The Action of Nitric Acid on Tetradecylveratrol.—This ether apparently does not interact smoothly with nitric acid. Two grams of the veratrol were suspended in 12 cc. of concentrated nitric acid (sp. gr. 1.42) and the acid warmed sufficiently to melt the ether. This was then left in contact with the acid for about 10 minutes and then washed free from acid by pouring into cold water. The nitro compound was finally purified as follows: It was extracted with ether and dried over calcium chloride. After spontaneous evaporation of the ether, the nitro compound was purified further by crystallization from petroleum ether when it separated in the form of flakes which melted at 91–93°. The yield was small. A nitrogen determination agreed with the calculated value for a mononitro derivative—$CH_3(CH_2)_{13}.C_6H_2(NO_2)(OCH_3)_2$.

Calc. for $C_{22}H_{37}O_4N$: N, 3.69; found: N, 3.8.

Majima and Nakamura[1] observed that the mononitro derivative of the dimethylether of hydrourushiol melts at 72–73°.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

ELECTROMERS AND STEREOMERS WITH POSITIVE AND NEGATIVE HYDROXYL.

BY LAUDER WILLIAM JONES.

Received March 9, 1914.

Although hydroxylamine is one of the simplest inorganic compounds containing nitrogen, it has not escaped speculative controversy concerning the structural formula best suited to represent it. Two formulas have been proposed:

$$H_2N{-}OH \quad (I) \qquad\qquad H_3N{=}O \quad (II)$$

Many of its reactions in organic chemistry, as well as some of its physical constants,[2] seemed to justify the formula which the name, hydroxylamine, implies. Some of the reactions, however, and especially the dual role which hydroxylamine plays as an oxidizing agent and as a reducing agent, have inclined other investigators to support the second formula.

One of the earliest statements of this view was made by Kolotow,[3] who heated hydroxylamine with ammonia at 100°, but could not find a trace of hydrazine. From this vague experiment, he concluded that hydroxylamine did not react as a hydroxyl compound, and that the formula, $H_3N{=}O$ was consequently the more probable. Haber[4] found that hydroxyl-

---

[1] *Loc. cit.*

[2] Brühl preferred the formula, $H_2N{-}OH$, as more consistent with his spectrochemical findings. *Ber.*, **32**, 566 (1899).

[3] Kolotow, *Ber.*, **26**, 761 (1893).

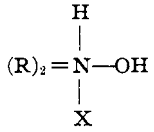
[4] Haber, *Ibid.*, **29**, 2444 (1896).

amine in alkaline solution oxidized ferrous hydroxide to ferric hydroxide, and was itself reduced to ammonia; while an acid solution, containing a hydroxylamine salt, reduced ferric salts to ferrous salts, with the evolution of a gas which was almost pure nitrous oxide. His conclusion was that the reactions of hydroxylamine could be interpreted best by assigning two different formulas to it, *viz.*, formula (I), or the salt, $NH_3(OH)Cl$, in acid solution, and formula (II) in alkaline solution.

In these disputed relations, as in other cases of a similar character, the opinion gradually emerged that hydroxylamine must be placed among the ever increasing number of tautomeric substances. The deportment of hydroxylamine with various alkylating and acylating agents shows all of the earmarks of the well known Protean reactions so commonly met with in the study of tautomeric substances. In my opinion, the experimental evidence is sufficient, not only to establish a tautomeric relationship in the ordinary structural sense, but also, as will be shown later, to confirm the belief that hydroxylamine and its derivative, in many of their reactions, behave tautomerically in the electronic sense[1] as well.

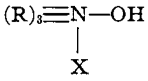
Structural Tautomerism of Hydroxylamine Derivatives.

The experiments of Dunstan and Goulding[2] suggested structural tautomerism, since they showed conclusively that direct alkylation of hydroxylamine led, in all cases, to salts of β- or N-alkyl hydroxylamines of the following types:



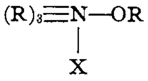
$$(R)_2=\overset{\displaystyle H}{\underset{\displaystyle X}{N}}-OH$$

(A)



$$(R)_3\equiv\underset{\displaystyle X}{N}-OH$$

(B)

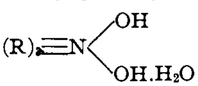


$$(R)_3\equiv\underset{\displaystyle X}{N}-OR$$

(C)

By the action of alkalies upon compounds of type (A), β-dialkyl hydroxylamines, $(R)_2N-OH$, were obtained. When compounds of type (B) were treated with silver oxide and water, they gave hydrated amine oxides,

$(R)_3\equiv N=O.2H_2O$ or



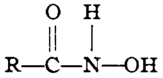
---

[1] Fry, *Z. physik. Chem.*, 76, 391 (1911); Jones, *Am. Chem. J.*, 48, 26 (1912); Bray and Branch, THIS JOURNAL, 35, 1440 (1913); Fry, *Ibid.*, 36, 265 (1914). W. A. Noyes (*Ibid.*, 35, 767 (1913)) has given some experimental evidence which seems to indicate the existence of a nitro-nitrogen trichloride, $N\overset{+}{\underset{+}{+}}(Cl^-)_3$, differing from the ordinary ammono-nitrogen trichloride, $N\equiv(Cl^+)_3$. The possibility of ammonia dissociating ionically to give $N\equiv$ and $N\overset{+}{\underset{+}{+}}$, with positive hydrogen in one case and negative hydrogen in the other, was assumed by Noyes in an early article (THIS JOURNAL, 23, 430 (1901)).

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

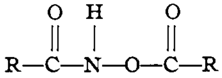
By careful dehydration of these substances, Meisenheimer[1] prepared anhydrous amine oxides, $(R)_3N=O$, which could be sublimed *in vacuo* to give solid crystalline compounds. The structural formulas assigned to them were confirmed by the fact that they all gave tertiary amines upon reduction, and that tertiary amines, when treated with hydrogen peroxide, were changed into amine oxides. Halogen alkyls reacted with the amine oxides to form derivatives of type (C). These experiments show that compounds obtained by the direct alkylation of hydroxylamine must be referred to the formula, $H_3N=O$.

When, however, halogen acyls or acid anhydrides react with hydroxylamine, the first acyl always replaces a hydrogen atom in the β- or N-position (I); but the second acyl group invariably assumes the α- or O-position (II).



$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-OH$

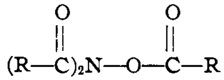
(I)



$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-O-\overset{\overset{O}{\|}}{C}-R$

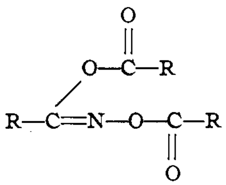
(II)

The third acyl group may substitute the remaining hydrogen atom in the β- or N-position,[2] or it may react with the hydroxamic form to give an oxygen-acyl derivative.



$(R-\overset{\overset{O}{\|}}{C})_2N-O-\overset{\overset{O}{\|}}{C}-R$

or



From these observations, the conclusion may be drawn that hydroxylamine reacts with acylating agents as if it had the formula, H_2N-OH. In fact, it was reactions of this particular character which induced Lossen[3] to decide that "the three hydrogen atoms of hydroxylamine were not equivalent,"[4] and to choose the formula H_2N-OH in preference to the formula $H_3N=O$. If the action of alkylating agents had been unravelled first, we should probably have used the formula $H_3N=O$, instead of formula (I).

In addition to these instances, the reactions of alkylating agents with aldoximes and with ketoximes furnish further evidence of a similar character. With compounds of these two classes, it frequently happens that one and the same reagent gives two types of alkyl derivatives during the same reaction.[5]

---

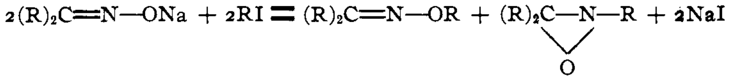
[1] Meisenheimer, *Ann.*, **385**, 117 (1901).

[2] Jones, *Am. Chem. J.*, **20**, 15 (1898); 48, 19 (1912).

[3] Lossen, *Ann.*, **161**, 347 (1872); **175**, 271 (1874); **186**, 1 (1877); **252**, 170 (1889); *Ber.*, **17**, 1587 (1884).

[4] Lossen, *Loc. cit.*

[5] Beckmann, *Ber.*, **22**, 1536 (1889).



$$2(R)_2C{=}N{-}ONa + 2RI = (R)_2C{=}N{-}OR + (R)_2\underset{\diagdown\ O\ \diagup}{C{-}N}{-}R + 2NaI$$

The Oxidation and Reduction of Hydroxylamine and Its Derivatives.

Before the evidence in favor of tautomerism in the electronic sense is presented, attention may be called to the fact that the controversy regarding a formula for hydroxylamine is based upon arguments which are very closely allied to those advanced for hydrogen peroxide. In fact, a number of chemists have emphasized the striking similarity in behavior of these two substances. Both compounds act as oxidizing agents and as reducing agents; and, to explain these contrasting reactions, analogous structural formulas have been proposed for each.

Hydroxylamine: $H_2N{-}OH$ and $H_3N{=}O$

Hydrogen peroxide: $HO{-}OH$ and $H_2O{=}O$

Wagner[1] called attention to this resemblance, and stated that hydroxylamine might be regarded as hydrogen peroxide in which one hydroxyl group had been replaced by the amido group. From this point of view, hydroxylamine would be the *amide* of hydrogen peroxide, and hydrazine would be its diamide

$$H{-}O{-}OH \qquad H{-}O{-}NH_2 \qquad H_2N{-}NH_2.$$

Hydroxylamine and its derivatives are so prone to engage in reactions involving either intramolecular or intermolecular oxidization and reduction that there is no difficulty in finding siutable cases to illustrate this behavior; a few chosen at random will suffice.

In the first place, it has been shown that the instability of hydroxylamine itself may be explained by changes involving mutual oxidation and reduction. The reactions are expressed approximately by the following equations:

$$3NH_3O = N_2 + NH_3 + 3H_2O \text{ (major)}$$

$$4NH_3O = N_2O + 2NH_3 + 3H_2O \text{ (minor)}$$

The β-disubstituted hydroxylamines, $(R)_2N{-}OH$, form a class of compounds which seem to lie close to the border line of instability. By very slight changes in the physical or chemical conditions, they generally decompose to give products which would be expected to result by a process of intramolecular oxidation.[2] Thus, Walder[3] found that β-dibenzyl hydroxylamine, $(C_7H_7)_2N.OH$, in the presence of acetyl chloride, or even with hydrogen chloride and acetic acid (Beckmann's mixture), gave chiefly

---

[1] Wagner, *Z. Russ. phys. chem. Soc.*, **30**, 721 (1899); C. B., **1**, 244 (1899); see also Angeli, *Chem. Zentr.*, **11**, 804 (1910); Stieglitz and Curme, *Ber.*, **49**, 1011 (1913); Stieglitz, THIS JOURNAL, **36**, 282 (1914) note.

