REACTIONS AND REAGENTS IN LIQUID AMMONIA[1]

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I. INTRODUCTION

Aside from water, liquid ammonia is the only solvent concerning which there exists a body of knowledge sufficiently extensive to warrant our speaking of it as having a chemistry of its own. From the chemical point of view, the importance of a solvent medium is determined by the number and variety of the reactions that may be carried out in it and this, in turn, depends upon the number, variety, and convenience of the reagents that the solvent affords. When a given substance reacts with a large number of other substances in the same or in a similar manner, we call it a reagent.

Reagents may be conveniently divided into five principal groups: namely, (*1*) acids and (*2*) bases; (*3*) oxidizing and (*4*) reducing agents; and (*5*) reagents that effect the transfer of atoms or groups of atoms from combination with one atom to combination with another. The members of the last group of reagents may be termed "synthetic reagents". In water we have a large number of strong acids and bases as well as strong oxidizing agents, but we have only weak, although numerous, reducing agents and few synthetic reagents.

The rather considerable differences that have been found to exist between the chemistry of solutions in liquid ammonia and in water are, in the main, due to the greater inertness of the H—N bond over that of the H—O bond. Because of the high reactivity of the hydrogen atoms in water, salts of the weaker acids and bases are largely, if not completely, hydrolyzed, and reducing agents stronger than hydrogen react with water with evolution of hydrogen. The chemistry of liquid ammonia solutions is characterized by reagents of high reducing power and by stable solutions of salts of exceedingly weak acids,—if, indeed, certain of these substances may be termed acids at all.

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II. ACIDS AND BASES

Acids and bases in liquid ammonia are relatively weak when compared with corresponding solutions in water. While the number and variety of acids that may be obtained in liquid ammonia (as ammonium salts) is, if anything, larger than in water, the number of bases is exceedingly limited; only the alkali-metal amides have any considerable solubility in ammonia. The study of acid–base reactions in liquid ammonia has, nevertheless, proved very fruitful, largely owing to the fact that in liquid ammonia solution one may study the salts of many acids which are largely, if not completely, hydrolyzed in water.

Since the acids are much weaker chemical agents in ammonia than they are in water, they may frequently be employed advantageously where side reactions are troublesome in aqueous solutions. Thus, germane may be prepared in yields up to 70 or 80 per cent by treating magnesium germanide with ammonium bromide in liquid ammonia; the corresponding reaction in water gives a yield of only about 20 per cent. The alkali-metal amides, in addition to reacting as bases, also are useful reagents for introducing the amide group into combination with various elements, such as carbon. In reactions of this type, the amides act as synthetic reagents rather than as bases; their reactions will be further discussed below.

III. OXIDIZING AGENTS

Oxidizing agents are less conveniently used in liquid ammonia than in water and are much less powerful. The halogens, as such, are not stable in liquid ammonia solution. Nitric and sulfuric acids form the corresponding ammonium salts and have little or no oxidizing power. Alkali-metal permanganates and chromates are soluble and may be employed as rather weak oxidizing agents. On the other hand, liquid ammonia supplies nitridizing agents which, at times, find useful application.

IV. REDUCING AGENTS

Elementary reductions

The strongest homogeneous reducing agents known to chemistry are the solutions of the alkali and alkaline-earth metals in liquid ammonia. These metals in ammonia solution dissociate into normal positive ions and electrons. The reducing power of these solutions is due to the electrons and is practically identical for solutions of all metals.

The metals in ammonia solution react with many of the more electronegative elements according to the equation:

$$A^n + nM = M_nA^n$$

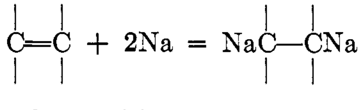
where A^n is an element of valence n and M is an atom of an alkali metal or an equivalent of an alkaline-earth metal. Thus, sodium and potassium react with all these elements from chlorine to lead, inclusive, with the exception of nitrogen, carbon, silicon, and, probably, germanium. Excepting the alkali-metal halides, compounds of the type M_nA^n are not appreciably soluble in liquid ammonia, but practically all react with additional atoms of the element A to form highly soluble poly salts. Thus, we have such compounds as Na_2S_x, Na_2Te_2, Na_2Te_x, Na_3Sb_7, and Na_4Pb_9, all of which are readily soluble and all of which are electrolytes in liquid ammonia solution.

