

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

IONIZATION OF TRIMETHYLETHOXYAMMONIUM HYDROXIDE, TRIMETHYLAMINE OXIDE AND THEIR DERIVATIVES

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Some time ago J. H. Hibben¹ and I reported on some experiments which seemed to show that the ionization of trimethylethoxyammonium hydroxide, $(\text{CH}_3)_3(\text{OC}_2\text{H}_5)\text{NOH}$, is much less, in aqueous solutions, than that of trimethylethoxyammonium bromide. More recently, Stewart and Maeser² have shown that in solutions 0.01 or 0.013 *M* for hydroxide ion the association of either trimethylethoxyammonium hydroxide or of trimethylmethoxyammonium hydroxide is of the same order as the association of sodium hydroxide. All of these compounds ionize almost completely in very dilute solutions. Hantzsch and Kalb³ have also shown that methylpyridinium hydroxide, $(\text{CH}_3)\text{C}_5\text{H}_5\text{NOH}$, ionizes almost completely in dilute solutions, although pyridine solutions contain very few hydroxyl ions and methylpyridinium hydroxide would be expected to show considerable association if the observations of Hibben and myself were correct as reported.

Since the solutions used in our experiments were supposed to be approximately 0.18 *M*, it has seemed possible that there might be much more association in solutions of this concentration than in the solutions examined by Stewart and Maeser. I have, therefore, tested the question by determining the resistance of more concentrated solutions of trimethylethoxyammonium hydroxide and of the same solution after the addition of hydrobromic acid. Since the conductance of the hydroxide ion is much greater than that of the bromide ion, the addition of an amount of hydrobromic acid insufficient for the complete neutralization of the hydroxide should cause an increase in the resistance if the association of the hydroxide is similar to that of the bromide, while it should cause a decrease of the resistance if the association of the hydroxide is much greater than that of the bromide, as our former results had led us to suppose. I have tried similar experiments with trimethylphenylammonium hydroxide, $(\text{CH}_3)_3\text{C}_6\text{H}_5\text{NOH}$, and with trimethylamine-oxide hydrate, $(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$. The results fully confirm the results of Stewart and Maeser. The hydroxides are very completely ionized but the amine-oxide hydrate solution contains very few hydroxide ions.

The solution of the trimethylamine-oxide hydrate was prepared by shaking a solution of trimethylhydroxyammonium bromide with silver oxide, with the thought that the conductance of a solution prepared in

¹ Noyes and Hibben, *THIS JOURNAL*, **45**, 357 (1923).

² Stewart and Maeser, *ibid.*, **46**, 2583 (1924).

³ Hantzsch and Kalb, *Ber.*, **32**, 3117 (1899).

this manner might be greater than that of a solution of the crystallized amino-oxide hydrate. There was a little indication that the resistance increased on standing but I am not sure that this is significant.

The measurements were made in a cell of the dumb-bell form recommended by Washburn.⁴ The resistance of the cell containing 0.1 *M* potassium chloride solution was 2034 ohms at 25°, which corresponds to a cell constant of 0.0382.² The results of the measurements⁵ are given in Table I.

Substance	Molal concentration	Resistance, ohms (25°)
KOH	0.54	213
{ KBr	.51 }	387
{ KOH	.03 }	
(CH ₃) ₃ C ₆ H ₅ NOH }	.509	249
{ (CH ₃) ₃ C ₆ H ₅ NBr }	.494 }	794
{ (CH ₃) ₃ C ₆ H ₅ NOH	.015 }	
[(CH ₃) ₂ NOC ₂ H ₅]OH	.159	1039
{ [(CH ₃) ₂ NOC ₂ H ₅]Br }	.135 }	2140
{ [(CH ₃) ₂ NOC ₂ H ₅]OH }	.024 }	
(CH ₃) ₃ NO.2H ₂ O	.5	93,000 ^a
{ [(CH ₃) ₂ NOH]Br }	.2 }	2780 ^a
{ (CH ₃) ₂ NO.2H ₂ O }	.3 }	

^a At 0°.

