggested for the compound. Hantzsch and Holl claimed to have isolated free trisulfimide but later found that the product was an impure sample of imidodisulfamide.[6] Further attempts to prepare free trisulfimide have been unsuccessful. When sulfamide is heated above its melting point, the following reactions are postulated:

$$3SO_2(NH_2)_2 \longrightarrow (NHSO_2)_3 + 3NH_3$$

$$2SO_2(NH_2)_2 \longrightarrow NH(SO_2NH_2)_2 + NH_3$$

It has been suggested that trisulfimide is formed from the decomposition of sulfamyl chloride, which may be an intermediate in the reaction of an aryl chlorosulfonate with ammonia.[7]

$$\begin{array}{l} C_6H_5OSO_2Cl + NH_3 \longrightarrow NH_2SO_2Cl + C_6H_5OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad (SO_2NH)_3 + 3HCl \end{array}$$

In an investigation of the reaction of phosgene with sodium amide Perret and Perrot noted the formation of melanuric acid and its chloride derivatives.[8] Because of the similarities existing between trisulfimide and melanuric acid, it seemed possible that trisulfimid may be obtained from the reaction of sulfuryl chloride and sodium amide. By fractional precipitation of the reaction products with silver nitrate, silver trisulfimide, $(SO_2NAg)_3$, was obtained. Hantzsch and Holl[2] prepared trimethyl trisulfimide in the following manner:

$$3CH_3I + (SO_2NAg)_3 \longrightarrow (SO_2NCH_3)_3$$

Tribenzoyl trisulfimide has also been prepared in a similar manner.

<u>SULFANURIC CHLORIDE</u>:

The reaction of sulfamic acid with phosphorous pentachloride was investigated by Ephraim and Gurewitch[9], who claimed to have isolated a binary compound of sulfamyl chloride, based on the following equation:

$$NH_2SO_2OH + 2PCl_5 \longrightarrow Cl_2 + HCl + POCl_3 + ClSO_2NH_2 \cdot PCl_3$$

Kirsanov[10] has shown recently that this reaction produces trichlorophosphazo sulfuryl chloride, according to the following equation:

$$NH_2SO_2OH + 2PCl_5 \longrightarrow 3HCl + POCl_3 + ClSO_2N{=}PCl_3$$

Trichlorophosphazo sulfuryl chloride is an extremely hygroscopic, white, crystalline compound; melting point at 35-36°. It is soluble in organic solvents and reacts with ammonia, amines, alcohol, and phenol. It hydrolyzes according to the equation:

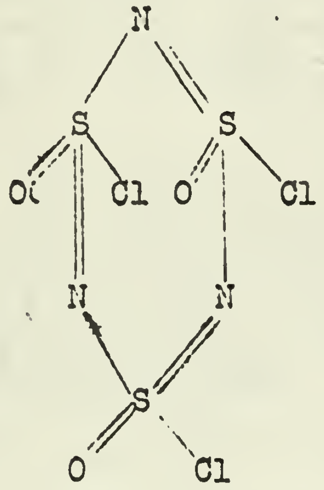
$$ClSO_2N{=}PCl_3 + 6H_2O \longrightarrow 4HCl + HOSO_2ONH_4 + H_3PO_4$$

Kirsanov[11] was able to prepare the sulfur analog of cyanuric acid, sulfanuric acid or 1-3-5trichloroxo-1-3-5 trithiatriazine, by the thermal cleavage of trichlorophosphazo sulfuryl chloride. The trichlorophosphazo sulfuryl chloride was distilled in vacuum and the residue obtained was a transparent brown liquid which contained the sulfanuric chloride. By fractional crystallization procedures, two products were obtained that corresponded to the formula $(NSOCl)_3$ these were designated by Kirsanov as α- and β-sulfanuric chloride. The α-sulfanuric chloride is a white crystalline product with a melting point of 144-145° and a boiling point of 270°; however, the

material explodes violently upon distillation. The β-sulfanuric chloride is also a white crystalline solid with a melting point of 42-43.

Sulfanuric chloride is soluble in ether and benzene; in alcohol the solution becomes acidic, probably involving the formation of esters of sulfanuric acid. Sulfanuric chloride reacts vigorously with ammonia, amines, and is slowly hydrolyzed by water.

Since sulfur in the hexavalent state, like carbon tends primarily to assume a tetrahydral configuration, sulfanuric chloride may exist as two geometric isomers, represented as the α and β forms.



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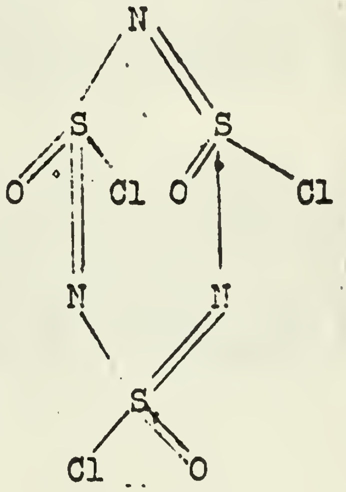

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ROLL CALL

THALLIUM TRIIODIDE

Robert H. Marshall April 21, 1953

Thallium triiodide was first prepared by Nicklès in 1864. Early methods of preparation involved the digestion of TlI and I_2 in ether, methanol, or ethanol solutions, followed by evaporation. A long period of digestion is necessary, however, owing to the low solubility of TlI and an intermediate iodide, Tl_3I_4. A better method has been reported by Sharpe, in which TlI is dissolved in a solution of I_2 in concentrated hydriodic acid(1). Evaporation at room temperature yields the TlI_3.

