REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. II. THE ACTION OF SODIUM ON PHENYL HALIDES IN LIQUID AMMONIA

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The investigation of the reaction between sodium and chlorobenzene in liquid ammonia was begun in an attempt to prepare sodium phenyl under conditions which seemed very favorable to its isolation. No evidence for the formation of this compound in liquid ammonia was obtained.[1] The principal products of the reaction between sodium and chlorobenzene or iodobenzene in liquid ammonia are benzene, diphenylamine, triphenylamine and sodium halide.[2] A small amount of sodium cyanide is formed,[3] and traces of aniline and phenyl-carbylamine are occasionally detected, but these substances are of minor importance in the reaction. The sodium reacts with the aryl halide in the ratio of 1 atom of the former to 1 molecule of the latter, and the following equations suggest the course of the principal reactions: $6C_6H_5Cl + 6Na + NH_3 \longrightarrow 3C_6H_6 + (C_6H_5)_3N + 6NaCl$; $4C_6H_5Cl + 4Na + NH_3 \longrightarrow 2C_6H_6 + (C_6H_5)_2NH + 4NaCl$. Aniline is formed in small quantity in accordance with the equation, $2C_6H_5Cl + 2Na + NH_3 \longrightarrow C_6H_6 + C_6H_5NH_2 + 2NaCl$. In the presence of a slight excess of sodium the diphenylamine is partially converted into sodium diphenylamide: $(C_6H_5)_2NH + Na \longrightarrow (C_6H_5)_2NNa + 1/2H_2$, and the aniline into sodium anilide: $C_6H_5NH_2 + Na \longrightarrow C_6H_5NH.Na + 1/2H_2$, the free bases being re-formed on the subsequent addition of ammonium salts, water or alcohol.

The entrance of ammonia into the above reactions, with the transfer of one of its hydrogen atoms to the phenyl radical, is a noteworthy change. The sodium is largely ionized in liquid ammonia and on addition of chlorobenzene the sodium delivers its charge to the chloride with the formation of sodium chloride, while the organic reaction involved may be simply expressed as an interaction of the phenyl radical with the ammonia molecule: $Na \leftrightharpoons Na^+ + \epsilon^-$; $C_6H_5Cl + \epsilon^- \longrightarrow C_6H_5 + Cl^-$; $6C_6H_5 + NH_3 \longrightarrow 3C_6H_6 + (C_6H_5)_3N$.

[1] Further studies of liquid ammonia systems have indicated that a compound such as sodium phenyl would be immediately ammonolyzed in liquid ammonia, as has been pointed out in the preceding article.

[2] The formation of hydrocarbon and of aniline has been noted by Lebeau, *Compt. rend.*, **140**, 1262 (1905).

[3] The formation of cyanide in the reduction of organic halogen compounds in liquid ammonia has been pointed out by Clifford, THIS JOURNAL, **41**, 1051 (1919).

Experimental Part

Apparatus.—The reaction tube A was immersed in commercial liquid ammonia contained in a Dewar tube B as shown in the accompanying figure.
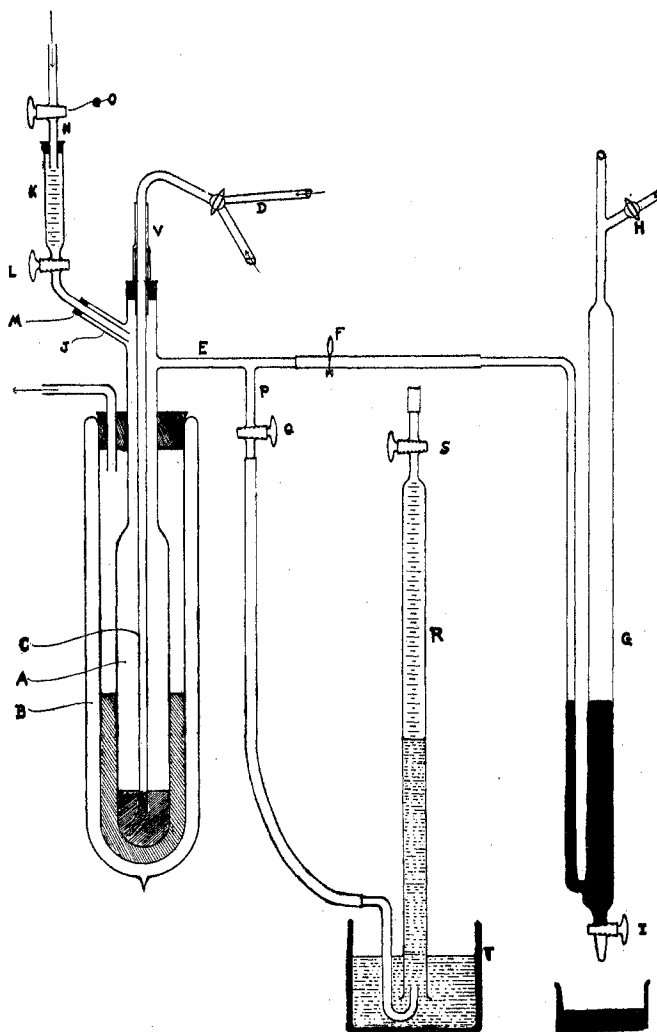
The apparatus employed in studying the reduction reactions in liquid ammonia solution.