Discussion

The conclusion which Stewart and Maeser reach that trimethylethoxy-ammonium hydroxide is very completely ionized in dilute aqueous solutions is certainly correct. The discordant result of our previous experiment was probably due to the ease with which the compound decomposes to trimethylamine and acetaldehyde. The concentration of the hydroxide in our solution was doubtless much less than we supposed.

I cannot, however, agree with the conclusion that the amine-oxide, so far as it exists as a base, has a different structure from that of the ethoxy compound. It seems to me far more probable that the base has the structure [(CH₃)₂NOH]OH, corresponding to that of the ethoxy compound, and that both the anhydrous amine-oxide and the larger part of the amine-oxide in solution have the structure (CH₃)₂N:: \ddot{O} , with a double union between the nitrogen and oxygen atoms. This compound may or may not be combined with water when in solution. My reasons for this opinion are as follows.

1. The assumption that "there is only one kind of hydration" does not agree with facts well established in another case. There are two isomeric

⁴ Washburn, *THIS JOURNAL*, **38**, 2450 (1916).

⁵ I wish to express my indebtedness to Dr. T. E. Phipps, who has kindly made the electrical measurements for me.

barium salts having the formulas, $(\overline{\text{OCC}_6\text{H}_4\text{SO}_2\text{N}})_2\text{Ba}\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_2\text{-SO}_2\text{C}_6\text{H}_4\text{CO.O})_2\text{Ba}\cdot 2\text{H}_2\text{O}$. The first of these salts is intensely sweet, while the second is nearly tasteless. Since benzoic sulfinide, $\overline{\text{OCC}_6\text{H}_4\text{SO}_2\text{NH}}$, is intensely sweet while the sulfamide of benzoic acid, $\text{HOCC}_6\text{H}_4\text{SO}_2\text{NH}_2$, is tasteless, the tastes of the salts demonstrate that their structures are as given and that the difference in structure of the hydrates persists in solution. The second of these hydrates resembles the hydrate of the amine-oxide, $(\text{CH}_3)_3\text{N}(\text{OH}_2)\cdot\text{H}_2\text{O}$, which I suppose to exist in only very small amount in the solution and which causes the conductivity. The other hydrate,⁶ $(\text{CH}_3)_3\text{N}=\text{O}\cdot 2\text{H}_2\text{O}$, which, I think, comprises the larger part of the oxide in solution, would not ionize appreciably.

2. The addition of hydrobromic acid to a solution of ammonia would cause an increase in the conductivity of the solution similar to that caused by the addition of the acid to a solution of the amine-oxide. This is explained for ammonia by assuming that the hydrogen of the acid adds to the nitrogen, and the bromine atom is then held by a polar valence. In a similar manner, the simplest explanation is that the hydrogen of the acid adds to the oxygen of the amine-oxide and that the bromine is held by a polar valence to the nitrogen.

3. Stewart and Maeser attach a good deal of importance to the low aqueous vapor pressure of trimethylamine-oxide hydrate and think this is connected with the slight conductivity of the compound. They seem to have overlooked the fact that the hydrate of potassium hydroxide, $\text{KOH}\cdot 2\text{H}_2\text{O}$, also has a very low, aqueous vapor pressure and that this does not interfere with its ionization. The trimethylethoxyammonium compounds are also excessively hygroscopic and evidently form hydrates, but they are highly ionized in solution.

4. The formula, $\text{R}:\overset{\text{R}}{\underset{\text{R}}{\text{N}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}: \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}: \text{H}$, which Stewart and Maeser give for

the associated hydroxide, includes a hydrogen atom with a covalence of 2. I know of no experimental evidence that hydrogen ever has a covalence of this sort.

⁶ A critic objects that these formulas imply that the nitrogen atom has a "sheath of ten electrons." Whether the pair of electrons which I assume to form the polar valence between the nitrogen and oxygen atoms is "in the sheath of the nitrogen atom," I do not know. Lewis, in his "Valence and the Structure of Atoms and Molecules," [American Chemical Society Monograph] p. 113, accepts a valence of five for phosphorus in phosphorus pentachloride and of six for sulfur in sulfur hexafluoride. I know of no reason, other than the octet hypothesis, why nitrogen may not have a valence of five. Our present knowledge of the actual function of the electrons is altogether too indefinite for us to be dogmatic on such a point as the exact positions of the electrons "in the sheaths of atoms."

