

curred. The mixture was then warmed to remove the excess of chlorine. This gave a white product of 2,5-dichloro-*p*-xylene which was recrystallized from acetic acid. It melted at 70–71°. The yield is not quantitative.

**Mesitylene.**—Mesitylene sulfonic acid was dissolved in water and a current of chlorine gas was passed into the solution. A white flocculent precipitate was obtained. After the solution was saturated with chlorine gas, it was warmed on a water-bath. The 2,4,6-trichloro-mesitylene formed was recrystallized from alcohol and then melted at 203–204°. The yield is not quite quantitative.

Subs., 0.1046: AgCl, 0.2010.

Calc. for  $C_6(CH_3)_3Cl_3$ ; Cl, 47.75. Found: 47.54.

#### Replacement by Iodine.

**Mesitylene.**—When an aqueous solution of potassium iodide was added to an aqueous solution of pure mesitylene sulfonic acid, a crystalline product was obtained which has been found to be the potassium salt of mesitylene sulfonic acid. This occurs when the solution of potassium iodide is concentrated. On this account a potassium iodate solution was added first. When, then, potassium iodide solution was added slowly to this solution, a flocculent precipitate containing iodine was formed. This mixture was heated until all free iodine had escaped, giving a liquid which collected at the bottom of the vessel, and solidified, when it was poured into ice-cold water. After recrystallization, it melted at 31°. It is mono-iodo-mesitylene. The yield is good.

Subs., 0.1032: AgI, 0.0980.

Calc. for  $C_6H_2(CH_3)_3I$ : I, 51.63. Found: 51.33.

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CALCUTTA, INDIA.

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

## THE STRUCTURES AND REACTIONS OF HYDROXYLAMINE AND ITS DERIVATIVES.

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Hydroxylamine is an endothermic compound, exploding violently at 70° to 80°, and acting as a reducing agent; on the other hand, it converts ferrous hydrate into ferric hydrate and zinc into zinc oxide, and in these instances apparently appears as an oxidizing agent. This, seemingly dual, chemical character, and other properties, of the base, have led some chemists to consider it a tautomeric substance, capable of reacting in the hydroxyl form,  $H_2NOH(I)$ , and the amine oxide form,  $H_2NO(II)$ .

Haber<sup>1</sup> called attention to the conversion of ferrous hydrate and of nitrites in the presence of alkali into higher oxidized compounds by hydroxylamine,<sup>2</sup> and to the reduction of ferric to ferrous sulfate in acid solution.<sup>3</sup>

<sup>1</sup> Haber, *Ber.*, **29**, 2444 (1896). Haber overlooked a paper by Dunstan and Dymond (*J. Chem. Soc.*, **51**, 655 (1888)), who found that ammonia and some nitrogen are formed in the reaction.

<sup>2</sup> Donath, *Ber.*, **10**, 766 (1877); Dunstan and Dymond, *loc. cit.*

<sup>3</sup> Meyerhinh, *Ber.*, **10**, 1042 (1877).

This chemist believes that these reactions are best explained by accepting the hydroxyl formula (I) in the salts, and, as it not only oxidizes ferrous hydrate but reduces cuprous oxide<sup>1</sup> in the presence of alkali, that in alkaline solution it exists in the 2 tautomeric forms. Ebler and Schott<sup>2</sup> arrive at almost the opposite conclusions in an extended critical discussion, and from an experimental investigation of the oxidation phenomena, *viz.*, that it possesses the amine oxide structure (II) in its salts, and in alkaline solution it exists only in the hydroxyl form (I).

De Bruyn<sup>3</sup> has shown that, while sodium and the free base react to form sodium hydroxylamate, ammonia and zinc oxide are formed in the reaction with zinc. The latter fact appears to support the amine oxide formula, *i. e.*,  $\text{H}_3\text{NO} + \text{Zn} = \text{NH}_3 + \text{ZnO}$ , but Elber and Schott<sup>4</sup> prove that zinc, and also calcium, react primarily by substituting the O-hydrogen of the base to form the corresponding hydroxylamates, and that these, almost explosive, products decompose under ordinary conditions with the liberation of ammonia and hydroxylamine, to leave the metallic oxides as residues. They<sup>5</sup> also show, contrary to Haber's results, that ammonia appears only towards the end of the action of ferrous hydrate upon hydroxylamine in alkaline solution, and that the proportion of the other products, nitrogen and nitrous oxide vary considerably, as the ferric hydrate formed in the reaction decomposes the base catalytically.

Ebler and Schott conclude from their experimental results that hydroxylamine in alkaline solution is not an oxidizing agent; certainly not in the sense "that it oxidizes strictly according to the equation  $\text{H}_3\text{NO} = \text{H}_3\text{N} + \text{O}$ ,"<sup>6</sup> and, since unstable, intermediate, metallic derivatives are first formed in the reactions, they believe it exists under such conditions only as the hydroxyl compound (I).

Recently, L. W. Jones<sup>7</sup> has also discussed the subject, and comes to the conclusion that the behavior of hydroxylamine towards "alkylating and acylating agents shows all the earmarks"<sup>2</sup> met with in the study of tautomeric substances, and that "the experimental evidence is sufficient, not only to establish a tautomeric relationship in the ordinary sense, but also to confirm the belief that hydroxylamine and its derivatives, in many of their reactions, behave tautomericly in the electronic sense as

<sup>1</sup> Lossen, *J. prakt. Chem.*, [I] 96, 462 (1866); Donath, *Ber.*, 10, 766 (1877).

<sup>2</sup> Ebler and Schott, *J. prakt. Chem.*, [II] 78, 289 (1908). A complete résumé of the literature up to the date of publication may be found in this paper.

<sup>3</sup> De Bruyn, *Rec. trav. chim.*, 11, 34 (1892).

<sup>4</sup> *Loc. cit.*, pp. 321-331.

<sup>5</sup> *Loc. cit.*, pp. 331-338. Ferric hydrate in aqueous, or ferric chloride in alcoholic, hydroxylamine, yield very unstable iron derivatives of the base, that are considered to be the intermediate products, as they give the same substances on decomposition, that should be formed in oxidations.

<sup>6</sup> *Loc. cit.*, p. 308.

<sup>7</sup> THIS JOURNAL, 36, 1268 (1914).

well."<sup>1</sup> Jones adopts the hydroxyl structure (I) for the base in acid solution, and the oxide (II) in alkaline. The latter view is erroneously ascribed to Haber, who, however, considered the alkaline solution to contain a mixture of the tautomeric forms, and, further, the important investigation of Ebler and Schott is overlooked, whose experimental results show that the base in alkaline solution reacts in the hydroxyl form.

