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TRANSFERENCE EXPERIMENTS WITH ELECTROMETRIC DERIVATIVES OF HYDROXYLAMINE

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In 1899, Dunstan and Goulding[1] prepared trimethylmethoxyammonium hydroxide, $((CH_3)_3NOCH_3)OH$, by the interaction of methyl iodide and trimethylamine oxide, $(CH_3)_5N:O$, and subsequent conversion of the methoxy iodide salt thus formed to the sulfate, which was treated with barium hydroxide. Meisenheimer[2] in 1913, by treating trimethylmethoxyammonium iodide with silver oxide, obtained the same compound. However, by treating trimethylhydroxyammonium chloride, $((CH_3)_3NOH)Cl$, formed from trimethylamine oxide and hydrochloric acid, with sodium methylate, he obtained, not trimethylmethoxyammonium hydroxide, but trimethylhydroxyammonium methylate, $((CH_3)_3NOH)OCH_3$.

On evaporating its aqueous solution, trimethylmethoxyammonium hydroxide decomposes into trimethylamine, formaldehyde and water, while trimethylhydroxyammonium methylate decomposes into trimethylamine oxide and methyl alcohol.

$$((CH_3)_3NOCH_3)OH \longrightarrow (CH_3)_3N + CH_2O + H_2O;\ ((CH_3)_3NOH)OCH_3 \longrightarrow (CH_3)_3N:O + CH_3OH$$

Meisenheimer[3] has also shown that salts of amine oxides of the type, $R_1R_2R_3N:O$, may be resolved into optically active isomers.

H. O. Jones,[4] on the other hand, has been unable to so resolve compounds of the type $R_1R_1R_2R_3NX$.

On the basis of these and similar facts, Meisenheimer[5] comes to the conclusion that in the amine oxides the oxygen is bound to the carbon by two valences which differ in character, one of them corresponding to the four valences of the ammonium group, while the fifth valence corresponds to that which holds the acid radical in ammonium salts. He assumes that all five groups are held by principal valences but that the fifth valence is in an outer zone and is different from the other four.

In his discussion the reference to the optical activity of sulfonium salts of the type, $R_1R_2R_3SX$,[6] is especially significant. The optical activity of such salts demonstrates[7] that the acid radical is held to a definite position

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[1] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 793, 1004 (1899).

[2] Meisenheimer, *Ann.*, **397**, 273 (1913).

[3] Meisenheimer, *Ber.*, **41**, 3966 (1908).

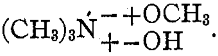
[4] H. O. Jones, *J. Chem. Soc.*, **83**, 1400 (1903).

[5] Meisenheimer, (a) Ref. 3, p. 3970; (b) *Ann.*, **399**, 371 (1913).

[6] Ref. 2, p. 281.

[7] An editorial critic suggests:

"I question the word 'demonstrates.' Unless there is definite evidence (which I doubt) that the compound, $R_1R_2R_3SX$, is a non-electrolyte, I do not see how the conin the molecule and, hence, is held by a principal valence although such salts ionize and the union with the acid radical is polar. He points out very forcibly that this union is similar to that which holds the acid radical in ammonium salts and we can scarcely doubt that the latter union is also due to a principal valence. This conclusion is also in accord with the evidence given by Potter and Noyes[8] that the union between an ammonium group and an acid group may hold an amino acid in a stable ring configuration. In spite of this, however, Meisenheimer[9] assumes that the acid radical, though held by a principal valence, "does not take a fixed place and hence has no influence on the asymmetry of the molecule." He rejected various other possible explanations, such as Werner's ammonium formula or the oxonium formula discussed by Willstätter,[10] Hantzsch and Graf,[11] Werner[12] and Fromm.[13]

It is well known that the 3 atoms of chlorine in nitrogen trichloride have the same oxidizing power as 6 atoms of elementary chlorine.[14] This has been explained by assuming that the chlorine atoms in this compound and in hypochlorous acid are positive. Considerable experimental evidence consistent with this explanation has been accumulated.[15] In a similar manner, L. W. Jones[16] assumes that amine oxides have the structure, $(CH_3)_3N\pm O$. Trimethylmethoxyammonium hydroxide would then have the structure,  $(CH_3)_3N\begin{matrix}-+OCH_3\\+-OH\end{matrix}$. In such a compound the positive valence of the oxygen atom would have twice the oxidizing power of a single valence of free oxygen. This gives a very satisfactory explanation of the formation of formaldehyde by the decomposition of the compound.

Langmuir[17] assumes that in the amine oxides "the nitrogen is quadricovalent." He should have added that on this supposition the oxygen is

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clusion can be drawn that the acid radical X is held to a definite position in the molecule. If it is an electrolyte, then the optical activity may be regarded as evidence that a pair of electrons or a positive charge is held to a definite position in the molecule."

Such an explanation appears to the writers of this paper altogether satisfactory. Applied to the nitrogen compounds described in this paper it would mean that there are *five* definite positions for the attachment of atoms or groups. We have shown in this paper that in some cases the ionization of the *fifth* group attached to the nitrogen atom is very slight.

