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REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. III. THE REDUCTION OF NITROBENZENE BY SODIUM IN LIQUID AMMONIA

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It has been pointed out by Kraus and White[1] that organic compounds of very diverse function react with the alkali metals in liquid ammonia. The field offered for investigation is very extensive, since at present insufficient data are at hand to explain the mechanism of many new reactions and to predict the character of the products which might be formed. The selection of the reduction of nitrobenzene as a basis for the present study seemed very desirable in view of the general interest in the reduction of nitro compounds and, further, in view of the progress which would probably be made for the future investigation of the behavior under similar conditions of compounds of closely related function.

Both nitrobenzene and sodium are soluble in liquid ammonia, so that conditions in such a system are ideal for the rapid reduction of the nitro compound by the electrons of the highly ionized metal. Reduction in fact takes place extremely readily, and it is important to compare the process with the more familiar reductions in heterogeneous systems.

The reduction of nitrobenzene by sodium in non-aqueous media has to a certain extent been investigated. Hofmann and Geyger[2] found that sodium readily reacts with an ethereal solution of chloronitro-benzene and of chloronitro-toluene with the production of compounds in which sodium has entered the nitro group. They were unsuccessful in reducing nitrobenzene under similar conditions. Schmidt,[3] however, was able to reduce nitrobenzene slowly in ethereal solution at ordinary temperature and rapidly in boiling toluene, that is, in the latter case, above the melting point of metallic sodium. He obtained a sodium compound to which he assigned the formula, $C_6H_5N(Na)ONa$, since it yielded β-phenylhydroxylamine when treated with acid. Schmidt also suggested the possibility that the disodium compound has the constitution $C_6H_5N(=O)Na_2$, and that it should thereby yield the hypothetical aniline oxide $C_6H_5N(=O)H_2$ with acids, aniline oxide then immediately rearranging to phenylhydroxylamine.

We have found that the same disodium derivative of phenylhydroxylamine as Schmidt obtained in toluene or ether solution is produced in

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[1] (a) Kraus and White, THIS JOURNAL, **45**, 768 (1923). See also (b) White, *ibid.*, **45**, 779 (1923).

[2] Hofmann and Geyger, *Ber.*, **5**, 915 (1872).

[3] Schmidt, *ibid.*, **32**, 2911 (1899).

liquid ammonia by the reduction of nitrobenzene. The compound is rather insoluble in liquid ammonia, being precipitated as a red crystalline solid. Either sodium oxide is formed as a by-product and then is more or less completely ammonolyzed,[4] or ammonia enters into the primary reaction with the formation of sodium amide and sodium hydroxide in equimolecular amounts. The reaction may then be expressed by the equation, $C_6H_5NO_2 + 4Na + NH_3 = C_6H_5N(Na)ONa + NaNH_2 + NaOH$. By the addition of water to the reaction mixture azobenzene and azoxybenzene were isolated. However, these were substances produced by the secondary reactions of phenylhydroxylamine in hot alkaline aqueous solution. By the use of ammonium chloride in liquid ammonia the disodium salt was converted into its corresponding ammono acid in the absence of water. $C_6H_5N(Na)ONa + 2NH_4Cl = C_6H_5N(H)OH + 2NaCl + 2NH_3$. β-phenylhydroxylamine was extracted from the mixture with anhydrous solvents. In liquid ammonia, then, reduction of nitrobenzene proceeds as in all other solvents, phenylhydroxylamine being the first product to be isolated (or the sodium derivative of it), while nitrosobenzene may be assumed to be an intermediate product since indirect methods have indicated its formation in aqueous solutions. Azo bodies are not formed primarily but may result from secondary reactions in aqueous alkaline solution.