The isomorphism of TlI_3 with RbI_3 and CsI_3 appears to establish the structure of the solid as thallium (I) triiodide. However, the absorption spectrum in methanol solution shows different maxima than those characteristic of the I_3^- ion. When such a solution is treated with aqueous Na_2CO_3 solution, Tl_2O_3 is precipitated. This reaction may be considered to occur in the following stages:

$$2\ TlI_3 \rightleftharpoons 2Tl^+ + 2I_3^-$$

$$2\ I_3^- + 4OH^- \rightleftharpoons 2OI^- + 4I^- + 2H_2O$$

$$2\ Tl^+ + 2OH^- + 2OI^- + 2H_2O \rightleftharpoons 2Tl(OH)_3 + 2I^-$$

$$2\ Tl\ (OH)_3 \rightleftharpoons Tl_2O_3 + 3H_2O$$

$$2\ TlI_3 + 6OH^- \rightleftharpoons Tl_2O_3 + 6I^- + 3H_2O$$

As evidence for such a series of reactions, it has been found that when I_2 and alkali are added to a solution containing Tl^+ ions, Tl_2O_3 is precipitated quantitatively. In addition, KI_3 solutions are immediately decolorized by alkali.

Thermal decomposition of the TlI_3 yields TlI and I_2 as final products. X-ray powder photography has shown Tl_3I_4 to be an intermediate product. Experiments were also carried out which indicate the dissociation pressures of various polyhalides to be:

$$Tl_3I_4 < CsI_3 < RbI_3 < TlI_3 < KI_3.$$

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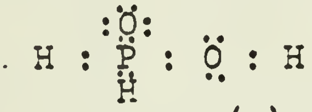
PREPARATION OF COPPER HYDRIDE IN AQUEOUS MEDIUM

N. E. Bojars April 28, 1953

A. INTRODUCTION.

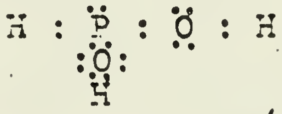
Hypophosphorous Acid as a Reducing Agent. Hypophosphorous acid reacts with copper (II) ions in water, yielding a red-brown reduction product. The constitution of this product has been the subject of controversy until recently. It has now been shown[1] that, under proper conditions, copper hydride (CuH) can be made in aqueous medium.

Several alkali salts of the monobasic hypophosphorous acid can be made from white phosphorus and the corresponding aqueous alkali.[2] A number of heavier metal salts has also been made.[3] The free acid can be prepared from barium hypophosphite and aqueous sulfuric acid,[4] or in resin exchangers.[5] Hypophosphorous acid is a colorless, crystalline compound, m.p. 26.5°C, readily soluble in water.[4] Two hydrogen atoms are attached to phosphorus (A).



$H:\overset{:\ddot{O}:}{\underset{H}{\ddot{P}}}:\ddot{O}:H$

(A)



$H:\underset{\underset{H}{:\ddot{O}:}}{\ddot{P}}:\ddot{O}:H$

(B)

Satisfactory proof has been advanced that a tautomer (B) does not exist[6-9]. However, two forms of the acid in a slow equilibrium with each other have been postulated[10,11] for aqueous solutions. The active reducing agent, according to Steele[12], is a hypothetical compound H_5PO_2, which is produced with measurable velocity. These assumptions are necessary to explain the rate of certain reactions,[13] where hypophosphorous acid is the reducing agent. The active form is produced, when the equilibrium amount is diminished [10,14]. Some objections against the current structural formulas for H_3PO_2 have been raised.[15] The ion $H_2PO_2^-$ is tetrahedral.[4] A study involving radioactive phosphorus has shown that mixtures of phosphates and hypophosphites do not exchange phosphorus, even upon heating to decomposition temperatures in closed vessels.[16]

Hypophosphorous acid is oxidized by many oxidizing agents and heavy metal ions[2,3,4,10,11]; in certain cases an induction period of the reaction is observed[17,18]. Hypophosphorous acid is useful for the production of nickel and nickel hydride alloys[19,20] via nickel hypophosphite, for electrode plating, and in ceramics, and as a stabilizer for iron (II) chloride[21]. The acid forms complexes with some metal ions.[22]

Hypophosphorous acid is a useful reducing agent in organic chemistry. A well-known example is the deamination,[23] involving the

replacement of the diazonium group by hydrogen. A method was found at the University of Illinois[34] for introducing deuterium into aromatic nuclei, in a similar way. The influence of various metal salts upon the deamination reaction has been studied and the mechanism has been discussed[25]. Hypophosphorous acid is also useful in the production of aryl phosphinic acids[26] and other organic compounds [27,28,29].

The use of the hypophosphorous acid in medicine[3] and biology[30], as a stabilizer for some polymers[31,32], and as a sensitizer for fumigating mixtures[33] can be mentioned.

B. The Reaction of Copper (II) Ions with Hypophosphite Ions.

It has long been known[34] that copper (II) ions are reduced by hypophosphite ions. Wurtz[35] obtained by such reduction a red-brown, amorphous precipitate, which he identified as copper hydride.

$$2\ Cu^{++} + 3\ H_2PO_2^- + 3\ H_2O \rightarrow 2\ \underline{CuH} + 3\ H_2PO_3^- + 4\ H^+ \quad (I)$$

Copper hydride then decomposes with evolution of hydrogen.

$$2\ \underline{CuH} \rightarrow \underline{2\ Cu} + H_2 \quad (II)$$

If excess of hypophosphite is present, hydrogen is evolved even during the initial stage of the reaction; with an excess of copper (II) salt copper only is precipitated[36,37]. The constitution of the product of the reaction (I) has been a subject of controversy[38] until recently. Thus, it has been maintained[2,36] that spontaneous decomposition and X-ray diffraction studies indicate that the product is a solution of hydrogen in copper as is the case with palladium, and that the red-brown precipitate is not a hydride analogous to the alkali hydrides.

The nature of metallic hydrides has been investigated recently[39]; Wiberg and co-workers[40,41,42] have developed methods for the preparation of hydrides in non-aqueous media. Lithium aluminum hydride[43] was found to be useful for the preparation of dry copper hydride.

$$4CuI + LiAlH_4 \rightarrow LiI + AlI_3 + 4\ CuH \quad (III)$$

Copper hydride can be dissolved in pyridine, and reprecipitated by ether. Thus it becomes evident that copper hydride is, after all, a definite chemical compound.

