23.5 g. of $(C_6H_5O)_3P$. The yield of $(C_6H_5O)_2PCl$ based on the $(C_6H_5O)_3P$ used up is 90%.

Table I given in the introduction to this paper summarizes the average of some 10 final experiments and shows the effect of varying the proportions on the yields of the various products.

Summary

1. Monophenoxy-, monomethoxy- and mono-ethoxy-dichlorophosphine were added to benzaldehyde in the presence of acetic acid. Mono-esters of the hydroxyphosphonic acid were formed.
2. Monophenoxy- and monomethoxy-dichlorophosphine were similarly added to benzalacetophenone giving mono-esters of the ketophosphonic acid.
3. Diphenoxy-chlorophosphine was added to benzaldehyde, several ketones and benzalacetophenone, yielding diphenyl esters of the corresponding phosphonic acids.
4. Diphenoxy-chlorophosphine was prepared by heating mixtures of phosphorus trichloride and triphenoxy-phosphine in sealed tubes. An equilibrium is thus established; the composition of the equilibrium mixture varies with the proportion of the 2 reactants employed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 23]

REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. I. PRELIMINARY INVESTIGATIONS

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Introduction

While the alkali metals and the metals of the alkaline earths are very strong reducing agents at ordinary temperatures, their use in the reduction of organic compounds has been much restricted, owing to the lack of a suitable solvent medium for the reacting constituents. Where reductions have been carried out with these metals as, for example, in the Fittig and the Würtz reactions, the metal has been introduced into a solution of the organic constituent in an inactive solvent. In such heterogeneous systems reaction is confined to the interface between the metal and the solution, as a result of which the rate of reaction is often very low, particularly when the products of reaction are insoluble and precipitate on the surface of the metal.

It has been recognized for some time that the alkali metals and the metals of the alkaline earths in solution in liquid ammonia afford an exceptionally strong and reasonably convenient means for the reduction of organic compounds. This method, moreover, possesses the advantage that the reductions may be carried out at low temperatures, at which the stability of organic substances is relatively great. A systematic study of such reduction reactions is lacking at the present time, although a number of isolated reactions of this type have been studied by various investigators. It is the purpose of the present series of articles to present the results obtained in a systematic investigation of reduction reactions in liquid ammonia solution. As will be shown below, the reactions are extremely varied and only after a detailed investigation of a large number of them will it be possible to gain a sufficiently comprehensive knowledge of the subject to enable us to predict the course of such reactions generally.

A discussion of the literature relating to this subject may be omitted for the sake of brevity. The following investigations may be mentioned: reduction of the alkyl halides by Lebeau[1] and Chablay;[2] the quantitative determination of the halogens in organic compounds by Dains, Vaughan and Janney[3] and Clifford;[4] the action of sodium and other metals on acetylene in liquid ammonia by Moissan,[5] Skosarewsky[6] and Cottrell;[7] the action of sodium on fluorene by Cottrell,[7] the action of the alkyl halides on sodium acetylide in liquid ammonia by Lebeau and Picon,[8] and further studies of sodium on various hydrocarbons by the same authors;[9] the action of sodium on the aliphatic acid amides and esters by Chablay.[10]

Experimental Studies

Hydrocarbons.—With a few exceptions, the alkali metals are without action on the hydrocarbons. In tertiary hydrocarbons containing large groups, the hydrogen of the tertiary carbon atom is often replaceable. Thus, triphenylmethane reacts with the alkali metals according to the equation: $R_3CH + Na = R_3CNa + {}^1/_2H_2$. The triphenylmethide formed is soluble in ammonia, with a strong red color. The compound is identical with that obtained by Schlenk and Thal[11] through the action of sodium amalgam on triphenylmethyl chloride in ethereal solution. This reaction will be discussed further in another paper.

Alcohols.—The alcohols react readily with sodium in liquid ammonia with the evolution of hydrogen and the formation of alcoholates. Sodium ethylate is practically insoluble in ammonia, whereas sodium butylate is appreciably soluble; 0.408 g. of sodium

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[1] Lebeau, *Compt. rend.*, **140**, 1042, 1264 (1905).

[2] Chablay, *ibid.*, **140**, 1262 (1905); *Ann. chim.*, [9] **1**, 469 (1914).

[3] Dains, Vaughan and Janney, This Journal, **40**, 936 (1918).

[4] Clifford, *ibid.*, **41**, 1051 (1919).