That disodium phenylhydroxylamine has the constitution, $C_6H_5N(Na)ONa$, is very probable, since sodium would more readily add to oxygen than to nitrogen. Further, the compound reacts with alkyl halides in liquid ammonia, but no dialkylaniline oxide could be isolated from such reaction mixtures. It is of interest to note that preliminary experiments indicate that an excess of methyl iodide reacts with the sodium compound in liquid ammonia with the formation of an unstable oil. This oil has certain of the characteristics of the primary product which Bamberger and Tschirner[5] obtained by the action of methyl iodide on dimethylaniline oxide and which they considered to be phenyldimethyl-methoxyammonium iodide, but which they found was too unstable to isolate. Such a compound could result from the disodium derivative of phenylhydroxylamine in liquid ammonia according to the following series: $C_6H_5N(Na)ONa \longrightarrow C_6H_5N(CH_3)OCH_3 \longrightarrow C_6H_5N(I)(CH_3)_2OCH_3$. We have further shown that potassium amide reacts with phenylhydroxylamine in liquid ammonia. A red crystalline precipitate is produced which has the same physical properties as the sodium or potassium compound resulting from the reduction of nitro or nitrosobenzene. To test these views on the structure of the

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[4] Unpublished observations of E. F. Whyte in this Laboratory have proved that sodium oxide in liquid ammonia is rapidly ammonolyzed to sodium amide and sodium hydroxide.

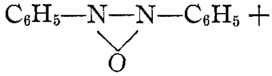
[5] Bamberger and Tschirner, *Ber.*, **32**, 1882 (1899).

disodium compound, a study of the formation of the alkyl derivatives of phenylhydroxylamine in liquid ammonia will be made.

Disodium phenylhydroxylamine is readily prepared by the reduction of nitrosobenzene in liquid ammonia: $C_6H_5NO + 2Na = C_6H_5N(Na)ONa$. As no by-products are formed, the reaction offers an especially good opportunity for further study of the structure of the sodium compound.

By the action of an excess of sodium in liquid ammonia, nitrobenzene is readily reduced to disodium anilide, which yields aniline by the action of ammonium chloride or water: $C_6H_5N(Na)ONa + 2Na + NH_3 = C_6H_5\text{—}NNa_2 + NaOH + NaNH_2$. Phenylhydroxylamine itself is reduced in liquid ammonia directly to aniline: $C_6H_5NHOH + 2Na + NH_3 = C_6H_5\text{-}NH_2 + NaOH + NaNH_2$.

A study of the reduction of azoxybenzene, azobenzene and hydrazobenzene in liquid ammonia has revealed the facts cited below.

Azoxybenzene is rapidly reduced to azobenzene:  $C_6H_5\text{—}\underset{\diagdown\, O\, \diagup}{N\text{—}N}\text{—}C_6H_5 + 2Na + NH_3 = C_6H_5\text{—}N{=}N\text{—}C_6H_5 + NaNH_2 + NaOH$. By the further action of sodium on azobenzene, sodium atoms add directly to the azo group in the azobenzene molecule, whereby a disodium ammono salt of hydrazobenzene results: $C_6H_5\text{—}N{=}N\text{—}C_6H_5 + 2Na = C_6H_5N(Na)\text{—}N(Na)\text{—}C_6H_5$. From this ammono salt hydrazobenzene may be obtained by the addition of ammonium salts of mineral acids or by the addition of water: $C_6H_5\text{—}N(Na)\text{—}N(Na)\text{—}C_6H_5 + 2H_2O = C_6H_5\text{—}N(H)\text{—}N(H)\text{—}C_6H_5 + 2NaOH$. The possible synthesis of quaternary hydrazines by the action of alkyl and aryl halides on the sodium salt of hydrazobenzene will be investigated.

The sodium derivative of hydrazobenzene is reduced by an excess of sodium to disodium anilide, $C_6H_5\text{—}N(Na)\text{—}N(Na)\text{—}C_6H_5 + 2Na = 2C_6H_5NNa_2$, from which compound aniline is obtained by the addition of water.

