

NON-AQUEOUS REDUCTION REACTIONS

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I. INTRODUCTION

The early investigators in the field of non-aqueous solutions were concerned chiefly with the study of the physical properties of such solutions. At the time—some thirty or more years ago—the theory of electrolytic solutions bulked large in the eyes of physical chemists and, while this theory had met with many notable successes, certain inconsistencies had been discovered that not only halted further progress but also threatened the general acceptance of the theory. It was hoped that the study of solutions—particularly of electrolytes—in non-aqueous solvents might throw light on the problem of electrolytic solutions generally and thus assist in the solution of the problem of aqueous solutions of electrolytes. To what extent these early hopes have been realized I shall not attempt to state, but, in any case, a great many investigators were led to study non-aqueous solutions and an extensive literature of the subject has developed. Perhaps the chief result has been to show that nearly all liquid media are capable of dissolving suitable electrolytes and of forming electrolytic solutions. On the other hand, it is now evident that few solvents are capable of dissolving ordinary salts quite generally.

The problem of electrolytic solution served to focus the attention of chemists on the physical rather than on the chemical properties of non-aqueous solutions. As a result we have, even today, only a fragmentary knowledge of the chemistry of solutions in solvents other than water. But, however complete our knowledge of the physical properties of non-aqueous solutions may be, these solutions will play only an unimportant rôle in

chemistry unless it can be shown that such solutions enable us to carry out important chemical reactions and processes that are not possible otherwise. As yet, little has been done to develop systematically the chemistry of solutions in non-aqueous solvents. Until this has been done it will be difficult to predict what will be the future of the chemistry of non-aqueous solutions. It is evident, however, that the number of solvents that give promise of extensive development as media for chemical reactions is very limited. Such solvents must be available in quantity at low cost, must permit of fairly ready manipulation and, finally, must be capable of dissolving a variety of chemically active substances. At the moment, only liquid ammonia and liquid sulfur dioxide seem to meet these requirements.

Despite this limited choice of non-aqueous solvents, there is good reason for believing that many reactions can be carried out more conveniently and efficiently in certain non-aqueous solvents than in water. To illustrate the importance of studying the chemistry of non-aqueous solutions, I shall discuss certain reduction reactions in liquid ammonia. Similar reactions may be carried out in other solvents, particularly the primary aliphatic amines. Although our knowledge of these reactions is still quite incomplete, the material already available is too extensive to permit of a full discussion here. It is hoped, however, to show that many new reactions are made possible by the use of liquid ammonia as a solvent and that new points of view are presented with respect to otherwise familiar reactions.

Liquid ammonia and the lower primary amines are unique in their power to dissolve the alkali metals and the metals of the alkaline earths (1). It has been shown that in these solutions the metals are ionized into normal positive ions and negative ions which are the same for all metals (2). These negative ions have been identified as electrons in solution. As was to have been expected, the electrons in solution are very active chemically, and, since the combination of an electron with an atom constitutes reduction, these metal solutions constitute the strongest reducing agents that we have at our disposal for reduction in a homogeneous phase.

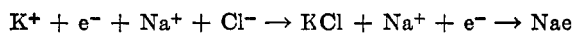
It may be pointed out that, while water is well adapted as a medium in which to carry out reactions with strong oxidizing agents, it is not well adapted to carrying out reactions with strong reducing agents. The reducing power of reducing agents in water is limited by the fact that stronger reducing agents than hydrogen set hydrogen free from water.

The strongest reducing agents that we have are the alkali metals and, since these metals either react with nonmetallic solvents or are insoluble in them, reductions by means of the alkali metals are greatly restricted in their application. As a result, the field of reduction reactions by means of strong reducing agents remains largely unexplored. In the study of such reactions, the solutions of the metals in liquid ammonia offer the only available means for systematic investigation.

The process of reduction by means of metals in liquid ammonia consists essentially in the combination of an electron with an atom (or group of atoms) or an ion. The positive ions of the metals are, of course, also present but they take no part in the reaction. The positive ions possess no metallic properties, and they are concerned in the process of reduction only to the extent of supplying the counterbalancing electrical charge for negative ions. When an atom undergoes reduction, a negative ion is formed. When a positive ion is reduced a neutral atom or group is commonly formed. Below are discussed some typical examples of various types of reduction reactions.