[5] Moissan, *Compt. rend.*, **127**, 911 (1898); **136**, 1217 (1903).

[6] Skosarewsky, *J. Russ. Phys. Chem. Soc.*, **36**, 863 (1904).

[7] Cottrell, *J. Phys. Chem.*, **28**, 85 (1914).

[8] Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913).

[9] Lebeau and Picon, *ibid.*, **157**, 137, 223 (1913); **158**, 1514 (1914); **159**, 70 (1914); **173**, 84 (1921).

[10] Chablay, *Compt. rend.*, **154**, 364 (1912); **156**, 1020 (1913).

[11] Schlenk and Thal, *Ber.*, **46**, 2843 (1913). See also Schlenk and Ochs, *ibid.*, **49**, 608 (1916).

was added to a liquid ammonia solution containing 0.916 g. of 99.5% ethyl alcohol. A white precipitate of sodium ethylate was immediately formed, and the reaction mixture became thick and mushy. After the first vigorous evolution of hydrogen, the reaction slowed up appreciably and at the end of 2$^1/_2$ hours the mixture was still blue, indicating that sodium was still present. In all likelihood, the slowness of the reaction may, in part, have been due to the pasty condition of the mixture, as a result of which a homogeneous distribution of the reacting constituents may not have been attained. At the end of the time stated, 159 cc. of hydrogen under standard conditions was collected as against a theoretical volume of 221 cc. It may be inferred that reaction takes place in the proportion of 1 molecule of alcohol to 1 atom of sodium. It would seem that the alcoholate is not reduced by the excess sodium present. However, the stability of the alcoholate may be only apparent, owing to its very low solubility. In the case of the higher alcohols, whose alcoholates may be soluble, it is possible that a reduction of the alcoholate may take place.

Phenols.—The phenols react with sodium, as do the alcohols, but the phenolates are much more soluble than the corresponding alcoholates. Sodium phenolate is moderately soluble in liquid ammonia. It reacts readily with various alkyl halides with the production of mixed ethers, but it is without action on aryl halides.

Thiophenols.—While there is no evidence of reaction between the alcohols or the more acidic phenols and the solvent ammonia, it is interesting to note that the thiophenols do so react. Thus, on adding thiophenol to liquid ammonia, a precipitate is immediately formed which, after evaporation of the excess solvent, is found to consist of a white crystalline solid, insoluble in petroleum ether, and which gradually decomposes in the open air with the evolution of ammonia, leaving behind a residue of liquid thiophenol. The solid is evidently the ammonium salt of thiophenol. It reacts readily with the theoretical amount of sodium in liquid ammonia with the formation of the corresponding sodium salt, according to the equation: $C_6H_5SNH_4 + Na \longrightarrow C_6H_5SNa + NH_3 + {}^1/_2H_2$. It has been found that the thio-ethers may readily be made in liquid ammonia solution through reaction of the sodium salt (and, in certain cases, of the ammonium salt) with various organic halides. These reactions will be described in another article.

Ethers.—The lower ethers appear to be entirely stable in the presence of sodium in liquid ammonia. On adding ordinary ether to a solution of sodium in liquid ammonia, separation takes place into two phases, one consisting chiefly of ammonia containing most of the sodium and the other consisting largely of ether containing only a relatively small amount of sodium. Such a solution of sodium in ether was left for 12 hours, at the end of which time there was no evidence of reaction.

Aldehydes.[12]—Aldehydes, or the products of reaction between aldehydes and ammonia, react readily with sodium in liquid ammonia. Aldehyde ammonia was prepared by leading ammonia gas into a dry ether solution of acetaldehyde. The resulting white precipitate was pressed, dried and used immediately. The aldehyde ammonia reacted rapidly with sodium in liquid ammonia solution, with the evolution of hydrogen. In one experiment, 1.429 g. of aldehyde ammonia required 0.528 g. of sodium to discharge the color characteristic of the free metal. This corresponds to a ratio of 0.956 atom of sodium to 1 molecule of aldehyde ammonia. A white precipitate, consisting of the sodium derivative, was formed. The reaction may be expressed by the equation: $CH_3CHOH.NH_2 + Na \longrightarrow CH_3ONa.NH_2 + {}^1/_2H_2$. On the addition of water to the reaction mixture and subsequent distillation, an aqueous solution was obtained which gave all the tests for acetaldehyde, indicating that the sodium derivative is stable in the

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[12] The experiments with acetaldehyde and the reduction of sodium acetate (described later) were performed by Charles C. Towne (*Thesis*, Clark University, **1922**).

presence of excess sodium. It is possible that if the sodium aldehyde derivative were soluble in liquid ammonia further reductions might take place.