The existence of trialkyl derivatives with amine oxide structures, and the formation of the salts of such substances in the action of alkyl halides upon hydroxylamine, has been advanced as strong evidence in favor of an amine oxide structure for hydroxylamine; indeed, Jones believes that "if the action of alkylating agents had been unravelled first, we should probably have used the formula  $H_3N = O$ , instead of Formula I."<sup>2</sup> Dunstan and Goulding<sup>3</sup> assume that in the reaction between hydroxylamine and methyl iodide a very unstable base,  $(H_3C)_2NOCH_3$ , is formed, which isomerizes at once to  $(H_3C)_3NO$ . This supposition involves not only an extraordinary instability in compounds of the O-alkyl-hydroxylamine group, that are quite stable under these conditions, but a spontaneous conversion of a derivative into an isomer with a larger content in free chemical energy,<sup>4</sup> and is untenable for this reason alone. Alkyl halides react upon ammonia only by addition to form primarily an alkyl-ammonium halide, from which product an alkylamine may be set free, and repetition of the processes leads finally to a salt of a tetra-alkyl-ammonium hydrate. From hydroxylamine the product  $(Alk)_2NOH$ <sup>5</sup> is formed, which by further addition passes over into  $(Alk)_3N(OH)I$ . This formula represents, however the salt formed from trialkyl-amine oxide and hydriodic acid,<sup>6</sup> which gives the amine oxide upon treatment with an alkali. On the other hand, if hydroxylamine had the amine oxide structure (II), the addition of methyl iodide to the nitrogen atom would be barred, since pentavalent nitrogen does not possess this additive property for the alkyl halides, and the only possible course would be similar to that shown in the anomalous reaction observed with the trialkyl-amine oxides.<sup>7</sup> It is evident that, *instead of indicating the structure  $H_3N = O$  for hydroxylamine, the formation of trialkyl-amine oxides can only be explained from the formula  $H_2NOH$ .*<sup>8</sup>

<sup>1</sup> *Loc. cit.*, p. 1269.

<sup>2</sup> *Loc. cit.*, p. 1270.

<sup>3</sup> Dunstan and Goulding, *J. Chem. Soc.*, **75**, 803, 1004 (1899).

<sup>4</sup> For definitions of the terms free and bound chemical energy, as used in this paper, see *THIS JOURNAL*, **32**, 990 (1910).

<sup>5</sup> Dunstan and Goulding, *J. Chem. Soc.*, **75**, 800-804 (1899).

<sup>6</sup> *Loc. cit.*, pp. 797, 802.

<sup>7</sup> *THIS JOURNAL*, **42**, 1232 (1920).

<sup>8</sup> The behavior of hydroxylamine towards acyl chlorides or acid anhydrides has not been altogether satisfactorily explained. A hydrogen atom in a basic amino group is readily replaceable by an acyl group, but for obvious reasons, it is much less so in

The theoretical objections to the formula  $H_2=O=O$  for hydrogen peroxide from the affinity-energy view-point, apply in an equal degree to the corresponding structure,  $H_3=N=O$ , for hydroxylamine, and, in this case, they are coupled with ample experimental evidence. The nitroso group in organic compounds is characterized by a more or less large content of free chemical energy, and its oxygen must exert intramolecularly a considerable attraction upon the hydrogens in the substance, which, *cat. par.*, will increase in extent with the spatial proximity between the atoms. An intramolecular rearrangement will take place, with the migration of a hydrogen to the oxygen, if the affinity-energy relations in the latter atom suffice to overcome the hindrance to a change, *i. e.*, the bound chemical energy between the hydrogen and the atoms to which it is directly and indirectly joined, and when a new product may be formed with an increase of entropy. The magnitude of the chemical work that the nitroso group is capable of performing is seen in the spontaneous transformation of primary and secondary nitroso alkanes into amphoteric, *i. e.*, intramolecularly well-neutralized, oximes.<sup>1</sup> Similarly, the structure  $H_3=N=O$ , supposing it were capable of existing at a very low temperature, should under ordinary conditions isomerize with a considerable increase in entropy into  $H_2NOH$ , as the affinity of hydrogen for nitrogen is much less than for oxygen, and the other energy conditions for the spontaneous rearrangement would evidently be present; indeed, the isomerization should take place with much less resistance than in the nitroso alkanes, as the hindrance to the migration of a hydrogen would be less and the oxygen richer in free chemical energy.

a neutral or amphoteric amido group, and it may become impossible with a further accumulation of negative radicals, or of a greater negative influence, on the nitrogen: *e. g.*, diacetimide is not acted upon by acetic anhydride (Hentschel, *Ber.*, 23, 2399 (1890)). Contrariwise, the hydrogen of an hydroxyl group is easily replaceable by an acyl group, even when its oxygen is directly joined to strongly negative radicals. In these relations may be found the explanation of the behavior of hydroxylamine; the first products being N-acyl derivatives, then the acyl group replaces the hydroxyl hydrogen to form compounds of the type  $(RCO)NH(OCOR)$ , whose N-hydrogen is now more or less protected. The third acyl group reacts either through the free chemical energy in the "polymolecule" of substance and reagent first converting the hydroxylamine derivative into a desmotropic form containing an easily acted upon hydroxyl group, *i. e.*,  $RC(OH) = N - (OCOR)$ , or, by substituting the remaining N-hydrogen atom; the course depending on the chemical nature of the substituents. The action of alkyl-halides on the sodium derivatives of the oximes, and the  $\beta$ -hydrocarbyl-hydroxylamines, proceeds partly with the direct replacement of the metal, partly by the addition of the halides to the nitrogen atom, whose additive capacity for these reagents has been greatly increased by the positive chemical influence of the metallic atom:  $R_2C = NONa + RI = R_2C = N(ONa)(R)I \xrightarrow{-NaI} R_2C = N(R)O \longrightarrow R_2C - \underbrace{N(R) - O}$  (see *THIS JOURNAL*, 42, 792 (1920)).

<sup>1</sup> J. Schmidt (*Ber.*, 35, 3727 (1902)); 36, 1765 (1903); 37, 532 (1904), and Piloty and Steinbock (*ibid.*, 35, 3103) succeeded in isolating several secondary nitroso derivatives, but they isomerize easily to the corresponding oximes.

The existence of the trialkyl-amine oxides in a free state corresponds to that of the tertiary nitroso alkanes; in these groups of substances the free chemical energy in the oxygen atoms is reduced by the spatial action of a large number of hydrogen atoms. A rearrangement is prevented in the alkane derivatives by the considerable hindrance, which would arise in the formation of a 3-membered ring, but the trialkyl-amine oxides undoubtedly rearrange to oximido derivatives,<sup>1</sup> before undergoing the decomposition by heat energy.

