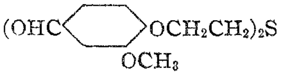
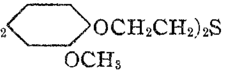
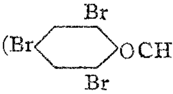
Name.	Formula.		M. p.
Bis(β,β-naphthoxy-ethyl) sulfide.......	$(\beta\text{-}C_{10}H_7.OCH_2CH_2)_2S$		129.0°
Bis(β,β-naphthoxy-ethyl) sulfone	$(\beta\text{-}C_{10}H_7.OCH_2CH_2)_2SO_2$		151.0°
Bis(β-vanilloxy-ethyl) sulfide..........	 $(OHC\underset{OCH_3}{\bigcirc}OCH_2CH_2)_2S$		131.5°
Bis(β-eugenoxy-ethyl) sulfide........	 $(CH_2 = CHCH_2\underset{OCH_3}{\bigcirc}OCH_2CH_2)_2S$		113.5°
Bis(β-tribromo-phenoxy-ethyl) sulfide.	 $(Br\underset{Br}{\overset{Br}{\bigcirc}}OCH_2CH_2)_2S$		118.5°
Bis(β-butyl-mercapto-ethyl) sulfide...	$(BuSCH_2CH_2)_2S$	b. p. 222–3°	17.5°
Bis(β-butyl-mercapto-ethyl) sulfoxide.	$(BuSCH_2CH_2)_2SO$		25.0°
Bis(β-butyl-mercapto-ethyl) sulfone..	$(BuSCH_2CH_2)_2SO_2$		73.7°
Bis(β-butyl-sulfinyl-ethyl) sulfoxide...	$(BuSOCH_2CH_2)_2SO$		196°.0
Bis(β-butyl-sulfinyl-ethyl) sulfone....	$(BuSOCH_2CH_2)_2SO_2$		171.0°
Bis(β-butyl-sulfonyl-ethyl) sulfone....	$(BuSO_2CH_2CH_2)_2SO_2$		266.5°
Bis(β-ethyl-mercapto-ethyl) sulfide...	$(EtSCH_2CH_2)_2S$	b. p. 173–5°	17.0°
Bis(β-ethyl-mercapto-ethyl) sulfone....	$(EtSCH_2CH_2)_2SO_2$		64.0°
Bis(β-ethyl-sulfonyl-ethyl) sulfone....	$(EtSO_2CH_2CH_2)_2SO_2$		223.0°
Bis(β-methyl-mercapto-ethyl) sulfone.	$(MeSCH_2CH_2)_2SO_2$		77.0°
Bis(β-propyl-mercapto-ethyl) sulfide..	$(PrSCH_2CH_2)_2S$	b. p. 193–5°	27.5°
Bis(β-propyl-mercapto-ethyl) sulfone.	$(PrSCH_2CH_2)_2SO_2$		75.5°
Bis(β-propyl-sulfonyl-ethyl) sulfone...	$(PrSO_2CH_2CH_2)_2SO_2$		254°.0
Bis(β-*iso*butyl-mercapto-ethyl) sulfone	$(i\text{-}BuSCH_2CH_2)_2SO_2$		94.2°
Bis(β-*sec.*-butyl-mercapto-ethyl) sulfone...........................	$((sec.)BuSCH_2CH_2)_2SO_2$		15.0°
Bis(β-amyl-mercapto-ethyl) sulfide...	$(AmSCH_2CH_2)_2S$		20.0°
Bis(β-amyl-mercapto-ethyl) sulfone...	$(AmSCH_2CH_2)_2SO_2$		91.0°
4-Phenyl-1,4-thiazan	$Ph.N < (CH_2CH_2)_2 > S$		108–111°
4-Phenyl-1,4-sulfanazan	$Ph.N < (CH_2CH_2)_2 < SO$		123.5°
4-*p*-Cresyl-1,4-sulfonazan	$p\text{-}CH_3.C_6H_4N < (CH_2CH_2)_2 > SO_2$		136.5°
4-*o*-Cresyl-1,4-sulfonazan	$o\text{-}CH_3.C_6H_4.N < (CH_2CH_2)_2 > SO_2$		135.0°
Bis(β-thio-ethyl acetate)............	$(CH_3COOCH_2CH_2)_2S$	b. p. 155–6°	(20 mm.)

BALTIMORE, MD.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, HARVARD UNIVERSITY.]

ON THE NONEXISTENCE OF VALENCE AND ELECTRONIC ISOMERISM IN HYDROXYLAMMONIUM DERIVATIVES.

BY ARTHUR MICHAEL.

Received March 9, 1920.

In 1894, Dunstan and Goulding[1] showed that trimethyl-hydroxylammonium iodide is the sole substitution product formed in the action of methyl iodide on an excess of hydroxylamine; later,[2] that the base set free from that salt represents a hydrated trimethylamine oxide. Further, that methyl iodide unites at ordinary temperature with the product to give the iodide of an ammonium base, to which they assigned the structure

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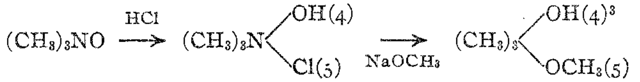
[1] *Proc. Chem. Soc.*, **10**, 138 (1894); *Chem. News*, **69**, 308 (1894).

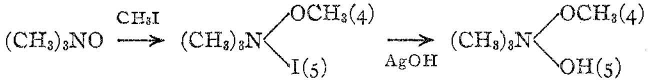
[2] *J. Chem. Soc.*, **69**, 839 (1896); **75**, 792, 1005 (1899).