5. Nitrogen has five valences in ammonium salts. The fifth valence is no less a real valence because it is highly polar. It has been shown that this fifth, polar valence may hold a nitrogen atom in a stable ring formation in solution.⁷ Evidently the static force which holds the nitrogen and oxygen atoms together in this case resides in these two atoms and not in the rest of the molecule.

6. The ammonium group is never stable unless the fifth, polar valence is satisfied in some way.

7. The double union between a carbon and an oxygen atom has a real meaning as shown by the replacement of the oxygen by two univalent chlorine atoms. The addition of hydrogen to the oxygen and of carbon, or of some other element to the carbon in a very great variety of reactions demonstrates that one of the unions is decidedly polar. I know of no compelling reason for thinking that the double union between the nitrogen and oxygen in the amine oxides has not a similar real meaning.

8. The distinction between polar and non-polar unions is one of degree and not of kind. This is so evident for the polar and non-polar unions of hydrogen atoms as to require no discussion.⁸ That chlorine atoms have a positive polar valence and yet show very little ionization has been shown for nitrogen trichloride and hypochlorous acid.⁹ Because the fifth valence of nitrogen is highly polar¹⁰ it does not follow that it is not a true valence any more than the trifling ionization of the hydrogen atoms of the ammonium group proves that these atoms are non-polar. In all the ordinary reactions of ammonia or ammonium compounds, whenever these atoms are replaced they react as hydrogen ions.

9. In all stable compounds containing a nitrogen atom combined with four hydrogen atoms or with four positive groups, the atom develops a fifth, polar valence. In all compounds of oxygen with well-established structures the oxygen atom has a valence of two or, less often, of four. It seems improbable that the amine oxides are exceptions to these general rules.

10. There is very strong evidence that a pair of electrons performing the function of a "covalence" balances only *one* positive charge on each of

⁷ Noyes and Potter, *THIS JOURNAL*, **37**, 192 (1915).

⁸ Noyes, *Trans. Faraday Soc.*, **19**, 521 (1923).

⁹ Noyes and Lyon, *THIS JOURNAL*, **23**, 463 (1901). Stieglitz, *ibid.*, **23**, 796 (1901). Noyes and Wilson, *ibid.*, **44**, 1630 (1922). Noyes and Haw, *ibid.*, **42**, 2167 (1920). Noyes, *ibid.*, **42**, 2175 (1920).

¹⁰ An editorial critic suggests that my "use of the concept of polar valence is rather indefinite." Those who follow the Lewis-Langmuir hypothesis understand by a polar valence one which ionizes in solution. Even in this sense, I have pointed out that the hydrogen of the methylene group of aceto-acetic ester is polar and that the chlorine atom is held to the hydroxyl of hypochlorous acid by a polar valence. I have, therefore, in another paper, extended the term polar to include compounds which separate into positive and negative parts during chemical reactions. Such compounds are rather common. See Noyes, *Bull. soc. chim.*, [4] **35**, 425 (1924); *Ber.*, **57**, 1233 (1924).

the atoms held together, while a pair of electrons which does not function as a covalence balances *two*. Thus ammonia, $\text{H}:\ddot{\text{N}}:\text{H}$ is electrically neutral

but as soon as the extra pair of electrons functions as a covalence the nitrogen atom develops a positive charge. The compound $\text{CH}_3:\ddot{\text{S}}:\text{CH}_3$ is electrically neutral but the group $\text{CH}_3:\ddot{\text{S}}:\text{CH}_3$ is a positive ion. A chlorine

atom with eight electrons in the outer shell is a negative ion but hydrogen chloride, in which one pair of the electrons probably forms a covalence between the hydrogen and chlorine atoms, is neutral.