On introduction into liquid ammonia, the aromatic aldehyde, *benzaldehyde*, yields a precipitate which is acted upon by sodium. This reaction has not been further investigated.

Acetone.—Acetone is miscible with liquid ammonia and sodium reacts with such solutions rapidly but quietly, with the evolution of no gas. One g. of sodium was found to react with 2.99 g. of acetone, which corresponds to a calculated ratio of 1 atom of sodium to 1.08 molecules of acetone. A small amount of white precipitate was formed in the above experiment, but this may have been sodium hydroxide or oxide introduced with the metal. The ammonia solution was colorless. The solvent was distilled under water,[13] no liquid insoluble in water being collected. The white crystalline residue in the reaction tube had an odor of acetone and ammonia. This residue, when exposed to the air, became yellow, brown, and finally black, with the evolution of a great amount of heat. In the course of oxidation, fumes having a camphor-like odor were given off, suggesting the possible formation of tri-acetone amine, or a similar condensation product. In another experiment, in which sodium was added to a liquid ammonia solution of acetone, water was added to the reaction mixture previous to distillation of the ammonia. On evaporation of the latter, two aqueous layers resulted, the upper one of which proved to be acetone, evidently thrown out of aqueous solution by the sodium hydroxide present. It would appear that sodium forms an addition product with acetone, or with acetone and ammonia, this product being decomposed on addition of water with the formation of ammonia, acetone and sodium hydroxide.

Benzophenone.—Sodium was found to act on a solution of benzophenone in liquid ammonia. The resulting solution was strongly colored, being violet-blue by transmitted light and green by reflected light. The proportion in which sodium reacts with benzophenone was not determined with certainty because of the difficulty of ascertaining the appearance of the blue color characteristic of excess sodium. However, in a mixture containing 1 g. of sodium and 3.95 g. of benzophenone, further addition of sodium produced no color change. This would appear to indicate that reaction takes place in the proportion of 2 atoms of sodium to 1 molecule of benzophenone. The ammonia was distilled from the reaction mixture under water with the separation of no gas or liquid insoluble in water. The residue consisted of a bluish-black crystalline powder, which yields a blue solution in ether. It rapidly oxidizes in air and probably hydrolyzes in moist ether and in water, an odor of benzophenone being distinguishable. This reaction requires further investigation.

Acids.—In attempting the reduction of sodium acetate, it was found advisable to introduce a weighed quantity of acetic acid into the reaction tube and thereafter to condense ammonia on the acid, whereby the ammonium salt was slowly formed and ultimately went into solution on the addition of sufficient ammonia. Sodium was then added until a permanent blue color was imparted to the mixture; 0.227 g. of sodium was found to react with 0.5814 g. of glacial acetic acid or, rather, the equivalent amount of the corresponding ammonium salt. Sodium in excess of this amount gave no signs of further reaction at the end of 2 hours. In the above experiment, therefore, sodium reacted with acetic acid in the proportion of 1.02 atoms of sodium to 1 molecule of acetic acid. Hydrogen was given off in the course of the reaction, as was evidenced by the inflammability of the collected gas. At the end of the reaction, the ammonia was evaporated and the white residue was found to be sodium acetate. Evidently, sodium acetate

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[13] This procedure, which was frequently employed, will be found described in the next article.

is not appreciably reduced by sodium in liquid ammonia, during a period of several hours, possibly owing to its insolubility in that solvent.

In a qualitative test, it was found that sodium reacts with sodium benzoate in liquid ammonia, even though sodium benzoate is only very slightly soluble in this solvent.