$(CH_3)_3N(OCH_3)I$, and which is decomposed by caustic potash into the amine oxide and methyl alcohol. A later examination of these reactions and products by Meisenheimer[1] has led to results and conclusions of great theoretical interest. This chemist, who prepared the amine oxide in a free state, found that the hydroxide obtained from the addition product with methyl iodide is capable of existing only in dil. aqueous solution, and decomposes on evaporation of the solvent into trimethylamine and formaldehyde, not into the amine oxide and methyl alcohol, as Dunstan and Goulding believed. On the other hand, by treating the amine oxide chlorohydrate with sodium methylate dissolved in absolute methyl alcohol, a solution was obtained which left the amine oxide as a residue on evaporation.

Meisenheimer[2] had previously assumed the particular valence in ammonium derivatives uniting the nitrogen with the acid radical to be different from the 4 other valences. Representing this valence by (5), it is evident that the structures of these 2 bases are identical, except that the hydroxyl and methoxyl groups are linked to nitrogen by different valences:



$$(CH_3)_3NO \xrightarrow{HCl} (CH_3)_3N\begin{matrix}OH(4)\\Cl(5)\end{matrix} \xrightarrow[NaOCH_3]{} (CH_3)_3\begin{matrix}OH(4)[3]\\OCH_3(5)\end{matrix} \qquad (I)$$



$$(CH_3)_3NO \xrightarrow{CH_3I} (CH_3)_3N\begin{matrix}OCH_3(4)\\I(5)\end{matrix} \xrightarrow[AgOH]{} (CH_3)_3N\begin{matrix}OCH_3(4)\\OH(5)\end{matrix} \qquad (II)$$

The existence of this remarkable kind of valence isomerism[4] was further confirmed by preparing 3 pairs of similarly constituted, bisubstituted derivatives that show the same striking contrast in the products of decomposition. For instance, the compound from the amine oxide and methyl iodide yields, by double decomposition with sodium ethylate or propylate, products that break up on evaporation of the alcoholic solution into trimethylamine, formaldehyde and ethyl or propyl alcohol. On the other hand, the isomeric derivatives, obtained from the addition products of ethyl and propyl iodides and sodium methylate, decompose

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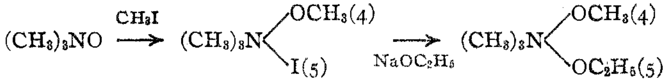
[1] *Ann.*, 397, 273 (1913).

[2] *Ibid.*, 385, 117 (1911).

[3] There is no decisive evidence that the solution before evaporation contained this product, as the reaction may proceed through the formation of $(CH_3)_3N(ONa)Cl$, which would decompose into the amine oxide and salt.

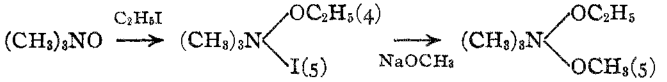
[4] Meisenheimer (*Ann.*, 397, 273 (1913)), believes that the non-equivalence or inequality of the 5 nitrogen valences is the cause of the assumed isomerism, and it seems, therefore, appropriate to designate its valence isomerism; although Werner has used that expression in a somewhat different sense. It is hardly conceivable that the bound energy holding the chlorine and hydrogen in the ammonium chloride molecule is equal in value, and, from that point of view, an inequality certainly exists between the energy relations in these atoms. It cannot cause isomerism, however, as a readjustment in the energy relations must take place with a chemical change in the molecule.

into ethyl, resp., propyl aldehyde, methyl alcohol and trimethylamine. The preparations and isomerism are expressed by:



$$(CH_3)_3NO \xrightarrow{CH_3I} (CH_3)_3N\begin{matrix}\diagup OCH_3(4)\\ \diagdown I(5)\end{matrix} \xrightarrow[NaOC_2H_5]{} (CH_3)_3N\begin{matrix}\diagup OCH_3(4)\\ \diagdown OC_2H_5(5)\end{matrix}$$

(III)

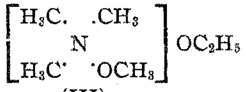


$$(CH_3)_3NO \xrightarrow{C_2H_5I} (CH_3)_3N\begin{matrix}\diagup OC_2H_5(4)\\ \diagdown I(5)\end{matrix} \xrightarrow[NaOCH_3]{} (CH_3)_3N\begin{matrix}\diagup OC_2H_5\\ \diagdown OCH_3(5)\end{matrix}$$

(IV)

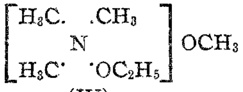
Meisenheimer calls attention to the fact, that it is always the alkyl radical joined by valence (4) which is split off as an aldehyde, and believes the "*reaction proves that the two alkyloxyl groups are not joined to the nitrogen atom in the same manner.*"[1] Willstätter[2] had suggested "oxonium" structures for the salts of the amine oxide, and also for the hydrated base, but Hantzsch and Graf[3] showed experimentally that the properties of the compounds are not compatible with such an interpretation. Later, Werner[4] expressed a similar view in terms of his ammonium hypothesis, but Meisenheimer in the first paper,[5] and later,[6] in a discussion of the subject with Fromm,[7] showed that the suggestion is not tenable.