[2] Victor Meyer, *Ber.*, **19**, 1629 (1886) note: An electronic interpretation was given by Jones, *Am. Chem. J.*, **49**, 422 (1913).

[3] Walder, *Ber.*, **19**, 1629. 3287 (1886); Behrend and Leuchs, *Ann.*, **257**, 233 (1890).

benzaldehyde and benzylamine. Dunstan and Goulding[1] stated that β-diethylhydroxylamine, when heated, gave acetaldehyde and ethylamine.

$$(C_2H_5)_2N—OH = CH_3CHO + C_2H_5—NH_2.$$

Bewad[2] studied the action of oxidizing agents upon many β-dialkylhydroxylamines. With β-ethyl-*sec.*-amylhydroxylamine, he obtained acetaldehyde, *sec.*-amylamine, diethylketone, ethylamine, with some ammonia and ethyl-*sec.*-amylamine. An interesting statement concerning the quantitative relationship existing between the amount of oxidation effected by the oxidizing agent and that due to intramolecular oxidation caused by the alkylhydroxylamine itself is found in Bewad's article. He said, "The oxygen from the hydroxylamine derivative participated in the reaction is such a way that the share of oxidation alloted to the oxidizing agent was *very much less* than that produced by the alkylhydroxylamine itself."

It is noteworthy that similar changes have been reported by Berg[3] in the study of dialkylchloroamines, $(R)_2N—Cl$. Thus, ethyl-isoamylchloramine, $(C_2H_5)(C_5H_{11})N—Cl$, upon treatment with alcoholic potash and then with acids, gave acetaldehyde, isoamylamine, isovalericaldehyde, and ethylamine. It will be observed that this reaction is strikingly like the one which has been shown to occur with β-ethyl-*sec.*-amylhydroxylamine, $(C_2H_5)(C_5H_{11})N—OH$.

There are many reasons for believing that this analogy is not superficial, but *highly significant;* and that the mutual oxidation and reduction of dialkylchloroamines and of β-disubstituted hydroxylamines have a similar underlying cause. The fact that the chlorine atom[4] in chloroamines must be considered as positive (Cl^+) in character suggests the possibility, and even the probability, that the hydroxyl group in β-dialkyl hydroxylamines may be positive[5] (HO^+) also.

---

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

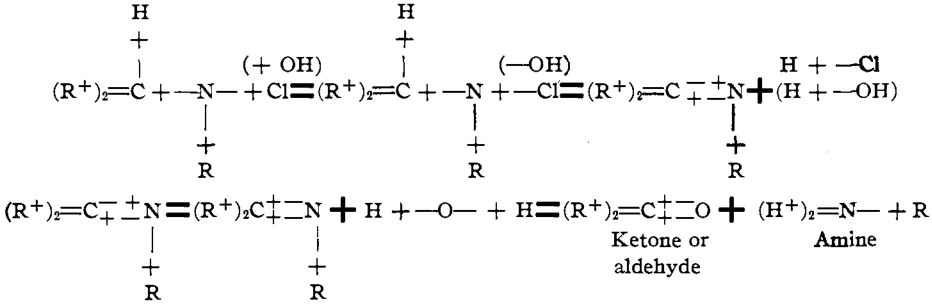
[2] Bewad, *J. prakt. Chem.*, **63**, 193 (1901).

[3] Berg, *Bull. soc. chim.*, [3] **17**, 297 (1897); Jones, *Am. Chem. J.*, **49**, 426 (1913).

[4] Two atomic weights of iodine are liberated for every atomic weight of chlorine in the chloroamine. Seliwanow, *Ber.*, **25**, 3617 (1892); Noyes and Lyon, THIS JOURNAL, **23**, 463 (1901); Noyes, *Ibid.*, **35**, 767 (1913); Stieglitz, *Ibid.*, **23**, 769 (1901); **29**, 51 (1903), etc.

[5] Stieglitz, THIS JOURNAL, **36**, 288 (1914) in a foot-note makes the following statement concerning positive hydroxyl: "The similar behavior of hydroxylamines and halogen amines, of hydroyxlamine and hydrogen peroxide, still more the fundamental similarity existing between hydroxylamines and ammonia and between their salts, and, above all, the fact that, as far as the writer is aware, no hydroxylamine derivative has been found to exchange hydroxyl for halogen by treatment with halogen acid or phosphorus halides are facts on which the writer's views are based. (According to a later private communication from Dr. Jones he has now reached the same conclusion on this question and has discovered further evidence supporting it.")

From this point of view, the analogy between these two reactions may be expressed by the following equations:

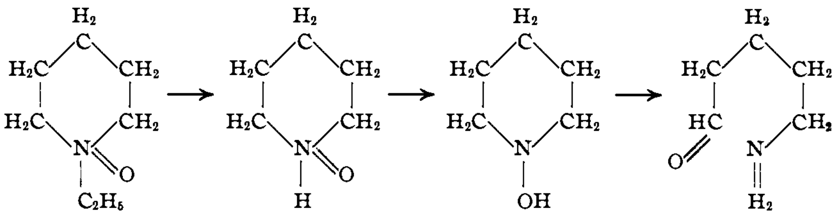


$$(R^+)_2{=}\overset{\substack{H\\+\\|}}{C} + \underset{\substack{|\\+\\R}}{-N-} \overset{(+\,OH)}{+\,Cl} \mathbf{=} (R^+)_2{=}\overset{\substack{H\\+\\|}}{C} + \underset{\substack{|\\+\\R}}{-N} \overset{(-OH)}{+\,-Cl} \mathbf{=} (R^+)_2{=}C^{-}_{+}{}^{+}_{-}\underset{\substack{|\\+\\R}}{N} \mathbf{+} \overset{H\,+\,-Cl}{(H + -OH)}$$

$$(R^+)_2{=}C^{-}_{+}{}^{+}_{-}\underset{\substack{|\\+\\R}}{N} \mathbf{=} (R^+)_2C^{+}_{+}{}^{-}_{-}\underset{\substack{|\\+\\R}}{N} \mathbf{+} H + -O- + H \mathbf{=} \underset{\text{Ketone or aldehyde}}{(R^+)_2{=}C^{+}_{+}{}^{-}_{-}O} \mathbf{+} \underset{\text{Amine}}{(H^+)_2{=}N- + R}$$

More conclusive evidence in support of this assumption will be presented later in this article.

The amine oxides, $R_3N{=}O$, furnish many interesting illustrations of intramolecular and intermolecular oxidation. Merling,[1] and later Wernick and Wolffenstein,[2] prepared members of this class of compounds by oxidizing *N*-alkylpiperidines and similar compounds with hydrogen peroxide. *N*-methylpiperidine oxide, $C_5H_{10}N({=}O)CH_3$, showed the surprising property of parting with its oxygen when a stream of hydrogen chloride was passed through it, or when it was gently heated. *N*-methylpiperidine was regenerated almost quantitatively. The corresponding ethyl derivative, when heated, decomposed in two ways: (*a*) to give *N*-ethylpiperidine and oxygen; (*b*) to give ethylene and δ-aminovalerianic aldehyde. Since δ-aminovalerianic aldehyde is formed by the action of hydrogen peroxide upon piperidine, it may be assumed that ethylene was produced first, and that the amino aldehyde resulted by a process of intramolecular oxidation resembling that described above in the case of β-dialkyl hydroxylamines.



Very similar reactions have been noted by Dunstan and Goulding,[3] by Mamlock and Wolffenstein[4] and by Meisenheimer[5] in the study of

---

[1] Merling, *Ber.*, **25**, 3123 (1892).

[2] Wernick and Wolffenstein, *Ber.*, **31**, 1553 (1898).

[3] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 799, 1004 (1899).

[4] Mamlock and Wolffenstein, *Ber.*, **33**, 159 (1900); **34**, 2499 (1901).

[5] Meisenheimer, *Ann.*, **385**, 117 (1911); **396**, 75 (1912); **397**, 273 (1912); **399**, 371 (1913); Fromm, *Ibid.*, **399**, 366 (1913).

simpler amine oxides. Thus, trimethylamine oxide readily decomposed in two ways: (*a*) to give trimethylamine and oxygen gas; (*b*) to give formaldehyde and dimethylamine.

$$2(CH_3)_3N{=}O = 2(CH_3)_3N + O_2.$$

$$(CH_3)_3N{=}O = (CH_3)_2N{-}H + CH_2O.$$

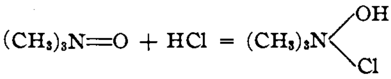
Dunstan and Goulding, in summing up the behavior of amine oxides, said, "From a careful study of amine oxides, we conclude that the oxygen is in the 'active' condition analogous to the oxygen atom in hydrogen peroxide." In connection with similar experiments, Hantzsch and Hillard[1] said, "Since, furthermore, this reaction (*viz.*, the loss of oxygen to give trimethylamine) occurs also when a solution of trimethylamine oxide is placed in contact with silver oxide; and since, in general, the properties of the base remind one of hydrogen peroxide, it seems plausible to assume that trimethyloxyammonium hydroxide may dissociate into trimethylamine and hydrogen peroxide."

$$(CH_3)_3N(OH)_2 \rightleftarrows (CH_3)_3N + H_2O_2.$$

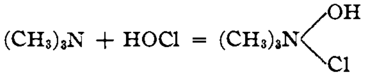
Hantzsch and Hillard suggested that the oxidation of tertiary amines by hydrogen peroxide to give hydrated amine oxides indicated that this reaction might be considered as reversible.

The Action of Hypochlorous Acid and of Bromine upon Tertiary Amines.