No support for the amine oxide structure can be found in the chemical behavior of hydroxylamine; on the contrary all observations confirm the hydroxyl constitution. For instance, trimethyl-amine oxide is very easily reducible by nascent hydrogen to trimethylamine,<sup>2</sup> and hydroxylamine, under the same conditions, should still be more readily converted into ammonia, if it contained a NO group, as the free chemical energy in the oxygen and its affinity for hydrogen would evidently be greater. Actually, however, it shows itself to be very stable towards the reagent.<sup>3</sup>

Nor is the chemical resemblance assumed to exist between hydroxylamine and hydrogen peroxide<sup>4</sup> more than a very superficial relationship, which is without value in determining the structure of the base. The 2 compounds are supposed to show a "striking" similarity in their behavior as oxidizing and reducing agents, but these properties are relative in the sense that they depend on the substances acted upon, and when this fact is taken into consideration the "striking" resemblance completely disappears.

A direct oxidizing capacity by hydroxylamine is apparently shown towards ferrous hydrate, but the affinity of this compound for oxygen is so enormous,<sup>5</sup> that the reaction may be looked upon rather as a reduction of the base; the reduction of stable oxygen derivatives might with equal justification be considered as an oxidation of nascent hydrogen. While hydroxylamine acts as a quite energetic reducing agent, hydrogen peroxide is an extremely powerful oxidizing agent, but, as Brodie and M. Traube have shown, it is only able to reduce metallic oxides, that may be considered mild oxidizing agents, *i. e.*, the reactions represent oxidations quite as much as they do reductions. For instance, silver oxide

<sup>1</sup> THIS JOURNAL, 42, 1236 (1920).

<sup>2</sup> Dunstan and Goulding, *J. Chem. Soc.*, 75, 796 (1899).

<sup>3</sup> Lossen, *Z. Chem.*, 1868, p. 399; *Ann.*, Suppl. 6, 246 (1868).

<sup>4</sup> C. B. Wagner, *Centralbl.*, 61, I, 244 (1899); Tanatar, *Ber.*, 32, 241 (1899); Ebler and Schott, *J. prakt. Chem.*, [2], 78, 310 (1908); C. B. Angeli, *Centralbl.*, 84, II, 861 (1910); Stieglitz and Curme, *Ber.*, 46, 911 (1913); Stieglitz, THIS JOURNAL, 36, 287, footnote (1914); Jones, *ibid.*, 1271; Langmuir, *ibid.*, 42, 285 (1920).

<sup>5</sup> For instance, Zorn (*Ber.*, 15, 1258 (1882)) showed that ferrous hydrate reduces sodium nitrite and nitrate in aqueous solution, even when the mixtures are cooled, with the formation of much nitrous oxide, ammonia, nitrogen and some hyponitrite.

and the peroxide give silver, but so does aldehyde, and in this case the metallic oxide may be considered as the oxidizer. Hydroxylamine reacts upon ferrous hydrate because of the comparatively weak affinity of nitrogen, and the strength of that of ferrous hydrate, for oxygen; and hydrogen peroxide upon silver oxide, because the bound chemical energy between hydrogen and oxygen and silver and oxygen in these compounds is comparatively slight. A "striking" similarity should not be assumed on such slight resemblances between extreme relations in chemical properties.<sup>1</sup> Moreover, as will be shown farther on, the veritable aliphatic amine oxide derivatives by no means act as oxidizing agents, and whatever oxidizing capacity is shown by hydroxylamine and its derivatives, is strictly in keeping with the affinity-energy relations that should be manifest if the compound have hydroxyl structures.

De Bruyn<sup>2</sup> found that the anhydrous base could be kept, under 15° and in flasks that had been treated with acids, for several years with but slight decomposition; in extent, however, it increased noticeably with the alkalinity of the glass of the container. The products consisted of ammonia, nitrogen, water, a little nitrous oxide and also, when the extent of the decomposition became relatively considerable, of traces of nitrous acid. The decomposition is evidently catalytic, and due to the alkali or alkaline product set free by the action of hydroxylamine upon glass,<sup>3</sup> and which connects the extent with the alkalinity of the glass. It is extremely doubtful whether auto-oxidation would enter at all into the decomposition of pure hydroxylamine, since the conditions for such an oxidation are extremely favorable in the rapid breaking up of the substance and, even under these conditions, the appearance of nitrous oxide in very small proportion among the products, nitrogen, water and ammonia, is a matter of doubt.

The instability of hydroxylamine towards heat arises from the comparatively weak affinity of nitrogen for hydrogen, which is decreased by the influence of the hydroxyl group, and the still less of nitrogen for that group, in contrast with the much greater between hydrogen and hydroxyl; an affinity relationship that is favored with rise of temperature. These energy relations find an expression in the thermal values, for Berthelot and André<sup>4</sup> emphasize that the heat generated in the conversion of ammonia into hydroxylamine is so small that "it hardly responds, properly speaking, to an oxidation," while the union of hydrogen with hydroxyl is highly exothermic. The facile elimination of water represents, therefore, an energetic tendency, and the decomposition should proceed with

<sup>1</sup> See Brühl, *Ber.*, 32, 507 (1899).

<sup>2</sup> *Ibid.*, 27, 967 (1894).

<sup>3</sup> De Bruyn, *Rec. trav. chim.*, 11, 27 (1892).

<sup>4</sup> *Compt. rend.*, 110, 833 (1910).

the formation of the products that are most stable towards heat energy and which represent the possible maximum entropy of the reaction, *i. e.*, water, nitrogen and ammonia.

These chemical energy relations are materially changed in the union of this very weak base<sup>1</sup> with a strong acid. The new product contains negative, acidic energy in excess, and, although the affinity of the oxygen in the basic component for the nitrogen has been decreased by the introduction of the acid, that of the hydrogens for the hydroxyl has apparently fallen off to a greater degree, for the salts are far more stable towards heat energy than the free base. The surplus of free negative chemical energy in the salt must strive towards the conversion of the slightly basic, hydroxylamine component into as strong a basic part as possible, as the maximum increase of entropy will be realized by the most complete neutralization of the acidic energy. This condition of intramolecular neutralization is obtained in the formation of the corresponding ammonium salt,<sup>2</sup> and in the presence of an oxidizable substance the salt parts with the hydroxylamine oxygen more or less readily,<sup>3</sup> according to the capacity of the oxidizable substance to assist in overcoming the hindrance to the separation of the oxygen.

The presence of alkali greatly accelerates the decomposition of the base,<sup>4</sup> and Kolotoff<sup>5</sup> found that the relative proportion of ammonia increases at the expense of nitrogen, and that nitrous oxide appears now in considerable and nitrite in appreciable amount.<sup>6</sup> Hydroxylamine and sodium from an hydroxylamate, in which the great amount of free positive, chemical energy still remaining in the metal manifests itself in the product spontaneously oxidizing on the air; at times with combustion, with the formation of nitrite. When hydroxylamine is dissolved in aqueous

<sup>1</sup> MacKay, *Centralbl.*, **79**, I, 1908, (1918).