Meisenheimer's explanation is based on a modified interpretation of Werner's ammonium hypothesis, and he assigns the following structures to III and IV:



$$\left[\begin{matrix}H_3C. & & .CH_3\\ & N & \\ H_3C\cdot & & \cdot OCH_3\end{matrix}\right]OC_2H_5$$

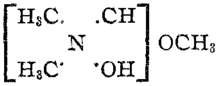
(III)



$$\left[\begin{matrix}H_3C. & & .CH_3\\ & N & \\ H_3C\cdot & & \cdot OC_2H_5\end{matrix}\right]OCH_3$$

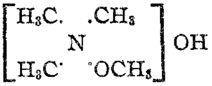
(IV)

but with the reservation that they only represent the structures correctly, if, in opposition to Werner's views, "*all five radicals are joined to nitrogen by main valences, four in the inner and one in the outer zone.*"[8] According to this interpretation the isomeric trimethyl-methoxylammonium hydrates, designated above as I and II, are represented by:



$$\left[\begin{matrix}H_3C. & & .CH\\ & N & \\ H_3C\cdot & & \cdot OH\end{matrix}\right]OCH_3$$

(I)



$$\left[\begin{matrix}H_3C. & & .CH_3\\ & N & \\ H_3C\cdot & & \cdot OCH_3\end{matrix}\right]OH$$

(II)

The subject has also been considered by L. W. Jones[9] from the viewpoint of the "electronic" hypothesis. This chemist assumes that the methoxyl

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[1] *Loc. cit.*, 277.

[2] *Ber.*, **33**, 1638 (1900).

[3] *Ibid.*, **38**, 2154 (1915).

[4] "Neuere Anschauungen," pp. 210, 204 (1909).

[5] *Loc. cit.*, 278.

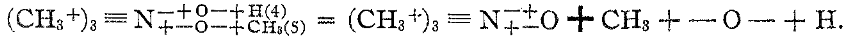
[6] *Ann.*, **399**, 371 (1913).

[7] *Ibid.*, 366 and 377.

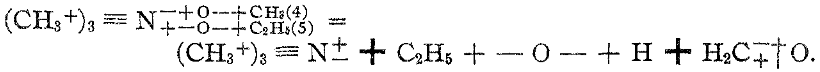
[8] *Ann.*, **397**, 283 (1913).

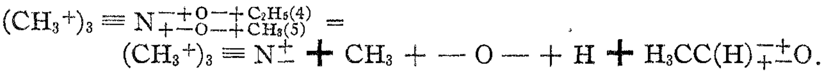
[9] THIS JOURNAL, **36**, 1284–88 (1914).

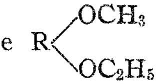
group is positive in II and III and negative in I and IV, and represents the isomerism, and decompositions of the isomeric products, as follows:

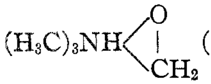
I 
$(CH_3{}^+)_3 \equiv N\substack{-+O-+H(4)\\ +-O-+CH_3(5)} = (CH_3{}^+)_3 \equiv N\substack{-+\\ +-}O \boldsymbol{+} CH_3 + -O- + H.$

II 
$(CH_3{}^+)_3 \equiv N\substack{-+O-+CH_3(4)\\ +-O-+H(5)} = (CH_3{}^+)_3 \equiv N\substack{-+H\\ +-O-+H} \boldsymbol{+} H_2C\substack{-+\\ +-}O.$

III 
$(CH_3{}^+)_3 \equiv N\substack{-+O-+CH_3(4)\\ +-O-+C_2H_5(5)} =$
$(CH_3{}^+)_3 \equiv N\substack{+\\ -} \boldsymbol{+} C_2H_5 + -O- + H \boldsymbol{+} H_2C\substack{-\\ +}\dagger O.$

IV 
$(CH_3{}^+)_3 \equiv N\substack{-+O-+C_2H_5(4)\\ +-O-+CH_3(5)} =$
$(CH_3{}^+)_3 \equiv N\substack{+\\ -} \boldsymbol{+} CH_3 + -O- + H \boldsymbol{+} H_3CC(H)\substack{-+\\ +-}O.$

It is evident that the acceptance of either of these interpretations involves far-reaching modifications in the present conception of valence and its relation to chemical properties. Even if it were granted that the values of the valences joining the hydroxyl and methoxyl groups to the nitrogen in I and II differ quantitatively, or in the "electronic" relations, there is no precedent in chemistry for the assumption that a methoxyl group on hydrolysis should yield formic aldehyde; on the contrary, all established facts point unmistakably to that of methyl alcohol. If it is admitted that the valence of an atom may exist in several modifications, and that these may cause such radical differences in chemical properties, then a permanent correlation between the valence theory and chemical behavior no longer exists, and the theory will lose much of its precision and usefulness in coördinating properties with structure. These remarks apply also to the explanations given for the breaking up of III and IV in different directions. The properties of substances of the type  $R\substack{OCH_3\\ OC_2H_5}$ are well established, and, without exception, they show considerable stability towards heat energy. To suppose that the hydroxylammonium derivatives have such structures, and, notwithstanding, are so unstable that they break up on evaporation of the absolute alcoholic solution *in vacuo* is scarcely conceivable chemically. And, quite as much opposed to chemical precedents, is the formation of aldehydes and different products of decomposition from substances with such structures, irrespectively whether they are interpreted according to the Werner hypothesis, or, whether with Jones, positive and negative signs are arbitrarily connected with certain of the atoms.

There is, however, no necessity to modify our conceptions on the relations between the valence phenomenon and the structures and chemical properties of substances. Derivative I, if it is formed in the action of sodium methylate on the chlorohydrate of the amine oxide, must have the formula $(H_3C)_3N(OH)OCH_3$, and such a derivative should decompose easily into the amine oxide and methyl alcohol. The isomeric product II, which is prepared from the addition product of the amine oxide and methyl iodide by double decomposition with silver oxide, has the structure  $(H_3C)_3NH\left\langle\begin{array}{l}O\\ |\\ CH_2\end{array}\right.(OH)$, and the formation of the corresponding iodo derivative becomes evident when the properties of organic nitroso compounds are taken into consideration.