[8] Noyes and Potter, THIS JOURNAL, **37**, 189 (1915).

[9] Ref. 2, p. 283.

[10] Willstätter, *Ber.*, **33**, 1638 (1900).

[11] Hantsch and Graf, *ibid.*, **38**, 2161 (1905).

[12] Werner, "Neuere Anschauungen," **1909**, pp. 204–210.

[13] Fromm, *Ann.*, **399**, 366 (1913). Ref. 5b.

[14] Seliwanow, *Ber.*, **25**, 3117 (1892).

[15] Noyes and Lyon, THIS JOURNAL, **23**, 460 (1901). Noyes and Haw, *ibid.*, **42**, 2167, 2174 (1920). Noyes and Wilson, *ibid.*, **44**, 1630 (1922).

[16] L. W. Jones, *ibid.*, **36**, 1273 (1914).

[17] Langmuir, *ibid.*, **42**, 280 (1920).

unicovalent. Such assumptions seem very improbable in the light of the fact that all ordinary groups having a quadricovalent nitrogen atom in which three or more of the groups combined with the nitrogen atom are alkyls, are ammonium groups carrying a positive charge and the further fact that there seem to be no other organic compounds containing unicovalent oxygen atoms.

According to the views of Meisenheimer, L. W. Jones, Lewis or Langmuir, the hydroxyl group should form a part of the positive ion of trimethylhydroxyammonium methoxide, $(CH_3)_3NOH)OCH_3$, but it should form the negative ion of trimethylmethoxyammonium hydroxide. It has seemed to us worth while to test this conclusion by actual transference experiments. Attempts to prepare these two compounds in a condition of sufficient purity for such a purpose were not successful. We have, however, carried out transference experiments with trimethylhydroxyammonium sulfate, trimethylhydroxyammonium chloride, trimethyliodo-methylammonium hydroxide, trimethylamine oxide hydrate, trimethylmethoxyammonium iodide, trimethylethoxyammonium bromide, and trimethyl ethoxyammonium hydroxide.

To demonstrate the migration of the ions the substances were dissolved in a warm 5–7% solution of agar-agar and the solution was cooled and solidified in the lower part of a U-tube. Dil. hydrochloric acid or, in one case, sulfuric acid was placed above the agar-agar on the cathode side and silver nitrate on the anode side. It was demonstrated by qualitative tests that no appreciable diffusion of sulfate or chloride ions into the acid on the cathode side occurred. Platinum electrodes were used and the U-tube was kept in ice water. The anion was easily identified by the formation of silver sulfate, chloride, bromide, iodide or oxide on the anode side. After the electrolysis the solution on the cathode side was poured out and the chloride or sulfate of the cation, which had been formed, was either identified as such or converted into the chloro-aurate, and the gold in the latter determined.

The resistance offered by the solution of the hydrate of the trimethylamine oxide and that of the trimethylethoxyammonium hydroxide, $((CH_3)_3NOC_2H_5)OH$, seems very significant. While the chloride, bromide, iodide or sulfate could be electrolyzed easily with a 10-volt circuit, an e.m.f. of 110 volts was required with the hydroxide to secure a transfer sufficiently rapid for practical purposes According to the view of Lewis or of Langmuir the hydroxide is a polar compound in which the hydroxyl group is not localized by any definite point of attachment and it is difficult to understand why it should not be highly ionized in solution, as is trimethylammonium hydroxide. On the other hand, if the hydroxyl is held to the nitrogen atom by a localized, principal valence, the low ionization seems much more natural.

Experimental Part

Preparation of Compounds.—Trimethylamine oxide hydrate was prepared both from hydroxylamine through the trimethylhydroxyammonium iodide as first described by Lobry de Bruyn,[18] and by treatment of trimethylamine with hydrogen peroxide.[1,2] In neither case did the compound reduce Fehling solution or liberate iodine from potassium iodide as stated by Hantzsch and Hilland.[19] Anhydrous trimethylamine oxide was prepared by heating the hydrate slowly to 120° in a 500cc. Erlenmeyer flask immersed in an oil-bath and connected through a calcium chloride tube to an oil pump which reduced the pressure to 10 mm. After heating for about 20 minutes at 120° the temperature was slowly raised to 140–150° and the heating at the latter temperature was continued for 20 minutes. As the hydrate used was pure, it was not necessary to sublime the oxide, as recommended by Bratring.[20] Trimethylhydroxyammonium chloride and sulfate were prepared from the trimethylamine oxide hydrate. Trimethyliodomethylammonium iodide was prepared from trimethylamine and methylene iodide according to the directions of Hofmann[21] and Litterscheid.[22] Trimethylmethoxyammonium iodide and trimethylethoxyammonium bromide were prepared by adding methyl iodide and ethyl bromide, respectively, to the anhydrous amine oxide essentially as described by Bratring.[20] The yield of the latter compound was much better than that obtained by Bratring, probably because the alcohol used was more nearly absolute. Trimethylethoxyammonium hydroxide was prepared by dissolving 3 g. of the bromide in 10 cc. of alcohol, adding an excess of freshly precipitated silver oxide and shaking for 5 hours, until the solution gave no precipitate of silver bromide on treatment with silver nitrate and nitric acid. The filtered solution was mixed with the warm solution of agar-agar, the solution cooled and electrolyzed.