The Dewar tube had a capacity of about 800 cc.; it was 45 cm. long and 6 cm. bore. The reaction tube was 60 cm. long, the enlarged portion immersed in the liquid ammonia being about 25 cm. long and 4.5 cm. in diameter. Liquid ammonia dried with sodium was introduced into the reaction tube through the inlet tube C. The side tube D permitted the introduction of air, oxygen, or other gas at will. By means of the tube E

the reaction tube was in connection through the pinchcock F with the mercury manometer G. Mercury could be introduced into the manometer through the stopcock H and withdrawn below through the stopcock I, whereby the pressure could be varied as desired.

The reaction tube also had a side tube J into which led a 20cc. buret K with stopcock L. Connection between the buret and side tube was made through the rubber stopper M. Air pressure could be exerted on any liquid in the buret through the tube N with Stopcock O.

The tube P with Stopcock Q was connected with the side-tube E of the reaction tube, and by this means, ammonia and any accompanying substances could be diverted from the manometer outlet and could be collected over water in the inverted 50cc. buret R. The buret could be filled with water from the vessel T as occasion demanded by applying suction at the stopcock S.

Procedure.—In performing various experiments mercury was first run into the manometer to a height of about 15 cm. Then with D, L and Q closed and F open, 20 to 30 cc. of ammonia was condensed in the reaction tube. Sodium could be added in small weighed amounts through the arm J which in this case was closed by a solid rubber stopper instead of being connected with the buret K. After the sodium had dissolved, the solution being hastened by stirring with a stream of ammonia gas, weighed quantities of the organic reagent were introduced. If the organic substance was solid, it was introduced into the tube in the same manner as was the sodium; liquids were added either from pipets or, when it was desired to prevent the entrance of air, they were injected into the reaction tube under air pressure from K.

At any time during the reaction tests could be made qualitatively or quantitatively for the formation of gaseous products by closing the pinchcock F, opening the stopcock Q, and collecting any gas insoluble in water in the buret R. In the same way benzene could be carried over and collected over water in the buret R.

To study the nature of the products in the reaction tube at the end of any experiment, various procedures were employed. The ammonia could be distilled from the reaction tube on removal of the latter from the Dewar tube, benzene thus being carried over and non-volatile products left in the tube for subsequent examination; or before distillation of the ammonia, water, alcohol, or an ammono acid, ammonium chloride or ammonium nitrate was added, whereby any slight excess of sodium or any sodium salts of weak acids were converted into sodium hydroxide, ethylate, chloride or nitrate. The reaction tube was then removed from the Dewar tube and the liquid ammonia allowed to evaporate at a pressure above atmospheric in order to prevent excessive frothing. Finally the tube was placed in a water-bath and practically all of the gaseous ammonia removed by warming. The residue in the tube was then ready for analytical study.

General Observations on the Reaction between Phenyl Halides and Sodium in Liquid Ammonia.—Many preliminary experiments showed that the aryl halide was best added to the liquid ammonia solution of sodium; when the sodium was added to the aryl halide in liquid ammonia the sodium became coated with the precipitate formed and then did not enter into the reaction completely. With no diluent present the reaction was very violent, crackling sounds were heard, and it was necessary to wire the stopper of the reaction tube and all connections in order to prevent disruption of the apparatus. The mixture became red immediately and a gummy mass was precipitated, consisting of benzene, aryl amines, and so-

dium chloride (when chlorobenzene was employed). As the addition of the halide (forced in under air pressure) was continued, the contents of the reaction tube became exceedingly viscous, the heat of the reaction causing the ammonia to boil vigorously. The reaction came to completion in about 2 hours.