Dunstan and Goulding's assumption that methyl iodide adds to the amine oxide to form a methoxylammonium salt certainly appears to be a consistent theoretical conclusion, and, that the addition does not proceed in this manner, is due to the following reasons. Owing to the presence of the negative hydroxyl group, hydroxylammonium hydrate has much less strongly developed basic properties than ammonium hydrate,[1] which manifests itself in the marked tendency to form stable halhydric salts with the acid component in a smaller molecular proportion than in the corresponding ammonium salts;[2] indeed, as by-products in the preparation of trimethyl amine oxide, di- and trihydroxylamine iodohydrates are formed, but none of the normal salt.[3] The intramolecular neutralization of the atomic forces in trimethyl-methoxylammonium iodide is, therefore, less complete than in the tetramethyl ammonium compound, and the tendency to form a derivative of that type should be less pronounced. The course of the addition of alkyl iodides to the amine oxide is mainly directed, however, by the energy and affinity relations of the atoms in the nitroso group, that are so characteristically shown in the spontaneous isomerization of the primary and secondary nitrosoalkanes to oximes. Trimethylamine oxide also contains a nitroso group, but, like the tertiary nitrosoalkanes, it represents a stable product under ordinary conditions, because the free energy in the atoms of the group has been converted to a very considerable extent into bound energy and heat, through the direct and spatial intramolecular action of the numerous hydrogen and carbon atoms.

According to the le Chatelier-van't Hoff equilibrium law the effect of heat on the structure of trimethylamine oxide should be to strive to change it into one with a greater energy content. It may be expected, therefore, that at a certain temperature the amine oxide will have absorbed sufficient energy to isomerize to $(H_2C) = N(CH_3)_2OH$; a change that is favored by the increase in the affinity relation of hydrogen for oxygen over that for carbon with the rise of temperature. The isomerized substance represents a condensation product of an aldehyde and dimethylammonium hydrate, and, as such derivatives are very easily hydrolyzed, and, as the hydrated amine oxide on heating under ordinary pressure

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[1] Mac Kay, *Centr.*, **1908**, I, 1918.

[2] Lossen, *Ann.*, **160**, 242 (1871).

[3] Dunstan and Goulding, *loc. cit.*

parts with its water with difficulty,[1] the following changes take place:[2]

$$(CH_3)_3NO, H_2O \longrightarrow H_2C = N(CH_3)_2OH + H_2O = (H_3C)_2NH + HCHO + H_2O.$$

On heating the amine oxide sulfate with dil. sulfuric acid, formaldehyde and dimethylammonium sulfate are formed, and at a much lower temperature (110°).[3] The decomposition is greatly facilitated under these conditions, for, in starting from the sulfate, a product much richer in free energy is not only used, but the quality is such, that it will be largely converted into bound energy and heat by the strong base formed in the reaction. Then, the affinity of the hydroxyl group for nitrogen, and that of the methyl hydrogen atom for the carbon, is decreased by such negative influence,[4] and the additive capacity of water to unsaturated compounds is enormously accelerated by the intramolecular, dynamic conditions prevailing in the dilute, aqueous solution of the acid.[5]

The isomerization of nitrosomethane to formaldoxime represents an intramolecular reduction of the oxygen and oxidation of the carbon; the hydrogen passing over to the oxygen not only on account of the quality and quantity of the free energy in it, but because in so doing an intramolecularly well-neutralized, amphoteric substance is formed.[6] The other course of isomerization is evidently barred, for a substance with the formula $H_2C = NH(= O)$ would be vastly richer in free energy; indeed, if it could be prepared in another way, it should, on account of the much greater affinity of hydrogen for oxygen than for nitrogen and the energetic relations in these atoms, spontaneously convert itself into the oxime. The primary reaction between the amine oxide and methyl iodide

$$(H_3C)_3NO + CH_3I = (H_3C)_3NH(OCH_2I)$$

represents an intermolecular reduction of the nitrogen and an oxidation of the carbon in the iodide. A hydrogen of the iodide passes over to the nitrogen, for the contrary course of addition would lead to the formation of iodomethyl-trimethylammonium hydrate, $(H_2CI)(H_3C)_3NOH$, which would be a strongly basic substance, and, as it would have a far greater content in free energy, its production would not represent the possible maximum entropy of the reaction.[7] The formula $(H_3C)_3NH$-

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[1] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 796 (1899).

[2] *Loc. cit.* Dunstan and Goulding state, "near 180° the base suffers decomposition, formaldehyde and trimethylamine being among the products," but give no analytical details. There can be no doubt that dimethylamine must also be formed, as otherwise the appearance of formaldehyde would be quite inexplicable.

[3] *Loc. cit.*

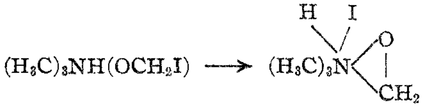
[4] THIS JOURNAL, **32**, 996 (1910).

[5] Michael and Brunel, *Am. Chem. J.*, **41**, 118 (1909); **48**, 266 (1912).

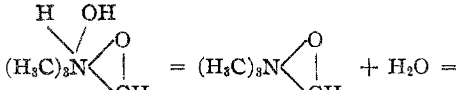
[6] Michael, THIS JOURNAL, **32**, 1000 (1910).