C. The Procedure for the Preparation of Copper Hydride in Aqueous Medium.

To obtain the desired results, the old method of Wurtz[35] was properly modified[1]. According to the equation (I), stoichiometric amounts of 0.4 M aqueous copper (II) sulfate and 0.6 M aqueous sodium hypophosphite containing 1.25% free sulfuric acid were allowed to react in a hydrogen atmosphere at 20°C for 15 to 20 hours. Precautior were made to exclude traces of oxygen, since otherwise some copper (I oxide appears as an impurity in the product.

Wet copper hydride was precipitated; all attempts to dry it led t a decomposition[1,44], even below 45°C. However, a satisfactory analysi was obtained by a special procedure[1]. In more than 100 separate experiments a light red-brown product was always obtained[1]. It was shown by analysis to contain 98.45% Cu and 1.55% H, in excellent

agreement with the calculated values for CuH.

The earlier workers had obtained analytical values up to 1.50% H and about 98.50% Cu. An aqueous suspension of copper hydride has been shown to act as a reducing agent; an attempt to devise a quantitative titrimetric procedure has not been entirely successful because of difficulties in estimating the end point[1].

Thus it has been definitely proved[1] that copper hydride can be made in aqueous medium. Silver (I) ions yield silver metal only under similar conditions[36].

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INORGANIC PAPER CHROMATOGRAPHY

Mary Joane Sirotek May 5, 1953

HISTORY

Inorganic analyses on strips of absorbent paper were first described over a century ago. Weil and Williams (1) credit the first recorded experiments on capillary analyses to F. F. Runge, who in 1850 analyzed a mixture of dyes on blotting paper and whose interest extended to the possibility of using capillary ascent of solution in blocks of wood for the separation of solutes. At a later date this was more fully investigated by Schoenbein and his student, Goppelsroeder. Schoenbein, who has usually been regarded as the pioneer of capillary analysis of inorganic compounds, showed that if a strip of paper is dipped into water containing inorganic salts, the water rises in the paper and carries the salts with it. The solutes concentrated in distinct zones as the solution was drawn into the strip. He predicted its later use as an analytical tool (2). In 1878, Bayley (3) noted a similar phenomenon. Fischer (4) knew of this work and applied it to the quantitative investigation of the separation of sodium and barium, and of certain double salts. By separating the cations in a double salt, such as ferrous ammonium sulfate, he demonstrated the absence of a complex ion.

The true discovery of chromatography is credited to Tswett (5), who separated the pigments in leaves by passing a petroleum ether extract of leaves through a column of calcium carbonate. He named the method and stated, erroneously however, that it was based on purely physical reactions. Tswett vigorously denied that his work was related to the work of Schoenbein and Goppelsroeder.

In 1909, Krulla (6) recommended adsorption on filter paper as a simple qualitative test for salts which give a color reaction and as a measure of the concentrations of dilute solutions.

Chromatography was then nearly completely forgotten for almost 25 years. But lately much has been done to develop the usefulness of this tool.

Strain (7) has defined chromatography as the technique of analysis and/or preparation in which there is a dynamic partition or distribution of dissolved or dispersed materials between two immiscible phases, one of which is moving past the other.

PROCEDURE

Chromatographic separations may be run on either columns or paper strips.

The procedure for paper chromatography is essentially this: a spot of the solute to be analyzed is applied to one end of the paper and the developing solvent is made either to ascend or descend the paper, with the result that different solutes appear in different zones.

Many variations of this simple procedure have appeared using simple filter paper or blotting paper in the form of strips, disks, sheets, and piles. Consden et al (8) and Strain (9) have described a descending method. Williams and Kirby (10) and Rockland and Dunn (11) used an ascending procedure. Other variations of the method have been developed by Brown (12), Muller and Clegg (13), Rutter (14), Ma and Fontaine (15) and Datta et al (16). Attempts to apply paper chromatography to a larger scale have been made by Mitchell and Haskins (17), Porter (18) and Yanofsky et al (19).

Burstall and Kember (21) have given an excellent description of the practical problems involved in running a chromatogram. In general the following things must be considered:

a. <u>The test solution</u>
In general the concentration should be about 1 mg./0.05 ml. for a one inch wide strip.

b. <u>Transfer of test solution to paper strip</u>
For qualitative analysis, a 0.05 ml. pipet may be used. For quantitative analysis a micrometer syringe or capillary buret should be used. Novellie (21) has described a simple method of application.

c. <u>Type and size of paper</u>
A strip one inch wide and eight to sixteen inches long of Whatman No. 1 or 3 is usually satisfactory. Scribner and Wilson (22) have stated that paper cannot be considered inert even towards water and have set up standards for filter paper. Cassidy (23) has found that some paper gives bands due to the presence of copper. Different papers may even invert the order of the spots. The machine direction of the paper should also be considered. Flood (24) has used paper impregnated with alumina.

d. <u>Atmospheric conditions</u>
The chromatogram should be produced in a closed tank so that the atmosphere will be saturated with the vapor of the solvent to prevent evaporation.

e. <u>Temperature</u>
The temperature should be kept somewhat constant. Gordon (25) states that with rising temperature the adsorption decreased and the salt becomes more motile.

f. <u>Time and distance of solvent movement</u>
The time varies for fifteen minutes to thirty-six hours. For complete separation of a large group, the solvent front should move twelve inches. For some separations, two to three inches is sufficient.

g. <u>Choice of solvent</u>
The best method is to try one of each of the following types: alcohols, ketones, ether, carboxylic acids, esters, etc. When the best type has been found, different members of its homologous series are tried, usually with the addition of 1-2% mineral acid. The solvent is usually saturated with water. Lacourt et al (26) have shown the importance

of choosing the proper initial solvent.

h. Development and detection of zones
Physical methods include use of fluorescent indicators (27), photoelectric cells, interferometry, and radioactive tracers (28). Chemical methods may consist of spraying or streaking with a color producing reagent.