It is important to note in connection with these reductions that sodium does not react with free hydrazobenzene in liquid ammonia with the formation of the disodium derivative and the evolution of hydrogen, but that the molecule splits, and monosodium anilide is formed: $C_6H_5\text{-}NHNHC_6H_5 + 2Na = 2C_6H_5NHNa$. The reduction of hydrazobenzene and of azobenzene to the mono- and disodium anilides, respectively, proceeds rapidly, and this method for the preparation of these latter compounds in liquid ammonia offers many advantages over the method of direct interaction of sodium and aniline.[6]

Considering the small quantities of reagents employed in the various experiments, good yields of phenylhydroxylamine, azobenzene and hydrazo-

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[6] Ref. 1b, p. 784. See also Picon, *Compt. rend.*, **175**, 1213 (1922).

benzene were obtained by the reduction of nitrobenzene, azoxybenzene and azobenzene, respectively. The method may prove of practical application in the synthesis of more valuable reduction products of other nitro and azo compounds.

Experimental Part

Apparatus and Procedure.—The apparatus and the experimental method employed were essentially identical with those described in the second article of this series.[7]

Materials.—The nitrobenzene used was redistilled thrice and had only a faint tinge of yellow color. Azoxybenzene, azobenzene and hydrazobenzene were obtained by reduction of nitrobenzene in alkaline aqueous solution, and β-phenylhydroxylamine by reduction of nitrobenzene in neutral solution in the usual manner. Nitrosobenzene was prepared by oxidation of phenylhydroxylamine. These nitrobenzene reduction products were recrystallized until pure as evidenced by their melting points.

The Reduction of Nitrobenzene

General Observations.—Franklin and Kraus[8] have observed that the aromatic nitrohydrocarbons are more or less soluble in liquid ammonia, solutions of nitrobenzene being very little colored, but those of the polynitro compounds often being highly colored. Solutions of nitrobenzene showed no electrical conducting power, while those of dinitrobenzene evidenced a conductance which increased up to a maximum with time. Solutions of trinitrotoluene were found to attain their final conductance values at once.

In conformity with the above we have noted that nitrobenzene, which is very soluble in liquid ammonia, is colored red to violet in ammonia solution when only partially purified by distillation. Distillation of the compound three or four times gave a product which was colorless in ammonia solution. The impurities in the colored solutions were very probably traces of polynitro compounds which would act as pseudo acids, exhibiting the phenomena of "slow neutralization" observed by Franklin and Kraus and yielding colored ammonium salts of their *aci* forms. These observations substantiate the conclusions drawn from the following experiments, that nitrobenzene exhibits no desmotropic character in liquid ammonia solution and that no metallic derivatives of it are formed in such solutions.

As sodium was added in successive portions to colorless solutions of nitrobenzene in liquid ammonia, the solutions became yellow, then orange, dark red and finally dark brown, while a precipitate which at first appeared to be white darkened as the reduction proceeded. The color phenomena varied somewhat in the different experiments because minute amounts of certain of the colored reduction products had a marked effect on the appearance of the others. The reaction of the metal solution with the

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[7] Ref. 1b, p. 780.

[8] Franklin and Kraus, *Am. Chem. J.*, **20**, 382 (1898); **23**, 277 (1900).

nitro compound was rapid but was characterized by no excessive violence when the sodium was added in small portions. In the presence of a large excess of sodium, however, the reaction was very violent and explosions were apt to occur. On partial reduction of nitrobenzene, if the ammonia was then evaporated before addition of water and the reaction products exposed to the air, violent explosions resulted, accompanied by flame and the deposition of carbon.[9]

No hydrogen was evolved in any of the reductions.

When nitrobenzene was treated with sodium in the proportion of 1 molecule of the former to 1, 2 or 3 atoms of the latter, there was only partial reduction of the nitrobenzene, some of this substance being recovered from the mixture of reaction products.