Bond reductions

Closely allied to the above reactions are those between the alkali metals and univalent and divalent groups such as triphenylmethyl, dimethyltin, and the like. On treating these groups with an alkali metal, there are obtained salts of which the following are examples: $(C_6H_5)_3CNa$, $(CH_3)_3SnNa$, $(C_6H_5)_3GeNa$, $(C_2H_5)_3SiLi$, $(C_6H_5)_3PbNa$, $(CH_3)_2SnNa_2$, and $(C_6H_5)_2GeNa_2$. These compounds are all salts and are valuable as synthetic reagents. Their reactions will be discussed below.

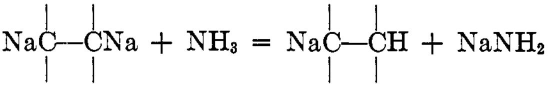
In a sense, the above reactions involve the splitting of a bond of the type A—A. If the bond is not very stable, fission takes place readily, but as the bond becomes more stable, a point is reached where reaction no longer occurs. Thus, the Sn—Sn bond is readily broken whether the substituent groups be aliphatic or aromatic. The same is true of germanium, but the Si—Si bond is not reduced by the alkali metals in ammonia solution. In the case of carbon, the triarylmethyls are readily reduced by the alkali metals, but corresponding reactions in which aliphatic groups are present do not occur.

Double bonds of the type A═A are readily reduced in the case of tin and germanium and either one or both bonds may be broken, depending upon the amount of metal used. With carbon, the C═C bond is not broken in the case of aliphatic compounds (so far as is known), but one bond is often broken in the case of aromatic compounds. Benzene is stable toward the alkali metals in liquid ammonia, but naphthalene and diphenyl are reduced. Reaction takes place as follows:

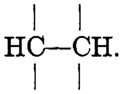


$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + 2\mathrm{Na} = \mathrm{Na}\overset{|}{\underset{|}{\mathrm{C}}}{-}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{Na}$$

Generally, one ion of the resulting salt ammonolyzes according to the equation:



$$\mathrm{Na}\overset{|}{\underset{|}{\mathrm{C}}}{-}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{Na} + \mathrm{NH_3} = \mathrm{Na}\overset{|}{\underset{|}{\mathrm{C}}}{-}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H} + \mathrm{NaNH_2}$$

In some cases, the resulting uni-univalent salt is stable; in others, it ammonolyzes to the hydrocarbon  $\underset{|}{\overset{|}{HC}}{-}\underset{|}{\overset{|}{CH}}$. Any of these salts may be converted to the corresponding hydrocarbon by the addition of an ammonium salt.

Reduction of salts

When salts of soluble metals are treated with other soluble metals in liquid ammonia, a metathetical ionic reaction occurs, the reaction being controlled by solubility relations. Thus, calcium reduces potassium from its bromide because of the low solubility of calcium bromide. In some cases, metals that have no appreciable solubility in liquid ammonia may reduce alkali metals from their salts because of the great depression of the concentration of the ions due to the reducing metal. Potassium, for example, is reduced from its amide by aluminum because aluminum amide is formed, which, being an amphoteric base, forms potassium ammonoaluminate with excess potassium amide, thus depressing the normal concentration of aluminum ions in the solution. The net result is that electrons, due to aluminum, and potassium ions, due to potassium amide, remain in solution as metal.

When a reducing metal reacts with a salt of another metal which is insoluble in liquid ammonia, the latter metal is, in general, reduced to the elementary state. When the reduced metal is inactive toward an alkali (or alkaline-earth) metal, it remains in the free state. Thus, when a silver salt is treated with alkali metal, metallic silver is precipitated. In other cases, when the precipitated metal is capable of reacting with the alkali metal, as with mercury or lead, for example, the reduced metal forms a compound with the alkali metal. (It should be noted in this connection, that, in many instances, a precipitated metal catalyzes the reaction between the reducing metal and ammonia and the resulting amide reacts further with the originally precipitated metal.)

Reduction of covalent compounds

Turning now to reactions of metals with compounds other than salts, we have several types of reactions:

(*1*) with hydrides, we have the reaction:

$$A{-}H + M = AM + \tfrac{1}{2}H_2, \text{ and}$$

(*2*) with other elements, we have the reactions:

$$AX + M = MX + A$$

$$A + M = MA$$

Here X is a univalent electronegative element, such as a halogen, and A is a univalent group, such as triphenylmethyl, trimethyltin, or the like.

