

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE CONSTITUTION OF ABNORMAL AMMONIUM SALTS¹

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Investigations of the systems in which abnormal ammonium salts are reported to exist are far from numerous. Kuriloff² studied the system, ammonium nitrate-hydrogen nitrate, and showed that the only abnormal compound was $\text{HNO}_3 \cdot 4\text{NH}_3$. Kendall and Davidson³ investigated the systems of ammonia with halogen hydrides, and demonstrated the existence of the compounds $\text{HX} \cdot 4\text{NH}_3$ in which X is chlorine, bromine and iodine and also the compound $\text{HI} \cdot 5\text{NH}_3$. These authors state that the compounds of the types $\text{HX} \cdot 2\text{NH}_3$ and $\text{HX} \cdot 7\text{NH}_3$ reported by Troost⁴ do not exist. They found no abnormal compounds in the hydrogen fluoride system and no compounds in any of these systems in which the ratio of acid to base was greater than one.

While there are, apparently, no investigations of the systems of amines with halogen hydrides,⁵ there are numerous compounds in the literature which belong to these systems. The compounds reported by Berliner and Hann⁶ of the type $\text{Base} \cdot 4\text{HF}$ are especially interesting. The bases were aromatic amines of the most diverse sorts. Three of the hydrogen fluoride molecules were "titratable with alkali" while the last was combined as the normal salt of the base. These compounds are all solids and are well characterized by elementary analysis for carbon, nitrogen and fluorine.

Most of the other compounds which are reported in the literature⁷ have been reported on the basis of absorption experiments. In general, the method was to pass the anhydrous halogen hydride over the dry normal salt until no further absorption took place at the particular temperature chosen. Kauffer and Kunz,⁸ using this method, reported a dihydrochloride

¹ The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Gordon D. Byrkit in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1929. This paper was prepared by the junior author after the death of Dr. W. H. Hunter, which occurred on August 19, 1931. [L. I. SMITH.]

² Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).

³ Kendall and Davidson, *THIS JOURNAL*, **42**, 1141 (1920).

⁴ Troost, *Compt. rend.*, **88**, 578 (1879); *ibid.*, **92**, 715 (1881).

⁵ Except that of Leopold [*Z. physik. Chem.*, **71**, 59 (1910)] on the system aniline-hydrogen chloride. This investigation, however, is incomplete in the range 19.6 to 49.7 mole per cent. of aniline, in which abnormal compounds of the type $\text{C}_6\text{H}_5\text{NH}_2 \cdot n\text{HCl}$ ($n = 2, 3$ or 4) would occur.

⁶ Berliner and Hann, *J. Phys. Chem.*, **32**, 1142 (1928).

⁷ Scholl and Escales, *Ber.*, **30**, 3134 (1897); Korczynski, *ibid.*, **41**, 4379 (1908); *ibid.*, **43**, 1820 (1910); Weinland and Reischle, *ibid.*, **41**, 3671 (1908); Weinland and Lewkowitz, *Z. anorg. Chem.*, **45**, 39 (1905); Rohler, *Z. Elektrochem.*, **16**, 431 (1910).

⁸ Kauffer and Kunz, *Ber.*, **42**, 385, 2482 (1909).

of dimethylamine, liquid di- and trihydrochlorides of trimethylamine and also reported that methylammonium chloride absorbed no hydrogen chloride. This is a series of abnormal compounds in which the maximum number of halogen hydride molecules added is equal to the number of alkyl groups in the amine. The influence of alkyl groups in this case would constitute an exception to the usual view, since the effect of the type and number of alkyl (and aryl) groups on the character of the ammonium salts formed is usually very small with respect to all other properties. Except for the work of Wieland⁹ and Rheinboldt,¹⁰ who showed that the number of molecules of desoxycholic and other bile acids¹¹ which added to one molecule of fatty acids, esters, etc., was directly dependent on the number of methyl and methylene groups in the molecule, there seems to be no work indicating a relation between the size and character of alkyl groups and the additive power of the molecule.