The Formation of Disodium Phenylhydroxylamine.—Four and a half g. of sodium was added to a liquid ammonia solution of 6 g. of nitrobenzene, which corresponds to a ratio of 4 atoms of sodium to 1 molecule of the nitro compound. Before the last small portion of sodium was added the mixture was bright red in color but became dark brown on addition of the remainder; 11 g. of ammonium chloride was then introduced into the reaction tube and the mixture thoroughly stirred. All sodium compounds were thereby decomposed with the formation of insoluble sodium chloride. The resulting mixture was light yellow. The ammonia was evaporated and the dry residue extracted thrice with hot anhydrous benzene. The mixture was filtered and the benzene extract treated with an equal volume of anhydrous petroleum ether. After the solution had cooled, 1.9 g. of colorless crystals of β-phenylhydroxylamine (m. p., 80–82°) was obtained; yield, 36%. These were soluble in water, and the aqueous solution readily reduced ammoniacal silver nitrate and Fehling solutions.

The precursor of phenylhydroxylamine in the above experiment might be its disodium derivative, $C_6H_5N(Na)ONa$, or the disodium derivative of aniline oxide, $C_6H_5N(=O)Na_2$. In the latter case, aniline oxide, the hypothetical tautomer of phenylhydroxylamine, would, after being set free by addition of ammonium chloride, instantaneously rearrange into the hydroxylamine. It was found that the sodium reduction product reacted with methyl iodide in liquid ammonia with great readiness, but all attempts to isolate dimethylaniline oxide, $C_6H_5N(=O)(CH_3)_2$, were unsuccessful. On the other hand the following experiment indicates the formation of a dimethyl derivative of phenylhydroxylamine.

Three and six-tenths g. of nitrobenzene was reduced by 2.7 g. of sodium in liquid ammonia, whereby the disodium compound was produced; 16.8 g. of methyl iodide was then added, or twice as much as was required to form a dimethyl derivative of phenylhydroxylamine. The mixture was at first red but soon changed to a yellow color, and on the addition of 4 g. of ammonium chloride a clear yellow oil was formed which coagulated to an amorphous precipitate. After evaporation of the ammonia and extraction of the residue with ether, from the ether extract a reddish oil was isolated which when warmed had the odors of dimethylaniline and formaldehyde. These latter substances were likewise found by Bamberger and Tschirner[5] to be formed when the unstable

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[9] Schmidt, Ref. 3, has noted the explosive properties of disodium phenylhydroxylamine.

product of the reaction between dimethylaniline oxide and methyl iodide spontaneously decomposed.

Dipotassium Phenylhydroxylamine.—Several experiments proved that potassium reacts with nitrobenzene in liquid ammonia just as does sodium. A red, crystalline precipitate was formed and from this phenylhydroxylamine was prepared.

The following experiment confirms the assumed structure of the metallic compounds: 1.02 g. of potassium was dissolved in liquid ammonia and was converted into potassium amide by the catalytic action of ferric oxide; 1.5 g. of phenylhydroxylamine was then added. The colorless solution immediately became deep red in color and a red crystalline precipitate slowly separated. The following tentative reaction may be written: $C_6H_5N(H)OH + 2KNH_2 = C_6H_5N(K)OK + 2NH_3$.

Disodium Anilide.—One g. of nitrobenzene was reduced by 1.1 g. of sodium, that is, in the ratio of 1 molecule of the nitro compound to 6 atoms of sodium. The complete reduction was rather slow, and the mixture was allowed to stand for 24 hours. A brownish-green solution was obtained to which water was added. An oil, separated from this mixture, proved to be aniline.

The Formation of Sodium Amide.—To test for the formation of sodium amide in the reduction of nitrobenzene, 3.6 g. of nitrobenzene in liquid ammonia, was reduced by 2 g. of sodium, and then 9 g. of α-bromonaphthalene was added. Vigorous boiling of the liquid ammonia indicated that a reaction ensued. Water was then added, the ammonia evaporated, and the aqueous mixture acidified with hydrochloric acid. This mixture was extracted with ether to remove azoxybenzene and any unchanged bromonaphthalene, and the aqueous solution was then made alkaline. A small amount of α-naphthylamine separated from the solution. The synthesis of this compound in liquid ammonia may then be formulated thus: $\alpha\text{-}C_{10}H_7Br + NaNH_2 = \alpha\text{-}C_{10}H_7NH_2 + NaBr$.

