ferric hydroxide when treated with sulfuric acid or the electric current, and obeyed the characteristic tests for colloids. Dialysis gave the crystalloids which were analyzed and found to be, in each case, the nitrate of the metal. In fact the colloids formed by starting directly with ferric nitrate were deeper in color than when nitric acid was employed to first form the nitrate.

The conclusions arrived at are: that hydrolysis was temporarily possible only at the boiling temperature when nitric acid was present in excess; that the addition of a metal combining with the nitric acid formed as a product of the reaction, when the nitrate was used; and with the excess acid when ferric nitrate was formed in the presence of the free acid, favored hydrolysis by destroying the effect of the nitric acid present; that the most favorable condition under which colloidal ferric hydroxide is formed would be one in which the nitric acid was completely removed; and that the finer the state of division of the metal which is used to remove the nitric acid, the deeper red the colloidal solution, since the completeness of the removal of the nitric acid would favor the degree of hydrolysis of the ferric nitrate to colloidal ferric hydroxide.

Experiments are also being carried out to determine whether the nitrates or other salts of the metals would behave similarly, or whether the metals in the electromotive series could be advantageously employed, as was the case with iron and copper salts, to bring about colloidal reactions by precipitating a metal from its solution by one that is more electropositive.

COMMERCIAL HIGH SCHOOL, CHEMICAL LABORATORY,
BROOKLYN, N. Y.

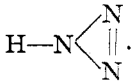
THE REDUCTION OF HYDRONITRIC ACID. II. THE STRUCTURES OF THE TRINITRIDE RADICLE.

BY J. W. TURRENTINE.

Received November 12, 1913.

It is the purpose of this paper to show that Fisher's interpretation of the reaction yielding diazobenzeneimide, on which is based the conception of the cycloid structure of the trinitride radicle, is erroneous, since that reaction in all essentials is an oxidation of hydrazine; that in no instance where the oxidation of hydrazine has been studied has a reaction been observed analogous to the one in this case proposed by Fisher. It will be maintained that the interpretation of a reaction which is open to such doubt can not be taken as a sufficient basis for the structure of a compound resulting from this reaction. A new open-chain structure will be proposed for the trinitride radicle and evidence adduced from new reactions observed in a study of the reduction of hydronitric acid and its salts will be brought to bear in support of that structure.

Historical.

Curtius[1] first prepared hydronitric acid from its sodium salt, obtainable from benzoyltrinitride by saponification with sodium hydroxide. Fisher[2] had ascribed the cycloid form to the trinitride group of diazobenzeneimide, previously suggested by Kekulé,[3] from which Curtius logically concluded that the structural formula for free hydronitric acid was  $\mathrm{H{-}N}\Big\langle\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}$.

Fisher prepared diazobenzeneimide, formerly described by Griess,[4] by heating phenylnitroso-hydrazine in a dilute solution of potassium hydroxide. He expressed the reaction by the equation,

$$C_6H_5.N_2H_2.NO = C_6H_5.N_3 + H_2O,$$

and regarded it merely as a splitting-off of water, or a dehydration. Phenylnitroso-hydrazine was prepared from phenylhydrazine hydrochloride by treatment, in cooled solution, with sodium nitrite,[5] as indicated by the equation:

$$C_6H_5.N_2H_3.HCl + NaNO_2 = C_6H_5.N_2H_2.NO + NaCl + H_2O.$$

In hot solution, or in acid solution, the reaction would have gone directly to diazobenzeneimide.[6] Phenylnitrosohydrazine, therefore, can be regarded as an intermediate oxidation product of phenylhydrazine to diazobenzeneimide, or of hydrazine to hydronitric acid. Concentrated sulfuric acid and a few related reagents are capable of extracting the water-forming elements from compounds, but dilute caustic potash can scarcely be so regarded. On the contrary, it is rather a hydrolyzing or saponifying agent. The reaction, then, could not have been a splitting-off of water, but since water was a product of the reaction through the combination of oxygen and hydrogen, it was an oxidation (or reduction).