<sup>2</sup> The heat of neutralization of hydroxylamine by acids is much smaller than that of ammonia. (Thomsen, *J. prakt. Chem.*, [2], **13**, 241 (1876)).

<sup>3</sup> von Meyer, *J. prakt. Chem.*, [2], **29**, 497 (1884); Nietzcki and Benchiser, *Ber.*, **19**, 303 (1876); Biltz, *ibid.*, **29**, 2080 (1896); Piccini, *ibid.*, **27** I, ref.; Stähler, *ibid.*, **37**, 4732 (1904).

<sup>4</sup> De Bruyn, *Rec. trav. chim.*, **11**, 31 (1892).

<sup>5</sup> Kolotoff. The fullest account in a non-Russian journal of this work is in *Bull. soc. chim.*, **12**, 871 (1894). The résumé in the *Ber.* (ref. **26**, 761 (1893)) misprinted in the formula  $\text{NaNO}_3$  for  $\text{NaNO}_2$ ; an erratum that has led Jones (*THIS JOURNAL*, **36**, 1279, 1281 (1914)) to state that nitric acid is formed, although nitrous acid is correctly given in the text.

<sup>6</sup> De Bruyn, *Rec. trav. chim.*, **11**, 32 (1892). The difference between the behavior of hydroxylamine towards solid alkali, and on adding it to a strong, aqueous solution without cooling off, which this chemist considered "remarkable," is evidently due to the decomposition of the base by the considerable heat generated in the solution of the solid alkali. No decomposition was noticed when the operation was done under cooling.

alkali a certain proportion of the substance, increasing with the concentration of the alkali, must exist as hydroxylamate in the solution. As the alkali derivative shows a very great affinity for oxygen, it takes it, if a more available source is not present, from the unchanged hydroxylamine, with the formation of ammonia and of  $\text{HN}(\text{OH})\text{ONa}$ , which may. (1) decompose to yield nitrous oxide,<sup>1</sup> (2) form hyponitrite, through polymerization of the intermediate product  $\text{NONa}$ ,<sup>2</sup> or (3) be oxidized further to nitrite. It is evident that the presence of alkali must accelerate the decomposition of hydroxylamine, and, also, that it tends so to change the products formed as to neutralize the excess of positive chemical energy in the hydroxylamate; *i. e.*, to form hyponitrite and nitrite in a direct relation to the concentration of the alkali derivative.<sup>3</sup> And, also, that the catalytic influence of the alkaline material from the glass container must act in the same direction. Further, it is very probable that the small amount of nitrous oxide, appearing with the slow, spontaneous decomposition of the base, has its origin in the oxidation to  $\text{HN}(\text{OH})_2$  by the oxygen of the air under these catalytic influences, which breaks up to yield the oxide and water.<sup>4</sup>

According to Jones,<sup>5</sup> "The  $\beta$ -disubstituted hydroxylamines,  $(\text{R}_2)\text{NOH}$ , form a class of compounds which seem to lie close to the border line of instability. By very slight changes in the physical and chemical conditions they generally decompose to give products which would be expected to result by a process of intramolecular oxidation. Thus, Walder<sup>6</sup> found that  $\beta$ -dibenzyl-hydroxylamine,  $(\text{C}_7\text{H}_7)_2\text{NOH}$ , in the presence of acetyl chloride, or even with a hydrogen chloride and acetic acid, gave chiefly benzaldehyde and benzylamine."

Instability as a general chemical expression is indefinite,<sup>7</sup> but many of the properties of these substances certainly cannot be classified under it. For instance, the dibenzyl derivative in question may be heated considerably above its melting point with only a slight change, and may be boiled

<sup>1</sup> Nitrous oxide is the main, and hyponitrous acid a very subordinate, product in the oxidation of hydroxylamine, or in the reduction of nitrous or nitric acids in alkaline solutions.

<sup>2</sup> For an explanation of the reaction, see Michael, *J. prakt. Chem.*, [2] 60, 299 (1899).

<sup>3</sup> Bertoni (*Liebig's Jahresber.* 1879, 211) found that in the oxidations by dichromate and permanganate the percentages of nitrite and nitrate increase in the presence of alkali.

<sup>4</sup> Feist (*Ber.*, 25, 332 (1892)) found that diaceto-diketo-hexamethylene dicarboxylate is oxidized with the loss of 2 nuclear hydrogens by hydroxylamine in the presence of alkali. Such a reduced benzene derivative should be easily oxidizable, and the action undoubtedly takes place through the hydroxylamate.

<sup>5</sup> Jones, *THIS JOURNAL*, 36, 1271 (1914).

<sup>6</sup> Walder, *Ber.*, 14, 1629, 3287 (1886).

<sup>7</sup> *THIS JOURNAL*, 40, 1686, footnote (1918).



with concentrated hydrochloric acid without decomposition.<sup>1</sup> Jones<sup>2</sup> explained the formation of benzaldehyde and benzylamine with acetyl chloride by the elimination of water to form benzal-benzylamine and its addition to that compound in the reverse direction, while Walder and V. Meyer<sup>3</sup> believed it to be due to "intramolecular auto-oxidation."<sup>4</sup>

Although the first explanation is undoubtedly correct in principle, it cannot be accepted without modification in this particular reaction, as the water generated in the formation of benzal-benzylamine would be immediately decomposed by the excess of acetyl chloride present. When an excess of that reagent is avoided, the O-acetyl derivative is formed,<sup>5</sup> and there is no apparent reason why it should not be the primary product when the reagent is used in an excess. The replacement of the hydroxyl-hydrogen by acetyl decreases the affinity between the nitrogen and the oxygen, and these affinity changes are increased when the hydrochloric acid formed in the reaction unites with the new product to form a salt. That product should lose acetic acid readily under the influence of the affinity between it and acetyl chloride, and the benzal-benzylamine hydrochloride thus formed belongs to a class of substances that assimilate water very readily to form the salts of strong primary bases and aldehydes. If the reaction product containing this salt should be extracted with moist ether, benzaldehyde would be formed, and would pass over into the ether extract, as Walder<sup>5</sup> observed.

The same products are formed when  $\beta$ -dibenzyl-hydroxylamine is boiled

<sup>1</sup> Walder, *Ber.*, **19**, 1629, footnote 2 (1886).

<sup>2</sup> *Am. Chem. J.*, **50**, 422 (1913).

<sup>3</sup> *Ber.*, **19**, 1629, footnote 1 (1886).