THEORY

A theory to be adequate should describe the formation and development of zones, their rate of movement, and their spatial as well as concentration dimensions. It should make it possible to calculate beforehand the state of development after a given amount of developer has been applied and should clarify the findings of experiment. Unfortunately the time has not arrived when a new substance can be placed on a paper, a developer added, and the results accurately predicted.

Many attempts have been made to develop a theory. Wilson (29) has devised a theory in terms of the adsorption isotherm which is used to express the relationship between solute and adsorbent at equilibrium. However, this does not take into account the effect of one solute upon another at varying concentrations. He neglects all diffusion and lack of equilibrium.

In 1941, Martin and Synge (30) introduced partition chromatography, in which the difference between partition coefficients in the aqueous and nonaqueous phases of the components of a mixture gave refinement in the normal chromatographic separation which depends upon adsorption characteristics. In 1944, Consden et al (8), extended this to the use of paper strips. Martin and Synge developed a plate theory for chromatography analogous to that used for distillation columns. They consider the column or strip to consist of a number of theoretical plates (H.E.T.P.) within each of which perfect equilibrium occurs and relate the partition coefficient to the rate of movement of the bands.

Thus, A = cross-sectional area of paper + nonmobile phase + mobile phase
A_L = cross-sectional area of mobile phase i.e., solvent phase
A_S = cross-sectional area of nonmobile phase i.e., water phase
α = partition coefficient = $\dfrac{\text{conc. in } H_2O \text{ phase}}{\text{conc. in solvent phase}}$.

$$R_f = \frac{\text{movement of band}}{\text{movement of advancing front of liquid}} = \frac{RA_L}{A} = \frac{A_L}{A_L + \alpha A_S}$$

$$\alpha = \frac{A_L}{R_f A_S} - \frac{A_L}{A_S} = \frac{A_L}{A_S}\left(\frac{1}{R_f} - 1\right)$$

Other attempts at development of a theory have been made. Flood (31) has related the zone radii to the concentration. Hopf (32) has developed Flood's formula further. Brimley (33) assumes that the spots spread by diffusion in a way analogous to the theory of heat flow. Thomas (34) discusses a theory of kinetics leading to a Langmuir type of isotherm at equilibrium.

However, no completely satisfactory theory has been devised.

MECHANISM

All chromatographic methods are based on the differential migration of solution through polyphase systems in which the phases have a preferential affinity for the solutes.

In considering the mechanism of chromatography, Arden, et al (35) have listed these factors as requiring consideration.

a. Selective extraction of the salts of the organic solvent, an effect prevailing at the test patch.

b. Where substantially immiscible solvents are used, partition of the inorganic substance between organic solvent and aqueous layer, since water is present as a normal constituent of the adsorbent paper and is usually added to the organic solvent. This partition therefore takes place as the liquid mixture moves down the paper, and separations are due to slight changes in conditions at different points on the adsorbent strip.

c. Adsorption of the metallic ions by the paper.

d. Formation of complexes with high solubilities in organic media under specific conditions.

Feigl (36) has compared the mechanism to a process of fractional precipitation. Muller and Clegg (37) have described the mechanism on circular filter paper. In the chromatographic field, it is often a moot question as to whether the separation is due to adsorption, ion exchange, liquid-liquid distribution or a combination of two or three of these. The predominant force varies with the solvents and the solute. Thus, Pollard, et al (27) state that for butanol mixtures in cation analysis the separation is essentially partition chromatography whereas in collidine, complex formation and selective extraction play the dominant role.

APPLICATIONS

The most obvious application of paper chromatography is the qualitative detection of substances. Although most of the ground work has been done with amino acids, recently applications to the detection of cations and anions have become more abundant. Lederer (38) has devised a method for the separation of the noble metals. Arden et al. (35) have found a method for the separation of several metal ion groups, namely, Ca Sr Ba; Al Ga In Zn; Co Cu Fe Mn Ni; and Pb Cu Bi Cd Hg. A more intensive investigation by Pollard, et al (39) has resulted in a scheme for the separation of Pb, Ag, Hg, As, Sb, Cr, Mn, Cu, Co, Ni, Bi, Fe, Sn, Sr, Ba, Cd, Zn, Al, Mg, Ca, Na, and K. Later Pollard, et al (40) extended the scheme to include Ce, Li, Mo, Tl, Ti, U, V, and W. Anion analysis has developed more slowly, but Lederer (41) has devised a scheme for the separation of the chloride group anions. Fillinger (42) has devised a simple scheme to be used in elementary qualitative analysis. She makes use of alumina columns but the procedure could also be applied to paper.

A method of two dimensional chromatography has been discussed by Consden (43) and Tolley (44). The "maps" produced by this method can be used for identification of more difficult substances since two solvents may be used.

Methods for quantitative analysis have developed more slowly. For semi-quantitative work, the stain is compared with those made by known amounts of substance. For more accurate work, the color band is cut out and the metal content determined accurately by colorimetric, polarographic, and spectographic techniques. Fischer (45) has described several simple methods for the quantitative assay of amino acids. This method is applicable to other problems. Bull et al. have plotted the % transmission on semi log paper versus the distance along the strip and by means of a planimeter have estimated the concentration of amino acids.

Anderson and Lederer (47) have combined quantitative analysis with electrochromatography on paper. Strain (48) has used two and three way electrochromatography for the resolution of mixtures.

An application for the determination of molecular structure has been described by Strain (9). He has done this work by studying the adsorption sequences and relative rates of migration. Strain (7) has also studied the effect of ionic charge, radius and mass on the degree of separability.

ADVANTAGES AND DISADVANTAGES

Some of the advantages of paper chromatography include its use for the separation of substances too unstable to be distilled, the concentration of dilute solutions, and the determination of the purity, homogeneity, and components of solutions. It is also a rapid, simple, and inexpensive method.