Superficially, it would appear that the oxidation was intramolecular. It probably is of little moment whether the reaction was intramolecular or resulted from the interaction of the saponification or hydrolysis products of phenylnitrosohydrazine. The reaction, it is maintained, is an oxidation of an organic derivative of hydrazine; and it will be shown in the following paragraphs that the oxidation of hydrazine, or its derivative, yields ammonia, or its derivative, as an additional oxidation product wherever hydronitric acid or its derivative has been produced by that oxidation. There is no reason to suppose that this reaction is an exception.

---

[1] *Ber.*, **23**, 3023.

[2] *Ann. Chem.* (*Liebig*), 190, 67.

[3] *Lehrbuch*, **3**, 230.

[4] *Ann.* (*Liebig*), 137, 65.

[5] Fisher, *Loc. cit.*

[6] Altschult, *J. prakt. Chem.*, [2] **54**, 496.

The Oxidation of Hydrazine.

Inorganic.—Due to the researches of Browne and Shetterly on the oxidation of hydrazine[1] it now has become possible to classify the reactions between hydrazine and the oxidizing agents containing no oxynitrogen radicle into three groups: (1) those yielding fairly large amounts of hydronitric acid and ammonia; (2) those yielding little or no hydronitric acid, but large amounts of ammonia, and (3) those yielding little or no hydronitric acid and ammonia.[2] The main point brought out in this investigation, having a bearing on the present discussion, is that, in every instance where hydronitric acid was a product of the oxidation of hydrazine, ammonia also was evolved. This work, as well as that of certain others, also emphasizes the fact that when hydrazine is oxidized by this class of oxidizing agents there is a strong tendency for ammonia to be formed. In fact, in every instance where the oxidation of hydrazine is not complete, that is, does not go completely to nitrogen and water, ammonia is a product of the reaction.

In the work of Browne and Shetterly, ammonia was looked for among the products of the oxidation by 24 oxidizing agents, and in 23 instances it was found to be present. In the 24th case, the oxidation by mercuric chloride, ammonia could not be identified positively. In one other case, that of the oxidation by cupric sulfate, ammonia was present only in traces.

The oxidation of hydrazine by oxidizing agents containing the oxynitrogen group, or a group made up of nitrogen united to negative elements, does not lend itself to such a satisfactory classification. This, probably, in the main, is due to the lack of systematic study of the reactions involved. From an examination of the literature of the subject it becomes evident that in some cases the same reacting substances have given entirely different and even contradictory results in the hands of the different investigators.

Angeli[3] obtained a precipitate of silver trinitride when he allowed silver nitrite, in cold saturated solution, to react with a saturated hydrazine sulfate solution. He proposed the following equation to represent the reaction:

$$H_2N.NH_2 + NO_2H = H_2NN : NOH(+ H_2O) = N_3H + H_2O.$$

Ammonia appears not to have been looked for among the reaction products. Dennsted and Göhlich[4] prepared hydronitric acid from hydrazine sulfate and potassium nitrite in sulfuric acid solution. The presence of ammonia

---

[1] THIS JOURNAL, **29**, 1305 (1907); **30**, 53 (1908); **31**, 221 (1909); **31**, 783 (1909).

[2] *Ibid.*, **31**, 783 (1909); cf. p. 793.

[3] *Ber.*, **26**, 885 (1893); *Atti accad. d. Lincei Roma*, [5] **2**, I, 569; *Chem. Centr.*, **1893**, II, 559.