In this connection, some experiments of Willstätter and Iglauer,[2] and of Hantzsch and Graf[3] are significant. Willstätter studied the action of hypochlorous acid upon trimethylamine. From structural considerations alone, it would seem probable that this reaction might give the same compound which had been obtained previously by the action of hydrogen chloride upon trimethylamine oxide. *E. g.*,

(I) 

$$(CH_3)_3N{=}O + HCl = (CH_3)_3N\Big\langle\begin{matrix}OH\\Cl\end{matrix}$$

(II) 

$$(CH_3)_3N + HOCl = (CH_3)_3N\Big\langle\begin{matrix}OH\\Cl\end{matrix}$$

As a matter of fact, a totally different reaction occurred, which Willstätter expressed by the following equations:

$$(CH_3)_3N + HOCl = (CH_3)_2N{-}Cl + CH_3OH.$$

The salt (I) obtained from trimethylamine oxide *does not yield either of these products under any circumstance.*[4] Hantzsch and Graf discussed these

---

[1] Hantzsch and Hillard, *Ber.*, 31, 2058 (1898).

[2] Willstätter and Iglauer, *Ber.*, 33, 1636 (1900).

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

[4] Meisenheimer, *Ber.*, 46, 1149 (1913). Trimethylamine oxide was treated with hypochlorites, but not a trace of dimethylchloroamine could be found.

puzzling experiments, and decided to represent the two possible compounds as "coördination isomers" in accordance with Werner's hypothesis.

$[(CH_3)_3NOH]Cl.$ From $(CH_3)_3N{=}O$ and HCl.
$[(CH_3)_3NCl]OH.$ From $(CH_3)_3N$ and HOCl.

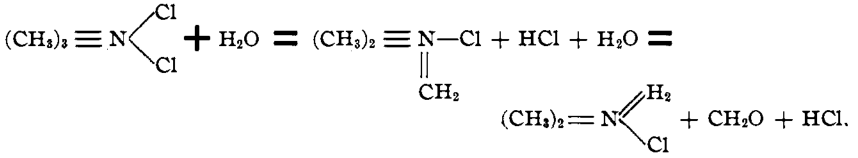
The experiments of Willstätter and Iglauer were repeated by Meisenheimer,[1] who used not only hypochlorous acid, but also hypochlorites. His experiments showed that a serious mistake had been made in the interpretation of the reaction; *formaldehyde was produced, not methyl alcohol.* In addition to dimethylchloroamine, he isolated monomethyldichloroamine, $CH_3{-}NCl_2$.

$$(CH_3)_3N + 2HOCl = (CH_3)_2N{-}Cl + CH_2O + H_2O + HCl.$$

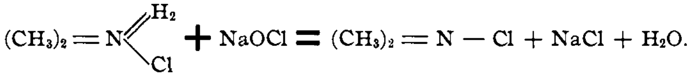
$$(CH_3)_2N{-}H + 2HOCl = (CH_3)N{=}Cl_2 + CH_2O + H_2O + HCl.$$

The reaction required a large excess of hypochlorite. When only two mol equivalents were used, the formation of the chloroamine was scarcely perceptible; the chief products in that case were unchanged tertiary amine, and a secondary amine accompanied by formaldehyde.

Meisenheimer accounted for these results by assuming that the free chlorine present in the hypochlorite reacted by addition with the tertiary amine to give $(R)_3NCl_2$, which was subsequently changed in accordance with the following equations:



$$(CH_3)_3 \equiv N\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix} + H_2O = (CH_3)_2 \equiv \underset{\underset{CH_2}{\|}}{N}{-}Cl + HCl + H_2O = (CH_3)_2 = N\begin{smallmatrix}\diagup H_2\\ \diagdown Cl\end{smallmatrix} + CH_2O + HCl.$$



$$(CH_3)_2 = N\begin{smallmatrix}\diagup H_2\\ \diagdown Cl\end{smallmatrix} + NaOCl = (CH_3)_2 = N - Cl + NaCl + H_2O.$$

In my opinion, it is quite unnecessary to assume that the dichloride is responsible for these changes, although, as will be shown later, in the case of the corresponding dibromide, it would lead to the similar reactions if it were formed. It seems entirely sufficient to assume that the hypochlorous acid reacts with the tertiary amine to give trimethylchloroammonium hydroxide, $(CH_3)_3NCl(OH)$, and that this is the substance undergoing change in these reactions. In fact, if the dichloride were formed, it would not persist to any extent as such in an alkaline medium of the character of sodium or calcium hypochlorite, but would be expected to give trimethylchloroammonium hydroxide.

The behavior of bromine towards tertiary amines led to similar anomalies. Hantzsch[2] obtained the dibromide of trimethylamine as a reddish

---

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

[2] *Loc. cit.*

yellow solid which melted at 85°. It had a distinct odor of bromine, and decomposed rapidly in moist air. As Hantzsch himself suggested, structural relations, pure and simple, would lead one to expect that such a dibromide might react with alkalies in much the same fashion that lead dibromide, or other similar inorganic salts, have been found to react; and that the action of alkalies upon the dibromides of tertiary amines might yield hydrated amine oxides. *E. g.*,

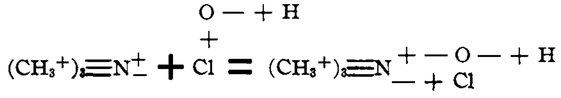
$$Pb(Br)_2 + 2KOH = Pb(OH)Br + KBr + KOH = Pb(OH)_2 + 2KBr.$$

$$(R_3)N(Br)_2 + 2KOH = (R)_3N(OH)Br + KBr + KOH = (R)_3N(OH)_2 + 2KBr.$$

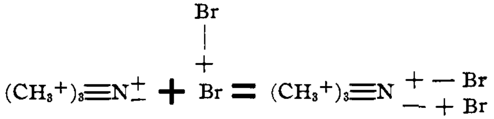
But this was not the case. Potassium hydroxide reacted with the dibromide of trimethylamine to give trimethylamine, potassium hypobromite, and potassium bromide, with small amounts of dimethylbromoamine, *but not a trace of trimethylamine oxide or its hydrate could be found.*

An Electronic Explanation of the Action of Hypochlorous Acid and of Bromine upon Tertiary Amines.

Several important conclusions may be drawn from these experiments, *viz.*, that both the bromine molecule and the hypochlorous acid molecule add to tertiary amines in such a way that the *two groups of each molecule preserve all of their distinctive electronic characteristics even after the addition has taken place.* From an electronic point of view, bromine in hypobromous acid is positive (Br^+), while it is negative (Br^-) in hydrogen bromide. The bromine molecule may be represented by the electronic formula,[1] $Br+—Br$. Similarly, hypochlorous acid, in accordance with its usual behavior towards organic compounds, may be written $H + —O— + Cl$.[2] In terms of these symbols, the addition reactions discussed above may be represented in the following manner:



$$(CH_3^+)_3\equiv N^{+}_{-} + \overset{O-+H}{\overset{+}{Cl}} = (CH_3^+)_3\equiv N\begin{smallmatrix}+ & -O-+H\\ - & +Cl\end{smallmatrix}$$



$$(CH_3^+)_3\equiv N^{+}_{-} + \overset{Br}{\overset{|}{\overset{+}{Br}}} = (CH_3^+)_3\equiv N\begin{smallmatrix}+ & -Br\\ - & +Br\end{smallmatrix}$$

In at least one essential particular, the reaction of bromine upon metallic lead differs from the action of bromine upon trimethylamine, *viz.*, both bromine atoms in lead dibromide are eliminated by alkalies in the form of bromide, and must be represented as negative.[3]

---

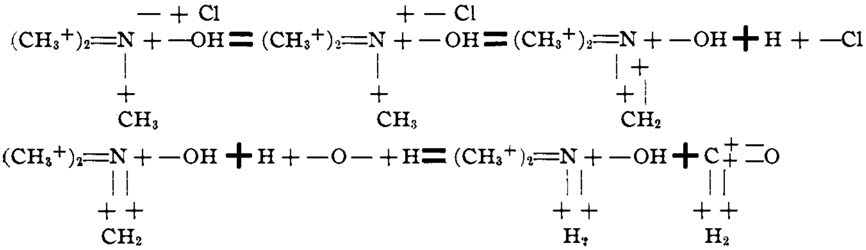
[1] The chlorine molecule was given a corresponding formula, $Cl+ — Cl$, by W. A. Noyes, THIS JOURNAL, 23, 463 (1901); Stieglitz, *Ibid.*, 23, 797 (1901). See Walden, *Z. physik. Chem.*, 43, 385 (1903).

[2] Stieglitz, *Loc. cit.*

[3] It is very probable that between these two extremes, there may be many cases

$$\mathrm{Pb} \boldsymbol{+} \mathrm{Br} + - \mathrm{Br} = \left[\mathrm{Pb} \begin{matrix} - + \mathrm{Br} \\ + - \mathrm{Br} \end{matrix}\right] = \mathrm{Pb} \begin{matrix} + - \mathrm{Br} \\ + - \mathrm{Br} \end{matrix}$$

The results obtained by Willstätter and Iglauer in their experiments with hypochlorous acid and tertiary amines may be interpreted electronically by assuming that the intermediate product with positive chlorine and negative hydroxyl was transformed in much the same manner as the dialkylchloroamines studied by Berg were found to change; *viz.*, through intermolecular oxidation brought about by positive chlorine. The reactions may be represented by the following equations:



$$(\mathrm{CH_3^+})_2{=}\underset{\substack{|\\+\\\mathrm{CH_3}}}{\mathrm{N}}\overset{-\,+\,\mathrm{Cl}}{+\,-\mathrm{OH}} = (\mathrm{CH_3^+})_2{=}\underset{\substack{|\\+\\\mathrm{CH_3}}}{\mathrm{N}}\overset{+\,-\,\mathrm{Cl}}{+\,-\mathrm{OH}} = (\mathrm{CH_3^+})_2{=}\underset{\substack{|\,+\\+\,|\\\mathrm{CH_2}}}{\mathrm{N}} + -\mathrm{OH} \boldsymbol{+} \mathrm{H} + -\mathrm{Cl}$$

$$(\mathrm{CH_3^+})_2{=}\underset{\substack{||\\+\,+\\\mathrm{CH_2}}}{\mathrm{N}} + -\mathrm{OH} \boldsymbol{+} \mathrm{H} + -\mathrm{O} - + \mathrm{H} = (\mathrm{CH_3^+})_2{=}\underset{\substack{||\\+\,+\\\mathrm{H_2}}}{\mathrm{N}} + -\mathrm{OH} \boldsymbol{+} \underset{\substack{||\\+\,+\\\mathrm{H_2}}}{\mathrm{C}}\substack{+\\+}\substack{-\\-}\mathrm{O}$$

$$(\mathrm{CH_3^+})_2{=}\mathrm{N} - + \mathrm{H} \boldsymbol{+} \mathrm{H} + -\mathrm{O} - + \mathrm{Cl} = (\mathrm{CH_3^+})_2{=}\mathrm{N} - + \mathrm{Cl} \boldsymbol{+} \mathrm{H} + -\mathrm{O} - + \mathrm{H}$$