Unfortunately, at the present time there is a considerable degree of empiricism involved in chromatography. There is a great deal of physical data to be worked out. Paper chromatography is not applicable to large scale work. There is always the chance of chemical change in the adsorbed solute.

Because there is some confusion in nomenclature, Dent (49) has recommended the use of the word "papyrography" as a substitute for paper chromatography, but his suggestion has not been carried out very widely.

Much work remains to be done in this subject, especially in the way of further quantitative studies of its physico-chemical nature, including kinetic studies so as to evaluate the various factors involved in a more quantitative and predictable fashion.

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INORGANIC COLUMN CHROMATOGRAPHY

S. A. Bartkiewicz May 12, 1953

Chromatography, a simple and ingenious method of chemical analysis by adsorption, was invented in 1906 by M. Tswett, a Russian botanist, while working with plant pigments. The method was used sporadically in biological research; but, it was almost thirty years later before chromatography found any serious application in the inorganic field. (24,27,36) It has been used in inorganic chemistry chiefly for the resolution and identification of mixtures of cations. Chromatography has also been applied to some extent in the separation of elements, detection of anions, purification of inorganic compounds, and the separation of isotopes. Some attempts have been made to apply this method quantitatively.

Strain (24) describes the mechanism of chromatography as a dynamic process which depends upon the continuous and simultaneous adsorption, desorption, or elution and readsorption of the substances being resolved upon the column. Concepts regarding the details of the adsorption process itself are not entirely clear. (16,19,28,34) In adsorption columns several types of adsorptive forces may come into play. These may be of the physical type, Van der Waal's forces, or ential chemical reaction, chemadsorption.

The choice of column size, adsorbent and solvent, is determined to a large extent by the quantity and the adsorbability of the materials to be resolved, the physical and chemical nature of the adsorbent, the solubility of the materials to be adsorbed, and by the activity and solubility of the adsorbent. (16,19,27,30) Final selection is usually, however, made by empirical methods. (27) Le Rosen (37) attempted to standardize chromatography, and suggested a method for determining the characteristics of an adsorbent which would aid researchers in reproducing the work of other people.

Terminology indicates limitation to colored substances only. Modification of the process and the procedure, however, makes it possible to work with colorless materials and to locate colorless bands. (9,27)

It should be kept in mind that most of the above material has been derived and postulated with reference primarily to organic materials. Much of it undoubtedly does apply to inorganic materials as well.

The first extensive work done in inorganic chromatography was by Schwab and Jockers. (19) They examined a variety of substances which could be used as adsorbents and used several of the standard reagents for developers. Using Al_2O_3 as an adsorbent and primarily H_2S and $(NH_4)_2S$ as developers, they obtained a definite series order of adsorption for a number of cations. Working with Dattler (20,21) Schwab found that by treating Al_2O_3 with HNO_3 an anionic series could be obtained--the cations being used as developers. An endeavor was made to arrive at the quantitative possibilities of chromatography by attempting to correlate band widths with concentration of the ion. Srikantan and Krishman (25) applied the method to the quantitative

determination of various constituents of alloys such as brass and steel. They report that 99% accuracy can be obtained by careful control of the method. Kubli (17) investigated the work of Schwab and Dattler (20) with anions and extended the series order to almost twice its original number. Schwab and Ghosh (22) investigated the possibilities of the application of chromatography to qualitative analysis. Some success was obtained with the HCl, H_2S and $(NH_4)_2S$ groups. Bishop recommends the use of chromatography in teaching qualitative analysis and cites two examples that can be used. Fillinger and Troftan (15) have reported the successful application of chromatography to some degree in undergraduate qualitative analysis at Hollins College, Virginia. Schwab and Ghosh (23) investigated the use of chromatography in micro analysis and found that the sensitiveness of the method is as great and in some cases greater than by the drop method. They also made separations of the noble metals, using Al_2O_3 as an adsorbent. No developers were required since the compounds used were themselves colored. Tanaka and co-workers (29) found that the presence of .001γCo, 0.001γ of Ni, 0.001γ of Zn, and 0.5γ of Cu could be determined using an Al_2O_3 column and $(NH_4)_2S$ as a developer. Venturello and Saini (32) report the separation of the Pt group upon Al_2O_3 using various developers. Venturello and Agliardi (31) investigated the work of Schwab and Jockers (19) and further extended the cationic series. Erlenmeyer and co-workers also extensively investigated the use of chromatography in inorganic analysis. Using 8-hydroxyquinoline as the adsorbent Erlenmeyer and Dahn (12) succeeded in resolving a series of ions. No developer was needed since the oxime itself served the purpose. Working with Violuric acid as an adsorbent, Erlenmeyer and Schoenauer (14) were successful in separating Na^+, and K^+ as well as most of the alkaline earths. Erlenmeyer and Schmidlin (13) extended the work upon the Na-group. Robinson (33) working with a mixture of starch and 8-hydroxyquinoline further extended the series order of Erlenmeyer and Dahn. He also successfully determined the Zn content of Cu - Ni brazing alloys by the method of band width measurements. Dean (10) using a combination of chromatography and colorimetry successfully isolated and determined Cobalt in ferrous and non-ferrous alloys. Several successful separations of ions have been reported using cellulose as an adsorbent. (4,6,7,8,34) Kutzelnigg (18) using ZnS as an adsorbent successfully obtained the following series order: Au, Os, Ru, Pd, Hg, Ag, Bi, Cu, Fe, U, Pt, Rh, and Ir. The formation of sulfides produced sharply defined zones which can be identified by their color. Traces of Ni have been determined by the use of D.M.G. as an adsorbent. (5) Metals in the form of dithizone complexes have been separated upon an Al_2O_3 column by Bagh (2) and by Dunabin. (11) Al-Mahdi and Wilson (1) have resolved Co^{+2}, Cu^{+2}, Fe^{+3}, and Ni^{+2} as diethyldithiocarbamates.