The metal amide formed in the reduction of nitrobenzene in liquid ammonia does not react with any excess of the nitro compound. This was proved by a test experiment in which nitrobenzene was treated with potassium amide. The nitrobenzene was recovered unchanged.

The Secondary Formation of Azoxybenzene and Azobenzene

These compounds may be obtained when water is added to the mixtures of partially reduced nitrobenzene and liquid ammonia, and result from the familiar reactions of phenylhydroxylamine in alkaline aqueous solution.

Two g. of sodium was added to an ammonia solution of 3.6 g. of nitrobenzene. The final mixture was reddish-yellow. Water was added, the ammonia was evaporated, and the cooled aqueous solution filtered. The yellow residue was recrystallized from methyl alcohol; 1.8 g. of azoxybenzene, m. p. 34–36°, was obtained.

Two and eight-tenths g. of sodium was added to an ammonia solution of 3.6 g. of nitrobenzene. Water was added, and the insoluble residue obtained was twice crystallized from alcohol; 0.9 g. of azobenzene, m. p. 68.5°, was obtained.

The Oxidation of Disodium Phenylhydroxylamine

Three and six-tenths g. of nitrobenzene was reduced by 2.7 g. of sodium in liquid ammonia. Air was blown through the liquid ammonia mixture for $^3/_4$ hour. The color became very dark red; 6.4 g. of ammonium chloride was then added and a dark tarry mass separated. The ammonia was evaporated and anhydrous ether was added. The ether solution was green which would indicate the possibility of the presence of some nitrosobenzene, although none of the compound was isolated. The ether extract yielded considerable nitrobenzene, but no phenylhydroxylamine. The experiment proved that disodium phenylhydroxylamine is oxidized to nitrobenzene in liquid ammonia.

The Reduction of Nitrosobenzene

Nitrosobenzene is insoluble in liquid ammonia. It was found to react with either potassium or sodium with great rapidity. A dark red solution was formed at first, but after 2 equivalents of the alkali metal were added a red crystalline precipitate slowly formed. This would indicate that the metallic derivatives of phenylhydroxylamine are to a certain extent soluble in liquid ammonia. Phenylhydroxylamine was isolated by the same procedure as described above in connection with the reduction of nitrobenzene.

The Reduction of Phenylhydroxylamine

Phenylhydroxylamine is extremely easily soluble in liquid ammonia. To a solution of 2 g. of this compound was added 0.84 g. of sodium. A light yellow precipitate (sodium amide and sodium hydroxide) formed, but no hydrogen was evolved in the reduction. The mixture became blue on the addition of 0.7 g. of sodium over the above amount, so that 2 atoms of sodium reacted with 1 molecule of the phenylhydroxylamine. The ammonia was evaporated leaving an oily residue from which aniline was extracted.

The Reduction of Azoxybenzene

Azoxybenzene is difficultly soluble in liquid ammonia, the solution being colored yellow; 4.3 g. of the substance was reduced by 1 g. of the sodium (1 molecule of azoxybenzene to 2 atoms of sodium). The reaction was very rapid, fine yellow crystals of azobenzene separating out of solution. These were isolated and crystallized from alcohol; yield, 77%; m. p., 63–68°.

The Reduction of Azobenzene

Formation of Hydrazobenzene.—Azobenzene dissolves to a slight extent in liquid ammonia with the production of a yellow solution; 3.95 g. of azobenzene was treated with 1 g. of sodium in liquid ammonia (in the ratio of 1 molecule of azobenzene to 2 atoms of sodium). The action was rapid and a blood-red solution was formed containing no precipitate. On addition of water a faintly yellow precipitate resulted. After evaporation of the ammonia the aqueous solution was filtered and the residue crystallized from alcohol. White crystals of hydrazobenzene were obtained; m. p., 126–129°; yield, 75%. No aniline was formed in the reduction.