The formation of monomethyldichloroamine also is easily accounted for. Dimethylchloroamine, like the compounds of the same class studied

in which the tautomeric equilibrium is more easily shifted by comparatively slight changes in physical or chemical conditions. Thus, phosphorus trichloride reacts with chlorine to give phosphorus pentachloride. When phosphorus pentachloride is treated with water, all of the chlorine is eliminated as hydrogen chloride. This suggests the electronic formula,

$$(\mathrm{Cl^-})_3\substack{+\\+\\+}\;\begin{matrix}+-\mathrm{Cl}\\+-\mathrm{Cl}\end{matrix}$$

But phosphorus pentachloride dissociates slightly at ordinary temperature, and much more completely at elevated temperature, to give phosphorus trichloride and chlorine. Assuming that the electronic formula given above represents the state of the chlorine atoms in the pentachloride, a dissociation of this kind presupposes an intramolecular oxidation, and, therefore, a condition of electronic equilibrium expressed in the following equations:

$$(\mathrm{Cl^-})_3\substack{+\\+\\+}\mathrm{P}\begin{matrix}+-\mathrm{Cl}\\+-\mathrm{Cl}\end{matrix} \rightleftarrows (\mathrm{Cl^-})_3\substack{+\\+\\+}\mathrm{P}\begin{matrix}-+\mathrm{Cl}\\+-\mathrm{Cl}\end{matrix} \rightleftarrows (\mathrm{Cl^-})_3\substack{+\\+\\+}\mathrm{P}\substack{+\\-} \boldsymbol{+} \mathrm{Cl} + -\mathrm{Cl}$$

Many other dissociations require similar electronic explanations. Mercuric oxide reacts with acids to give a mercuric salt and water; but when it is heated it dissociates into metallic mercury and oxygen:

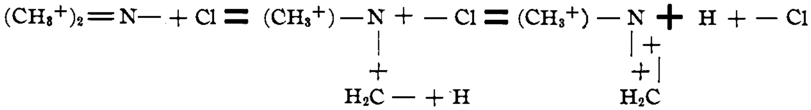
$$2\mathrm{Hg}\substack{+\\+}\substack{-\\-}\mathrm{O} \rightleftarrows 2\mathrm{Hg}\substack{-\\+}\substack{+\\-}\mathrm{O} \rightleftarrows 2\mathrm{Hg}\substack{-\\+} \boldsymbol{+} \mathrm{O}\substack{+\\-}\substack{-\\+}\mathrm{O}$$

Even water, since at high temperature it shows an appreciable dissociation into hydrogen and oxygen, must be represented thus:

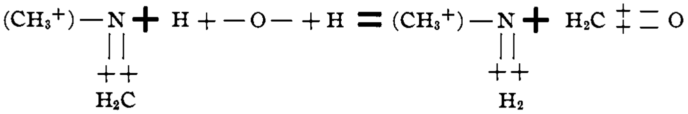
$$2\mathrm{H} + -\mathrm{O}- + \mathrm{H} \rightleftarrows 2\mathrm{H} + -\mathrm{O} + -\mathrm{H} \rightleftarrows 2\mathrm{H} + -\mathrm{H} \boldsymbol{+} \mathrm{O}\substack{+\\-}\substack{-\\+}\mathrm{O}$$

These cases are merely illustrative of countless others which might be cited.

by Berg (see p. 1272) would undergo intramolecular oxidation to give a chloride, methylamine, and formaldehyde.



$$(CH_3^+)_2{=}N{-}+Cl \boldsymbol{=} (CH_3^+){-}\underset{H_2C\,-\,+H}{\underset{+}{\underset{|}{N}}}+\,-Cl \boldsymbol{=} (CH_3^+)-\underset{H_2C}{\underset{+|}{\underset{|+}{N}}} \boldsymbol{+} H+-Cl$$



$$(CH_3^+){-}\underset{H_2C}{\underset{++}{\underset{||}{N}}} \boldsymbol{+} H+-O-+H \boldsymbol{=} (CH_3^+){-}\underset{H_2}{\underset{++}{\underset{||}{N}}} \boldsymbol{+} H_2C\,{}^{+}_{+}{}^{-}_{-}\,O$$

Methylamine would then be changed to methyldichloroamine by the action of the hypochlorite,

$$(CH_3^+)-N^{-+H}_{-+H} \boldsymbol{+} 2H+-O-+Cl \boldsymbol{=} (CH_3^+)-N^{-+Cl}_{-+Cl} \boldsymbol{+} 2H+-OH.$$

The hydrolysis of trimethylamine dibromide by means of alkalies may be explained as follows: If complete hydrolysis occurs, the products will be trimethylammonium hydroxide, or a tertairy amine and water, a hypobromite, and a bromide.

$$(CH_3^+)_3\equiv N\,{}^{-}_{+}{}^{+}_{-}{}^{Br}_{Br} \boldsymbol{+} 2K+-O-+H \boldsymbol{=}$$

$$(CH_3^+)_3\equiv N\,{}^{-}_{+}\,\vdots\,{}^{+H}_{-OH} \boldsymbol{+} K+-O-+Br \boldsymbol{+} K+-Br.$$

If only partial hydrolysis takes place, the reaction may be represented by the following equation:

$$(CH_3^+)_3\equiv N^{-+Br}_{+-Br}+K+-O-+H = (CH_3^+)_3\equiv N^{-+Br}_{+-OH}+K+-Br.$$

This intermediate product should be the same as one which would be formed by the addition of hypobromous acid to trimethylamine. It would either be hydrolyzed further, or dissociate directly, into hypobromus acid and trimethylamine. On the other hand, it might undergo intramolecular oxidation, and lose formaldehyde to give dimethylamine, which would then be converted into dimethylbromoamine by the action of the hypobromite. (See reactions, (p. 1277) in the case of hypochlorous acid.) These interpretations account for all of the aberrations actually observed by Willstätter and Iglauer and by Hantzsch.

Electronic Tautomerism of Hydroxylamine and its Derivatives.

If hydroxylamine is considered from the electronic point of view, the variety of its reactions, as well as those of its derivatives, may be explained in a more satisfactory way than it has been found possible to explain them upon the basis of ordinary structural formulas. Furthermore, by simple hypotheses concerning the exchange of electrons between atoms composing these substances, the chemical changes involving oxidation and reduction, as well as molecular rearrangement, find consistent interpretations.

The spontaneous decomposition of hydroxylamine has been mentioned above. Lobry de Bruyn[1] found that samples of pure hydroxylamine, which had been kept in clean sealed glass tubes for about two years, were only partially decomposed; they all contained ammonia, nitrogen and nitrous oxide, but only two of them showed traces of nitrous acid. Lobry de Bruyn speaks of these processes as "Selbstoxidation und Reduction" in which "one part of the hydroxylamine gives oxygen and forms ammonia, while a second part suffers oxidation to hyponitrous acid and to nitrous acid which undergo further changes." Many investigators have mentioned the tremendous effect which alkalies have in accelerating this decomposition. If hydroxylamine is poured upon solid potassium hydroxide, it may even take fire and burn. Kolotow[2] studied the action of solutions of sodium hydroxide upon hydroxylammonium sulfate. The following products were formed which he expressed quantitatively in values for nitrogen based upon the fractional part of total nitrogen (16.41%) furnished by the sulfate.

		Per cent.
NH_3	=	7.12
N_2	=	6.68
N_2O	=	2.22
$NaNO_3$	=	0.39

From these experiments, and many others which might be given, it will be found that the decomposition of hydroxylamine gives chiefly ammonia and nitrogen, with some nitrous oxide, nitrous acid and nitric acid. It has also been shown that hyponitrous acid is one of the products.

If the assumption be made that the hydrogen atoms function positively in all of the following cases, the electronic equilibrium of hydroxylamine may be shown as follows:

$$\begin{tikzcd}
\text{(I)} & (H^+)_2 = N - + O - + H \arrow[r, shift left] \arrow[d, shift right] & (H^+)_3 \equiv N \pm \mp O \arrow[l, shift left] \arrow[d, shift right] & \text{(I}a\text{)} \\
\text{(II)} & (H^+)_2 = N + - O - + H \arrow[r, shift left] \arrow[u, shift right] & (H^+)_3 \equiv N \overset{+}{+} \overset{-}{-} O \arrow[l, shift left] \arrow[u, shift right] & \text{(IIa)}
\end{tikzcd}$$

A consideration of these formulas will show that (I) and (I*a*), (II) and (II*a*) represents pairs of structural tautomers, while (I) and (II), (I*a*) and (II*a*), respectively, denote pairs of electronic tautomers or electromers;[3] that is, compounds which, in the ordinary structural sense, are identical, but mutually transformable by an exchange of negative electrons between the atoms composing the molecules.

---

[1] Lobry de Bruyn, *Ber.*, **27**, 967 (1894).

[2] Kolotow, *J. Russ. Phys. Chem. Soc.*, **1**, 295 (1893); *Ber.*, **26**, 701 (1893). The figures given are those of Kolotow. With the present values of atomic weights, the percentage of nitrogen would be 17.07, instead of 16.41%.

[3] The word "electromer" was coined by H. S. Fry, and used by him in an article which appeared in the *Z. physik. Chem.*, **76**, 387 (1911).