While the reasons given seem to the writer to demonstrate conclusively that the fifth, polar, negative atom or group is held by the static charge of the nitrogen atom and not by the group as a whole, it does not follow from this that it is localized on the periphery of the nitrogen atom. We need further evidence before a conclusion on that point can be reached. The optical activity of allylbenzylphenylmethylammonium bromide¹¹ proves that the four positive groups of this compound are localized with reference to each other on the periphery of the nitrogen atom and the optical activity of carboxymethyl-ethylmethylsulfonium chloroplatinate,¹² $[(\text{CH}_2\text{CO}_2\text{H})\cdot\text{CH}_3\cdot\text{C}_2\text{H}_5\cdot\text{S}]_2\text{PtCl}_6$, demonstrates that a group held by a polar valence, or the unoccupied electrons of a polar group, may be one of the four groups localized with reference to one another on the periphery of an asymmetric sulfur atom. It might seem possible that the polar valence could be localized on the periphery of the nitrogen atom but there is no similar pair of electrons to perform this function and I know of no experimental evidence which points to such a localization. The failure to obtain optically active compounds of the type $\text{RR}'\text{R}''\text{NX}$ is some evidence that the polar valence cannot be localized. Compounds of the type $\text{RR}'\text{R}''\text{HNX}$ have, also, not been resolved into optical isomers. The theory furnishes no good reason for this failure other than the mobility of the hydrogen atoms. Amine-oxides of the type $\text{RR}'\text{R}''\text{NO}$, in which the ion is $\text{RR}'\text{R}''\text{NOH}^+$, have been resolved.

Summary

The conclusion of Stewart and Maeser that trimethylethoxyammonium and trimethylmethoxyammonium hydroxides are highly ionized in aqueous solutions has been confirmed and the erroneous observations of the author in a previous paper have been corrected.

Reasons are given for believing that the fifth, polar valence of ammonium compounds is a real valence residing in the nitrogen atom and not in

¹¹ Pope, *J. Chem. Soc.*, 75, 1127 (1899).

¹² Pope and Peachy, *ibid.*, 77, 1072 (1900).

the group as a whole; also, for thinking that the amine-oxide retains the structure $(\text{CH}_3)_3\text{N}::\ddot{\text{O}}$ in solution, the nitrogen having its usual valence of five (one being polar) and oxygen its valence of two.

The hypothesis of Stewart and Maeser that the amine-oxide has the structure $\text{R}:\text{N}:\ddot{\text{O}}:\text{H}:\ddot{\text{O}}:\text{H}$ in solution is questioned.

Reasons are given for believing that the polar valence of ammonium compounds is properly considered as a "primary valence" and that the differences between "polar" and "non-polar" valences are differences of degree rather than of kind.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ISOXAZOLINE OXIDES

IV. BENZOYL-DIPHENYL-ISOXAZOLINE OXIDE

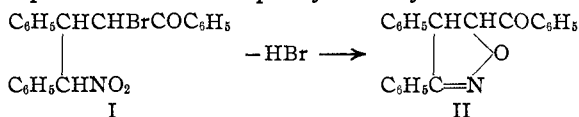
Second Paper

BY E. P. KOHLER

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In the first paper¹ I described the products obtained by the action of potassium acetate on the various stereomeric forms of a highly phenylated α -bromo- γ -nitroketone (I). This reaction always gave almost exclusively a substance melting at 123° , but in one case it was possible to isolate an isomer melting at 151° in an amount barely sufficient to show that it was enough like the main product to justify the conclusion that the two compounds were stereoisomers. These substances were assumed to be the two possible forms of diphenyl-benzoyl-isoxazoline oxide.



The properties of the main product (123°) were in fairly good agreement with this interpretation, but two facts provoked some doubt: the substance had no oxidizing power, and it gave the normal reaction of ketones with Grignard reagents. These facts were not completely irreconcilable with the proposed formula but the discovery that triphenyl-isoxazoline oxide,² whose structure could be established with more precision, liberates chlorine from phosphorus pentachloride and is reduced by Grignard reagents, necessitated a reëxamination of the problem. As a result, it is now clear that the substance melting at 123° is not an isoxazoline oxide. This conclusion has been reached in the following manner.

¹ Kohler, *THIS JOURNAL*, **46**, 1733 (1924).

² Kohler and Barrett, *ibid.*, **46**, 2105 (1924).