In one such experiment, after the air had been driven from the reaction tube, all the gas evolved during the later reaction was collected over water; this amounted to 2 or 3 cc. (air), although 17 cc. of chlorobenzene entered into reaction. Hence, no hydrogen was evolved in the reaction, and the formation of amines resulted in the transfer of the ammonia hydrogen to the phenyl radical.

The reaction mixture became so dark in color that the end-point could not be observed by disappearance of the blue color due to the sodium, but when an excess of sodium over the ratio of 1 atom of sodium to 1 molecule of phenyl halide was employed, this excess was clearly indicated on the subsequent addition of water; and when the reagents were used in exactly this ratio, no phenyl halide, or only traces, could be detected after the reaction was completed.

In a preliminary experiment of this kind 20 cc. of chlorobenzene was allowed to react with an excess of sodium, water was added to the mixture (while still cooled in the Dewar tube) the dark brownish red color became lighter, and a yellow-red oil separated. Depending on the rate of addition of the phenyl halide this oil varied in color from yellow-red to black in various experiments, and it occasionally had a carbylamine odor. The reaction tube was removed from the Dewar tube and the ammonia was distilled. The oil was then separated from the aqueous solution, dried by solid sodium hydroxide, and distilled. A fraction (b. p., 80–82°), consisting of benzene, was first evolved; then successively, a few drops boiling at 182°, giving a violet color with hypochlorite and suggesting traces of aniline; a fraction boiling at 250–290° having the odor of diphenylamine and giving in conc. hydrochloric acid a deep blue color with sodium nitrite solution; and a fraction boiling at 290–315°, which on recrystallization from petroleum ether proved to be triphenylamine (m. p., 120°), and gave a blue color with conc. sulfuric acid.

Experiments of a similar nature with iodobenzene showed that the reaction was identical with that of chlorobenzene.

Benzene, a Primary Reaction Product

To 6.05 g. of sodium dissolved in liquid ammonia was slowly added 29.6 g. of chlorobenzene. At the end of the reaction the ammonia was distilled into an inverted buret filled with water saturated with benzene, preliminary experiments having proved that benzene will distil from the reaction mixture with the ammonia gas; 9.6 cc. of impure benzene was thus collected; this was combined with benzene obtained by a similar experiment, the mixture dried with phosphorus pentoxide, and filtered; $d_4^{21.5}$ 0.9052. On distillation, this product proved to be mainly benzene (b. p., 80.5–85°), while a small fraction (b. p. 85–125°) contained a little chlorobenzene. Therefore, 7.7 g. of pure benzene was thus obtained, or 75% yield on the basis of 1 molecule of benzene by the action of 2 atoms of sodium.

The experiment proved that benzene is formed without the addition of water or alcohol and that sodium phenyl is not a reaction product.

Formation of Diphenylamine and Triphenylamine

To a solution of 6 g. of sodium in liquid ammonia were added 10 cc. of toluene and a solution of 29.4 g. of chlorobenzene in 50 cc. of toluene, the reaction proceeding with less violence than in the absence of the toluene.   After 3 hours, 10 cc. of ethyl alcohol was added, and the ammonia carefully evaporated by removing the reaction tube from the Dewar tube.   Great care was necessary in the evaporation to overcome the tendency to excessive frothing.   The tube was placed in a water-bath and the toluene, excess alcohol, benzene, and chlorobenzene were distilled in a vacuum in a gentle stream of ammonia gas.   During the distillation the fluid mixture changed in color from a red to a brownish-yellow, and gave a white residue of sodium chloride together with red to brown amorphous masses (aryl amines).   The residue was extracted with ether, the ether extract filtered and evaporated on the water-bath, and the residue distilled in a vacuum in a current of ammonia gas at 20–25 mm. pressure.   After the rejection of that fraction distilling below 200° (consisting of traces of benzene, toluene and chloro-benzene), 9.1 g. was left, consisting of diphenylamine and triphenylamine.   According to the equations given above, 11.0 g. of diphenylamine or 10.7 g. of triphenylamine would be obtained if the reaction proceeded quantitatively in one or the other direction, indicating a yield of 83% to 85% of combined amines.