Structural tautomers (I) $\rightleftarrows$ (I*a*)
(II) $\rightleftarrows$ (II*a*)
Electronic tautomers[1] (I) $\rightleftarrows$ (II)
(I*a*) $\rightleftarrows$ (II*a*)

In terms of the electronic formulas proposed above, the spontaneous decomposition of hydroxylamine may be explained. Since the hydroxyl group in formula (I) is positive, there is no chance for this form to lose water. It is to be expected that a substance corresponding to formula (I) (or in view of the reactions of amine oxides, to formula (I*a*)), would act as an oxidizing agent, and would readily dissociate into "active oxygen" and ammonia.

$$(H^+)_3 \equiv N \mp \pm O = (H^+)_3 \equiv N \pm + \mp O.$$

In the case of amine oxides, the oxygen either escaped as free oxygen or was used to bring about oxidation intramolecularly or intermolecularly. Similarly, hydroxylamine in alkaline solution oxidizes ferrous hydroxide to ferric hydroxide, and is converted into ammonia.

On the other hand, formula (II) would represent a substance which could lose one molecule of water, since the hydroxyl group in this case is negative,

$$(H^+)_2 = \underset{\bullet}{N} + - O - + H = H + - N \mp + H + - O - + H.$$

This product of dissociation, *active imide*, corresponds in form to the univalent nitrogen derivatives which are assumed to play so important a role in the Beckmann rearrangement.[2] A substance of such a formula would be a powerful reducing agent, and would combine with the oxygen given by the dissociation of the form $(H^+)_3 \equiv N \mp \pm O$, or with oxygen furnished by other oxidizing agents, or with oxygen of the air, to give an electromer of hyponitrous acid.

$$H + - N \pm + O \pm \mp N \equiv (H^+)_3 = H + - N \mp \pm O + (H^+)_3 \equiv N \pm.$$

The form, HNO, would rearrange to give hyponitrous acid, or nitrous oxide and water.

$$2H + - N \mp \pm O = 2H + - N \substack{+\\+} \substack{-\\-} O = (H + - O - + N \pm)_2.$$

---

[1] A third electromer, $(H^+)_3 \equiv N \substack{-\\-} \substack{+\\+} O$, might result from either (I*a*) or (II*a*) by an exchange of negative electrons between oxygen and nitrogen. This formula leads to no corresponding tautomer of the formula H_2N-OH, since rearrangement is precluded by the fact that positive oxygen cannot hold positive hydrogen. The improbability of this formula is increased by the fact that no compounds NH_5, NR_5, etc., have been made. Furthermore, the compounds $(R^+)_3 \equiv N \substack{- + Br\\+ - Br}$ do not seem to show any tendency to become $(R^+)_3 \equiv N \substack{- + Br\\- + Br}$.

[2] For the conception of univalent nitrogen as applied to the Beckmann rearrangement, see Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); Stieglitz and Earl,

Granting these statements, we are in a position to explain the fact that nitrous oxide is the chief product obtained during the action of the majority of oxidizing agents upon hydroxylamine. It may be assumed that, in the presence of an active oxidizing agent, it would not be necessary for the oxygen to be furnished by hydroxylamine itself, but that it might be taken largely, or exclusively, from the oxidizing agent, and that, especially in acid solution, this might force the hydroxylamine to react almost quantitatively through the dissociation product,[1] $H+-N^{+}_{-}$, to give nitrous oxide.

If, however, no oxidizing agent, except hydroxylamine itself, is present, the chief products are ammonia and nitrogen, with small amounts of nitrous oxide, and still smaller amounts of nitrous acid and nitric acid. The formation of ammonia and nitrous oxide has been explained. To account for the nitrogen, it may be assumed that the speed of spontaneous decomposition is relatively slow, and that hyponitrous acid, formed by the oxidation of active imide, reacts with hydroxylamine to give hydroxylammonium hyponitrite, which might be expected to decompose at once to yield nitrogen and water.

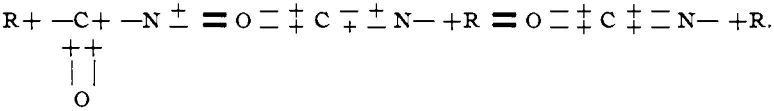
$$(NH_3(OH)ON)_2 = 2N_2 + 4H_2O.$$

In a similar manner, Wislicenus[2] found that nitrous acid reacted with hydroxylamine to give nitrous oxide and water.

Ibid., 30, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, 28, 3266 (1896); 34, 1613 (1902), etc.

For an electronic interpretation in terms of univalent nitrogen see Jones, *Am. Chem. J.*, 48, 26 (1912); 50, 440 (1913); Stieglitz, THIS JOURNAL, 36, 280 (1914).

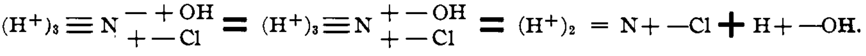
The formula, $H + - N^{+}_{-}$, would act also as an oxidizing agent. It is this specific property of univalent nitrogen derivatives which has been shown to be accountable for the Beckmann rearrangement. Thus



$$R+ -\underset{\substack{++\\ |\,|\\ \mathrm{O}}}{C}+ -N^{+}_{-} = O{}^{-}_{-}{}^{+}_{+}C{}^{-}_{+}{}^{+}_{-}N- +R = O{}^{-}_{-}{}^{+}_{+}C{}^{+}_{+}{}^{-}_{-}N- +R.$$

During the rearrangement the carbon atom is oxidized by losing two negative electrons which are gained by the nitrogen atom.

[1] In acid solution, the presence of the salt, $NH_3(OH)Cl$, must be taken into consideration. Electronically, a loss of water would give a chloroamine, $H_2N + - Cl$, with negative chlorine.



$$(H^+)_3 \equiv N\begin{smallmatrix}- + OH\\ + - Cl\end{smallmatrix} = (H^+)_3 \equiv N\begin{smallmatrix}+ - OH\\ + - Cl\end{smallmatrix} = (H^+)_2 = N+ -Cl + H+ -OH.$$

This chloroamine might lose hydrogen chloride to give active imide $H + - N^{+}_{-}$. It may be that this reaction is partially responsible for the changes observed in acid solution. In explaining the Beckmann rearrangement of oximes, Stieglitz has made similar assumptions concerning the intermediate products. Thus, in the case of ketoximes, Stieglitz (THIS JOURNAL, 36, 281 (1914)) assumes the intermediate product:

$$(R^+)_2{}^{-}_{-}C{}^{+}_{+}{}^{-}_{-}N + - Cl.$$

[2] Wislicenus, *Ber.*, 26, 77 (1893).

$$\mathrm{NH_3(OH)—ON{=}O} = \mathrm{N_2O} + 2\mathrm{H_2O}.$$

If the form $\mathrm{H+—N{=}O}$, or hyponitrous acid, continued to be oxidized, nitrous acid or even nitric acid would result.

In many respects, the reactions of hypochlorous acid resemble those of hydroxylamine, and may be explained in a very similar way by assuming positive and negative hydroxyl. It is well known that hypochlorous acid, in addition to its ability to substitute chlorine for hydrogen in organic compounds, acts as an oxidizing agent and as a reducing agent. Furthermore, on exposure to light, it dissociates into oxygen and hydrogen chloride. All of these reactions find a happy explanation if the assumption be made that hypochlorous acid behaves as a tautomeric substance in the electronic sense. Thus:

$$\underset{\text{(I)}}{\mathrm{H}+—\mathrm{O}+—\mathrm{Cl}} \rightleftarrows \underset{\text{(II)}}{\mathrm{H}+—\mathrm{O}—+\mathrm{Cl}}$$

There is also a possibility of having structural tautomers, similar to those proposed for hydroxylamine.

$$\underset{\text{(I}a\text{)}}{\mathrm{H}+—\mathrm{Cl}\substack{-\\+}\substack{+\\-}\mathrm{O}} \rightleftarrows \underset{\text{(II}a\text{)}}{\mathrm{H}+—\mathrm{Cl}\substack{+\\+}\substack{-\\-}\mathrm{O}}.$$

Formula (I) explains the dissociation of hypochlorous acid in the light.

$$2\mathrm{H}+—\mathrm{O}+—\mathrm{Cl} = 2\mathrm{H}+—\mathrm{Cl} + \mathrm{O}\substack{-\\+}\substack{+\\-}\mathrm{O}.$$

Owing to the tautomeric equilibrium between (I) and (II), which seems to be shifted by the action of light, hypochlorous acid gradually dissociates into oxygen and hydrogen chloride. This reaction may be catalyzed in many other ways.

When hypochlorous acid acts upon organic compounds as a chlorinating agent, it does so according to formula (II), and substitutes *positive* chlorine for positive *hydrogen*. In some cases the chlorine in the organic compound retains its positive character, that is, its ability to liberate iodine from an acidulated solution of an iodide, etc. This is the case with chloroamines, chloroimidoesters, nitrogen trichloride and many other compounds. It has been shown that tetraiodomethane reacts with water to give iodoform and hypoiodous acid.[1]

$$\mathrm{I_3C—+I} + \mathrm{H+—O—+H} = \mathrm{I_3C—+H} + \mathrm{H+—O—+I}.$$

Bolas and Grove[2] and later Nef[3] found that tetrabromomethane, when heated with alcohol or with alcoholic potash gave bromoform, acetaldehyde and potassium bromide, but not a trace of carbonate could be found. Similarly, Nef[4] found that tetrachloromethane, with one equivalent of sodium ethylate, gave chiefly orthoformic ethyl ester, but no carbonate.

---

[1] Gustavson, *Ann.*, **172**, 176 (1874).

[2] *J. Chem. Soc.*, **23**, 164; **24**, 783; *Ann.*, **156**, 60; **160**, 160.

[3] Nef, *Ann.*, 308, 329 (1899).

[4] Nef, *Loc. cit.*, p. 330.

Tetraiodomethane when heated with alcohol at 100° gave a quantitative yield of iodoform. Another interesting case of a similar character was reported by Nef.[1] Chlorocyanogen and bromocyanogen, when treated with alkalies are converted into cyanates together with chlorides or bromides. But iodocyanogen under the influence of the same reagents gave a *cyanide* and an *iodate*. These reactions would suggest the following electronic formulas for these three compounds:

$$N\equiv C+\!-Cl \qquad N\equiv C+\!-Br \qquad N\equiv C-\!+I$$

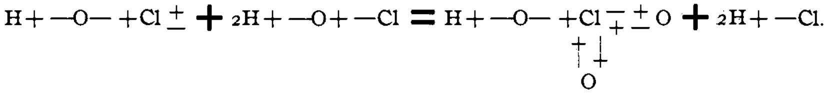
The possibility of the halogen atoms being linked to nitrogen must be taken into account, but that would not alter the conclusion concerning the positive or negative nature of the halogen atoms.