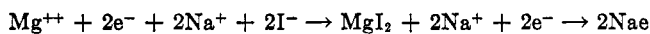
II. METATHETIC REACTIONS

There are numerous reactions of the metals that are of the metathetic type. If we add an alkali metal, M_1e , to a salt, M_2X , of another metal, we have in solution the ionic species: M_1^+ , M_2^+ , X^- and e^- , where e^- represents the electron. By metathesis, four binary ionic combinations are possible (3), namely: M_1X_1 , M_2X_2 , M_1e and M_2e . No reaction will occur unless one of the binary products is removed from solution. For example, on treating sodium chloride with metallic potassium, we have the possible reaction:



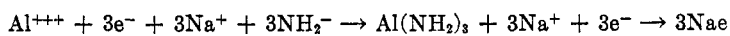
If the solution is dilute, no reaction occurs; but, if the solution is concentrated, reaction takes place from left to right because potassium chloride is the least soluble of the four possible binary products and is precipitated. The sodium ions, together with the electrons, remain in solution, from which they may be recovered as metallic sodium by evaporating the solvent.

A better example of metathesis is the reduction of sodium from sodium iodide by means of magnesium (4). Here the reaction proceeds as follows:



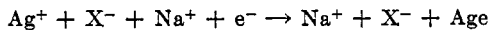
Sodium is reduced from its iodide by means of magnesium because of the very low solubility of magnesium iodide, even though metallic magnesium is only slightly soluble in liquid ammonia.

A corresponding reduction occurs when sodium (or potassium) amide is acted upon by less electropositive metals that are not measurably soluble in liquid ammonia, such as aluminum (5). Thus we have the reaction:



The reaction proceeds as it does because of the very low solubility of aluminum amide. Similar reactions occur in the case of other elements such as beryllium, manganese and zinc.

Another type of metathetic reaction is that in which a weakly positive metal is reduced from its salt by means of an alkali metal (3). The reduction of silver from its salts by means of sodium may serve as example (6). Here we have the ionic reaction:

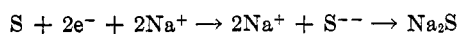


The symbol Age represents neutral or metallic silver. The reaction occurs because of the low solubility of metallic silver, Age.

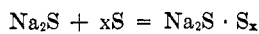
III. REACTION OF ELECTRONS WITH NEGATIVE ELEMENTS

If an electronegative element is introduced into a solution containing electrons (metal), the atoms of this element combine

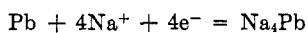
with the electrons to form negative ions. In other words, a salt is formed. Thus, for example, in the case of sulfur (7), we have the reaction:



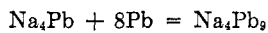
Sodium sulfide is only slightly soluble in liquid ammonia and is therefore precipitated. It should be pointed out, however, that the normal sulfide combines readily with additional sulfur atoms to form soluble polysulfides, thus:



Sodium sulfide and the polysulfides are well known and the reaction of electrons with sulfur presents nothing essentially new. However, while in aqueous solution the representatives of the poly type of salts are very limited, in liquid ammonia they are quite numerous. They may all be formed by the direct interaction of electrons with electronegative or amphoteric elements (8). For example, if metallic lead is treated with a solution of sodium in liquid ammonia, the electrons are taken up directly by the lead atoms to form a normal plumbide according to the equation:



The normal plumbide, like the corresponding sulfide, is insoluble in liquid ammonia and, like the sulfide, reacts with additional lead atoms to form soluble polyplumbides (9). If lead is present in excess, we have the reaction:



The compound, Na_4Pb_9 , is a metallic alloy in the pure state. It may be obtained from the solution by evaporating the solvent, and it is redissolved when the solvent is again added. Although this polyplumbide is a metallic alloy in the pure state, it is a true salt in solution. If a solution of the plumbide, Na_4Pb_9 , is electrolyzed between lead electrodes, $2\frac{1}{4}$ atoms of lead are dissolved at the cathode and precipitated on the anode per equiva-

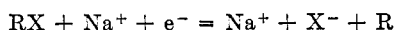
lent of electricity (10). This shows conclusively that the plumbide in solution is a true electrolyte and that it comprises an anion in which nine atoms of lead are associated with four negative charges of electricity.