Trimethylhydroxyammonium Sulfate, $((CH_3)_3NOH)_2SO_4$, was electrolyzed with an e.m.f. of 110 volts and a 40-watt electric lamp in series. With hydrochloric acid on the cathode side, trimethylhydroxyammonium chloride melting at 205–206° (Dunstan and Goulding give 205–210°) was obtained.

Analyses. Calc.: Cl, 31.79. Found: 30.90, 31.29.

Trimethylhydroxyammonium Chloride, $((CH_3)_3NOH)Cl$, gave in the same way, with dil. sulfuric acid on the cathode side, trimethylhydroxyammonium sulfate melting at 156°. Dunstan and Goulding give 155–156°. Silver chloride was found on the anode side but no chlorine was found on the cathode side.

Trimethyliodomethylammonium Hydroxide, $((CH_3)_3NCH_2I)OH$, gave, with hydrochloric acid on the cathode side, trimethyliodomethylammonium chloride, melting at 180°. Litterscheid[22] gives 178–179°.

Analysis. Calc.: Cl, 15.07. Found: 15.14.

The double salt with mercuric chloride was also prepared and melted at 173.5°. Litterscheid gives 174–175°.

One g. of trimethylamine oxide hydrate, $(CH_3)_3NO.2H_2O$, was dissolved in 30 cc. of a 7% solution of agar-agar and electrolyzed for 4 hours, with hydrochloric acid on the cathode side, using an e.m.f. of 110 volts and no other resistance in series. The current increased slowly from 0.014 to 0.025 amperes. The cathode portion was poured off and evaporated to dryness in a vacuum desiccator. The residue, after recrystallizing from absolute alcohol, melted at 210–211°. A mixture with pure trimethyl-

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[18] Lobry de Bruyn, *Rec. trav. chim.*, **15**, 185 (1896).

[19] Hantzsch and Hilland, *Ber.*, **31**, 2059 (1898).

[20] Bratring, *Inaug. Dissertation*, Berlin, **1913**.

[21] Hofmann, *Chem. Centr.*, **31**, 170 (1860).

[22] Litterscheid, *Ann.*, **337**, 69 (1904).

hydroxyammonium chloride melted at the same temperature, while the pure chloride melted at 212°. An Anschütz thermometer was used.

Trimethylmethoxyammonium Iodide, $((CH_3)_3NOCH_3)I$.—One g. of the salt was dissolved in 30 cc. of a 7% solution of agar-agar and was electrolyzed for 7 hours, with hydrochloric acid on the cathode side, using an e.m.f. of 10 volts. The cathode portion was drawn off and the chloro-aurate of the base was precipitated by adding chloroauric acid. The salt was recrystallized from hot water.

Analysis. Calc. for $((CH_3)_3NOCH_3)AuCl_4$: Cl, 45.95. Found: 45.47.

Trimethylethoxyammonium Bromide, $((CH_3)_3NOC_2H_5)Br$.—One g. of the salt was dissolved in 30 cc. of a 7% solution of agar-agar and electrolyzed for 12 hours with hydrochloric acid on the cathode side and an e.m.f. of 10 volts. The current was 0.013 amperes. From the cathode portion the chloro-aurate was prepared.

Analysis. Calc. for $((CH_3)_3NOC_2H_5)AuCl_4$: Cl, 44.49. Found: 44.06.

Trimethylethoxyammonium Hydroxide, $((CH_3)_3NOC_2H_5)OH$.—An alcoholic solution of the base prepared from 3 g. of the bromide as described above was mixed with a hot solution of agar-agar and the cooled solution was electrolyzed for 7 hours with hydrochloric acid on the cathode side and an e.m.f. of 110 volts. The current increased slowly from 0.01 to 0.017 amperes. The chloro-aurate was prepared and analyzed as before.

Analysis. Calc.: Au, 44.49. Found: 44.6.

Summary

Transference experiments have been carried out with trimethyl amine oxide, trimethylhydroxyammonium salts, trimethylmethoxyammonium iodide, trimethylethoxyammonium bromide, trimethyliodomethylammonium hydroxide and trimethylethoxyammonium hydroxide. It has been demonstrated that in each case a hydroxy, methoxy or ethoxy group remains with the nitrogen as a part of the cation. The attachment of these groups to the nitrogen must be very different from that of the hydroxyl or other atom or group which travels toward the anode during the electrolysis.

The resistance offered by the solutions of trimethylamine oxide hydrate and of trimethylethoxyammonium hydroxide seems more consistent with the hypothesis that the hydroxyl ion of these compounds is attached to the nitrogen by a principal valence of such a character that it is only slightly ionized than with that of the unlocalized polar valence assumed by Lewis and Langmuir.

We wish to express our indebtedness to Mr. P. K. Porter for the preparation of some of the compounds used and for carrying out some of the transference experiments.

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