Propyl Iodide.—To a liquid ammonia solution containing 10 g. of *n*-propyl iodide was added 1.35 g. of sodium. Reaction took place rapidly, a colorless gas being evolved and a clear colorless solution being formed; 932 cc. of propane under standard conditions was collected over water, corresponding to approximately 1.8 g. The calculated yield from the equation, $2C_3H_7I + 2Na + NH_3 \longrightarrow C_3H_8 + C_3H_7NH_2 + 2NaI$, would be 1.3 g., so that the above equation perhaps expresses the course of the reaction in the main. In an experiment in which 5 g. of sodium was allowed to react with 37 g. of *n*-propyl iodide, about 0.3 cc. of a volatile oil was collected over water. This oil boiled from the aqueous mixture at about 75°, leaving a few drops of dark colored oil which was heavier than water. Evidently, the oil originally collected over water consisted of *n*-hexane (b. p., 69°) mixed with a small amount of propyl iodide. The strongly alkaline solution, obtained in the last experiment by passing ammonia into water, was neutralized with hydrochloric acid, evaporated to dryness, and the residue extracted with absolute alcohol. Upon evaporation of the alcohol extract, a residue was obtained which, when treated with a little water and solid potassium hydroxide, yielded approximately 2 cc. of liquid on distillation. This liquid had a strong ammoniacal odor and a boiling point of 50–60°. Apparently, this liquid was an impure *n*-propylamine (b. p., 49°).

***Tert*-Amyl Iodide.**—Six g. of sodium was dissolved in liquid ammonia and *tert*-amyl iodide was slowly added,[14] until 50.7 g. of amyl iodide was used up, which corresponds very closely with 51.7 g. required theoretically, if reaction takes place between 1 atom of sodium and 1 molecule of amyl iodide. The final reaction mixture consisted of 2 colorless layers, the upper of which was evidently a light oil. On distillation of the ammonia, this light oil was carried over and collected over water. When it was treated with hydrochloric acid, there was no evidence of action. The oil distilled at 30–41°, and evidently consisted mainly of *sec.* pentane (b. p., 30.4°). In another experiment, carried out under conditions otherwise identical with the preceding, when the reaction was approximately $^1/_2$ complete, a portion of the ammonia was distilled and collected over an aqueous solution of sulfuric acid. Along with the oil, which was formed as in the previous case, a considerable quantity of gas was given off which was not soluble in the acid. On replacing the acid with water and collecting as in the preceding experiment, the amount of insoluble gas diminished but did not cease entirely. At about this time, the tube containing the reaction mixture exploded with considerable violence. It is not improbable that, in the course of certain of these reactions, unstable reduction products of nitrogen may be formed, and the explosion in this case may have been due to the presence of such products. Lacking further evidence, however, conjecture regarding the cause of the explosion is of little value.[15]

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[14] On the addition of larger quantities of the iodide to a sodium solution, the mixture separates into 2 liquid phases, the upper of which contains the sodium and the lower the iodide. Reaction takes place as the sodium in the upper layer diffuses into the iodide solution. Later in the course of the reaction, a third layer is formed, consisting of the hydrocarbon which is a product of the reaction. The initial separation into 2 liquid phases is quite common. It may be compared with the salting-out effect observed in aqueous solutions on adding an electrolyte to a solution of an organic compound.

[15] Due caution should be observed in working with liquid ammonia solutions. Not only may unforeseen accidents occur, but the Dewar tubes are liable to collapse. This is particularly true of tubes constructed of ordinary glass.

Ethylene Chloride.[16]—One g. of sodium was added in portions to 2.15 g. of ethylene chloride in liquid ammonia. The reaction proceeded rapidly, a white precipitate of sodium chloride settling and a gas being evolved. The ammonia was distilled into water and 480 cc. of gas under standard conditions was collected; 481 cc. of ethylene under corresponding conditions would be required to satisfy the reaction equation given below. The gas had a sweetish odor and burned with a smoky flame. It decolorized bromine water but did not give a test for acetylene with ammoniacal cuprous chloride. These properties are characteristic of ethylene. An aqueous solution of the residue in the reaction tube gave an odor of carbamine on treating with chloroform and caustic potash. From the amount of ethylene evolved during the reduction, it is clear that very little ethylene diamine, if any, was formed.[16a] The principal reaction may be formulated as follows: $C_2H_4Cl_2 + 2Na \longrightarrow C_2H_4 + 2NaCl$.