Just as the metallic elements, when dissolved in liquid ammonia, dissociate into normal positive ions and a common negative ion, the electron, so the metallic compounds, when dissolved in ammonia, dissociate into normal positive and negative ions, the latter comprising the more electronegative constituent of the compound.

Soluble salts of the poly type are formed quite generally by the direct interaction of electrons with the elements of the fourth, fifth and sixth groups (11). The only exceptions are silicon, carbon and perhaps oxygen. Oxygen reacts directly with the alkali metals in liquid ammonia solution to form, in the first instance, dioxides which, in the case of potassium, rubidium and cesium, are further oxidized to tetroxides (12).

IV. REACTION OF ELECTRONS WITH NEGATIVE ELEMENTS IN ORGANIC COMPOUNDS

If we have a compound containing electronegative elements not in the ionic condition, reaction ordinarily takes place with electrons, the negative elements going into the negative ionic condition (13). Familiar examples are the organic halides of the type RX , where R is an organic group and X is a halogen. Such compounds react with the alkali metals in liquid ammonia solution according to the equation:



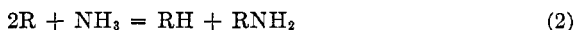
The halogen invariably goes into the state of a negative ion and remains in solution, or is precipitated in the form of the corresponding salt of the alkali metal. This reaction of electrons with halogens occurs even in the case of highly halogenated organic compounds and serves as a convenient method for the analysis of organic compounds for the halogens (14).

The organic residue, R , reacts variously, depending upon its

nature. In some instances, two groups polymerize (15) according to the equation:



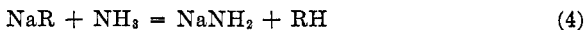
More frequently, however, the organic group reacts with the solvent. The final products are in accordance with the reaction equation:



It is possible that in some instances the mechanism of the reaction actually corresponds to that of equation 2. It is probable, however, that in most cases, reaction takes place as follows:



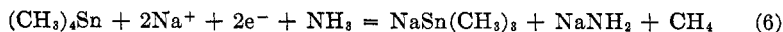
In other words, a salt of the organic group is formed (15, 16). Such salts are not usually stable in the presence of liquid ammonia and ammonolysis occurs according to the equation:



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

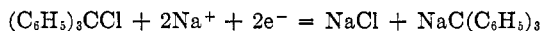


We have some direct evidence that the organic group, R, does not react directly with ammonia according to equation 2. For example, when tetramethyl tin is treated with sodium in liquid ammonia, we have the reaction:

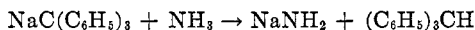


Since, in this reaction, there is present no substance with which sodium amide reacts, the formation of the amide becomes evident (17). It is probable that in other reactions, such as those of the organic halides, the hydrocarbon is formed, as it is in the case of tetramethyl tin, by ammonolysis according to equation 4, while an amine is formed as the result of the action of sodium amide on the original unreacted halide according to equation 5.

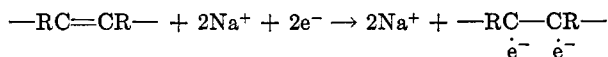
In the case of certain aromatic carbon derivatives, the intermediate formation of a more or less stable sodium salt is clearly evidenced by the formation of colored solutions, the color being due to the presence of these salts (18). This is, for example, the case with triphenylmethyl derivatives. If triphenylmethyl chloride is reduced by means of sodium, the following reaction occurs:



Sodium triphenylmethide is soluble in liquid ammonia, to which it imparts an intense red color. If this solution is evaporated, there are left behind, in addition to sodium chloride, sodium amide and triphenyl methane (19). In other words, ammonolysis occurs with the generation of the hydrocarbon and sodium amide according to the equation:



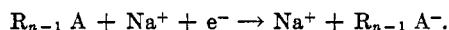
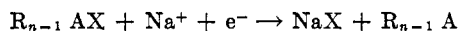
With the exception of triarylmethanes, the electrons do not react with the saturated hydrocarbons (20). They do not react with the doubly bonded aliphatic hydrocarbons, but they frequently react with aromatic hydrocarbons containing double bonds. Thus, they react with diphenyl (21) and with naphthalene (22). What happens is that the double bond is broken according to the equation:



There is formed a disodium salt which, in general, will be more or less completely ammonolyzed. Frequently one of the valences undergoes ammonolysis, while the other remains stable. Mention might also be made of the fact that the aryl ketones react with the alkali metals to form solutions of the metal ketyls (23). The alkali metals react with many organic compounds containing sulfur, selenium, nitrogen, phosphorus, tin, lead, etc. The organic oxygen compounds are, in general, rather stable toward the electrons in ammonia. Thus, the alkali metals do not react with the ethers and, in many cases, probably not with the carboxyl group of acids (20).

V. REACTION OF ELECTRONS WITH COMPOUNDS CONTAINING AMPHOTERIC ELEMENTS

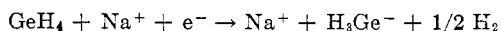
An amphoteric element A of valence n , of which $n - 1$ valences are satisfied by hydrocarbon groups, forms compounds of the type $R_{n-1}AX$, where X is an electronegative element or group. Such compounds are reduced to the free state by means of electrons in liquid ammonia. The free radicals, $R_{n-1}A$, may be further reduced to salts of the type $NaAR_{n-1}$. The reactions may be written as follows:



Salts of the type $NaAR_{n-1}$ are well known in the case of oxygen. The alcoholates and phenolates are familiar examples. Salts of oxygen acids belong to this class of substances, the organic substituent consisting of an $RCO-$ group. Corresponding compounds of other elements are not well known. The mercaptides, $RSNa$, are known, but the corresponding compounds of elements of the fourth and fifth groups have received little attention. It may be stated, however, that all the elements of the fourth, fifth and sixth groups form stable salts of the type $NaAR_{n-1}$ and many of them form the free groups, AR_{n-1} , which usually exist in the bimolecular form.

In recent years groups of the type R_3A , derived from the elements of the fourth group, have been extensively studied. The groups in the free state resemble the triarylmethyls. They form salts with the alkali metals in liquid ammonia that are analogous to the metal alkyls of Schlenck. For the elements silicon (24), germanium (25), and tin (26), organic derivatives corresponding to the metal alkyls have been prepared by reduction by means of the alkali metals in liquid ammonia or ethylamine.

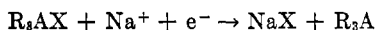
In the case of germanium, sodium germanyl, $NaGeH_3$, the analog of sodium methyl, has been prepared (27). Monogermane, GeH_4 , reacts directly with sodium in liquid ammonia to form sodium germanyl according to the equation:



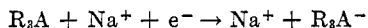
Sodium germanyl is a colorless salt which is readily soluble in liquid ammonia and whose solutions conduct the electric current with considerable facility. It is entirely stable in solution and shows no tendency to ammonolyze. The corresponding derivatives of heavier elements of the fourth group would probably not prove stable.

Since compounds of the type R_3ANa have been prepared in the case of silicon, germanium and tin, it is of interest to compare their properties. The silicon derivatives show a markedly greater tendency to ammonolyze than do the corresponding derivatives of germanium or tin. Sodium germanyl is much more stable toward ammonolysis than is sodium triethylgermanide (28).

If a compound of the type R_3AX is completely reduced by means of sodium, reduction takes place in two stages. First, the neutral group is formed according to the reaction equation:



Then the group AR_3 is further reduced to the state of a negative ion according to the equation:

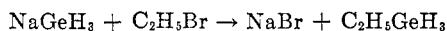


These compounds are true salts in which the groups AR_3^- act as anions. They are very highly ionized in liquid ammonia. Thus, the conductance of sodium triphenylmethide, sodium triphenylgermanide and sodium triphenylstannide has been measured in liquid ammonia solution (29). The results indicate an ionization greater than that of ordinary salts such as sodium bromide.