(*1*) The first reaction might be looked upon as the action of an acid on a metal having a reducing power greater than that of hydrogen. Actually, this relationship is only a formal one; reactions of this type take place with substances which have no acidic properties. Triphenylmethane reacts slowly with potassium to produce potassium triphenylmethide and hydrogen. A better example is the reaction of sodium (or potassium) with monogermane:

$$GeH_4 + Na = NaGeH_3 + \tfrac{1}{2}H_2$$

This reaction takes place readily and is quantitative. The compound sodium germanyl, the analog of sodium methyl, is a true salt and is stable in liquid ammonia at its boiling point; the germanyl ion is not reduced further by sodium. A similar reaction takes place between the alkali metals and arsine, as Warren C. Johnson has shown. Doubtless such reactions would occur between alkali metals and other hydrides, such as silane, phosphine, and the like. The reaction of the alkali metals with certain boranes has recently been studied by H. I. Schlesinger and his coworkers at the University of Chicago, with most interesting results.

(*2*) The reactions of the second type are very common in liquid ammonia solution. They are often complicated by side reactions in which that solvent takes part. The compound AM often ammonolyzes in liquid ammonia according to the equation:

$$AM + NH_3 = AH + MNH_2$$

The resulting amide, in turn, reacts with the original halide according to the equation:

$$AX + MNH_2 = MX + ANH_2$$

The net result of the complete reaction is as follows:

$$2AX + 2M + NH_3 = 2MX + AH + ANH_2$$

When, for example, methyl chloride reacts with sodium in liquid ammonia, methane and methylamine are formed in equivalent quantities. The actual mechanism of the above reaction remains uncertain, but it is well established that an alkali-metal amide is formed as an intermediate reagent. When tetramethyltin is treated with sodium in liquid ammonia, reaction occurs as follows:

$$(CH_3)_4Sn + Na + NH_3 = (CH_3)_3SnNa + CH_4 + NaNH_2$$

Since tetramethyltin is stable toward sodium amide, this substance remains in solution or is precipitated. It is by no means certain, however, that sodium methyl, $NaCH_3$, is actually formed as an intermediate compound which later ammonolyzes to sodium amide and methane.

The most convenient method of preparing compounds of the type MA is to treat the halides AX with an excess of metal. This avoids the necessity of an initial reduction of the compound to the free group A. The chief difficulty met with is due to the fact that the halides of elements of lower atomic number ammonolyze in liquid ammonia. For this reason, the method is usually inapplicable in the case of silicon and, in some instances, germanium. Sometimes the difficulty can be overcome by dissolving the halide in ethylamine, which has a lower hydrolyzing tendency. In this way, the compound $LiGe(C_2H_5)_3$ has been obtained. This method is not applicable in the case of silicon, but it was found possible to reduce triphenylsilicon chloride to triphenylsilicon in ethylamine solution by means of lithium, owing to the formation of a compound between triphenylsilicon and ethylamine. The precise nature of this compound has not been established.

Any highly halogenated compound reacts with the alkali metals in liquid ammonia, but the tendency of such compounds to ammonolyze is so great that few of the lighter elements can be reduced by this method. Cases in point are the boron and silicon halides. Highly halogenated carbon compounds react with the alkali metals, the halogen being quantitatively converted to halide salt. The method is a very general and convenient one for determining halogens in organic compounds. What happens to the carbon residue, however, remains undetermined. The reactions are complicated, owing to the formation of alkali-metal amide which, in turn, reacts with the halides. Carbon tetrachloride reacts immediately with the alkali metals in liquid ammonia with quantitative formation of sodium chloride, but the residual carbon atom enters into a series of exceedingly complex reactions and these reactions cannot be unravelled until it is known how the alkali-metal amide reacts with carbon tetrachloride. This question will be touched upon below.

The bonds between carbon atoms and the less electronegative elements are, in general, rather stable; thus, the bonds between carbon and germanium and silicon are not reduced by the alkali metals. The carbon–tin and the carbon–lead bonds are both reduced; in the case of tetraaryl tin compounds only one bond is reduced, but in the case of lead, complete reduction may occur. We have no knowledge as to how the bonds between carbon and other metallic elements behave in this respect.