[4] *Chem. Ztg.*, **21**, 876; *Chem. Centr.*, **1897**, II, 1073.

was not noted among the products of the oxidation. The resulting reaction is expressed as follows:

$$3N_2H_4.H_2SO_4 + 6KNO_2 + 3H_2SO_4 = 3N_3H + 8H_2O + 6KHSO_4 + 2O + 2N_2O.$$

Tanatar[1] oxidized hydrazine with nitrogen trichloride in alkaline solution. A gas, supposedly nitrogen, was evolved. The presence or absence of ammonia was not mentioned. De Girard and de Saporta[2] employed hydrazine in the determination of copper sulfate and sodium nitrite. The following equation is given to represent the reaction taking place between hydrazine and sodium nitrite:

$$N_2H_4.H_2SO_4 + 2NaNO_2 = N_2 + Na_2SO_4 + 2NOH.$$

It is not stated that ammonia was looked for. In striking contrast with this equation is that proposed by Dennsted and Göhlich, above. In both instances the reaction was carried out in acid solution, hydrazine sulfate, as is well known, gives an acid reaction. Francke[3] records the formation of ammonia as the result of the oxidation of hydrazine by nitrous acid, and has determined the following equation to be a quantitative expression of that reaction:

$$N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O.$$

This equation again is in striking contrast with those proposed by Dennsted and Göhlich and by de Girard and de Saporta. M. J. Brown[4] corroborates Francke's observation relative to the formation of ammonia from the action of nitrous acid on hydrazine (potassium nitrite in sulfuric acid solution), but notes also that hydronitric acid is produced. Thus, practically the same reacting substances, under approximately similar conditions, have yielded four dissimilar sets of results in the hands of as many different experimenters. Thiele[5] observed the formation of hydronitric acid as the result of the action of a nitrite on hydrazine in alkaline solution. No reference is made in the account of the experiment to the simultaneous production of ammonia.

In every case where it is definitely known that ammonia was looked for among the products resulting from the oxidation of hydrazine by the class of oxidizing agents under discussion, ammonia was found. In the one case where ammonia was looked for as an additional oxidation product to hydronitric acid, ammonia was found. This fact appears significant. In the instances cited, ammonia, if not looked for particularly, would have escaped the notice of the investigator. Only a negative result to a definite test can be taken to mean its absence. However, it is scarcely

---

[1] *Ber.*, 32 1399 (1899).

[2] *Chem. Centr.*, 1904, II, 731.

[3] *Ber.*, 38, 4102 (1905).

[4] THIS JOURNAL, 31, 792 (1909); cf. footnote 6.

[5] *Ber.*, 41, 2681 (1908).

justifiable, in the absence of such tests, to assume the formation of ammonia in every case, however grateful to the argument such an assumption would be, or however strongly such an assumption might appear to be warranted.

The oxidation of hydrazine by that class of oxidizing agents containing no nitro-group is susceptible of such precise classification, and the reactions resulting readily fall into such distinct types, that one is surprised that an analogous classification is not possible with the oxidizing agents containing the nitro-group. It is strongly indicated that a full understanding of the chemistry involved would make possible such a classification, and it is believed that the reaction recorded by M. J. Brown would be typical of a group instead of an isolated instance as it now stands. Still, other results, at variance with that of Brown might ensue through secondary reactions involving the two products of the oxidation, NH_3 and HN_3, causing the elimination of one or the other. On the other hand, it must be admitted that a simultaneous oxidation by the oxygen and nitridation by the nitrogen of the oxy-nitrogen group might induce an entirely different order of reaction, one that is in no wise analogous that by the non-nitrogenous oxidizing agents.

Organic.—In the oxidation of organic hydrazines a similar tendency to form ammonia, or organic derivatives of ammonia, is exhibited. The analogy of the reactions of hydrazine with those of the organic derivatives of hydrazine with oxidizing agents has been pointed out by Browne and Shetterly.[1] Fisher[2] obtained benzene and aniline as the products of the oxidation of phenyl hydrazine by Fehling's solution. Curtius[3] has reviewed a number of reactions involving the oxidation of hydrazine, in all of which ammonia and hydronitric acid, in the form of their derivatives, are formed. Chattaway and Aldridge,[4] in the intramolecular oxidation (reduction) of organic hydrazines, found that (*a*) a primary hydrazine yielded a primary amine, nitrogen and ammonia; (*b*) an unsymmetrical secondary hydrazine yielded a secondary amine, nitrogen and ammonia, and (*c*) a symmetrical secondary hydrazine yielded a primary amine and an azo-compound. In the case of each of the six hydrazines of the various types studied, ammonia or a derivative was an invariable product of the oxidation.