Acetylene Dibromide.—One g. of sodium was added to 4.05 g. of acetylene dibromide (that is, in the ratio of 2 atoms of sodium to 1 molecule of the dibromide). On the addition of sodium, the solution of dibromide became yellow, and finally reddish-orange, a gas being evolved. This gas had a garlic-like odor and gave a red precipitate when passed into ammoniacal cuprous chloride solution. The amount of this gas varied in several experiments in which the above quantities of reagents were employed. From 100 to 150 cc. of gas was collected, whereas 487 cc. would be required according to the following reaction equation: $C_2H_2Br_2 + 2Na \longrightarrow 2NaBr + C_2H_2$. After evaporation of the ammonia, the residue in the reaction tube was light brown in color, which, when exposed to air, changed over to a grayish hue. The odor of acetylene was very noticeable. The residue was readily soluble in water and the aqueous solution gave a precipitate with ammoniacal cuprous chloride solution, indicating that acetylene had resulted from the hydrolysis of sodium acetylide. Taking into account the work of Moissan,[17] it is probable that the reaction between sodium and acetylene dibromide takes place partly according to the equation above and partly according to the equations following: $C_2H_2Br_2 + 4Na \longrightarrow 2NaBr + C_2Na_2 + H_2$. $C_2H_2 + 2Na \longrightarrow C_2Na_2 + H_2$.

Benzyl Chloride.—Benzyl chloride reacts readily with sodium in liquid ammonia. To 1 g. of sodium, 4.2 g. of benzyl chloride was added, a white precipitate being formed, along with a solution which exhibited a beautiful pink color. On the addition of 0.5 g. more of the chloride, a white precipitate settled out of a colorless solution and there was no change on further addition of chloride. Sodium reacts with the benzyl chloride, probably in the proportion of 1 atom of metal to 1 molecule of chloride. The nature of the reaction products was not further investigated.

Phenyl Halides.—The phenyl halides react with sodium in liquid ammonia solution with considerable violence. Reaction takes place in the ratio of approximately 1 atom of sodium to 1 molecule of the halide. The chief products of reaction are diphenyl- and triphenylamine and benzene. These reactions are discussed more fully in a later article.

Chlorotoluene.—To 1 g. of sodium dissolved in liquid ammonia, *o*-chlorotoluene was slowly added. The reaction was vigorous; no gas was evolved. There was a marked color change from blue to red when 3.2 g. of the halide had been added, whereas 5.5 g. would be required if the metal reacted in the proportion of 1 atom of metal to 1 molecule of the halide. On allowing the reaction mixture to stand, it was seen that there

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[16] The experiments with ethylene chloride and acetylene dibromide and those on the action of magnesium on organic halides were performed by Walter D. Wood (*Thesis*, Clark University, 1922).

[16a] Since writing the above, an investigation of Chablay's [*Compt. rend.*, **142**, 93 (1906)] has come to our notice. Our observations confirm these earlier results.

[17] See Refs. 8 and 9.

was a clear red solution, with a white precipitate, probably sodium chloride, or *o*-toluidine, or its sodium derivatives. On evaporation of the ammonia, the solution lost its red color and a sirupy solution was left behind. Water was added to the residue and the reddish oil formed was extracted with ether. This ether extract was dried and distilled. A combustible fraction boiling at 100–125°, evidently consisted mainly of toluene. The residue had the physical characteristics of *o*-toluidine.

While the above experiment would appear to indicate that 2 atoms of sodium react with 1 molecule of *o*-chlorotoluene, it is uncertain that the end product of the reaction was reached. It is probable that the reaction is similar to that of the phenyl halides, in which case it would be expressed by the following equation: $2CH_3C_6H_4Cl + 2Na + NH_3 \longrightarrow C_6H_5CH_3 + CH_3C_6H_4NH_2 + 2NaCl$.

Since *p*-chlorotoluene solidifies at liquid ammonia temperatures, ammonia was condensed on 2.75 g. of the halide previously introduced into the reaction tube; 1 g. of sodium was added and a violent reaction occurred, but without the evolution of gas. A slight excess of sodium was present and 0.4 g. of the halide was further added, whereby the mixture lost its blue color, becoming reddish-brown. On the basis of 1 atom of sodium to 1 molecule of *p*-chlorotoluene, 5.5 g. of the latter would be required against the 3.15 g. actually used. The ammonia was evaporated and a solid brown residue was left behind. This was treated with water and the separated oil extracted with ether, dried and distilled. A liquid boiling at 100–125° was obtained which consisted chiefly of toluene, whereas the residue in the flask slowly solidified and appeared to be *p*-toluidine. The reaction is evidently similar to that of the *ortho* compound. Due allowance must be made for the difficulty of determining the end-point in these reductions, in which both colored and insoluble products are formed.