The behavior of bromophenylacetylene and iodophenylacetylene, also studied by Nef,[3] indicates that the halogen atoms in these compounds must be considered as positive, since they react with sodium ethylate or potassium hydroxide to give chiefly *phenylacetylene*, *aldehyde* (resin) and a *halogen salt*.

In other cases the characteristic properties of positive halogen are lost entirely, which implies that, after substitution has occurred, an exchange of electrons between the atom linked to halogen and positive halogen gives compounds with negative halogen.[3] This is the case with methyl chloride, chloroform, trichloracetic acid, etc.

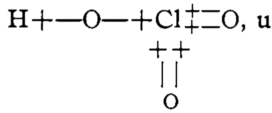
$$H_3C-\!+H \;\mathbf{+}\; H+\!-O-\!+Cl = H_3C-\!+Cl \;\mathbf{+}\; H+\!-O-\!+H = H_3C+\!-Cl \;\mathbf{+}\; H+\!-O-\!+H.$$

Formula (II) also explains the reducing action of hypochlorous acid which occurs when hypochlorites change to chlorates.



$$H+\!-O-\!+Cl{}^{+}_{-} \;\mathbf{+}\; 2H+\!-O+\!-Cl = H+\!-O-\!+\underset{\substack{+|\ |+\\ O}}{Cl}{}^{-}_{+}{}^{+}_{-}O \;\mathbf{+}\; 2H+\!-Cl.$$

By intramolecular oxidation and reduction, this electromer may pass to the form H+—O—+Cl‡═O, usually assigned to chloric acid.



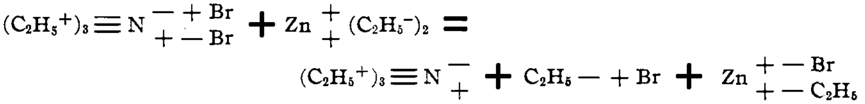
$$H+\!-O-\!+\underset{\substack{+\,+\\ |\,|\\ O}}{Cl}{}^{+}_{+}{=}O$$

---

[1] Nef, *Loc. cit.*, p. 320.

[2] Nef, *Loc. cit.*, pp. 292, 310, 316.

[3] Lachmann, *Am. Chem., J.* **18**, 372 (1896), in an unsuccessful attempt to prepare $N(C_2H_5)_5$, found that zinc diethyl reacted with triethylamine dibromide to give triethylamine, ethyl bromide, and zinc ethyl bromide. Electronically expressed:



$$(C_2H_5^{+})_3\equiv N\begin{smallmatrix}-\,+\,Br\\ +\,-\,Br\end{smallmatrix} \;\mathbf{+}\; Zn\begin{smallmatrix}+\\ +\end{smallmatrix}(C_2H_5^{-})_2 = (C_2H_5^{+})_3\equiv N\begin{smallmatrix}-\\ +\end{smallmatrix} \;\mathbf{+}\; C_2H_5-\!+Br \;\mathbf{+}\; Zn\begin{smallmatrix}+\,-\,Br\\ +\,-\,C_2H_5\end{smallmatrix}$$

Here again negative ethyl may be assumed to combine with positive bromine to give in the first place, $C_2H_5 - + Br$, which passes to the usual ethylbromide, $C_2H_5 + - Br$, that is, to the ethyl bromide which gives ethylalcohol and hydrogen bromide upon hydrolysis.

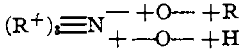
Electromers and Stereomers with Positive and Negative Hydroxyl or Alkoxyl.

It has been shown in a fairly conclusive manner that the hydroxyl group in hydroxylamine may function positively. If the hydroxyl group in hydroxylamine be regarded as positive, and if this condition of the hydroxyl group be retained in the alkyl (aryl) derivatives, two inferences concerning the behavior of substituted hydroxylamines must follow logically.

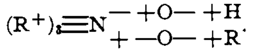
(1) Compounds containing in their formula the group $>N—OH$ or the group $>N—OR$ should show different physical and chemical properties, depending upon the nature of the hydroxyl or alkoxyl group, *i. e.*, whether it is negative (I) or positive (II).

$$\underset{\text{(I)}}{>N+—O—+R} \qquad \underset{\text{(II)}}{>N—+O—+R}$$

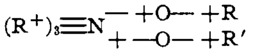
Then, again, provided one of the hydroxyl groups is positive and the other negative, compounds of the type, $(R)_3N(OH)_2$, should exist in two isomeric forms (electromers) when one of the hydrogen atoms is replaced by a single radical, R; and, furthermore, there should be two distinct isomers (electromers) if two of the hydrogen atoms are replaced simultaneously by dissimilar radicals, R and R′.



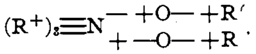
$$(R^+)_3\equiv N\begin{matrix}—+O—+R\\+—O—+H\end{matrix}$$



$$(R^+)_3\equiv N\begin{matrix}—+O—+H\\+—O—+R\end{matrix}.$$



$$(R^+)_3\equiv N\begin{matrix}—+O—+R\\+—O—+R'\end{matrix},$$



$$(R^+)_3\equiv N\begin{matrix}—+O—+R'\\+—O—+R\end{matrix}.$$

(2) Compounds of the formula, $R,R',R'',N(OH)_2$, in which there are three different alkyl (aryl) radicals linked to the nitrogen atom should exist in *stereoisomeric modifications*, provided one hydroxyl group is *negative* and the other one is *positive*. By the action of an optically active acid, *e. g.*, *d*-bromocamphorsulfonic acid or *d*-tartaric acid, a racemic compound obtained by synthesis should be resolved into a dextro- and a levo-modification. Optical activity might even persist in the corresponding amine oxides, $R,R',R'',N\mp\pm O$. Although the two hydroxyl groups are *structurally alike*, they are totally different *electronically*. Consequently, the nitrogen atom is linked to "*five different radicals*," and, in this respect, compounds of these types may be compared to substituted ammonium compounds of the type $R,R',R'', R''', N—X$, which have been repeatedly resolved into optically active forms.[1]

It is a remarkable fact that experimental evidence supporting both of

---

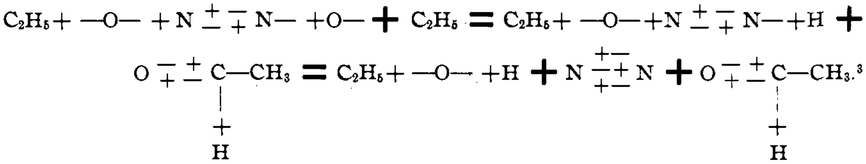
[1] LeBel, *Compt. rend.*, **112**, 724 (1891); **129**, 548 (1899); *Ber.*, **33**, 1003 (1900); Wedekind, *Ber.*, **32**, 517, 3561 (1899); **35**, 766 (1902); **36**, 3791 (1903); **38**, 1838 (1905); Wedekind and Oberheide, *Ibid.*, **37**, 2712, 3894 (1904); Wedekind and Froelich, *Ibid.*, **38**, 3438 (1905); Pope and Peachey, *J. Chem. Soc.*, **75**, 1127 (1899); Pope and Harvey, *Ibid.*, **79**, 828 (1901).

these deductions has been presented quite recently, and a brief survey of the facts may be taken up here.

1. Electromers.—In the first place, the chemical behavior of "diazo-ethoxane," studied by Zorn[1] many years ago, may be described. Zorn noted, with some surprise, that hydrolysis of this compound, structurally an ester of hyponitrous acid, did not give hyponitrous acid. This fact even caused him to write the formula with a question mark after it.[2] When an attempt was made to hydrolyze this compound by heating it with water, the products were *ethyl alcohol*, *acetaldehyde*, and *nitrogen*.

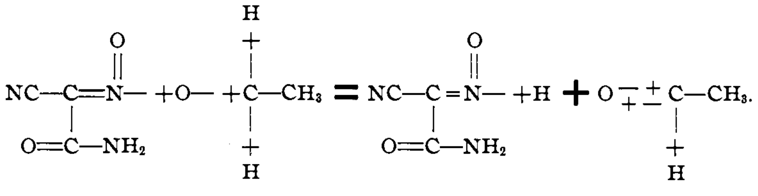
$$C_2H_5{—}O{—}N{=}N{—}O{—}C_2H_5 = C_2H_5{—}OH + N_2 + CH_3CHO.$$

This singular reaction finds a plausible interpretation, if the assumption be made that the two ethoxy groups are different electronically; *i. e.*, one of them negative and one of them positive. The following equations would then portray the reaction:



$$C_2H_5+ {—}O{—} +N \overset{+}{\underset{-}{}}\overset{-}{\underset{+}{}} N{—} +O{—} + C_2H_5 = C_2H_5+ {—}O{—}+N \overset{+}{\underset{-}{}}\overset{-}{\underset{+}{}} N{—}+H +$$
$$O \overset{-}{\underset{+}{}}\overset{+}{\underset{-}{}} \underset{\underset{\displaystyle H}{\overset{|}{+}}}{C}{—}CH_3 = C_2H_5+ {—}O{—} +H + N \overset{+-}{\underset{+-}{\overset{-}{\underset{+}{}}\overset{+}{\underset{-}{}}}} N + O \overset{-}{\underset{+}{}}\overset{+}{\underset{-}{}} \underset{\underset{\displaystyle H}{\overset{|}{+}}}{C}{—}CH_3.^3$$

There are many other instances of a similar kind in which esters of oximes or isonitro compounds have changed to aldehydes and oximido compounds. Thus, when Nef[4] heated the ethyl ester of fulminuric acid with water, he found that it gave desoxyfulminuric acid (cyanisonitroso-acetamide) and acetaldehyde. Here, again, it is highly probable that the ethoxy group should be represented as positive ($+O{—}+C_2H_5$), and that the reaction proceeded as follows:



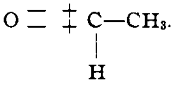
$$NC{—}\underset{\underset{\displaystyle O{=}C{—}NH_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}}{=}N{—} +O{—} +\underset{\underset{\displaystyle H}{\overset{|}{+}}}{\overset{\overset{\displaystyle H}{\underset{|}{+}}}{C}}{—}CH_3 = NC{—}\underset{\underset{\displaystyle O{=}C{—}NH_2}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}}{=}N{—} +H + O \overset{-}{\underset{+}{}}\overset{+}{\underset{-}{}} \underset{\underset{\displaystyle H}{\overset{|}{+}}}{C}{—}CH_3.$$

This nitroso compound would rearrange to give the isonitroso compound; and the aldehyde, an electromer of acetaldehyde, would become $O\overset{-}{\underset{-}{}}\overset{+}{\underset{+}{}}CH(CH_3)$. Another instance of a similar character was described by

---

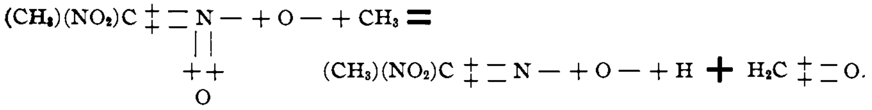
[1] Zorn, *Ber.*, **11**, 1630 (1878); **15**, 1008 (1882).