[7] Meisenheimer (*loc. cit.*, 289) found that ethyl and propyl iodides scarcely react on the hydrated, but readily on the anhydrous amine oxide. This difference in be-

(OCH_2I) is evidently in accord with the formation of trimethylamine and formaldehyde by hydrolysis, but not with that of a platinichloride and aurichloride from the corresponding chloro derivative, nor with the great chemical mobility of the halogen atom. In fact, all the addition products of the amine oxides and alkyl iodides act like salts of not very strong bases, as they are hydrolyzed by water to the extent of forming strongly acidic solutions.[1] It must be assumed, therefore, that the CH_2I group in the above compound reacts intramolecularly and additively on the basic nitrogen atom



to form the hydriodic acid salt of a condensation derivative of the unstable trimethylammonium hydrate and formaldehyde. This structure complies in every respect with the properties of the substance. The iodo compound, which may be called form-trimethyl-ammoniumhydroxide hydroiodide, owes its comparative stability to the intramolecular conversion of positive energy, centered at the nitrogen atom, by the negative of the halogen,[2] and a corresponding decrease in that property follows the replacement of the halogen by the much less negative hydroxyl group. Indeed, the hydroxide may exist only for a short time even in aqueous solution, and on evaporation of the solvent, a quantitative decomposition into formaldehyde and trimethylamine takes place:[3]



$$(H_3C)_3NHOH + CH_2O = (H_3C)_3N + H_2O + CH_2O.$$

The properties and decompositions of the isomeric compounds, obtained

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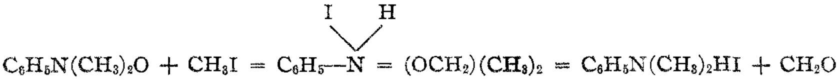
havior is undoubtedly due to the loss of free energy in the nitroso group accompanying hydration; the oxide is extremely hydroscopic, and the process undoubtedly proceeds exothermically, *i. e.*, with conversion of some of its free chemical energy into heat.

[1] Hantzsch and Graf (*Ber.*, **38**, 2156 (1905)) believe that a slight hydrolysis only takes place with solution, but Meisenheimer (*loc. cit.*, 284) states that the solutions are strongly acidic.

[2] Bamberger and Tschimer (*Ber.*, **32**, 1886 (1899)) found that the less basic dimethylaniline oxide with methyl iodide gives formaldehyde and dimethylaniline iodohydrate on standing. This reaction proceeds in a similar manner to that with the fatty amine oxides, *i. e.*,

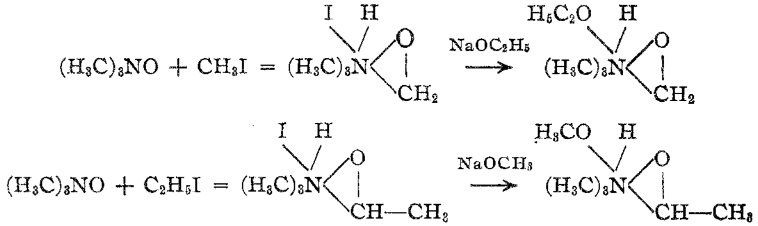


$$C_6H_5N(CH_3)_2O + CH_3I = C_6H_5\overset{I\ \ H}{-N} = (OCH_2)(CH_3)_2 = C_6H_5N(CH_3)_2HI + CH_2O$$

but the addition product is even less stable. Formaldehyde reacts in an analogous manner, and the addition product breaks down into formic acid and the iodohydrate.

[3] Meisenheimer, *loc. cit.*, 284.

on treating the addition products of the amine oxide and alkyl iodides with different alkylates, may now be explained. For instance, the reactions between the amine oxide and methyl and ethyl iodides, and those of the addition products with sodium ethylate, respectively, methylate, may be represented as follows:



It is evident, that substances of these structures must be quite unstable towards heat and water; indeed, Meisenheimer[1] found that they exist only in absolute alcoholic solutions, breaking up on concentration into trimethylamine and an alcohol and aldehyde.[2] Further, the aldehyde must correspond to the alkyl iodide, since that product is oxidized in the addition to the amine oxide, and the carbinol to the sodium alkylate, which relations agree with Meisenheimer's results.

Remsen and Norris[3] found that trimethylamine and chlorine unite to form a very unstable addition product, that decomposes easily in most air; with bromine a somewhat more stable product, $(H_3C)_3NBr_2$, was isolated, but it decomposes instantly with water, liberating an atom of the halogen as hydrobromic acid. The same product is formed in the action of bromine on trimethylammonium bromide, and this formation, together with the behavior towards water, led Norris[4] to change the formula into $(H_3C)_3NBr_3$, HBr. This conclusion implied the formation of hydrobromic acid, and it could be shown[5] that, on adding bromine in ether to trimethylamine in the same solvent, a precipitate of the bromohydrate is deposited, as long as the base is in excess.

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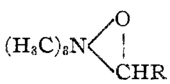
[1] *Loc. cit.*, 277.

[2] The facility of decomposition into carbinols and  is self-evident; the latter compound is a derivative of the unstable trimethylammonium hydroxide, and its existence as a derivative in solution is due to substitution of the 2 hydrogens by an alkylidene group. Cyclic derivatives of this nature are easily decomposed, even when the nitrogen is trivalent, and a ring derivative with a pentavalent nitrogen could not show more than a slight stability. Other substances containing halogen are known, in which the nitrogen has a higher valence than 5, *e. g.*, $(H_5C_2)_4NI_3$ and $(H_3C)_4NI_5$ (Weltzein, *Ann.*, **91**, 33 (1854)).

[3] *Am. Chem. J.*, **18**, 91 (1896).

[4] *Ibid.*, **20**, 51 (1898).