Experimental Method

The purposes of the present investigation were two: first, to determine whether or not the compounds reported by Kaufler and Kunz exist, and, second, to investigate further the systems obtained from amines and halogen hydrides, in order to ascertain whether there is a discoverable relation between the number and nature of the groups in a substituted ammonia and the amount of halogen hydride which may be added to it. Two types of measurements accordingly were made. We determined the amounts of halogen hydride absorbed by the amines at various temperatures, and also investigated the thermal behaviors of the systems thus formed.

Preparation of Materials

Dimethylammonium Chloride.—Kahlbaum's liquid dimethylamine was dissolved in ice cold toluene and dry hydrogen chloride passed into the cold solution until precipitation was complete. The crystals were filtered off, washed with dry benzene and dried; m. p. 167°.

Trimethylammonium Chloride.—This was prepared by students from ammonium chloride and paraformaldehyde. A solution of this material was made strongly alkaline, the base distilled into concentrated hydrochloric acid and the salt crystallized out. The process was repeated and the salt recrystallized several times from water, finally being dried over anhydrous calcium chloride in a desiccator; m. p. 273–275°, with decomposition.

Tetramethylammonium Chloride.—This was prepared by dissolving dry trimethylamine in purified methanol and saturating this solution with methyl chloride. The solution was concentrated to crystallization and the product recrystallized from methanol. The salt was treated with silver oxide in aqueous solution and, on crystallizing it

⁹ Wieland and Weil, *Z. physiol. Chem.*, **80**, 287 (1912); Wieland and Sorge, *ibid.*, **97**, 1 (1916); Wieland, *Z. angew. Chem.*, **42**, 421 (1929).

¹⁰ Rheinboldt, *ibid.*, **37**, 834 (1924); Rheinboldt, Pieper and Zervas, *Ann.*, **451**, 256 (1926); Rheinboldt, König and Otten, *ibid.*, **473**, 249 (1929).

¹¹ Boedecker, *Ber.*, **53**, 1853 (1920).

from methanol, a product was obtained which gave no odor of trimethylamine with aqueous alkali.

Methylphenylammonium Chloride.—Vacuum distilled methylaniline was dissolved in dry toluene and dry hydrogen chloride passed in to complete precipitation. The salt was filtered off, washed with dry benzene, dried and recrystallized from purified acetonitrile; m. p. 123.7–124.2°.

Absorption Experiments

Dry hydrogen chloride was passed over a weighed quantity of the normal salt in a weighed absorption bulb placed in a constant temperature bath until no more absorption took place. The increase in weight is the amount of hydrogen chloride absorbed by the salt. Results, expressed as the ratio of moles of hydrogen chloride to moles of base in the saturated mixture at various temperatures, are given in Table I. In most cases the resulting product was liquid.

TABLE I
ABSORPTION OF HYDROGEN CHLORIDE BY AMINES AT VARIOUS TEMPERATURES

Temp., °C.	$\frac{\text{Moles HCl}}{\text{Moles Me}_2\text{NH}}$	$\frac{\text{Moles HCl}}{\text{Moles Me}_2\text{N}}$	$\frac{\text{Moles HCl}}{\text{Moles Me}_2\text{NCl}}$	$\frac{\text{Moles HCl}}{\text{Moles MePhNH}}$
31.8		2.41		
Room				1.928
24.0		2.50		
21.9		2.48		
0.0		2.99	1.079	
– 3.6	2.45			
– 13.1			1.181	
– 21.8		3.81		
– 22.0		3.82		
– 24.7 ^a		4.02		
– 24.8 ^a		3.95		

^a It was difficult to maintain these low temperatures constant, hence the variation in results.