Work in this field is still fragmentary due to the lack of proper adsorbents. (16) With the development of a more universal adsorbent, a complete scheme of analysis, qualitatively and possibly quantitatively, will probably be conceived.

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AMMONOLYSIS AND AMINOLYSIS OF SOME SUBSTITUTED SILICON HALIDES

A. S. Hay May 19, 1953

In general the halosilanes are uniformly more reactive than their carbon analogs[1]. Trichlorosilane and tetrachlorosilane are hydrolyzed even by moist air. As the halogen atoms are replaced by alkyl or aryl groups the ease of hydrolysis decreases[2,3] and the stability also increases as bulkier groups are put into the molecule[4]. With increasing bond polarizability the ease of hydrolysis also increases in the order F, Cl, Br, I.

All of the halosilanes (with the exception of the fluoro compounds) react with ammonia at room temperature, or with liquid ammonia[5]. In this manner the silicon analogs of primary and secondary amines can be prepared[6,7]. Miner et al[8] treated t-alkoxychlorosilanes with ammonia and found that the type of product resulting from the reaction depended on the ratio of chlorines to silicon in the molecule. The mono- and dichlorosilanes formed the corresponding mono- and diaminosilanes, but the trichlorosilanes reacted with ammonia to give only resinous condensation products. Trisilylamine, prepared from tetrachlorosilane and ammonia, is the only known analog of a tertiary amine. They also found that the presence of at least one tertiary alkoxy group in the molecule is essential for the existence of a stable compound containing two amino groups on the same silicon atom.

In contact with water these t-alkoxyaminositanes react rapidly with evolution of ammonia to give silanols. They also react rapidly with most primary and secondary alcohols at room temperature with the evolution of one mole of ammonia.

$$(RO)_2Si(NH_2)_2 + R^1OH \rightarrow (RO)_2(R^1O)SiNH_2 + NH_3$$

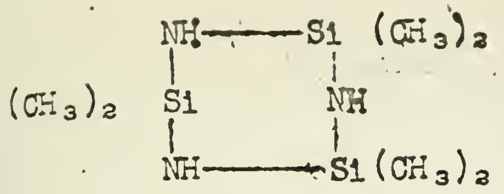
With methanol both amino groups react readily but heat is needed for the reaction with higher alcohols. At elevated temperatures with primary alcohols the second amino group reacts readily, with secondary alcohols the reaction is slower, and with tertiary alcohols the first amino group reacts slowly and the second not at all.

Generally trialkylchlorosilanes react with ammonia to give the corresponding disilazanes but triethylchlorosilane is reported to give some triethylaminosilane also.

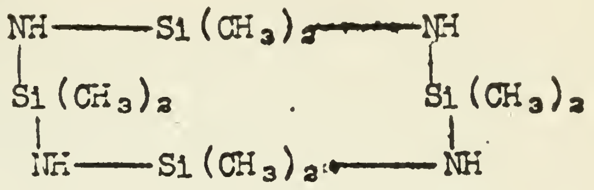
Similarly the reaction of tetrachlorosilane with alkylamines yields the corresponding N-alkyldisilazanes. Trimethylchlorosilane and methylamine react to form trimethyl-N-methylaminosilane. Reaction with a further molecule of trimethylchlorosilane gives heptamethyldisilazane.

$$(CH_3)_3SiCl + CH_3NH_2 \rightarrow (CH_3)_3SiNHCH_3 \rightarrow [(CH_3)_3Si]_2NCH_3$$

By reaction of ammonia with dimethyldichlorosilane Larsson and Smith[9] obtained hexamethylcyclotrisilazane(I) and octamethylcyclotetrasilazane(II). Both are hydrolyzed by water.



I



II

Dimethyldichlorosilane and methylamine or ethylamine in a 1:4 ratio yield as the main products dimethyl-bis-(methylamino)-silane and dimethyl-bis-(ethylamino)-silane, respectively.

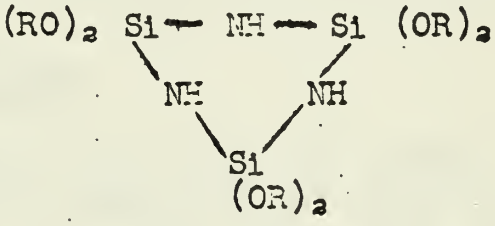
$$4RNH_2+(CH_3)_2SiCl_2\rightarrow(CH_3)_2Si(NHR)_2+2RNH_3Cl$$

Schwarz and Weigel[10] prepared some aminosilanes and studied their conversion to the disilazanes. They prepared triisopropoxyaminosilane by introducing dry ammonia into an ether solution of triisopropoxychlorosilane. It is very sensitive to moisture. When heated under reflux, ammonia is evolved and after 48 hours a 50 percent yield of the disilazane was obtained. When triphenoxyaminosilane, prepared in a similar manner, is heated it is converted quantitatively to the disilazane.

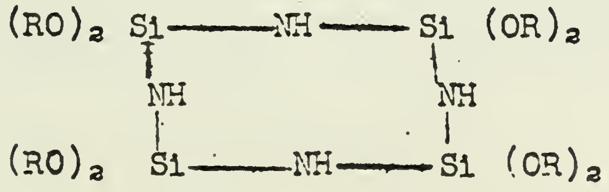
The preparation of diisopropoxydiaminosilane was attempted in a manner analogous to that for the monoaminosilanes. It could not be prepared but instead a mixture of tetraisopropoxydisilazane(III) and hexaisopropoxycyclotrisilazane(IV) was obtained. In order to determine whether the cyclic compound was formed by a further condensation of the disilazane, some of the latter was heated for some time at 180 deg. Under these conditions a mixture of the cyclotrisilazane(IV) and cyclotetrasilazane(V) was obtained. These compounds, as all other aminosilanes are sensitive to water, ammonia being split out.