Dichlorobenzene.—3.2 g. of *o*-dichlorobenzene was added to a solution of 1 g. of sodium in liquid ammonia; that is, in the proportion of 1 molecule of the former to 2 atoms of the latter. The reaction was vigorous and no gas was evolved. The mixture became dark red and appeared quite viscous. Some of the halide was isolated from the final reaction mixture, whose physical nature may have prevented completion of the reaction. The ammonia was distilled and the dry residue was extracted with ether. No benzene was obtained from this ether extract, the benzene formed (see below) being carried over with the stream of ammonia gas in the course of distillation. From the ether extract a colorless fraction boiling at 230–256° was obtained. Some of this fraction was dissolved in hydrochloric acid and precipitated from solution by sodium hydroxide. The solid was *o*-phenylenediamine (b. p., 256°).

Five g. of sodium in liquid ammonia solution was treated with 15.9 g. of *o*-dichlorobenzene as before, and the ammonia was distilled under water; 1.58 g. of benzene was obtained, or about 37% of the theoretical as calculated according to the equation given below. There was considerable tarry matter left in the residue at the end of the distillation, and the gummy character of the reaction products doubtless interfered with the smooth course of the reaction. The reaction may be tentatively formulated as follows: $2C_6H_4Cl_2 + 4Na + 2NH_3 \longrightarrow C_6H_6 + C_2H_4(NH_2)_2 + 4NaCl$.

α-Bromonaphthalene.—One g. of sodium was treated in ammonia solution with 9 g. of α-bromonaphthalene. The reaction was vigorous, and the solution formed was quite viscous; its color was initially red, and finally changed to a greenish-black. No gas insoluble in water was evolved. On vaporization of the ammonia and slight warming of the reaction tube, crystals of naphthalene sublimed over to the cooler portions of the tube. Any other reaction products possibly formed were not investigated.

Nitrobenzene.—On reduction of nitrobenzene with metallic sodium in liquid ammonia, the union of the nitrogen with the carbon atom is not affected. The final product of reduction is aniline with azoxybenzene, azobenzene, and hydrazobenzene, or their sodium derivatives, as intermediate products. These reduction reactions will be discussed in detail in a forthcoming article.

Phenyl Mustard Oil.—Phenyl mustard oil is another benzene derivative in which nitrogen is directly connected to the ring and it is interesting to note that, on reduction with metallic sodium in liquid ammonia, no benzene is obtained. One g. of sodium was dissolved in liquid ammonia and phenyl mustard oil slowly added. The reaction appeared to take place in definite stages. After the introduction of 1.42 g. of the mustard oil, a red precipitate was formed which persisted until another 1.42 g. had been added. On a third addition of 1.42 g. of mustard oil, the mixture became yellow, while on the fourth addition of the same amount the solution became clear with a somewhat brownish color, no precipitate being present. The total amount of mustard oil used corresponds to a ratio of 1 molecule of the isothiocyanate to 1 atom of sodium. On distilling the ammonia under water, no benzene was collected. The oily residue was treated with water and the resulting oily layer gave considerable quantities of aniline on distillation, as well as a few crystals of diphenyl. The aqueous layer contained sodium sulfide but gave no test for cyanide. The reaction cannot be formulated on the basis of existing data.

Benzonitrile.—Benzonitrile reacts rapidly but quietly with sodium in liquid ammonia. On adding 2.25 g. of the nitrile to a solution of 1 g. of sodium in liquid ammonia, a wine-red solution and a white precipitate were formed. The amounts of the reagent used correspond to a ratio of 2 atoms of sodium to 1 molecule of benzonitrile. No change could be observed on the further addition of 2.25 g. of benzonitrile. On evaporating the ammonia and adding water to the residue, a red precipitate was formed which was found to be insoluble in water and ether. Only a trace of sodium cyanide was present in the residual aqueous solution.

Sodium **Benzenesulfonate.**—To a solution of 0.56 g. of sodium in liquid ammonia sodium benzenesulfonate was added. Reaction took place rapidly and quietly, a yellowish-white precipitate being formed. Altogether 2.05 g. of sulfonate was required to discharge the blue color. This amount corresponds fairly closely with 2.19 g. required if the constituents react in the ratio of 2 atoms of sodium to 1 molecule of sodium benzenesulfonate.