Since the work of Chattaway and others has shown that invariably the intramolecular oxidation of organic hydrazine derivatives results in the formation of ammonia or its derivatives, it is indeed anomalous that ammonia was not a product—if it was not—of the reaction recorded by Fisher. To regard the reaction, as one must, as an oxidation of hydrazine,

---

[1] THIS JOURNAL, **31**, 783 (1909); cf. p. 799.

[2] *Ann.*, **190**, 67 (1878).

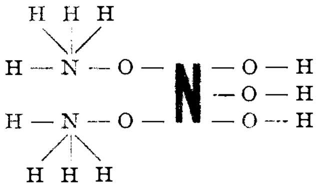
[3] *Ber.*, **26**, 1263 (1893).

[4] *J. Chem. Soc.*, **99**, **100**, 404.

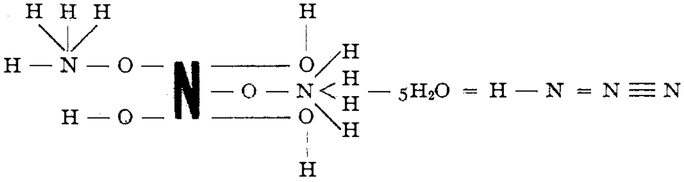
whether ammonia was formed or not, precludes the acceptance of Fisher's proof of the structure of diazobenzeneimide. To establish the formation of ammonia or a derivative in this reaction, would absolutely falsify this proof.

The Derivation of the Chain Structure from Certain Theoretical Considerations.

Mendeléeff[1] regarded hydronitric acid as theoretically obtainable from the secondary ammonium ortho-nitrate by the abstraction of five molecules of water. Erdmann[2] prepared orthonitric acid and determined its composition as $N(OH)_5$ or $N_2O_5.5H_2O$. The secondary ammonium salt would be $(NH_4)_2H_3NO_5$. Regarding the oxygen atoms of the orthonitric acid as united to hydrogen to form hydroxyl groups, the structure of the secondary ammonium salt could be represented thus:



In subtracting five molecules of water it should be true that the hydrogen atoms united to oxygen to form hydroxyl would remain so united and would go to make up a corresponding number of molecules of water. On the removal of water, then, there would remain the nuclear pentavalent nitrogen united to the nitrogen of the two ammonia groups, to one of which is attached the only remaining hydrogen atom, one which originally composed a part of an ammonia group. This hydrogen, with the nitrogen to which it is attached, forms an imide group. The result of this dehydration would have to be represented thus:



giving hydronitric acid a chain structure.

Mendeléeff[3] advanced the suggestion that one of the nitrogen atoms of hydronitric acid should be pentavalent and, in attempting to conform to the cycloid conception held by Curtius,[4] proposed the structure,

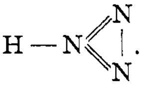
---

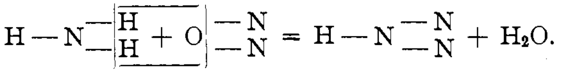
[1] "Principles of Chemistry," second edition, 1, 267.

[2] *Z. anorg. Chem.*, **32**, 431 (1902).

[3] "Principles of Chemistry," first Eng. Ed., **2**, appen. 3, 460; cf. footnote 3, p. 27.

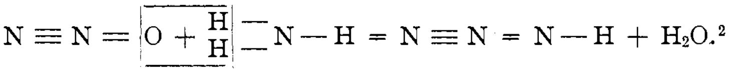
[4] *Ber.*, **23**, 3023.