V. SYNTHETIC REAGENTS

When a salt, MA, of a strongly positive ion, M^+, and a weakly negative ion, A^-, is treated with a compound, RX, containing a strongly electronegative atom, reaction occurs. The negative atom, X, originally combined with another atom or group of atoms, R, goes into the ionic condition and the residual groups are coupled; thus:

$$MA + RX = MX + RA$$

Reagents of this type (MA) are very common in liquid ammonia solution and they are frequently useful for purposes of synthesis. The reactions are similar to those of the metal alkyl salts, such as LiC_2H_5, and they are used chiefly to combine various elements or groups of elements with carbon or with other similar atoms.

Negative ions containing hydrogen

The alkali-metal amides are typical examples of this class of reagents. They react as follows:

$$MNH_2 + RX = MX + RNH_2$$

where R may be an organic group or a group in which the central atom is other than carbon. With methyl chloride, for example, we have the reaction:

$$KNH_2 + CH_3Cl = KCl + CH_3NH_2$$

With triphenylsilicylchloride, we have

$$(C_6H_5)_3SiCl + KNH_2 = KCl + (C_6H_5)_3SiNH_2$$

These reactions are similar to those of the hydroxides and alcoholates with alkyl halides in water or in alcohol. The alcoholates and the phenolates act similarly in liquid ammonia, with the advantage that hydrolysis of these salts does not occur. Thus we have reactions of the type:

$$C_6H_5OK + C_2H_5Br = KBr + C_6H_5OC_2H_5$$

Similar reactions occur with sulfur and doubtless with selenium and tellurium, although these latter reactions have not been studied.

The reactions are particularly valuable in the case of the elements of the third and fourth groups. Warren C. Johnson, of the University of Chicago, has shown that the compound $NaAsH_2$, the arsenic analog of sodium amide, reacts with alkyl halides as follows:

$$NaAsH_2 + RX = Na + RAsH_2$$

With germanium, we have the reaction:

$$NaGeH_3 + CH_3Cl = NaCl + CH_3GeH_3$$

Substituting a hydrogen atom in methylgermane and treating with an alkyl halide, we have:

$$NaGeH_2 \cdot CH_3 + RCl = RGeH_2 \cdot CH_3 + NaCl$$

In this way, the four hydrogen atoms of germane may successively be substituted by any desired alkyl groups.

With phenyl halides, sodium germanyl reacts in a radically different manner.

$$2NaGeH_3 + 2C_6H_5Br = 2NaBr + 2C_6H_6 + Ge_2H_4$$

Evidently, phenylgermane is unstable; benzene splits off, leaving behind a germane of the ethylenic type. Since the product of the above reaction is a solid, it seems reasonable to assume that the structure in the solid state is complex. It is, however, readily soluble in liquid ammonia. With sodium, it yields the salts $NaGeH_2 \cdot GeH_2Na$ and Na_2GeH_2. The fact that these two salts may be formed indicates that the second germanium bond is reasonably stable. Both bonds are broken down in the presence of an excess of reducing metal. The above reaction requires further study.

In preparing potassium (or sodium) germanyl by the action of the metal on monogermane in liquid ammonia, the reaction takes place quantitatively. In preparing the salts of the partially substituted germanes in a similar manner, the reaction is not quantitative; side reactions occur involving the solvent, as a result of which hydrogen is evolved. Similar side reactions occur in the case of other elements. When triethylsilane is treated with lithium in ethylamine solution, the following reaction takes place quantitatively:

$$(C_2H_5)_3SiH + Li + C_2H_5NH_2 = (C_2H_5)_3Si \cdot NH \cdot C_2H_5 + Li + H_2$$

The lithium merely acts as a catalyst for the reaction; an atom of hydrogen is lost by a molecule of silane and by one of amine and the silicon and nitrogen atoms are coupled.