<sup>4</sup> Bamberger (*ibid.*, **33**, 3193 (1900)) found that  $\beta$ -benzylhydroxylamine is oxidized by air, in the presence of water, to form benzaldehyde, benzyl-isobenzal-aldoxime, benzalaldoxime and other products; and, Behrend and Leuchs (*Ann.*, **257**, 222, 233 (1890)) that the dibenzyl derivative is readily oxidized by red prussiate into benzyl-isobenzal-aldoxime, which is also formed by intermolecular oxidation and reduction when the substance is boiled with alcoholic benzyl chloride. These basic substances may decompose with the elimination of water, are very easily oxidized, and form salts that are comparatively easily reducible; and the course of the chemical change, including "intramolecular oxidation," depends on the relative facility of the several processes in one or the other direction, that is on their chemical structures and the employed reagents.

Meyer used "intramolecular auto-oxidation" in the accepted sense, that is the oxidation to benzaldehyde is effected by oxygen coming from within the molecule. This conception of the process is essentially different from that of Jones (*Amer. Chem. J.*, **50**, 423 (1913)), who states that "before benzylamine and benzaldehyde can be formed there must be an 'intramolecular Selbst-oxidation,' as Victor Meyer called it, or the carbon atom must yield negative electrons which are at once combined with the nitrogen atom to give a new electromere" of benzalbenzylamine. To call a change in the electronic signs in a hypothetical "electromer," an "intramolecular auto-oxidation" evidently leads to confusion in the use of the expression.

<sup>5</sup> Walder, *Ber.*, **19**, 1627 (1886).

for several hours with a saturated solution of hydrochloric acid in glacial acetic acid, while heating with conc. hydrochloric acid leads only to the salt of the unchanged base.<sup>1</sup> In the latter instance the presence of water prevents its elimination from the hydrochloride, but it is brought about with the use of the dehydrating hydrochloric-acetic acid solution.

As further evidence that these derivatives "lie close to the border line of instability," Jones<sup>2</sup> quotes from Dunstan and Goulding<sup>3</sup> "that  $\beta$ -diethyl-hydroxylamine when heated, gave acetaldehyde and ethylamine." These chemists<sup>4</sup> found, however, that the base distills, apparently without decomposition, between 130–134°, and noticed such a change only when it was heated to 180° with acetic acid in excess.

It was mentioned above that the hydroxyl group in hydroxylamine is loosely joined to the nitrogen atom, and that this relationship, and its strong affinity for hydrogen, are the main reasons of the slight stability of the base towards heat energy. If the N-hydrogen atoms of the base are replaced by primary or secondary hydrocarbon radicals, the new products should and do show a far greater stability towards heat, since the separate hydrogen can now come only from a hydrocarbon group, and much more energy is not only required to remove it than from an amino group, but it is spatially farther removed. Any structural change in the  $\beta$ -derivative, that decreases the expenditure of energy necessary to separate the oxygen from the nitrogen, or the eliminated hydrogen from the hydrocarbon group, must favor decomposition, and, also, the use of a reagent with a decided affinity for water. The behavior of  $\beta$ -dibenzyl-hydroxylamine may be taken in illustration. The reaction should be facilitated by hydrochloric acid for several reasons. It is a weak base, and, as the considerable negative energy of the acid cannot be neutralized in the salt formed, it must cause a decrease in the affinity between the nitrogen atom and the hydroxyl group. Further, the benzal-benzylamine hydrochloride, formed by the elimination of water, is the salt of a weak base, and it has, too, negative chemical energy in large excess, which will be largely converted into bound chemical energy and heat through the formation of benzylamine hydrochloride, following the addition of water. And, finally, the latter process is enormously facilitated by the presence of a strong mineral acid in an aqueous solution.<sup>5</sup> In this particular instance, the presence of water in the acid prevents the realization of the first phase of the reaction, but it is brought about by boiling the substance with the dehydrating mixture of hydrochloric and acetic acids,<sup>6</sup> and the reaction then goes to completion.

<sup>1</sup> Walder, *Ber.*, 19, 1629 (1886).

<sup>2</sup> *Loc. cit.*, p. 1272.

<sup>3</sup> Dunstan and Goulding, *J. Chem. Soc.*, 75, 793 (1899).

<sup>4</sup> *Ibid.*, p. 801.

<sup>5</sup> Michael and Brunel, *Am. Chem. J.*, 48, 272 (1912).

<sup>6</sup> Walder, *Ber.*, 19, 1629 (1886).

The influence of hydrocarbon radicals on the facility and quantitative course of these reactions has not been studied with hydroxylamine derivatives, but the results should be closely allied to those found by Berg<sup>1</sup> with the corresponding chloro-amines. The halogen in that class of compounds has not only a much slighter affinity for nitrogen than hydroxyl, but its content in free chemical energy is greater, and, also, its affinity for hydrogen. A chloro-amine, consequently, loses hydrochloric acid very much more readily than the corresponding hydroxyl derivative parts with water.<sup>2</sup> With ethyl-iso-amylchloro-amine, where the alkyl groups are of different sizes, Berg obtained 4 products of decomposition; a mixture of acetic and isovaleric aldehydes and ethyl and iso-amyl amines. This result agrees with the theory, as the difference between the influence of the methyl and isobutyl radicals on the affinity-energy relations of the hydrogens in the 2 methylene groups joined directly to the nitrogen, cannot, according to the "*principle of partition*,"<sup>3</sup> suffice to throw the elimination phase entirely in one direction, and the 2 unsaturated compounds thus formed must give by hydrolysis the 4 products mentioned above. Berg did not determine the relative proportions between the products of decomposition, but it may be estimated theoretically by a consideration of the relative influence of the alkyl groups on the affinity of the methylene hydrogen for the halogen, and the energy required to separate them from the carbons to which they are directly joined. These influences work in the same direction, *viz.*, the affinity factor increases and the hindrance factor decreases with the relative positivity of the alkyls joined to the methylene groups.<sup>4</sup> Since the iso-amyl is decidedly more positive than the ethyl group, with the chloro-amine in question, the proportion of isovaleric aldehyde and ethylamine should be considerably larger than that of acetic aldehyde and iso-amylamine.<sup>5</sup>

Jones<sup>6</sup> has called attention to the analogy between this reaction and the results obtained by Bewad<sup>7</sup> in the behavior of a number of  $\beta$ -dialkylhydroxylamines towards ferric and copper sulfates in the presence of alkali. Thus, with  $\beta$ -ethyl-*sec.*-amylhydroxylamine a mixture of acetic aldehyde, diethylketone, ethylamine and *sec.*-amylamine are formed, and, besides, some ammonia and ethyl-*sec.*-amylamine. Bewad<sup>8</sup> concluded from the relative proportions of the products that the oxygen from the

<sup>1</sup> Berg, *Bull. soc. chim.*, [3] 17, 297 (1897).

<sup>2</sup> THIS JOURNAL, 42, 1241 (1920).