[2] Meyer and Jacobson, "Lehrbuch," I, p. 308.

[3] This formula represents an electromer of acetaldehyde.  $O \overset{-}{\underset{-}{}} \overset{+}{\underset{+}{}} \underset{\underset{\displaystyle H}{|}}{C}{—}CH_3$. The same may be true of the formula assigned to nitrogen with respect to nitrogen.

[4] Nef, *Ann.*, **280**, 328 (1894); Schultz, *Ber.*, **42**, 738 (1909).

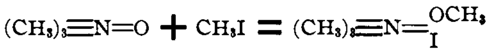
Nef.[1] The silver salt of dinitroethane reacted with methyl iodide to give formaldehyde and ethylnitrolic acid. It may be assumed that the intermediate ester with positive methoxyl, $+O—+CH_3$, was unstable and dissociated at once.



$$(CH_3)(NO_2)C \substack{+\\+} \substack{-\\-} \underset{\substack{|\,|\\++\\O}}{N} - + O - + CH_3 = (CH_3)(NO_2)C \substack{+\\+} \substack{-\\-} N - + O - + H + H_2C \substack{+\\+} \substack{-\\-} O.$$

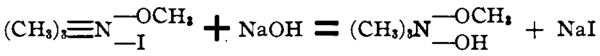
Certain experiments described by Meisenheimer[2] are still more interesting. In an article[3] concerning the "Non-equivalence of the Five Valences of Nitrogen," Meisenheimer describes the preparation of two isomeric compounds of the type $(R)_3{\equiv}N(OCH_3)(OH)$. The *first* isomer was prepared by the action of methyl iodide upon trimethylamine oxide, and the subsequent replacement of iodine by hydroxyl. Thus:

1.



$$(CH_3)_3{\equiv}N{=}O + CH_3I = (CH_3)_3{\equiv}N{=}\genfrac{}{}{0pt}{}{OCH_3}{I}$$

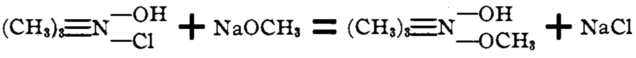
2.



$$(CH_3)_3{\equiv}N\genfrac{}{}{0pt}{}{-OCH_3}{-I} + NaOH = (CH_3)_3N\genfrac{}{}{0pt}{}{-OCH_3}{-OH} + NaI$$

(A)

The *second* isomer was secured by the action of sodium methylate upon the salt obtained by treating trimethylamine oxide with hydrogen chloride.

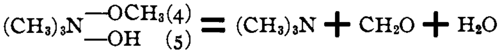


$$(CH_3)_3{\equiv}N\genfrac{}{}{0pt}{}{-OH}{-Cl} + NaOCH_3 = (CH_3)_3{\equiv}N\genfrac{}{}{0pt}{}{-OH}{-OCH_3} + NaCl$$

(B)

The two forms, (A) and (B), are identical *except for the order in which the hydroxyl group and the methoxyl groups were introduced.* In (B), as Meisenheimer said, the methoxyl group is linked to the "*fifth* valence," or the one which usually engages the *acid radical;* while it is linked to the "*fourth* valence" in formula (A). But these two substances are fundamentally different. This is easily demonstrated by a study of their solutions. When a water solution of trimethylmethoxyammonium hydroxide (A) was heated, it decomposed quantitatively in accordance with the following equations:

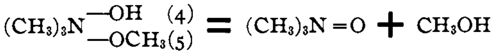
(A)



$$(CH_3)_3N\genfrac{}{}{0pt}{}{-OCH_3(4)}{-OH\ \ (5)} = (CH_3)_3N + CH_2O + H_2O$$

While trimethylhydroxyammonium methylate (B) showed a totally different behavior.

(B)



$$(CH_3)_3N\genfrac{}{}{0pt}{}{-OH\ \ (4)}{-OCH_3(5)} = (CH_3)_3N{=}O + CH_3OH$$

---

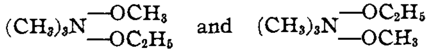
[1] Nef, *Loc. cit.*, p. 282.

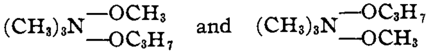
[2] Meisenheimer, *Ann.*, **385**, 117 (1911); **396**, 75 (1912); **397**, 213 (1912); **399**, 371 (1913).

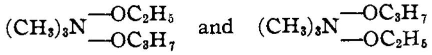
[3] Meisenheimer, *Ann.*, **397**, 273 (1913).

In addition to these compounds, Meisenheimer prepared a number of isomeric mixed dialkyl compounds.

E. g.,

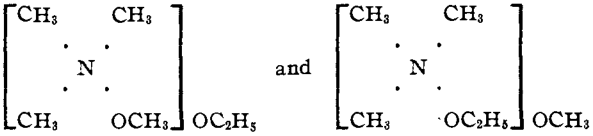
1.

$(CH_3)_3N\begin{matrix}-OCH_3\\-OC_2H_5\end{matrix}$ and $(CH_3)_3N\begin{matrix}-OC_2H_5\\-OCH_3\end{matrix}$

2.

$(CH_3)_3N\begin{matrix}-OCH_3\\-OC_3H_7\end{matrix}$ and $(CH_3)_3N\begin{matrix}-OC_3H_7\\-OCH_3\end{matrix}$

3.

$(CH_3)_3N\begin{matrix}-OC_2H_5\\-OC_3H_7\end{matrix}$ and $(CH_3)_3N\begin{matrix}-OC_3H_7\\-OC_2H_5\end{matrix}$

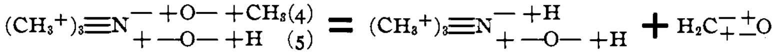
In every case, water decomposed each of these six compounds to give a tertiary amine, an alcohol, and an aldehyde; but, invariably, the radical which was eliminated as aldehyde was the radical which occupied "position four (4)"and the group eliminated as alcohol always occupied "position five (5)." Meisenheimer stated that he never obtained even recognizable traces of the aldehyde, which should have resulted if the group attached in position five had separated in that form. His conclusions may be stated in his own words: "Durch diese Reaktion ist bewiesen, dass die beiden Alkoxygruppen nicht in gleicher Weise an das Stickstoffatom gebunden sind."

Meisenheimer considered various possible explanations, such as the oxonium formula, Werner's ammonium formula, and the oxonium formula of Werner. The discussion of these points cannot be taken up here, but may be found by reference to the original articles. After presenting evidence for and against various views, Meisenheimer finally decided to formulate his compounds in the symbolism of Werner's ammonium theory. Thus:

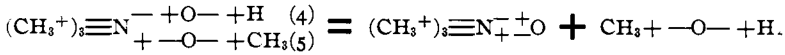

$$\left[\begin{matrix}CH_3 & & CH_3\\ & \cdot\,\cdot & \\ & N & \\ & \cdot\,\cdot & \\ CH_3 & & OCH_3\end{matrix}\right]OC_2H_5 \quad \text{and} \quad \left[\begin{matrix}CH_3 & & CH_3\\ & \cdot\,\cdot & \\ & N & \\ & \cdot\,\cdot & \\ CH_3 & & OC_2H_5\end{matrix}\right]OCH_3$$

However, he was not entirely satisfied with Werner's symbols, and said, "Dass die obigen Formeln nur dann richtig sind wenn mann sie anders interpretiert als A. Werner es tut." Meisenheimer, in contrast to Werner, assumed that all five radicals are bound by "haupt" valences to nitrogen, four in the inner zone and one in the outer zone. But he considered that the ammonium compounds differed from such compounds as $(CrCl_2(OH_2)_4)$-Cl, etc., in that all four coördination positions of nitrogen are occupied by radicals with "haupt" valences, and that the one in the outer zone is also linked by a "haupt" valence, but it does not have so firm a linking.

The key to these disputed relations is easily furnished, in terms of the electronic conception, by assuming that the one hydroxyl (or alkoxyl group) is positive and the other negative; or, translated into Meisenheimer's[1] language, the "fourth valence" of nitrogen is linked to a positive hydroxyl or alkoxyl group, while the "fifth valence," or the one which usually engages the acid radical, is linked to a negative hydroxyl or alkoxyl group. Thus:

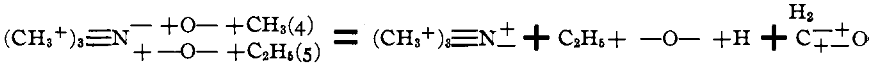
(A) 

$$(\mathrm{CH_3^+})_3{\equiv}\mathrm{N}\begin{smallmatrix}-\;+\mathrm{O}-\;+\mathrm{CH_3}(4)\\+\;-\mathrm{O}-\;+\mathrm{H}\quad(5)\end{smallmatrix} = (\mathrm{CH_3^+})_3{\equiv}\mathrm{N}\begin{smallmatrix}-\;+\mathrm{H}\\+\;-\mathrm{O}-\;+\mathrm{H}\end{smallmatrix} + \mathrm{H_2C}{\mp}{\pm}\mathrm{O}$$

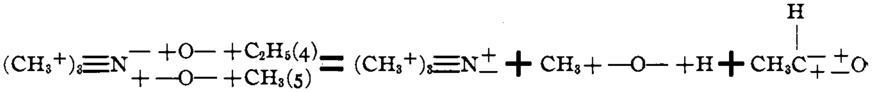
(B) 

$$(\mathrm{CH_3^+})_3{\equiv}\mathrm{N}\begin{smallmatrix}-\;+\mathrm{O}-\;+\mathrm{H}\quad(4)\\+\;-\mathrm{O}-\;+\mathrm{CH_3}(5)\end{smallmatrix} = (\mathrm{CH_3^+})_3{\equiv}\mathrm{N}{\mp}{\pm}\mathrm{O} + \mathrm{CH_3}+-\mathrm{O}-+\mathrm{H}.$$

To illustrate the decomposition of the di-derivatives, one set of equations may be given.