$[(RO)_2Si]_2NH$

III

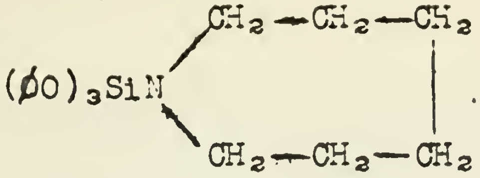


IV



V

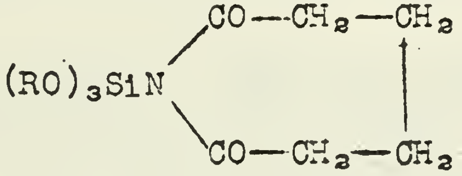
Triphenoxychlorosilane and hexamethylenediamine react in methylene chloride at the boiling point to give a mixture of triphenoxyaminosilane and triphenoxyhexamethyleniminosilane(VI). After six days



VI

in a desiccator over phosphorus pentoxide the cyclic compound crystallized out of the mixture. In contrast to other aminosilanes and disilazanes described, it is comparatively stable to moisture. Several hours in contact with water at room temperature produces only a slight amount of hydrolysis.

In an attempt to prepare a molecule containing the grouping -SiNHCO - four moles of triisopropoxyaminosilane and one mole of adipoyl chloride were condensed in refluxing ether solution. A mixture of triisopropoxyadipimidosilane(VII) and hexaisopropoxydisilazane was obtained. The cyclic compound could be purified by crystallization from benzene. It is extraordinarily susceptible to hydrolysis and gives by reaction with water, ammonia, adipic acid, and hexaisopropoxydisilazane which undergoes further hydrolysis to yield hexaisopropoxydisiloxane.



VII (R = $(CH_3)_2CHO-$)

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Thesis Report

Niels C. Nielsen May 26, 1953

The preparation and study of the structures and properties of some metal derivatives of azo and azomethine dyes has led to interesting results with respect to the theoretical aspects of coordination chemistry and may well be of practical value to the dye industry which has used these "lakes" for many years. One aspect of this problem concerns the donor properties of the azo group.

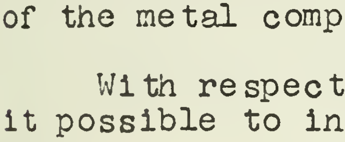
The earlier characterization of the metal lakes of azo dyes as Werner-type coordination compounds was accomplished by Morgan and Drew, and their associates and students, who prepared, analyzed, and performed various substitution reactions on these compounds. This work showed the necessity of having substituents such as -OH, NH_2, etc. in at least one position ortho to the azo group in order to form stable complexes. The later workers also indicated that the azo group was involved in the formation of only one coordinate covalent bond.[1]

Callis and Nielsen[2,3] continued this investigation and, by the use of magnetic susceptibility measurements, was able to establish the configuration of a large number of complexes. Further work by Liu[4] and the measurement of stability constants by Snavely and Fernelius[5] permits a rather complete evaluation of the metal complexes of the azo dyes.

With respect to the azo group as a donor, Feigl[6] has found it possible to induce color changes in solutions of azo dye indicators by the addition of $Pd(CN)_2$. The dyes used did not contain any ortho substituents, and the change, apparently, cannot be produced by any other compound.

Since the azo group does contain enough atoms to furnish two pairs of electrons, in addition to π electrons from the double bond, it may be possible to form two coordinate covalent bonds with this group. In examining the absorption spectra of various dyes and their metal complexes in neutral, acid, and alkaline solution, some evidence has been found for the addition of a proton to the azo group without completely rupturing the coordinate bond previously established with a metal ion. The resulting spectra are also being evaluated with respect to the affect of chemical constitution on the color of these compounds.

In an effort to induce the azo group to form more than one bond, the following dyes are being prepared:



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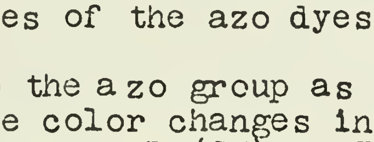

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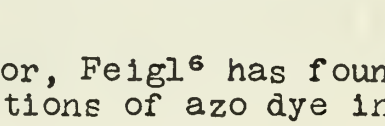

A study of the metal complexes of these dyes should provide some clarification of the donor properties of the azo group.

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THESIS REPORT

The Synthesis of Hydrazine

Roger W. Sanftner May 26, 1953

Interest in an economic synthesis of hydrazine has been heightened of late by the use of hydrazine as a speciality fuel. Furthermore many uses, e.g. in polymers or agricultural chemicals, for substantial quantities of hydrazine are conceivable should a low cost procedure for manufacture of hydrazine be developed. Many approaches have been devised, but the Raschig synthesis (1), modified but slightly, still remains the principal technical process in operation in this country today.

Recently Mattair and Sisler (2) reported the isolation of hydrazine from the interaction of gaseous chlorine with liquid and gaseous ammonia. They stated that the yield of hydrazine is dependent upon the ammonia to chlorine ratio and upon the ammonium chloride concentration. Wiberg and Schmidt (3) report that chloramine and ammonia dissolved in anhydrous ether give no hydrazine whereas, with water present, hydrazine was reported to have been formed.

A study has been undertaken of the reaction of ethereal solutions of chloramine with liquid ammonia under various conditions in order to determine the effect of ammonium chloride on the ammonolytic reaction of chloramine and liqiid ammonia. The reaction between hydrazine and chloramine in liquid ammonia was also investigated.

McElroy (4) and Oldham (5) have found that chloramine will undergo an one electron reduction at the dropping mercury electrode in liquid ammonia. Hydrazine could be postulated as one of the products of such a reaction. Since chloramine undergoes such a reduction, it was suggested that chemical reduction of chloramine might result in the formation of hydrazine. The reaction of aqueous chloramine solutions with a variety of amalgams was investigated; it was found that under certain conditions small quantities of hydrazine are formed.