The above mixture on fractionation at 20–25 mm. in ammonia gas gave a fraction boiling at 205–225°, consisting of a clear yellow oil that crystallized at room temperature; crystallized from petroleum ether, this product melted at 42–44°; crystals from aqueous methyl alcohol melted at 42–45°; and finally when this substance was distilled in a vacuum at 0.001 mm. pressure, the product melted at 42–50°.   Further fractionation was impossible because of the small amount of material available.   This fraction was largely diphenylamine, and only by modifying the apparatus and carrying out the reaction on a larger scale does it seem that the pure product could be isolated (see below).

The highest-boiling fraction (above 225°) yielded a brownish-yellow distillate which readily crystallized; this was recrystallized from methyl alcohol and from petroleum ether, and melted at 126°.   The colorless and odorless crystals were practically pure triphenylamine and gave the color reactions of this substance.

The aqueous solution of the sodium chloride residue from the first ether extraction gave a prussian blue test for cyanide.

Melting Points of Mixtures of Diphenylamine and Triphenylamine.—On account of the difficulty of separating these amines by distillation or crystallization, a brief study of mixtures of them was made.   Triphenylamine was prepared by the method of Piccard and Kharasch[4] (for final purification from diphenylamine the solvent was changed from glacial acetic acid to methyl alcohol, as advised).   The melting points of various mixtures of this product (m. p., 127°) with diphenylamine (m. p., 52.6°)[5] were briefly investigated and it was clearly evident that the amines are partially miscible in the solid condition, the limits of miscibility being from about 13% to 75% of triphenylamine.   A liquid phase containing approximately 21% of the tertiary amine is in equilibrium with the eutectic mixture of the two solid solutions at a temperature of 43.6°.   The existence of these solid solutions is undoubtedly the cause of difficulties in the purification of small quantities, especially of the two amines.

Effect of Diluent.—In the presence of petroleum ether as an inert diluent, the reaction between the aryl halide and sodium in liquid ammonia could be readily controlled.   In experiments of this kind it was noted that

[4] Piccard and Kharasch, THIS JOURNAL, **40**, 1077 (1918).

[5] Rogers, Holmes and Lindsay, *J. Ind. Eng. Chem.*, **13**, 314 (1921), have shown that the melting point of diphenylamine given in the earlier literature is too high.

very little evidence for the formation of diphenylamine was obtained, and that triphenylamine seemed to be the only amine formed. It is believed that by this dilution the predominating tendency becomes for tertiary amine formation, and that by carrying the reaction out on a larger scale a rapid method for the preparation of this compound would be possible.

Sodium Diphenylamide.—Diphenylamine was added to a solution of sodium in liquid ammonia; hydrogen was evolved, and the solution lost its blue color, becoming slightly yellow. On the addition of water a white solid separated which was found to be diphenylamine, and sodium hydroxide was present in the aqueous solution. This reaction was not further investigated, but it is evident that the clear yellow liquid ammonia solution contained sodium diphenylamide.

Sodium Anilide.—It was found by a preliminary experiment that on the addition of sodium to a liquid ammonia solution of aniline reaction as evidenced by the evolution of gas was very slow and incomplete. Further study of this reaction was discontinued since sodium anilide was prepared very readily by a reaction which will be reported later.

Summary

1. Sodium reacts with phenyl halides in liquid ammonia with the formation of benzene and secondary and tertiary phenylamines, together with sodium chloride and occasional traces of aniline, phenyl carbylamine and sodium cyanide. The sodium and phenyl halide react in the ratio of 1 atom of the former to 1 molecule of the latter. Equations for the fundamental reactions have been given.

2. The benzene was proved to be a primary product of the reaction, sodium phenyl not being formed under the conditions.

3. Benzene distils readily, and toluene and chlorobenzene distil slowly, from liquid ammonia mixtures.

4. Diphenylamine and triphenylamine are partially miscible in the solid state, the limits of miscibility being approximately 13% and 75% of triphenylamine. A liquid phase containing about 21% of triphenylamine is in equilibrium with the eutectic mixture of the two solid solutions at a temperature of 43.6°.

5. The formation of the tertiary amine is favored by dilution of the reaction mixture with petroleum ether, and a new method of preparation of triphenylamine is suggested.

6. The ammono salts, sodium diphenylamide and sodium anilide, are formed by the action of sodium on diphenylamine and aniline in liquid ammonia.

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