Discussion of the Absorption Experiments

The data in Table I show that the amount of absorption of hydrogen chloride by the normal salts depends on the temperature; as this is lowered, the amount of absorption increases. It is true as Kaufler and Kunz state that trimethylammonium chloride absorbs two additional moles of the gas at 0°. However, since the amount of absorption shows a continuous change, so that any ratio whatever may be obtained by a proper choice of temperature, it appears that the report of the compound $(\text{CH}_3)_3\text{N}\cdot 3\text{HCl}$ is erroneous. The same authors report a dihydrochloride of dimethylamine on the basis of the amount of hydrogen chloride absorbed by the normal salt at ordinary temperatures.¹² This again seems to be a fortuitous choice

¹² Their statement⁸ "0.1624 g. Dimethylaminhydrochlorid nahmen bei gewöhnlicher Temperatur 0.971g. Chlorwasserstoff auf = 1.00 Mol HCl," however, is erroneous either in data or calculation. The data given correspond to the absorption of 13.26 moles of hydrogen chloride by the normal salt.

of temperature since at -3.6° the normal salt absorbs 1.45 moles of hydrogen chloride or a total of 2.45 moles per mole of base.

Other salts as well show a non-stoichiometric absorption of hydrogen chloride at various temperatures. In such experiments as these we seem to be determining the solubility of hydrogen chloride in the liquid phase present, and this changes gradually with the temperature without reference to the stoichiometric relation between the two components. *At the same time, there is a strong force acting between many of these normal salts and hydrogen chloride.* Trimethylammonium chloride, especially, absorbs the gas with an avidity which is comparable only with the absorption of water vapor by potassium hydroxide.

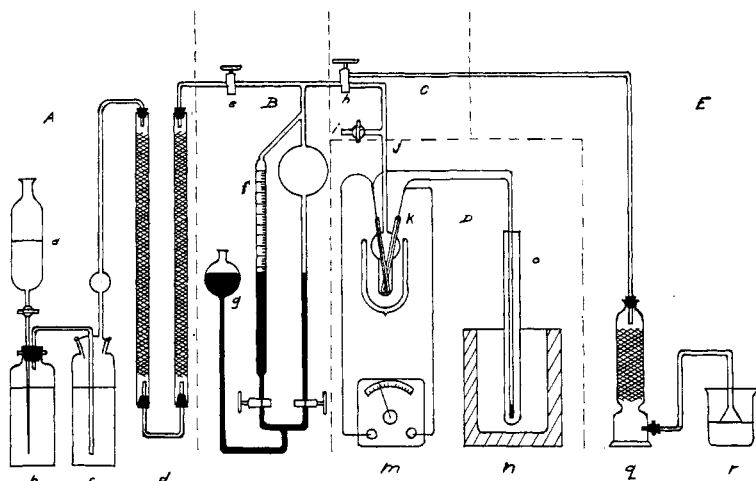


Fig. 1.

Thermal Investigation

Preparation of the Mixture.—The apparatus shown in Fig. 1 was used. The thermocouple tube, *k*, was first weighed, filled with pure normal salt,¹³ reweighed and sealed to the apparatus at *j*. Hydrogen chloride was generated in *b*. After passing through the bubbler of concentrated sulfuric acid, *c*, the gas continued through two long tubes, *d*, packed with anhydrous calcium chloride to remove oxides of sulfur. With both the buret and bulb filled with mercury and stopcock *h* opened to *E*, the system was flushed with hydrogen chloride until all the air was removed, while a water pump attached at *i* removed the air from the thermocouple tube. With *h* closed and the buret, *f*, filled with mercury, the calibrated bulb of five hundred cubic centimeters' capacity was filled with hydrogen chloride to the lower mark. With stopcocks *e* and *i* closed, *h* was opened to the bulb, *k*, which was surrounded by a Dewar flask of liquid air. Hydrogen chloride was condensed into *k* until when the stopcock, *h*, was closed and the mercury leveled, it stood at the upper mark of the calibrated bulb. The temperature and pressure were noted during this process. By using the bulb and/or buret (for quantities less than 500

¹³ On account of the great hygroscopicity of these salts, this operation was accomplished in a desiccator box.

cubic centimeters) any desired quantity of hydrogen chloride could be condensed into k, resulting in a mixture of any desired composition.