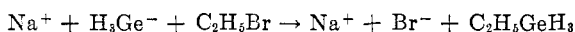
VI. REDUCTION BY MEANS OF WEAKLY ELECTRONEGATIVE IONS

In anions of the type R_3A^- , the electron is not firmly held. The energy effect (heat) accompanying the formation of such anions has been measured in the case of tin and found to amount to only a few thousand calories (30). The salts of such anions therefore serve as convenient reducing agents. In general, they react readily with negative elements or with compounds of such

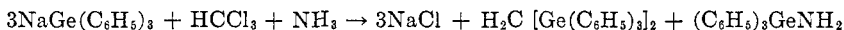
elements. Thus sodium germanyl reacts with ethyl bromide according to the equation (31):



Here we have a coupling of the germanyl group with the ethyl group. The reaction consists in the interchange of an electron and a C_2H_5 group and may be written thus:

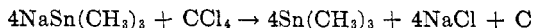


Such reactions are quite common, particularly in the case of the simpler halogen derivatives of hydrocarbons (26). In the case of the more highly halogenated hydrocarbons, the reactions are often more complex, and ammonia may take part in the reaction. Thus, when chloroform is treated with sodium triphenylgermanide, the following reaction occurs:



The reaction is actually the resultant of several coupled reactions that need not be discussed here (33).

When sodium trimethylstannide is treated with carbon tetrachloride in liquid ammonia, reaction occurs as follows:



Trimethyl tin and sodium chloride are formed quantitatively (32). It is not known what becomes of the carbon, but it is safe to assume that it reacts with ammonia. A similar reaction occurs on treating sodium triphenylgermanide with carbon tetrachloride in liquid ammonia (33).

The presence of ammonia may thus complicate the result by entering into reaction with the organic residue. This difficulty may be overcome by dissolving the salt in a neutral solvent, such as benzene or ether. Carbon tetrachloride reacts with sodium triphenylgermanide in benzene solution with the formation of sodium chloride and triphenyl germanium (34). What becomes of the carbon atom of carbon tetrachloride has not, as yet, been determined. Reactions of this type would seem to afford a

means for studying the chemical properties of the free valences of carbon.

Sodium triphenylgermanide reacts with silicon tetrachloride in benzene solution, sodium chloride and triphenyl germanium being formed (35). The silicon atom seems to react with the solvent, but the nature of the reaction remains to be determined. Without doubt salts of the type NaAR_3 will be found to react quite generally with the halogen derivatives of the elements of the fourth, fifth and sixth groups. As yet, this field has not been systematically investigated.

Compounds of the type NaAR_2 , of the elements of the fifth group, are less well known than the corresponding compounds of elements of the fourth group. The nitrogen derivatives are practically the only ones that have been studied. Sodium anilide $\text{NaN}(\text{H})\text{C}_6\text{H}_5$, and sodium diphenylamide, $\text{NaN}(\text{C}_6\text{H}_5)_2$, are excellent salts in liquid ammonia solution, particularly the latter (36). That these and similar compounds of other elements would react with compounds containing strongly electronegative elements or groups seems certain. Here, again, we have a fertile field for further investigation.

VII. CONCLUSION

The importance of non-aqueous solutions in modern chemistry depends upon their availability for the purpose of carrying out reactions that cannot be carried out in aqueous solutions or by other means. With respect to reduction reactions, the solutions of the metals in liquid ammonia afford a unique reagent. The electrons in these solutions are highly reactive toward electronegative and amphoteric elements, and an extensive field of chemistry, not hitherto cultivated, becomes accessible to investigation. The results already obtained serve to broaden our views regarding certain compounds; the elementary metals themselves appear as salts of the electron and certain metallic compounds appear as normal salts of the more electronegative constituent.

Such compounds as the alkali metal alkyls appear as examples of a numerous class of compounds of the elements of the fourth, fifth and sixth groups. They owe their existence to the ampho-

teric nature of these elements, particularly their tendency to go into the state of negative ions. These compounds are highly ionized in solution and constitute valuable reagents for the reduction of other elements or groups.

The systematic investigation of the chemistry of non-aqueous solutions cannot but lead to many valuable results. Substantial progress, however, will be made only when the chemistry of non-aqueous solutions is made a primary objective rather than a side line, incident to other investigations.

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