<sup>3</sup> *Ibid.*, 32, 1005 (1910).

<sup>4</sup> Michael, *J. prakt. Chem.*, [2] 60, 433 (1899).

<sup>5</sup> A quantitative investigation in this field would be of interest. See THIS JOURNAL, 41, 393 (1919).

<sup>6</sup> Jones, *ibid.*, 1272 (1914).

<sup>7</sup> Bewad, *J. prakt. Chem.*, [2] 63, 193 (1901).

<sup>8</sup> *Loc. cit.*, 207, 208.

hydroxylamine derivative enters into the oxidation to a much larger extent than that from the oxidizing agent.

Ebler and Schott<sup>1</sup> showed that ferric hydroxide unites with hydroxylamine in alcoholic solution to form a product that decomposes very easily with the formation of nitrogen, water, ammonia and nitrous oxide. Somewhat similar results were obtained by Adam and Overman<sup>2</sup> with copper sulfate; in alcoholic solution several unstable double compounds of the salt and hydroxylamine were isolated, one of which on addition of water is reduced to a cuprous derivative. When caustic soda is added to a solution of an hydroxylamine salt and copper sulfate, similar changes take place but they occur so rapidly that only the final products of decomposition could be separated, *viz.*, copper, cuprous oxide and nitrogen. This property of ferric and cupric hydroxide in the presence of alkali, which is evidently allied to catalysis as platinum black causes a similar decomposition,<sup>3</sup> appears also in their behavior towards the monoalkyl-hydroxylamines. For instance,  $\beta$ -methyl-hydroxylamine on warming with Fehling's solution gives methylamine, carbonic acid and ammonia;<sup>4</sup> the latter 2 products by an elimination and subsequent addition of water to the primarily formed methylene imine, with the complete oxidation of the formic aldehyde thus formed by the reagent. Corresponding changes undoubtedly take place in the decompositions of the dialkyl-hydroxylamines studied by Bewad, *i. e.*, the unstable metallic derivatives decompose in the presence of alkali; in part to give some of the secondary amines and ammonia, but to a greater degree not by oxidation but by a "catalytic" decomposition of the metallic derivative, occurring with an elimination of water and addition of that reagent to the alkylidene-alkylamines that are thus formed.

Halhydric acid is eliminated with facility when the halogen and hydrogen of the chloro-amines are conversely distributed in a compound, *i. e.*, the first element attached to the carbon and the latter to the nitrogen. When hydroxyl replaces halogen in such products, the structures are unstable under ordinary conditions as they isomerize to amides, but there can be no doubt that the elimination of water from amides takes place through the desmotropic hydroxyl form. According to the le Chatelier-van't Hoff equilibrium law, an organic substance with the increment of heat energy may, (1) pass over into the liquid or gaseous condition, (2) change its structure into an isomer with a greater content of free chemical energy, which may occur before, but usually after, the change in the state of aggregation, or

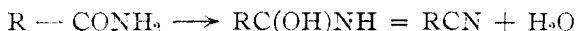
<sup>1</sup> Ebler and Schott, *J. prakt. Chem.*, [2], 78, 336-338 (1908).

<sup>2</sup> Adam and Overman, *THIS JOURNAL*, 31, 637 (1909).

<sup>3</sup> Tanatar, *Z. physik. Chem.*, 40, 475 (1901); 41, 37 (1902); Ebler and Schott, *loc. cit.*, 335.

<sup>4</sup> Kirpal, *Ber.*, 25, 1715 (1892).

undergo a chemical decomposition, which may take place before or subsequent to (2). If water may be eliminated by heat from the amide of a monobasic acid, Process 3 must occur after 2, for the carbonyl-oxygen will acquire free chemical energy with the absorption of heat energy until it possesses a sufficiently greater attraction for hydrogen than the nitrogen has as to cause an isomerization, in accordance with the above principle, from the carbonyl into the enol structure. And, if a reactive hydrogen is available, a condensation with elimination of water should then place. An amide, therefore, before losing water to form a nitrile, must pass over into the more energetic enol derivative,



and the first phase in the decomposition is favored by the increasing affinity of hydrogen for oxygen over that for nitrogen with rise of temperature.<sup>1</sup>

According to Jones, the amine oxides "furnish many interesting illustrations of intramolecular and intermolecular oxidation."<sup>2</sup> "Thus, trimethylamine oxide readily decomposed in 2 ways: (a) to give trimethylamine and oxygen gas; (b) to give formaldehyde and dimethylamine."<sup>3</sup> Further, that Dunstan and Goulding 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," and that, according to Hantzsch and Hillard,<sup>4</sup> trimethylamine oxide loses oxygen on contact with silver oxide, and its properties "remind one of hydrogen peroxide." In regard to the facile decomposition of trimethylamine oxide, Dunstan and Goulding<sup>5</sup> mention that when the hydrated product is "heated above 110°, water is expelled, and near 180° it suffers complete decomposition; formaldehyde and trimethylamine being among the products."<sup>6</sup> The

<sup>1</sup> It was shown some years back (Michael, *Am. Chem. J.*, 14, 533 (1892)) that all condensations occurring with an elimination of water, which take place in an intermolecular system and involve a carbonyl group, proceed primarily with the aldolization of that group. A similar law evidently applies to all intramolecular dehydrations in carbonyl derivatives, irrespectively whether the primary enolization or aldolization process takes place with absorption of heat energy, or of chemical energy, *i. e.*, by the union of the substance with the reagent to form "polymolecules" (THIS JOURNAL, 42, 798 (1920)). The actual dehydration must occur in the hydroxyl derivative, with the formation of an unsaturated or a cyclic substance, according to the structure of the compound. Reversely, an addendum containing more than one available hydrogen must always separate between a single hydrogen and the remaining radical. Thus, water and ammonia add by separating into hydrogen and the hydroxyl and amino groups, never, as is often assumed, into H<sub>2</sub> and O, resp. NH.

<sup>2</sup> THIS JOURNAL, 36, 1273 (1914).

<sup>3</sup> Jones, *loc. cit.*, p. 1274.

<sup>4</sup> Hantzsch and Hillard, *Ber.*, 31, 2058 (1898).

<sup>5</sup> Dunstan and Goulding, *J. Chem. Soc.*, 75, 796 (1899).