Similar side reactions occur when certain hydrides are treated with potassium (or sodium) amide. The reaction

$$GeH_4 + KNH_2 = KGeH_3 + NH_3$$

is not quantitative. About 10 per cent of the germane reacts in a complex manner with the amide and ammonia; nitrogen is coupled to germanium, and very large quantities of hydrogen are evolved. In the case of triethylsilane, the reaction is quantitative:

$$2(C_2H_5)_3SiH + KNH_2 = KN[Si(C_2H_5)_3]_2 + 2H_2$$

In working with liquid ammonia solutions, it is necessary always to be on the lookout for side reactions involving ammonia. When chloroform is reacted with potassium amide, reaction proceeds quantitatively according to the equation:

$$HCCl_3 + 4KNH_2 = 3KCl + KCN + 3NH_3$$

It might be expected that with carbon tetrachloride reaction would occur according to the equation

$$CCl_4 + 4KNH_2 = 4KCl + C(NH_2)_4$$

and that the carbon tetraamine would go to some lower deammonation product. Actually, an entirely different reaction occurs. When carbon tetrachloride is treated with potassium amide in liquid ammonia, reaction takes place immediately. Potassium chloride is formed quantitatively, and large quantities of gas, consisting of six parts of nitrogen to one part of hydrogen, are evolved. The solution, originally clear when the reaction is completed, soon becomes opalescent and gradually turns brown; finally, free carbon is precipitated. The amount of carbon precipitated is one-half that originally due to carbon tetrachloride; the remaining carbon must pass off in the form of a volatile compound. The details of this reaction have not been worked out. The reaction well illustrates the need for caution in generalizing in the field of liquid ammonia chemistry.

Substituted negative ions

While reagents of the type MA^nH_{n-1} are very useful, their number is limited. Corresponding compounds in which hydrogen has been substituted by organic groups are more stable as well as more numerous. Practically all the electronegative elements from sulfur to lead, inclusive, form compounds of the type MA^nR_{n-1}, where R is an alkyl or aryl group or, occasionally, hydrogen. In a few instances, the substituted groups (R) may themselves be metallo-organic groups. Thus, we have the reaction:

$$HSiCl_3 + 3NaGe(C_6H_5)_3 = 3NaCl + [(C_6H_5)_3Ge]_3SiH$$

(The corresponding reaction with chloroform does not take place.) The product of this reaction is beautifully crystalline. The hydrogen in the product may be substituted by halogens or other groups. It should be noted that the above reaction cannot be carried out in liquid ammonia, since silicochloroform is ammonolyzed by that solvent. The reagent, sodium triphenylgermanide, however, is easily prepared in liquid ammonia.

Reactions of the type

$$R_3ANa + R'_3AX = NaX + R_3A \cdot AR'_3$$

are readily carried out in the case of tin and germanium and less readily in the case of silicon. The difficulty with silicon compounds is that all the silicon halides are rather readily ammonolyzed by liquid ammonia.

Reactions of the type

$$R_3ANa + R'_3A'X = R_3A \cdot A'R'_3 + NaX$$

take place readily in liquid ammonia and provide a general means for coupling two groups through two different central atoms. Reactions of this type could doubtless be extended profitably to elements of the fifth group and, possibly, to others; they seem not to have been investigated thus far. It is of interest to note that bonds of the type A—A and A—A′ are fairly stable in the case of tin and much more stable in the case of germanium and silicon. The stability increases markedly with decreasing atomic number of the central element. The Sn—Sn bond seems to be somewhat more stable with aryl than with alkyl substituents. This is in contrast to what we find with carbon, where only the hexaaryl ethanes are broken down by reducing agents.

Divalent negative ions

With tin and germanium, it is possible to obtain divalent groups of the type R_2A. They are solids which oxidize readily; they evidently possess a complex structure, since they are quite non-volatile. They react readily with the alkali metals in liquid ammonia, as follows:

$$2R_2A + 2Na = NaAR_2 \cdot AR_2 \cdot Na$$

$$R_2A + 2Na = Na_2AR_2$$

These and other similar compounds are important reagents for building up chains of atoms other than carbon. Thus, treating the above salts with the monohalide R_3AX, we have:

$$NaAR_2 \cdot AR_2Na + 2R_3ACl = 2NaCl + R_3A \cdot R_2A \cdot R_2A \cdot R_3A$$

$$Na_2AR_2 + 2R_3AX = 2NaX + R_3A \cdot R_2A \cdot R_3A$$

Syntheses of this type have so far been confined to tin, germanium, and silicon. There is every reason for expecting that similar reactions would be even more readily applicable to the elements of the fifth and, perhaps, the higher members of the sixth group.