In Raschig's original work, a variety of mateials was investigated in an attempt to find a substance which would act as a catalyst for the reaction between hypochlorite and ammonia. It was found that glue and gelatin are effective in increasing the yields of hydrazine; it was first assumed that the increased viscosity of the solution served to in-

crease the yield. Subsequent investigations by Bodenstein (6,7) and Møeller (8) have shown this theory to be incorrect. These investigations have shown that the presence of small amounts of metallic ions catalize the decompositon of hydrazine during the course of the reaction; glue and gelatin serve as metallic deactivators. Many substances have been investigated as substitutes for glue and gelatin (1,9.10). These two materials still remain, however, the most satisfactory substances from the standpoint of yield. None the less many disadvantages arise from their use. An investigation was begun to determine the role of gelatin in its removal of metallic ions from solution and also to discover an effective agent which would not posses the disadvantages exhibited by gelatin. Many substances have been investigated and several promising alternative materials have been found. Furthermore, it is believed that the cause of effectiveness of gelatin has been found.

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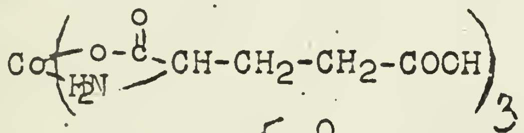
P.A.HORRIGAN May 26,1953

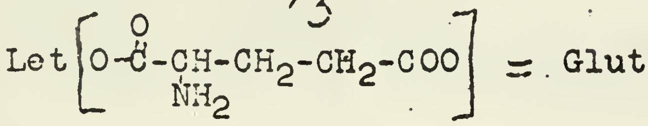
A Study of the Uncoordinated Carboxyl Groups in Glutamic Acid Complexes

There have been reports that uncoordinated functional groups on ligands react one way when the ligand is coordinated to a metal atom, and another when the ligand is "free".[1,2]

It was decided to prepare complexes of cobalt and copper with glutamic acid and study the properties of the uncoordinated carboxyl groups. The following compounds were prepared:

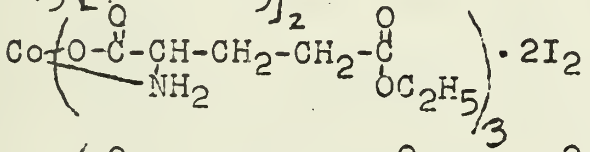


$$\mathrm{Co}\left(\begin{matrix}\mathrm{O{-}\overset{O}{C}}\\ \mathrm{H_2N}\end{matrix}\!>\mathrm{CH{-}CH_2{-}CH_2{-}COOH}\right)_3$$

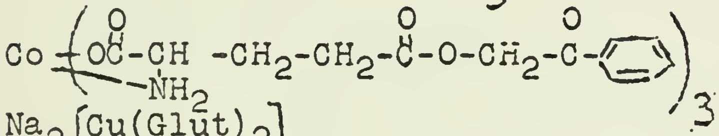


$$\text{Let}\left[\mathrm{O{-}\overset{O}{C}{-}\underset{NH_2}{CH}{-}CH_2{-}CH_2{-}COO}\right] = \mathrm{Glut}$$

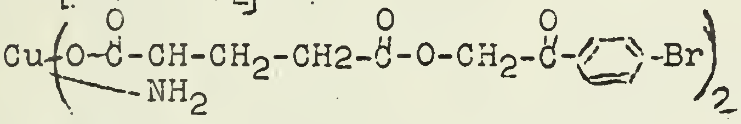
$\mathrm{Na_3[Co(Glut)_3]}$
$\mathrm{Ag_3[Co(Glut)_3]}$
$\mathrm{Co_3[Co(Glut)_3]_2}$



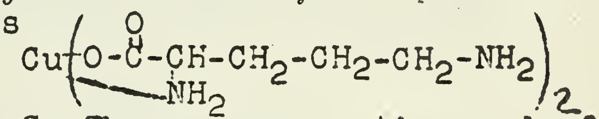
$$\mathrm{Co}\left(\mathrm{O{-}\overset{O}{C}{-}\underset{NH_2}{CH}{-}CH_2{-}CH_2{-}\underset{OC_2H_5}{\overset{O}{C}}}\right)_3\cdot 2\mathrm{I_2}$$



$\mathrm{Na_2[Cu(Glut)_2]}$
$\mathrm{Cu[Cu(Glut)_2]}$



As an extension of this study, the application of the "masking effect" is being attempted with some of these complexes. The "masking effect" was first illustrated by A.C.Kurtz[3,4], who prepared amino derivatives of such complexes as



$$\mathrm{Cu}\left(\mathrm{O{-}\overset{O}{C}{-}\underset{NH_2}{CH}{-}CH_2{-}CH_2{-}CH_2{-}NH_2}\right)_2$$

and, who then removed the metal with H_2S. Thus, one reactive end of the molecule was "masked" while the other was left free to form a derivative. The phenacyl derivatives mentioned above are being treated to yield the metal-free ligands.

This work has shown that the uncoordinated carboxyl groups in cobalt and copper glutamate complexes exhibit no anomalous properties.

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   Journal of Physical Chemistry (J. Phys. Chem.);
   Analytical Chemistry (Anal. Chem.);
   Industrial and Engineering Chemistry (Ind. Eng. Chem.);
   Journal of the Electrochemical Society (J. Electrochem. Soc.);
   Journal of the Chemical Society (J. Chem. Soc.);
   Nature (Nature);
   Science (Science);
   Transactions of the Faraday Society (Trans. Faraday Soc.);
   Proceedings of the Royal Society of London (Trans. Royal Soc. London);
   Journal of Chemical Physics (J. Chem. Phys.);

Zeitschrift für anorganische Chemie (Z. anorg. Chem. or Z. anorg. allgem. Chem.);
Angewandte Chemie (Angew. Chem.):
Chemische Berichte (Chem. Ber. or Ber.);
Comptes rendus (Compt. rend.);
Helvetica Chimica Acta (Helv. Chim. Acta)

3. Review:

Chemical Reviews (Chem. Revs.);
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Journal of Chemical Education (J. Chem. Educ.).