Formation of Disodium Anilide.—One g. of azobenzene was reduced with 0.5 g. of sodium in ammonia (1 molecule of azobenzene to 4 atoms of sodium). A red-brown opaque solution resulted. Water was added and aniline was isolated from the aqueous solution. To test for the formation of disodium anilide in this reduction in liquid ammonia, 5.0 g. of azobenzene was treated with 2.5 g. of sodium, and 17.0 g. of ethyl iodide was then added to the liquid-ammonia solution. Water was then added and an ether extract of the aqueous solution yielded an oil that boiled at 205–215° and evidently consisted mainly of diethylaniline. This substance was formed in ammonia by a reaction expressed by the equation, $C_6H_5NNa_2 + 2C_2H_5I = C_6H_5N(C_2H_5)_2 + 2NaI$.

The Reduction of Hydrazobenzene

Formation of Aniline.—Hydrazobenzene is readily soluble in liquid ammonia, yielding a pale yellow solution. When sodium was added to such a solution in the proportion of 1 molecule of hydrazo compound to 1 atom of sodium, the solution became dark red and a white gelatinous precipitate consisting probably of monosodium anilide (see below) was precipitated. No hydrogen was evolved in the reduction. After the addition of water at least $^1/_2$ of the original amount of hydrazobenzene was recovered and some aniline was also obtained. The test showed that there was insufficient sodium for complete reduction and that the hydrogen atoms of the hydrazine molecule were not replaced by sodium.

Two g. of hydrazobenzene was treated with 0.5 g. of sodium in liquid ammonia (1 molecule of hydrazobenzene to 2 atoms of sodium). After the addition of water, by the usual procedure an oil was isolated which gave a violet color with sodium hypochlorite solution and boiled at 184° and, therefore, was practically pure aniline. No hydrazobenzene was recovered from the reaction mixture.

Formation of Monosodium Anilide.—Four g. of hydrazobenzene was treated with 1 g. of sodium as in the preceding experiment. To the mixture was then added 6.8 g. of ethyl iodide. Water was added and an ether extract of this aqueous solution yielded an oil which gave on distillation 2 fractions, one boiling at 185° consisting of aniline, and a second boiling at 200–205° consisting of mono-ethylaniline. The latter compound was synthesized in liquid ammonia evidently according to the following equation: $C_6H_5NHNa + C_2H_5I = C_6H_5NHC_2H_5 + NaI$.

Summary

Nitrobenzene and nitrosobenzene are readily reduced by sodium in liquid ammonia with the formation of a disodium derivative of β-phenylhydroxylamine, the structural formula of which is probably $C_6H_5N(Na)ONa$. Phenylhydroxylamine is liberated from this salt in ammonia by the action of ammonium chloride, and the free phenylhydroxylamine may be isolated by extraction with anhydrous solvents after evaporation of the ammonia. By the further reduction of the disodium derivative in liquid ammonia, disodium anilide is formed and aniline is obtained from this by the action of ammonium chloride or water. Phenylhydroxylamine itself is reduced directly to aniline in liquid ammonia.

The disodium derivative of phenylhydroxylamine is oxidized in liquid ammonia to nitrobenzene by air.

Azoxybenzene and azobenzene are not formed as direct reduction products of nitrobenzene in liquid ammonia, but may be isolated after treatment of the partially reduced mixture with water. They result from the secondary reactions of phenylhydroxylamine in alkaline aqueous solution.

Azoxybenzene is reduced by sodium to azobenzene. Azobenzene is reduced to a disodium derivative of hydrazobenzene from which the latter compound may be obtained after treatment with ammonium chloride or water. The disodium derivative of hydrazobenzene may be further reduced by sodium in ammonia to disodium anilide, while hydrazobenzene itself is reduced by sodium to monosodium anilide.

Mono- and dialkylanilines may be synthesized in liquid ammonia by the action of alkyl halides on mono- and disodium anilides, respectively.

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