[5] *Loc. cit.*

Hantzsch and Graf[1] re-established the older formula, by showing that 2 atoms of iodine are liberated on adding potassium iodide to a solution of the substance in acetic acid. They endeavored to replace the bromine in the compound by hydroxyl, but found that metallic oxides or hydroxides give trimethylamine, with metallic bromides and hypobromites, but no amine oxide or its hydrate.[2] Hantzsch[3] used these results for speculations on the constitution of ammonium salts, and on the mechanism of double decomposition, which have a bearing on the subject discussed in this paper. That chemist compares the behavior of the amine dibromide with that of lead bromide

$$\mathrm{Pb}\begin{matrix}\diagup \mathrm{Br}\\ \diagdown \mathrm{Br}\end{matrix} \xrightarrow{\mathrm{KOH}} \mathrm{Pb}\begin{matrix}\diagup \mathrm{OH}\\ \diagdown \mathrm{Br}\end{matrix} \xrightarrow[\mathrm{KOH}]{} \mathrm{Pb(OH)_2} \longrightarrow \mathrm{PbO, H_2O}$$

and believes the amine dibromide should react in a corresponding manner. For trimethyl-hydroxylammonium bromide represents a "very stable salt,"[4] and the amine oxide is fairly stable. Hantzsch[4] believes the decomposition of the amine dibromide by potash into amine and hypobromous acid to be unexplainable from the commonly accepted structure of the compound; since $(H_3C)_3N(OH)Br$ should be the intermediate product of the reaction, and that substance cannot decompose in the above manner. He finds, however, an "entirely satisfactory" explanation of these results in Werner's ammonium hypothesis, and, accordingly, expresses the addition products with hydrobromic acid and bromine by $[N(CH_3)_3H]Br$ and $[N(CH_3)_3Br]Br$. The latter product should yield bromo-trimethylammonium hydrate, $[N(CH_3)_3Br]OH$, on hydrolysis, which should break up into trimethylamine and hypobromous acid.[5]

The behavior of triethylamine towards chlorine water has recently been studied by Meisenheimer,[6] who shows that it is converted into a mixture of the chlorohydrates of di- and tri-ethylamine and acetaldehyde. This interesting result is explained[7] by the decomposition of the first-formed product, $(H_5C_2)_3NCl_2$, into hydrogen chloride $(H_5C_2)_2(CH_3CH=)NCl$, and the hydrolysis of the latter substance into diethylamine chlorohydrate and aldehyde; the acid set free unites with unchanged tertiary base, and protects it from the action of the halogen. It is now possible to explain the apparently anomalous results obtained by Remsen and Norris in the behavior of bromine towards trimethylamine in excess, and that of the amine dibromide towards water. In the first reaction, some of the

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[1] *Ber.*, 38, 2157 (1905).

[2] *Ibid.*, 2161.

[3] *Ibid.*, 2162.

[4] *Loc. cit.*

[5] *Ibid.*, 2163.

[6] *Ber.*, 46, 1160 (1913).

[7] *Ibid.*, 1150.

amine forms the dibromide, which reacts with unchanged base to form a not isolated product,[1] undoubtedly $(H_3C)_2(H_2C=)NBr$, and the salt of the tertiary base. The amine dibromide with cold water undergoes the same decomposition, liberating $^1/_2$ of the halogen as hydrobromic acid.

The behavior of the trimethylamine dihalides towards water is a characteristic organic reaction.[2] The ease of the elimination process is due to the loosening of the affinity between carbon and hydrogen by the negative $NHal_2$ group,[3] and the slight affinity between nitrogen and halogen; the following phase is facilitated by the quality and quantity of the free energy at the unsaturated carbon and nitrogen of the intermediate product, $(H_3C)_2(H_2C=)NHal$, for water. With the formation of dimethylammonium halhydrate, the free energy in the NHal group is very largely converted into bound energy and heat, and the possible maximum increase of entropy in the system is realized.

The course of decomposition of the amine dibromide by water is determined by the strong affinity of water for hydrobromic acid, and the comparatively weak affinity for bromine. With the addition of alkali to the mixture a substance with a great capacity to directly neutralize the free chemical energy in the halogen atoms is introduced into the system, and, as the expenditure of energy necessary to separate them from the nitrogen atom is inconsiderable, the amine dihalide behaves chemically as if it were practically a mixture of amine and halogen. A second determining factor for this course of the reaction is the slight affinity of oxygen for nitrogen, which is so manifest in the negative values of the heats of formation of the oxides of nitrogen, and remains comparatively small, irrespective of the elements or groups to which the nitrogen atom may be joined.[4] For these reasons, when halogen in an organic substance is in direct union with nitrogen, it cannot be replaced by oxygen or hydroxyl. The reactions proceed either, (1) with the elimination of halhydric acid, (2) the direct removal of the halogen, or (3) its replacement by hydrogen, according to the chemical nature and structure of the substance, and the chemical character of the reagents.

When the behavior of trimethylamine dibromide and lead dibromide are viewed, not from a rigid application of the valence hypothesis, but from the affinity and energy conditions of nitrogen and lead, it is evident at once that similar reactions could not be expected. Nitrogen has only a small affinity for oxygen and much less for halogen, decreasing from iodine to bromine and then to chlorine; even when it is joined to 3

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[1] Norris, *loc. cit.*, 63.

[2] The dialkylchloroamines are decomposed by alkali in a similar manner (Berg, *Ann. chim. phys.*, [7] 3, 344 (1894)).

[3] THIS JOURNAL, 32, 996 (1910).