 Preferring to ascribe the simplest possible valence to nitrogen, however, he suggested as more probable the structure, $H-N\begin{matrix}-N\\-N\end{matrix}$. As a further argument in favor of this formula he cited the formation of the acid from nitrous oxide, whose structure he regarded as $O\begin{matrix}-N\\-N\end{matrix}$, and ammonia:



$$H-N\begin{matrix}-\\-\end{matrix}\boxed{\begin{matrix}H\\H\end{matrix}+O}\begin{matrix}-N\\-N\end{matrix} = H-N\begin{matrix}-N\\-N\end{matrix}+H_2O.$$

If nitrous oxide is derivable, however, from primary ammonium orthonitrate, as believed by Mendeléeff, its structure must be $N \equiv N = O$. This conclusion inevitably must be reached if the line of reasoning is followed which is suggested in the analogous derivation of the structure of hydronitric acid from the secondary ammonium orthonitrate. The formation of hydronitric acid from nitrous oxide and ammonia, or more strictly, the formation of sodium trinitride from nitrous oxide and sodium amide, is the basis of the Wislicenus method of preparing hydronitric[1] acid. The structure indicated by the interaction of these substances, therefore, is of special interest as also indicating the open chain structure:



$$N \equiv N = \boxed{O+\begin{matrix}H\\H\end{matrix}}\begin{matrix}-\\-\end{matrix}N-H = N\equiv N = N-H + H_2O.^2$$

Of interest in this connection is the discussion of the structure of trimethylene, ethylene and hydronitric acid by Armstrong, who first questioned the validity of Curtius's formula.[3] Armstrong[4] considered the determination of the structure of nitrous oxide[5] of special importance, "as it is one of a group of compounds including trimethylene, ethylene and diazoimide, all of which it is the fashion at the present moment to formulate as cycloids:

---

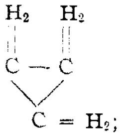
[1] *Ber.*, **25**, 2084; cf. also Dennis and Browne, THIS JOURNAL, **26**, 577 (1904).

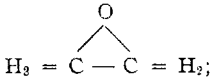
[2] In "designing" structures for compounds, one's ideas are apt to be formed from what one is able to produce on paper rather than by what, from deduction, one knows must be the conditions and relations existing within the molecule. In working out the structures supposedly resulting from the hypothetical reactions, for example, of Mendeléeff, one finds one's self attempting to draw structures wherein the oxygen atoms may be made to appear in juxtaposition to the hydrogen atoms, and, being carried away by this success, is apt to forget that chemical reactions probably take place in more than one plane.

[3] Cf. also Angeli, *Real. Accad. dei Lincei*, **16**, II, 790 (1907); **20**, I, 623 (1911).

[4] *Chem. News*, **67**, 153 (1893).

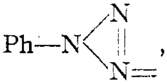
[5] Gladstone (*J. Chem. Soc.*, **45**, 241) regarded the value obtained by Liveing and Dewar for the molecular refraction of nitrous oxide as favoring the view that nitrogen in that compound has the low value which it exhibits in nitriles.



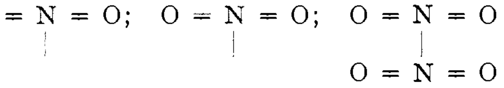


But apparently these is no valid evidence to justify the practice and it is in no way necessary to adopt such a practice."

Quoting further: "Passing now to nitriles and nitrous oxide, we have the most indefinite ideas as to the former: they are conventionally regarded as compounds of triad nitrogen, but this practice is but the outcome of formal obedience to certain artificial, dogmatic rules of valence, and has no real justification. As we must admit the existence of latent affinities in CO, which may be written $—C—O$, we may also admit the possibility of their existence in nitrogen and may represent the nitriles as compounds of the form: $X—\underset{\|}{C}—N—$. Nitrous oxide on this assumption would be $=N—O—N=$. Diazoimide in like manner, might be regarded as $=N—\underset{|}{N}—N=$, a formula which is implied in Mendeléeff's assumption that it is dinitrile."