<sup>6</sup> *Loc. cit.*, p. 806.

formation of formaldehyde involves that of dimethylamine, which must have been at least a considerable constituent of the basic product; as the latter does not appear to have been analyzed, no direct proof of the formation of trimethylamine, or of oxygen, has been given.<sup>1</sup> The statement by Jones, quoted above, on the "active" condition of the oxygen in the amine oxide, could not be found in the papers of Dunstan and Goulding. These chemists, quite to the contrary, in summing up the properties of the hydrated amine oxide, state "that there is no evidence to show that the oxygen atom is in the 'active' condition analogous to that of the oxygen atom in hydrogen peroxide."<sup>2</sup> And, that the corresponding triethyl and tripropyl derivatives have similar properties; the latter substance showing no "evidence of being a powerful oxidizing agent."<sup>3</sup> The anhydrous trimethylamine oxide is even more stable towards heat than the hydrated product, as it sublimes at  $180^{\circ}$  *in vacuo*, and melts at  $208^{\circ}$ , apparently with only slight decomposition.<sup>4</sup> In regard to the quotation by Jones from the research of Hantzsch and Hilliard, it was shown by Dunstan and Goulding<sup>5</sup> that those chemists worked with an impure preparation of the hydrated trimethylamine oxide, as the pure substance does not reduce Fehling's solution or set free iodine from potassium iodide, like hydrogen peroxide, and the accuracy of their observations on its properties is "entirely" questioned.

An oxidizing capacity in these compounds is apparently shown in the conversion of ferrous sulfate into ferric hydrate. The first phase in this reaction consists in the formation of ferrous hydrate and the sulfate of the amine oxide, and the further course of the reaction corresponds to that discussed above in the analogous hydroxylamine reaction, only in this case the methyl groups give a much greater stability to the compound towards oxidation and catalysis, and trimethylammonium sulfate is the main organic product formed in the reaction.

In further evidence of the oxidizing power of the amine oxides, the behavior of the *N*-alkylpiperidine oxides on heating is quoted by Jones.<sup>6</sup> It is stated that the methyl derivative "showed, according to Wernick and Wolfenstein,<sup>7</sup> 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." Further,<sup>2</sup> that the ethyl derivative "when heated decomposed into ethylpiperidine, "oxygen," ethylene and  $\delta$ -aminovaleric aldehyde,

<sup>1</sup> For an analysis of this reaction, see THIS JOURNAL, 42, 1237 (1920).

<sup>2</sup> Dunstan and Goulding, *loc. cit.*, p. 806.

<sup>3</sup> *Loc. cit.*, p. 1009.

<sup>4</sup> Meisenheimer, *Ann.*, 397, 287 (1912).

<sup>5</sup> *Loc. cit.*, p. 806.

<sup>6</sup> *Loc. cit.*, p. 1273.

<sup>7</sup> *Ber.*, 31, 1557 (1898).

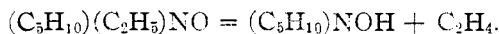
and that latter product "resulted by a process of intramolecular oxidation."

It was not possible to confirm all of these statements in the literature on the subject. Wernick and Wolfenstein<sup>1</sup> heated the methyl and ethyl derivatives to 200° in a sealed tube with hydrochloric acid, saturated at 0°, and, by this drastic treatment, were able to prove the formation of the corresponding alkyl piperidines and alkyl chlorides. The latter substances must have been formed with the separation of the alkyl group from the nitrogen atom; what became of the oxygen was not established, but it could not have been present as free oxygen, since the tubes opened under "a slight pressure only." These chemists found, further, that hydrogen chloride reacts upon the methyl derivative; not, as stated by Jones, when it "was passed through it, or when it was gently heated," but explosively at temperatures between 180° and 230°; the formation of N-methyl-piperidine was proven by the analysis of the double platinum salt, and a small yield of methyl chloride was noticed. Evidently it is not a question of the decomposition of the base in these reactions but of the hydrochlorides, and no experimental indication of the fate of the oxygen was offered.

It is not permissible, however, to conclude from this behavior of the hydrochloride in presence of hydrogen chloride and at a comparatively high temperature, that the amine oxide parted with its oxygen "when a stream of hydrochloric acid was passed through it." The excess of negative chemical energy introduced by the acid loosens the affinity of the oxygen for the nitrogen, and the structure permits, in the formation of hydrochloride of the far more basic methyl-piperidine, a much better neutralization of the chemical forces. That the affinity-energy relations in the salt decidedly affect the course of decomposition is evident from the behavior of N-ethyl-piperidine oxide on heating, when at 142° an energetic evolution of ethylene takes place, and some ethylpiperidine is

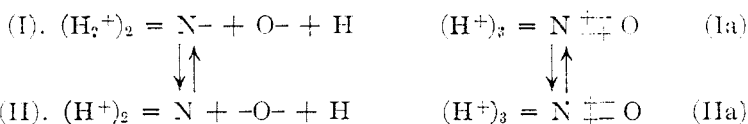
<sup>1</sup> Wernick and Wolfenstein, *Ber.*, 31, 1555 (1898). The fatty amine oxides obtained by Wolfenstein were not prepared in a pure state, and, therefore, were not analyzed; the products used in the experiments may have contained the hydrated oxides, and an impurity that occasioned the setting free of iodine from potassium iodide in the case of the tripropyl derivative (*ibid.*, p. 1559). The hydrated trimethyl amine oxide also showed such oxidizing properties in an impure state, but not when pure. (Dunstan and Goulding, *J. Chem. Soc.*, 75, 806 (1899)). Bamberger and Tschirner (*Ber.*, 32, 342 (1892)) found that dimethylaniline oxide melts at 153° under decomposition, to give formaldehyde, mono- and di-methylaniline and other products. In agreement with the above theoretical considerations, the acid sulfate on heating (Bamberger, *ibid.*, 1882) yields the acid sulfates of the stronger basic dimethylaniline and *o*- and *p*-dimethyl-aminophenol. This instance of "intramolecular oxidation" is evidently connected with the ease of nuclear oxidation in such tertiary aromatic bases, and that the affinity of the oxygen for the nitrogen in these aromatic amine oxides is less than in the fatty compounds.

formed, but mainly "δ-aminovaleric aldehyde." The latter product is not, as Jones stated, an aldehyde, for he overlooked a later paper,<sup>1</sup> where it was shown that it is not formed by intramolecular oxidation, as the supposed amino aldehyde is cyclo-pentamethylene-hydroxylamine.<sup>2</sup> That phase of the reaction proceeds, therefore, with the migration of hydrogen to the oxygen of the NO group, *i. e.*, a reaction similar in its nature to the isomerization process in other NO derivatives:



And, it is an admirable illustration of the capacity of the NO group to perform chemical work, as the splitting off of ethylene is without doubt aided by the considerable content in free chemical energy in the group, and the affinity for hydrogen residing in the oxygen atom.