[4] Berthelot and André, *Compt. rend.*, 110, 836 (1890).

alkyl groups, the affinity of nitrogen for halogen is slight, as is evident from the properties of the compounds. And, as these addition products are formed with a small conversion only of the free energy in the halogen atom into bound energy with the nitrogen atom, the energetic hindrance to a dissociation into the component parts is inconsiderable. On the other hand, the affinity of lead increases from oxygen to halogen, *i. e.*, in exactly the reverse relationship. And, a very considerable expenditure of energy is required to separate it from halogen, as the free energy of the halogen and of the metal has been largely converted in their union into bound energy and heat. The reaction between lead bromide and caustic alkali proceeds by double decomposition, because lead has a decided affinity for oxygen, as is shown in the considerable heat of formation of lead oxide and hydroxide, and the entropy increase with the formation of the latter compound and alkali bromide, must be far greater than it would be with that of metallic lead, alkali bromide and hypobromite.

Willstätter and Iglauer[1] found that hypochlorous acid reacts upon the tertiary base tropidine to form the N-chloro derivative of the secondary base norotropidine, and explained the result by assuming a decomposition of the primary product, $R(CH_3)N(OH)Cl$, into $RNCl$ and CH_3OH. Hantzsch and Graf[2] showed that trimethylamine and hypochlorous acid form at first the corresponding hypochlorite, and then dimethylchloroamine. Under the supposition that methyl alcohol is the second product of the reaction, Hantzsch[3] explains the result by assuming that the acid may ionize to a slight extent also into $Cl^{\cdot} + OH'$, and that it should, therefore, form some $[(H_3C)_3.NCl]OH$, which may break up into base and acid, or into the chloroamine and the carbinol. Even if the unproven and very doubtful ionization of hypochlorous acid into $Cl^{\cdot} + OH'$ be accepted, the addition of these ions to the amine[4] must proceed with the possible maximum increase of entropy, that is with the formation of the salt derivative, $[(H_3C)_3N(OH)]Cl$, and not with that of the basic substance $[(H_3C)_3NCl]OH$. But the first structure represents the product obtained from the amine oxide and hydrochloric acid, and that salt does not decompose in the manner assumed by Hantzsch.

[1] *Ber.*, 33, 1636 (1900).

[2] *Ibid.*, 38, 2156 (1905).

[3] *Ibid.*, 2163.

[4] Hypochlorous acid is always used in very dilute solution and must add as an electrolyte, to form primarily a hypochlorite, which may rearrange to a more stable chlorohydrol (Michael, *J. prakt. Chem.*, [2] 60, 452, 463 (1899); Michael and Leighton, *Ber.*, 39, 2157 (1906)). This assumption is essential to explain the course of such additions to unsaturated hydrocarbons. It is, therefore, unnecessary to suppose the presence of traces of $Cl^{\cdot} + OH'$, as the unstable amine hypochlorite may directly rearrange to the more stable chlorohydrol, but in that case, too, trimethylhydroxylammonium chloride should be formed.

Meisenheimer[1] showed later that hypochlorous acid does not react upon trimethylammonium chloride, and that it gives dimethylchloroamine in very small amounts with the free base. But better yields of that product are obtained by using the chloride and sodium or calcium hypochlorites, although these salts must be taken in a large excess. When 2 mol. equivalents only of the salts are used practically no chloroamine is formed, and the products are unchanged tertiary amine, with some dimethylamine and formaldehyde, which, and not methyl alcohol as was previously supposed, is the second product formed under all conditions. Meisenheimer[2] accounts for these results by the presence of free chlorine in the reagents, which unites with the base to form the dichloride, and which on decomposition yields the products mentioned above.[3]

L. W. Jones[4] objects to this experimental solution of the problem on the ground that the dichloride would not persist to any extent in an alkaline medium of the character of the hypochlorites used, but should give trimethyl-chloroammonium hydroxide.[5] The decomposition of that product into dimethylamine and formaldehyde is explained "electronically" as follows:[6]

$$(H_3C^+)_2(H_3C^+) \equiv N\begin{smallmatrix}-+\mathrm{Cl}\\+-\mathrm{OH}\end{smallmatrix} \longrightarrow (H_3C^+)_2(H_3C^+) \equiv N\begin{smallmatrix}+-\mathrm{Cl}\\+-\mathrm{OH}\end{smallmatrix} \xrightarrow{-HCl}$$

$$(H_3C^+)_2(H_2C^{\pm}) \underset{+}{\overset{=}{=}} N + -OH \longrightarrow (H_3C^+)_2(H_2C^{\substack{+\\+}}) \equiv$$

$$N + -OH \xrightarrow{+H_2O} (H_3C)_2NH + CH_2O + H_2O.$$

This explanation is untenable for several reasons. In order to lose hydrochloric acid the "electronic" signs between the nitrogen and chlorine of the primary product have to be inverted, but the "electromer" thus formed, which is the product assumed to undergo the decomposition, is no longer a derivative of chloroammonium hydroxide, but represents an unstable "electromeric" derivative of hydroxylammonium chloride, and should pass over into $(H_3C^+)_3 \equiv N\begin{smallmatrix}+-\mathrm{Cl}\\-+\mathrm{OH}\end{smallmatrix}$. That formula, however, represents the addition product of trimethylamine oxide and hydrochloric acid, which yields the amine oxide upon treatment with alkali. Further, how is it possible for Jones to assume the formation of the chloroammonium hydroxide, as the primary product of the action of hypochlorous acid upon trimethylamine, after Meisenheimer[7] has shown that the base may be even heated with a large excess of the acid, and yields dimethylchloroamine only in

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[1] *Ber.*, 46, 1148 (1913).

[2] *Loc. cit.*, 1150.

[3] See page 1240.

[4] THIS JOURNAL, 36, 1275 (1914).

[5] The dichloride does not "persist" (see page 1240), and the replacement of Cl by OH never occurs in such derivatives (see page 1241).