Melting Point Determination.—With stopcock h closed, the tube k was surrounded by liquid air until all of the hydrogen chloride had been condensed (five minutes was sufficient). Stopcock i was opened to the air,¹⁴ and the tube sealed off at j. The tube was then warmed until the contents were melted and thoroughly mixed. The thermocouple tube was air jacketed and fitted with the wires of the cold junction of the thermocouple while the hot junction was placed in a stirred bath of ice and water. The jacketed tube was surrounded by a cooling bath about 20° below the approximate freezing point of the mixture, and the millivoltmeter (calibrated at the freezing point of several highly purified organic liquids) was read at regular intervals. The horizontal portion of the cooling curve thus obtained represented the freezing (melting) point of the mixture and the corresponding temperature was read from the calibration chart of the thermocouple.

In cases in which the melting point of the mixture was near or above 0°, a tube without provision for the thermocouple junctions replaced k. The procedure for the preparation of the sample was precisely the same. The melting points were determined by placing the sealed tube in a stirred glycerin bath which was warmed very slowly. Several determinations, at twenty-four hour intervals, were made on each tube. The necessity for the long interval between determinations is, of course, the fact that as the temperature is raised to the melting point, hydrogen chloride passes into the vapor phase, which changes the melting point. More consistent results were therefore obtained if the contents of the tubes were allowed to return to equilibrium before a second determination was made.

The systems trimethylamine- and methylphenylamine-hydrogen chloride were investigated in this way. The results are given in Tables II and III and the corresponding Figs. 2 and 3.

TABLE II

THERMAL DATA ON THE SYSTEM TRIMETHYLAMINE-HYDROGEN CHLORIDE

Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.
55.4	270 dec.	66.6	56.3	72.5	-54.5
56.7	260 dec.	67.1	49.1	74.0	-87.3
59.6	199.6	68.1	15.4	75.0	-126.8
60.5	125-130	69.1	-1.4	76.6	-126.0
65.3	62.9	72.4	-54.5	78.1	-116.3

TABLE III

THERMAL DATA ON THE SYSTEM METHYLPHENYLAMINE-HYDROGEN CHLORIDE

Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.	Mole % HCl	M. p., °C.
60.10	79.5	66.99	36.4	72.95	34.0
61.99	55.4	67.50	36.6	75.37	31.2
63.36	38.4	68.03	34.8	77.48	20.9
63.96	32.8	68.39	38.4	80.22	1.3
64.48	33.7	68.94	36.8	81.53	-17
65.21	34.6	69.07	36.7	82.11	< -24
65.74	34.9	69.52	38.4	84.96	< -24
66.45	37.6	70.15	37.6		

¹⁴ When a tube prepared as described and surrounded by liquid air for five minutes was broken off at j and held at the mouth of a bottle of 28% ammonia, no fumes were formed; hence there was no loss of hydrogen chloride.

Investigations in the systems methylamine- and dimethylphenylamine-hydrogen chloride offered considerable difficulty and were finally laid aside. In the first case, the normal salt seemed to have no tendency to absorb hydrogen chloride and the pressures developed on warming were almost invariably greater than the glass tubes would stand. In the second case, the normal salt was too hygroscopic to be handled even in the desiccator box. Attempts to use the free base were also unsuccessful because of the high melting point of dimethylaniline (2°) which prevented the base from reacting with the hydrogen chloride as it was condensed into the bulb. Before the base was warm enough to react, the pressure of the hydrogen chloride was always sufficient to break the tube.