To 3.8 g. of sodium in liquid ammonia 15.0 g. of sodium benzenesulfonate was added, after which the ammonia was distilled under water. In this procedure, there was collected 5.3 cc. of a light oil which proved to be benzene. This corresponds to a yield of 71% of all the sulfonate, when calculated in terms of benzene.

In several experiments involving the reduction of sodium benzenesulfonate by means of sodium in liquid ammonia, it was found that no aniline was produced and that small quantities of diphenyl were formed. It was shown that the benzene was actually formed in the primary reaction and that it was not a product of the action of water on the initial products of the reduction. Sodium sulfite was present in the aqueous extracts obtained from these reactions.

Phenyl Sulfide.—Phenyl sulfide reacts readily with sodium in liquid ammonia. The sulfide was added slowly to an ammonia solution containing 1 g. of sodium, until a permanent red color was formed requiring 4.04 g., which corresponds to a ratio of 2 atoms of sodium to 1 molecule of phenyl sulfide. The ammonia was distilled into water and about 0.9 cc. of benzene was collected. Sodium sulfide was present in the residue and no other reaction products were isolated. The experiment illustrates the relative instability of thio-ethers as compared with that of the aliphatic oxygen ethers. During the distillation of the ammonia and collection of the benzene, large bubbles of insoluble gas were evolved, as in the reduction of *tert*-amyl iodide. This suggests the possible presence of some relatively unstable reaction product.

Metallo-organic Compounds.—The metallo-organic halides are reduced by the alkali metals in liquid ammonia solution, the corresponding salt of the halide being formed. In the case of the more stable metallo-organic groups, as for example in those of tin,[18] the bond between the metal and the adjacent carbon atom is not affected; the group, as a whole, takes up a negative electron, forming a salt of the alkali metal. In the case of other metallo-organic compounds, as in those of mercury,[19] for example, the union between the metal and the adjacent carbon atoms is broken down. The metal atom combines with the alkali metal to form a metallic compound, while the organic groups either react with each other or with the solvent, in which case amines are formed.

The compounds formed between the alkali metals and the metallo-organic groups, on reduction of the corresponding halides, are salts, and as such may be considered as derivatives of the corresponding acids. Such acids, when stable, react with the alkali metals to form salts, with evolution of hydrogen.[20]

Action of Magnesium on Organic Halides.[16]—To 1 g. of magnesium ribbon in liquid ammonia, 8.4 g. of iodobenzene was added, that is, 1 molecule of halide per atom of magnesium. There was but little evidence of reaction, until a crystal of ammonium chloride was introduced.[21] At the end of the reaction, the ammonia was distilled into water and 0.88 g. of benzene was collected. The odor of aniline was likewise noted. On adding water to the residue in the reaction tube, it was found that considerable magnesium remained behind in metallic form. The reaction may be formulated as follows: $2C_6H_5I + Mg + NH_3 = C_6H_6 + C_6H_5NH_2 + MgI_2$.

One g. of magnesium ribbon (twice that required according to the reaction given below) was treated with 6.4 g. of ethyl iodide in liquid ammonia. The ammonia was distilled into water and 482 cc. of gas (under standard conditions) was collected. This gas burned with a slightly luminous flame. Under standard conditions 289.1 cc. of the gas was found to weigh 0.3648 g., corresponding to a molecular weight of 28.3, whereas the molecular weight of ethane is 30. The aqueous solution in the above experiment was found to give a decided test for primary amines on treatment with chloroform and alcoholic caustic potash. The reaction in this case may be formulated as follows: $2C_2H_5I + Mg + NH_3 = C_2H_6 + C_2H_5NH_2 + MgI_2$.

Discussion

From the above described experiments it will be clear that the reactions between organic compounds and solutions of the metals in liquid ammonia are extremely varied and often quite complex. The course of the reaction in any given case cannot be predicted in the light of known facts. Nevertheless, some inferences may be drawn as to the nature of these reduction reactions and as to the type of compounds which may be expected to suffer reduction under the conditions in question.

It is evident that organic compounds containing strongly electronegative constituents (particularly univalent constituents) are generally reduced. While this phase of the reduction process is still somewhat obscure in certain respects, our knowledge of the properties of the solutions of the alkali

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[18] Kraus and Greer, THIS JOURNAL, 44, 2629 (1922).

[19] Observations by Herman F. Kurtz, to be published later.

[20] See, for example, Ref. 18.