[6] *Loc. cit.*, 1277.

[7] *Ibid.*, 1159.

traces?[1] Evidently, the hypochlorite first formed[2] simply dissociates on heating, as hypochlorous acid would react upon dimethylamine, if it were present, to give the corresponding chloroamine.

The theoretical objections to the Meisenheimer-Werner view,[3] apply with equal force to the "electronic" explanation. The hypochlorite is expressed "electronically" by $(H_3C^+)_3 \equiv N^{+-O-+Cl}_{-+H}$, which would have to change into $(H_3C^+) \equiv N^{+-O-+Cl}_{+-H}$, before it could rearrange to $(H_3C^+)_3 \equiv N^{+-OH}_{+-Cl}$. That formula represents one of the possible "electromers" of trimethylhydroxylammonium chloride, and is, indeed, the stable form of the "electronic" structure, which Jones[4] assumes to be formed in the addition of hypochlorous to the tertiary base, and which, as explained above, does break up by elimination of hydrochloric acid into $(H_3C)_2(H_2C=)NOH$, but into the amine oxide.[5]

The "coördination" and the "electronic" formulas are structurally closely connected: $[(CH_3)_3N(OH)]Cl$ and $(CH_3)_3N^{-+OH}_{+-Cl}$ representing a derivative of hydroxylammonium chlorohydrate, and $[(CH_3)_3NCl]OH$ and $(CH_3)_3N^{-+Cl}_{+-OH}$ one of chloroammonium hydroxide. Jones, in his endeavor to place the plus and minus signs in the "electronic" formula so as to permit the elimination of hydrochloric acid, overlooked that such a decomposition cannot possibly take place in a derivative with a salt structure. And, to conjecture on that possibility in derivatives of chloroammonium hydroxide is superfluous, as there is absolutely no experimental evidence indicating the existence of such compounds, which besides involve theoretically extremely improbable assumptions.

Conclusion.

Isomeric trialkyl-hydroxylammonium salts and trialkyl-dialkyloxylammonium derivates are not known, and there is, therefore, no experimental

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[1] Undoubtedly due to free chlorine, which is usually present in aqueous hypochlorous acid.

[2] Hantzsch and Graf, *Ber.*, 38, 2156 (1905).

[3] See page 1234.

[4] *Loc. cit.*, 1277.

[5] According to Jones (*loc. cit.*, 1278) the "electronic" formula of trimethylamine dibromide is $(CH_3^+)_3 \equiv N^{-+Br}_{+-Br}$, and the substance may be completely "hydrolyzed" by alkali to form the tertiary amine and a hypobromite and bromide, or, partially into $(CH_3+)_3 \equiv N^{-+Br}_{+-OH}$, which "would be formed by the addition of hypobromous acid to trimethylamine," and "would either be hydrolyzed further, or dissociate directly into hypobromous acid and trimethylamine. On the other hand, it might undergo intramolecular oxidation, and lose formaldehyde to give dimethylamine." A further discussion of this subject does not appear necessary, but, in view of Hantzsch's proof that the dibromide is decomposed by alkali only in one way, *i. e.*, that it practically falls apart into amine and halogen, and Meisenheimer's correction and explanation of Willstätter's abnormalities, the statement (Jones, *loc. cit.*) that these "electronic" interpretations account for all the "aberrations" observed by Hantzsch and Willstätter certainly requires elucidation.

evidence in this field to support Werner's ammonium or "coördination" hypotheses, or any modifications of them. Nor, are any facts known to substantiate "electronic" conceptions, or the existence of "electromers," in this group of compounds.[1]

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SOME OBSERVATIONS ON THE COLOR CHANGES OF THE DIPHENYLAMINE REACTION.

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The diphenylamine reaction is recognized as one of the most delicate qualitative tests for nitrate nitrogen. However, the utilization of this reaction as a microchemical test for nitrates in plant tissue presents numerous difficulties. Many substances occurring as normal constituents of the cells may diminish the intensity of the characteristic blue coloration, and in some rarer instances the coloration may be completely inhibited. But besides the interference of such substances there are grosser factors influencing the reaction, so that the results of a series of tests of the same tissue may be very inconsistent.

These latter inconsistencies directed the observations on the color changes[2] herein reported. Solutions containing only diphenylamine, nitric acid, sulfuric acid and water were used in the study of the factors controlling the production and intensity of the coloration. The factors studied were the concentration of sulfuric acid, the temperature, time and the order of mixing.

Of these factors, the concentration of the sulfuric acid is the most important. Fig. 1 shows the influence of this concentration throughout a close series from 20 to 96% sulfuric acid. The repetition of such series has always given essentially like results. Solutions were made up in 6 cc. shell vials. The total volume of solution was 5 cc., and through a single series the quantities of nitric acid and diphenylamine were constant, as, for example, in one of the best series each vial contained 0.4 mg. of diphenylamine and 0.06 mg. of nitric acid. The lower limit of blue color-

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[1] Stieglitz, (THIS JOURNAL, 38, 2053 (1916)) referring to the hydroxylammonium derivatives and to the paper by Jones, remarks "that the only electromers whose separate existence has been convincingly shown are the hydroxylamines."

[2] The chemistry of the reaction and its application to the qualitative determination of nitrates have been the objects of much previous work, to which some of the important references are as follows: Kehrman and St. Micewicz, *Ber.*, 45, 2641 (1912); Wieland, *ibid.*, 46, 3296 (1914); Withers and Ray, THIS JOURNAL, 33, 708 (1911); Coron, *Ann. chim. anal.*, 16, 211 (1911); Tillmans and Splittgerber, *Z. Nahr. Genussm.*, 25, 417 (1913).