Discussion of Thermal Investigations

That di- and trihydrochlorides of trimethylamine do not exist is evident from the thermal diagram of the system (Fig. 2), since there are no maxima at either $66\frac{2}{3}$ or 75 mole per cent. of hydrogen chloride. On the other hand, it is equally evident from Fig. 3 that a dihydrochloride of methylaniline is formed. That the high point of the curve is at 69 mole per cent. hydrogen chloride rather than at $66\frac{2}{3}\%$

is to be expected because at the temperatures at which these mixtures melted, much of the hydrogen chloride was in the vapor phase. Thus, while sufficient gas had been placed in the tube to give a mixture of the composition 69% hydrogen chloride, enough was probably in the vapor phase and therefore without effect on the melting point, to reduce the amount in the solid and liquid phases to $66\frac{2}{3}\%$.¹⁵

¹⁵ In general, the melting points below -83° (the boiling point of hydrogen chloride) are the most accurate. As the temperature of fusion rises, the observed melting points become higher and higher than they would be were all the hydrogen chloride in the solid and liquid phases. This accounts for the extreme flatness of the curves in the neighborhood of the normal salt.

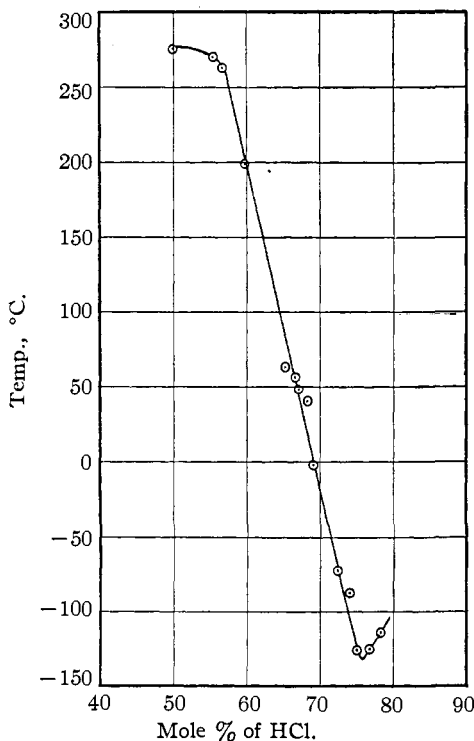
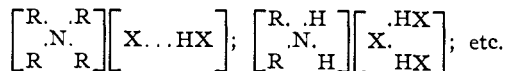


Fig. 2.—Trimethylamine-hydrogen chloride.

A General System of Molecular Compounds of Higher Order

Werner's¹⁶ formulation of normal and abnormal ammonium salts as $[H_3N \dots H]X$ and $[H_3N \dots H \dots NH_3]X$, respectively, is usually extended in the case of abnormal salts with extra ("exo")¹⁷ acid molecules by assuming the addition of the exo molecules to the anion of the salt, thus



However, these formulas do not express experimental facts in that, while ammonium chloride does not add hydrogen chloride,¹⁸ many substituted

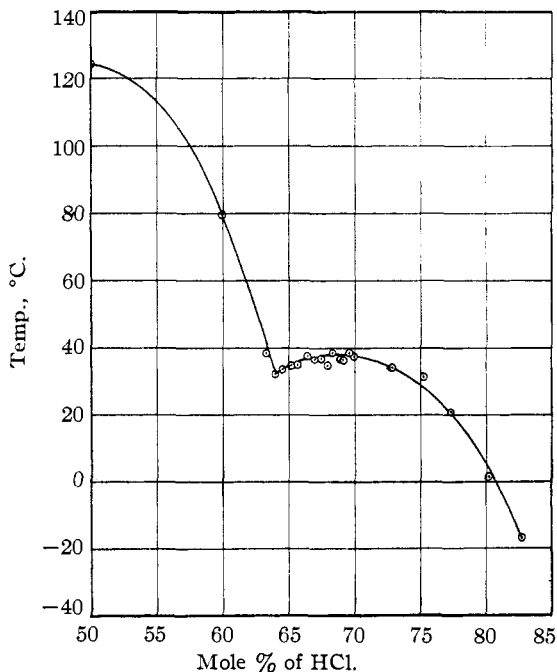


Fig. 3.—Methylphenylamine-hydrogen chloride.

ammonium chlorides do. Since the difference here is in the character of the cation of the salt, formulas for dihydrochlorides, etc., must be based on the cation of the salt, and must not involve the anionic chlorine, which is identical in both cases.