[21] The reaction may also be catalyzed by means of methyl iodide. The reaction of the catalyzer evidently depends on the removal of the external coating adhering to the metal whereby the fresh surface of the metal is exposed to the reagent.

metals in liquid ammonia enables us to hazard a guess as to the mechanism here involved. It has been shown that in liquid ammonia solution the alkali metals are ionized into an electropositive constituent which appears to be identical with the positive ion of a salt of the metal in solution in the same solvent, and a negative ion which appears to be identical in solutions of different metals and which consists, apparently, of a negative electron, associated with ammonia in dilute solutions, and perhaps unassociated with the solvent at high concentrations. Reactions of the metals with other substances are characterized by the combination of the negative electron with an electronegative element, or group of elements; and the process of reduction, so far as these electronegative elements are concerned, consists essentially in a combination of these elements with the negative electron.

It is to be expected that when an organic compound, containing a strongly electronegative constituent, is introduced into a solution of the metal in liquid ammonia, the negative electron will combine with the electronegative constituent, forming a normal anion of that constituent in the solution. Actually, the positive ion of the metal is not involved in the reaction, save in so far as the negative and positive charges in a solution at any time are necessarily equivalent. This stage of the reaction might be formulated as follows: $RX + \epsilon^- = R + X\epsilon^-$. In this process the organic group R is left free in which condition it will, in general, react with other organic groups, with molecules of the solvent or with negative electrons. In the last named case, this would result in the formation of an anion according to the reaction equation: $R + \epsilon^- = R\epsilon^-$, the group thus forming the anion $R\epsilon^-$ in solution. In a few instances, reactions of this type take place as, for example, in the reduction of triphenyl-chloromethane, in which the sodium salt, $NaC(C_6H_5)_3$, is formed, and in the reduction of trimethylstannic chloride, in which trimethylsodium stannide is formed.[18]

That a similar reaction will not take place in the case of most organic groups, as for example the methyl and the phenyl groups, may be expected, for the resulting compound RM is a salt of the very weak acid RH, which therefore would ammonolyze in liquid ammonia solution with the formation of the hydrocarbon RH and the corresponding amide, according to the equation: $RM + NH_3 = RH + MNH_2$. Reactions of this type take place in the case of the salts of triphenylmethane, as will be described in a succeeding number of this series. In no instance has there been found evidence of the formation of compounds of this type in the case of the simpler hydrocarbon groups.

It is only in exceptional cases that two hydrocarbon groups, resulting on reduction, combine to form a hydrocarbon, as in the Fittig reaction. As has been noted above, in a few instances diphenyl is formed in very small quantities. In the greater number of cases the group reacts with ammonia, which behavior is not unexpected when we take into account the great affinity of carbon for hydrogen, and the relative stability of the combination between the amine group and carbon in the amines. The reaction may be formulated as follows: $2R + NH_3 = RH + RNH_2$. In this connection, one may recall the tendency of organic halides to react with ammonia to form amines according to the reaction equation: $RX + NH_3 = RNH_2 + HX$. In the presence of ammonia, of course, the resulting acid combines with the solvent to form the corresponding ammonium salt.

What is striking in the case of many reduction reactions is the speed with which they take place. So far as may be judged, the reactions between the alkali metals and compounds containing strongly electronegative elements or groups of elements take place instantaneously in liquid ammonia solution; that is, the rate of these reactions cannot be measured or estimated. This fact is in harmony with the electronic interpretation of the initial stages of the reduction reactions as outlined above.

Lebeau[1] has suggested that, since the amines are formed in the course of many reactions and since the metal amides react with the alkyl halides with the formation of primary amines, in the reduction of organic compounds by means of the metals, the metal first reacts with the ammonia to form the corresponding amide, which then reacts with the halogen to form the amine. In view of the slowness with which the reaction takes place between the metals and the solvent, it is difficult to account for the extreme rapidity of the reduction reactions in the case of such substances as methyl and phenyl chlorides. Furthermore, as will be pointed out more in particular in a succeeding article, this view does not account for the formation of secondary and tertiary amines.

Summary

The action of metallic sodium on organic compounds containing electronegative groups has been studied. Organic compounds containing strongly electronegative groups are, in general, reduced, the groups or various elements of the groups forming salts with the reducing metal, while the organic radical thus freed undergoes various reactions, depending upon the nature of the radical in question and upon the nature of various other substances present. In most instances ammonia takes part in the reaction. Further than this no general scheme of these reduction reactions can be formulated.

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