According to Stieglitz,<sup>3</sup> "Convincing evidence of the separate existence of electromers has been uncovered by L. W. Jones<sup>4</sup> in a brilliant critical review of the chemistry of hydroxylamine derivatives." It was shown in a previous paper,<sup>5</sup> that such "electromers" are not known, and it is of interest to examine the other evidence and further explanations, that this chemist has brought forward in this paper in support of the view that hydroxylamine behaves "tautomericly in the electronic sense," and in "the ordinary structural sense."<sup>6</sup> To explain the properties of hydroxylamine, Jones<sup>7</sup> assumes that the hydrogens function positively, and represents the "electronic equilibrium" of the base as follows:



"Since the hydroxyl group in Formula I is positive," that form cannot lose water, but the elimination may take place in Formula II, forming "active imide,"  $H + -N \overset{+}{\equiv}$ , a powerful reducing agent, which would combine with the oxygen given by the amine oxide, Formula Ia, or with oxygen of the air or other oxidizing agents "to give  $H + -M \overset{+}{\equiv} O$ , an electromer of hyponitrous acid. The form HNO would rearrange to give hyponitrous acid, or nitrous oxide and water."<sup>8</sup> "In the presence

<sup>1</sup> Wernick and Wolfenstein, *Ber.*, 31, 1566 (1898).

<sup>2</sup> Haase and Wolfenstein, *ibid.*, 37, 3228 (1904).

<sup>3</sup> Stieglitz, *THIS JOURNAL*, 38, 2052 (1916).

<sup>4</sup> *Loc. cit.*, p. 1268.

<sup>5</sup> Michael, *THIS JOURNAL*, 42, 1232 (1920).

<sup>6</sup> Jones, *loc. cit.*, p. 1269.

<sup>7</sup> *Ibid.*, 1279.

<sup>8</sup> Some of these statements are difficult to follow, as " $H + -N \overset{+}{\equiv} O$ " is not "an electromer of hyponitrous acid," nor is it possible for such a structure to "rearrange" to give that acid.



of an active oxidizing agent,"<sup>1</sup> the oxygen may be taken "largely or exclusively" from it, and "that, especially in acid solution, this might force the hydroxylamine to react almost quantitatively through the dissociation product,  $H + -N^{\pm}$ , to give nitrous oxide."<sup>1</sup> It may, also, 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."<sup>1</sup>

These statements are coupled with improbable and impossible assumptions. There is no experimental indication of the existence of hydroxylamine or its derivatives in electronic forms, nor, as is shown above, of hydroxylamine in the amine oxide form. But, even if we suppose that hydroxylamine is a mixture of the tautomeric forms, it would not make the above explanations more probable. For, the amine oxide form should not "readily dissociate into 'active oxygen' and ammonia," supposedly in conformity with the tertiary amine oxides, as it was shown above that Jones' views on the decompositions of the latter group of substances is based on an imperfect knowledge of the literature. Again, there is as yet no experimental proof that hydroxylamine is an oxidizing agent in the accepted sense of the term, and the formation of nitrous oxide through that of the hypothetical "*active imide*" and of HNO does not appear possible. For, nitrous oxide is scarcely formed in the explosive decomposition of hydroxylamine,<sup>2</sup> which is the most favorable condition for its production, if the base decomposes into "*active imide*" and free oxygen. Equally difficult to understand is the explanation accounting for the production of nitrogen. Whether hydroxylamine decomposes fairly rapidly or explosively the products of decomposition consist of nitrogen, ammonia, water and perhaps a very little nitrous oxide.<sup>2</sup> Jones' assumption, that the formation of nitrogen depends upon the "speed of spontaneous decomposition"<sup>1</sup> being relatively slow, and, that hyponitrous acid may not only exist under such thermal conditions, but may unite with hydroxylamine, is inconsistent with experimental data. Hyponitrous acid is exceedingly unstable, even at a low temperature, and, at the high temperature of the rapid decomposition of hydroxylamine, it should at once decompose into water and nitrous oxide; but, even supposing it remained stable and reacted with a base, it should be largely upon the much stronger basic ammonia, when nitrous oxide, and not nitrogen, should be formed. Finally, it is not easy to understand why the oxygen of an oxidizing agent should be able or have to "force" hydroxylamine and its salts to dissociate into water and " $H + -N^{\pm}$ ," or into these products and an acid. The salts represent stable compounds, and to assume that oxidizing

<sup>1</sup> *Loc. cit.*, p. 1281.

<sup>2</sup> De Bruyn, *Rec. trav. chim.*, II, 27 (1892).

agents are capable of breaking them up in such a manner, in order to react upon a purely hypothetical radical, cannot be reconciled with their properties or with our present knowledge of the oxidation process.<sup>1</sup>

### Summary.

All the properties of hydroxylamine, those of its derivatives and salts, conform with and can only be satisfactorily explained by the hydroxyl structures. There is as yet no indication of the existence of such products in tautomeric amine oxide forms, which, for energy and affinity reasons, under ordinary conditions, should represent labile substances.

The chemical resemblance between hydroxylamine and hydrogen peroxide is superficial, and is without value in establishing the structure of the base. No theoretical nor experimental evidence is known pointing to the existence of hydroxylamine, its derivatives, salts, or hydroxylammonium products<sup>2</sup> in "electromeric" modifications, and the "electronic" explanations of the reactions of these compounds are not tenable.

Hydroxylamine, its alkyl derivatives and the trialkylamine oxides, are not oxidizing agents in the accepted sense of the term, and there is no reason for supposing that the hypothetical  $H_2NO$  would act as such a reagent. The property is somewhat more developed in the salts with strong acids. This is due to the decrease in the affinity between the nitrogen and the hydroxyl-oxygen, with the increase in the free negative chemical energy accompanying salt formation, and the possibility of a large increase of entropy with the generation of the corresponding ammonium salt.

All intra- and intermolecular condensations occurring in organic compounds with a loss of water or ammonia and involving a carbonyl- or nitrosyl group, proceed in the first phase through an enolization, or an aldolization of these radicals. The direct formation of water or ammonia by the union of a carbonyl- or nitrosyl oxygen with several hydrogens is energetically impossible, for the affinity and free chemical energy conditions reside in these oxygen atoms, which are necessary to overcome the chemical hindrance to the change, *i. e.*, the bound chemical energy between the migrating hydrogen and the atoms to which it is joined. Reversely, water, ammonia or other addenda with more than one available hydrogen, always function by separating into a single hydrogen and the remaining radical.

CAMBRIDGE 38, MASS.

<sup>1</sup> The oxidation of primary and secondary amines proceeds with the interception of oxygen between the nitrogen and hydrogen, and with the formation of the corresponding hydroxylamines (Bamberger, *Ber.*, **35**, 4293, 4299 (1902); **36**, 685, 701, 710 (1903); Dunstan and Goulding, *J. Chem. Soc.*, **85**, 1005 (1899); Mamlock and Wolfenstein, *Ber.*, **33**, 159 (1900); **34**, 2494 (1901)).

<sup>2</sup> See THIS JOURNAL, **42**, 1232 (1920).