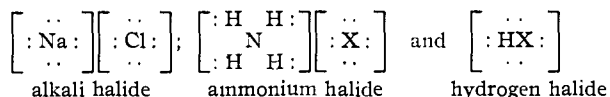
The attempt to correlate the additive properties with the change in character of the cation depends on a development of the conception of

¹⁶ Werner-Pfeiffer, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," fifth edition, Braunschweig, 1923.

¹⁷ Werner-Pfeiffer, Ref. 16, p. 310; Weinland, "Einführung in die Chemie der Komplex-Verbindungen," second edition, Stuttgart, 1924, p. 327.

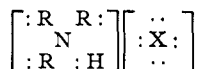
¹⁸ Kendall and Davidson, THIS JOURNAL, **42**, 1141 (1920).

"pseudo atoms" of Grimm¹⁹ and Glockler.²⁰ According to these authors, the well-known similarity of the ammonium and potassium ions, the former a pseudo atom of neon and the latter of argon, lies in that the L electrons of the nitrogen atom are so altered by the sphere of four protons (which are *inside* their respective electron pairs in the ammonium ion) that they behave almost as the M electrons of the potassium ion. That neither the alkali halides nor ammonium halides add halogen hydrides, as Kendall and Davidson³ observed, is not surprising when their electronic structure is considered



In the terminology of Sidgwick,²¹ these are all donors.

However, substituted ammonium halides do absorb halogen hydride even when there is no formation of definite compounds. It is conceivable that in these the alkyl and aryl groups are of such size that in replacing the protons they so distort the electronic arrangement of the atom that some or all of the remaining protons lie without the L shell, thus



With such a configuration as this, it is possible that the protons so "extrapolated" may possess the power of coordination in quite a weakened sense. It is possible to account on this basis for the absorption of hydrogen chloride, for example, by trimethylammonium chloride, even though the additive power of the extrapolated proton is insufficient to cause the formation of a definite compound. With methylphenylammonium chloride, on the other hand, the comparatively great size of the phenyl group, together with the methyl group, makes this extrapolation so pronounced that a definite compound, $\text{CH}_3(\text{C}_6\text{H}_5)\text{NH}\cdot 2\text{HCl}$, is formed. The exo molecule is bound in the "second sphere" of Werner,²² the substituted ammonium ion acting as the center of the complex. It is possible to conceive of a third zone in which the forces available to bind additional molecules are much weaker than those of the second sphere, and may even attract molecules without binding them in a stoichiometric way.

No matter how they may be written in a Werner type formula, it seems of great importance that these compounds with exo molecules form a transition from the coordination compounds of Werner, in which groups of definite number are geometrically arranged about a central atom, to the "ion atmosphere" of Debye and Hückel, in which there is an indefinite

¹⁹ Grimm, *Z. Elektrochem.*, **31**, 474 (1925).

²⁰ Glockler, *THIS JOURNAL*, **48**, 2021 (1926).

²¹ Sidgwick, "Electronic Theory of Valency," Oxford University Press, 1927.

²² Werner-Pfeiffer, Ref. 16, p. 234.

"cloud" of electrostatically attracted dipole molecules or ions about another ion or about another strongly dipolar molecule. These forces are often considered to be all of the same nature, that is, electrostatic,²³ and it is on this basis that an organization of our knowledge is possible with the aid of Table IV. In the compounds of the first and second orders, the groups about the central atom, which are definite in number and position in the molecule, are held by the strong forces of primary valence in the first-order compounds and by the weaker forces of secondary valence in the second-order compounds. Intermediate between these two types are the compounds in which, while the number and position of the groups about the central atom are definite, it is difficult to say whether the groups are held by primary or secondary valence. The nitroprussides, metal carbonyls, etc., are examples.

Compounds of the third order are those in which, while the number of added molecules is stoichiometric, it is at present impossible to determine the exact arrangement of the constituents of the molecule, as in many dihydrochlorides of monacid ammonium bases. Between the second and third orders are those compounds formed by addition to molecules already coördinatively saturated, as, for example, $\text{NiCl}_2 \cdot 8\text{NH}_3$.