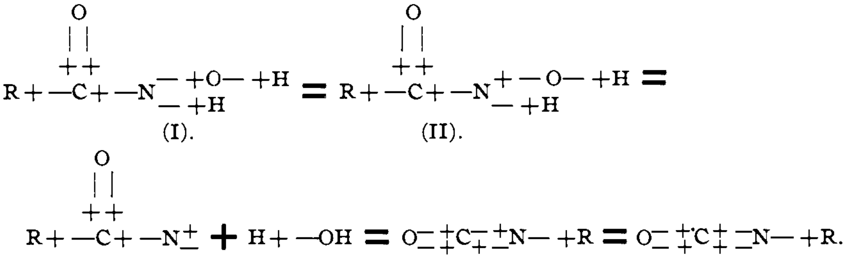


$$(\mathrm{CH_3^+})_3{\equiv}\mathrm{N}\begin{smallmatrix}-\;+\mathrm{O}-\;+\mathrm{CH_3}(4)\\+\;-\mathrm{O}-\;+\mathrm{C_2H_5}(5)\end{smallmatrix} = (\mathrm{CH_3^+})_3{\equiv}\mathrm{N}{\pm} + \mathrm{C_2H_5}+\;-\mathrm{O}-\;+\mathrm{H} + \overset{\mathrm{H_2}}{\mathrm{C}}{\mp}{\pm}\mathrm{O}$$



$$(\mathrm{CH_3^+})_3{\equiv}\mathrm{N}\begin{smallmatrix}-\;+\mathrm{O}-\;+\mathrm{C_2H_5}(4)\\+\;-\mathrm{O}-\;+\mathrm{CH_3}(5)\end{smallmatrix} = (\mathrm{CH_3^+})_3{\equiv}\mathrm{N}{\pm} + \mathrm{CH_3}+-\mathrm{O}-+\mathrm{H} + \mathrm{CH_3}\overset{\substack{\mathrm{H}\\ |}}{\mathrm{C}}{\mp}{\pm}\mathrm{O}$$

These facts make it highly probable that the hydroxyl group in hydroxylamine, and in its derivatives generally, may function positively. This applies to aldoximes, ketoximes, hydroxamic and hydroximic acids, isonitro compounds and many others which might be mentioned. The probability of tautomerism in the electronic sense, which would give compounds with negative hydroxyl, must be postulated for all such compounds. To illustrate this relation, the case of compounds undergoing Beckmann rearrangement[2] may be given.



$$\underset{\text{(I).}}{\mathrm{R}+-\overset{\substack{\mathrm{O}\\ \|\\ ++}}{\mathrm{C}}+-\mathrm{N}\begin{smallmatrix}-\;+\mathrm{O}-\;+\mathrm{H}\\-\;+\mathrm{H}\end{smallmatrix}} = \underset{\text{(II).}}{\mathrm{R}+-\overset{\substack{\mathrm{O}\\ \|\\ ++}}{\mathrm{C}}+-\mathrm{N}\begin{smallmatrix}+\;-\mathrm{O}-\;+\mathrm{H}\\-\;+\mathrm{H}\end{smallmatrix}} =$$

$$\mathrm{R}+-\overset{\substack{\mathrm{O}\\ \|\\ ++}}{\mathrm{C}}+-\mathrm{N}{\pm} + \mathrm{H}+-\mathrm{OH} = \mathrm{O}\begin{smallmatrix}-\\-\end{smallmatrix}\begin{smallmatrix}+\\+\end{smallmatrix}\mathrm{C}{\mp}{\pm}\mathrm{N}-+\mathrm{R} = \mathrm{O}\begin{smallmatrix}-\\-\end{smallmatrix}\begin{smallmatrix}+\\+\end{smallmatrix}\mathrm{C}\begin{smallmatrix}+\\+\end{smallmatrix}\begin{smallmatrix}-\\-\end{smallmatrix}\mathrm{N}-+\mathrm{R}.$$

Formula (I) must pass to Formula (II) before a molecule of water can be lost to give univalent nitrogen; this is accomplished by an exchange of negative electrons between the nitrogen atom and the oxygen atom; that is, formula (I) is a tautomeric electromer of Formula (II).

2. Stereomers.—Meisenheimer[3] was the first to observe that amine oxides with three different radicals, R, R′, R″, N=O, could be resolved into enantiomorphous modifications. Amine oxides of this kind were prepared by oxidizing tertiary amines with hydrogen peroxide or Caro's

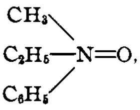
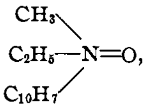
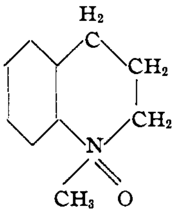
---

[1] Meisenheimer, *Ann.*, **399**, 372 (1913).

[2] Jones, *Am. Chem. J.*, **48**, 1 (1912); **50**, 414 (1913); Stieglitz, THIS JOURNAL, **36**, 288 (1914) note.

[3] Meisenheimer, *Ber.*, **41**, 3973 (1908); *Ann.*, **385**, 117 (1911).

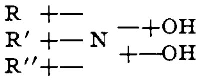
acid. Meisenheimer and his co-workers prepared methylethylaniline oxide, methylethyl-β-naphthylamine oxide and kairoline oxide

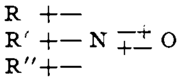
The racemates were resolved by means of *d*-bromocamphorsulfonic acid or *d*-tartaric acid. After fractional crystallization and separation, each salt was converted into the active picrate, which was changed to the corresponding active chloride, and finally, into the active amine oxide itself.

Previous attempts to resolve compounds with two like radicals, Na_2bcd, have been fruitless.[1] Even compounds more closely allied to these amine oxides in form, such as *N*-methylpicolinium salts, *N*-methylquinolinium salts, could not be resolved by H. O. Jones.[2] Meisenheimer takes it for granted that an explanation of the stereoisomerism is provided when he has called attention to the fact that, in the amine oxides, the doubly bound oxygen engages the valence which usually holds the acid radical, while in the case of the compounds studied by H. O. Jones, only non-ionizable valences have been displaced by doubly bound carbon.

It seems that a more consistent explanation may be offered in terms of the electronic view point. If the amine oxides and their hydrates have the following formulas:



$$\begin{array}{l}R\ +-\\R'\ +-\\R''+-\end{array} N \begin{array}{l}-+\mathrm{OH}\\+-\mathrm{OH}\end{array}$$



$$\begin{array}{l}R\ +-\\R'\ +-\\R''+-\end{array} N \begin{array}{c}-+\\+-\end{array} O$$

the nitrogen atom in either event *does not hold two like groups* since the properties of positive and negative hydroxyl are as divergent as those of positive and negative chlorine. In this respect, the conditions are not the same as those in ammonium compounds of the form, Na_2bcd.

It must be assumed that the linking $-N\begin{smallmatrix}-+\\+-\end{smallmatrix}O$ is similar to the grouping $-N\begin{smallmatrix}-+\mathrm{OH}\\+-\mathrm{OH}\end{smallmatrix}$ in so far as its effect upon the asymmetry[3] of the molecule is concerned. The question may be raised, "Why should compounds of the type RR′R″N=O show optical activity while compounds of the type RR′R″N=C< do not?" In a previous article[4] it was shown that systems containing the carbon nitrogen linking, C=N, tend to assume a condition in which the carbon atom is as fully oxidized as possible and

---

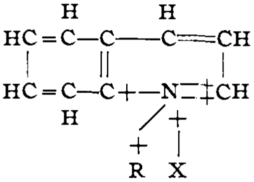
[1] Aschan, *Z. physik. Chem.*, 46, 293 (1903); Scholtz, *Ber.*, 43, 2121 (1911).

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

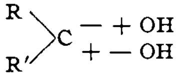
[3] The amine oxides dissolved in benzene often show very large rotations.

[4] Jones, *Am. Chem. J.*, 50, 440 (1913).

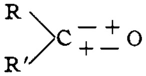
the nitrogen atom as fully reduced, *viz.*, $>\mathrm{C}\genfrac{}{}{0pt}{}{+-}{+-}\mathrm{N}-$ Therefore, in the cyclic compounds studied by H. O. Jones, we should have



In other words, the nitrogen atom is linked to only four different groups, since the linking $\equiv\mathrm{N}\genfrac{}{}{0pt}{}{-+}{-+}\mathrm{C}<$, is synonymous with $\mathrm{Na_2}$bcd. It does not seem improbable, however, that some day conditions may be found to stabilize the system $\equiv\mathrm{N}\genfrac{}{}{0pt}{}{-+}{+-}\mathrm{C}<$ in certain compounds, which may be expected to show optical activity. Furthermore, it may be predicted that compounds of the form



and



will be found to show activity if they are ever prepared. Many other possibilities of a similar character suggest themselves.

When the existence of isomers among organic compounds was first recognized, Faraday[1] said, "In reference to the existence of bodies composed of the same elements, and in the same proportion, but differing in their qualities, it may be observed, that, now we are taught to look for them, they will probably multiply on us." In the opinion of the author, we are in much the same position at the present time with respect to these new isomers which depend upon the distribution of electrons and their exchange; and it is not improbable that they will "multiply on us" in the future.

CINCINNATI, O.

[COMMUNICATION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN.]

FORMS OF SULFUR IN PLANT MATERIALS AND THEIR VARIATION WITH THE SOIL SUPPLY.[2]

BY W. H. PETERSON.

Received April 13, 1914.

Sulfur occurs in plant and animal tissues chiefly in the form of proteins, volatile compounds, as the mustard oils, and sulfates. In the proteins, it is known to exist as the amino acid, cystine, but in spite of much investigation, no other sulfur bearing compound has been isolated from the

---

[1] Faraday, *Phil. Trans.*, 440, (1825).

[2] This paper represents a thesis submitted to the Graduate Faculty of the University of Wisconsin in partial fulfillment for the degree of doctor of philosophy. Published with the permission of the Director of the Agricultural Experiment Station.