Those compounds in which the number of bound molecules is indefinite even though there is marked affinity between the two components (for example, trimethylammonium chloride and hydrogen chloride) lie between the compounds of the third order and the class of Debye and Hückel. In the latter there is an indefinite cloud of dipoles, which may be either oppositely charged ions or neutral molecules, about a central dipole, which again may be either an ion or a molecule. The exo compounds in which we have been especially interested include compounds of the third order and the intermediate types on both sides.

TABLE IV
COMPOUNDS OF HIGHER ORDERS

Order	First	Second	Third	Debye-Hückel
Type compounds	CCl_4	$[\text{Co}(\text{NH}_3)_6]^{+3}$	$[\text{MePhNH}_2 \cdot 2\text{HCl}]$	$[\text{K}^+(\text{Cl}^-)_n]$
Intermediate types	$[\text{Fe}(\text{CN})_5(\text{NO})]^{-4}$	$\text{NiCl}_2 \cdot 8\text{NH}_3$	$\text{Me}_3\text{NHCl} + \text{HCl}$	
Number of groups	Definite	Definite	Definite	Indefinite
Location of groups	Definite	Definite	Indefinite	Indefinite
Strength of binding	Strongest	----->	Decreases ----->	-----> Weakest
			←----- Exo compounds ----->	

Summary

1. It has been shown that di- and trihydrochlorides of trimethylamine do not exist. This is another example of the fallacy of assuming the

²³ Magnus, *Z. anorg. allgem. Chem.*, **124**, 289 (1922); van Arkel and de Boer, *Rec. trav. chim.*, **47**, 593 (1928). Compare also the cluster theory of gas reactions of Lind ["Chemical Effects of Alpha Particles and Electrons," New York, 1928].

existence of abnormal compounds on the basis of absorption experiments only.

2. The existence of a dihydrochloride of methylaniline has been shown by means of a thermal diagram of the system.

3. An explanation of the absorption of hydrogen chloride by the normal ammonium salts with and without the formation of stoichiometric compounds has been advanced.

4. An attempt has been made to bring all molecular compounds of higher orders into one general system.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

AN IMPROVED PROCEDURE FOR THE PREPARATION OF ORGANOLITHIUM COMPOUNDS

BY HENRY GILMAN, E. A. ZOELLNER AND W. M. SELBY

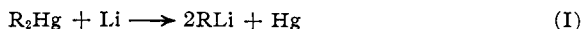
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Introduction

The chief and outstanding chemical difference between organometallic compounds containing alkali metals and those prepared from alkaline earth metals is the general tendency of the former to add to some ethylenic linkages and the absence of such addition with organometallic compounds like the Grignard reagent. There are, of course, occasional differences in a series of organolithium compounds, for example, just as there are differences between RMgX compounds. It is reasonable to expect that, in general, the mechanisms of reaction of these two groups of organometallic compounds with a given reactant would be similar and, in many cases, identical. However, the literature contains numerous cases where the mechanism proposed with organoalkali compounds does not agree with that established with organomagnesium compounds. It was in connection with such studies, as they concern terminal cumulated unsaturated linkages and allylic systems, that we needed phenyl-lithium in quantity.

Organolithium compounds were first prepared by Schlenk and Holtz¹ by the reaction of lithium with an R_2Hg compound in accordance with this general reaction, which has recently been shown to be reversible²



The technique in this operation was subsequently improved and excellent

¹ Schlenk and Holtz, *Ber.*, 50, 272 (1917). See, also, Groll, *THIS JOURNAL*, 52, 2998 (1930).

² Ziegler and Colonius, *Ann.*, 479, 135 (1930). For other studies on the reaction between RX compounds and lithium, see Spencer and Price, *J. Chem. Soc.*, 97, 385 (1910), and Wittig and Leo, *Ber.*, 64, 2395, 2405 (1930).