The refractive power of the phenyl derivative of diazoimide was determined by Dr. Perkin, the results of which examination did not indicate that diazophenimide was a dinitrile, "nor is it possible to deduce from them any special argument in favor of the formula, Ph—, the problem, in fact, remains unsolved."[1]

Much evidence is at hand favorable to Armstrong's idea of the latent valence of nitrogen. Nitrogen in ammonia, for example, is commonly regarded as trivalent, yet it shows a marked tendency to become pentavalent, without displaying any evidence of an oxidation. In fact, it may be made to change back and forth from the trivalent to the pentavalent form without an oxidation or a reduction. The same is true of both of the nitrogen atoms of hydrazine. That of nitric oxide, likewise, unites with oxygen to form the peroxide, which immediately polymerizes to a double molecule, in which the nitrogen atoms must be represented as pentavalent, as:



$$=\underset{|}{N}=O;\quad O=\underset{|}{N}=O;\quad \begin{array}{c}O=N=O\\ |\\ O=N=O\end{array}$$

Kanonikoff[2] determined the refractivity of the NO_2 group **through** measurements applied to picric acid; making allowances for the high dis-

---

[1] Armstrong, *Loc. cit.*

[2] *J. Russ. Phys. Chem. Soc.*, 1883, 434.

persive power of the latter, he concluded that the nitrogen in this group was pentatomic, with each of the oxygens united to it by a double bond.

It would be of distinct interest to see if the nitrogens in the trinitride group have the value characteristic of the nitrogen in nitric acid (5.1), or the lower value (4.1) of that in the cyanide group. The value for the trinitride group as now regarded, $—N = N \equiv N$, should be $(2 \times 4.1) + 5.1 = 13.3$; or, the first nitrogen, not occupying the terminal position, might have a still different value.

Before the discussion of the latent valences of nitrogen is concluded, it should be pointed out that nitrogen compounds enter into reactions of two distinct types, both of which involve a seeming change in valence. These are typified by the reaction of ammonia with water, or hydrochloric acid, a reversible reaction, and that of nitric acid on hydrazine, the latter a true oxidation (and reduction), and irreversible.

Experimental.

In a study of the electrochemistry of hydronitric acid and its salts,[1] certain anode reactions were observed which were explainable only on the basis of the supposition that hydronitric acid, or the trinitride ion, was acting as an oxidizing agent. Excessive anode efficiencies were obtained simultaneously with an anodic evolution of nitrogen. Ammonia and, in one case, hydrazine were found to be present in the solution which had undergone electrolysis. When certain reactions, which were supposed to be analogous to those hypothesized as taking place at the anode in trinitride solution, were induced chemically,[2] it was observed that hydronitric acid was an active oxidizing agent. Cuprous oxide in its presence became cupric trinitride, and formed ammonia and free nitrogen as the reduction products of the acid radicle. Metallic copper[3] reacted with the acid to become cupric trinitride, with the production of ammonia and free nitrogen.

The further study[4] of the free acid as an oxidizing agent established the fact that numerous metals lying below magnesium in the electrochemical series dissolved in a dilute aqueous solution of this acid with an evolution of nitrogen and gave rise to the formation of ammonia or of ammonia and hydrazine. This action is of especial importance in view of the fact that the literature dealing with the reactions of hydronitric acid

---

[1] Turrentine, THIS JOURNAL, **33**, 803 (1911).

[2] Turrentine and Moore, "The Reduction of Hydronitric Acid by Cuprous Oxide," THIS JOURNAL, **34**, 375 (1912). In this connection see "The Action of Hydronitric Acid on Cuprous Chloride and Metallic Copper," *Ibid.*, p. 382.

[3] Turrentine and Moore, *Loc. cit.*

[4] Turrentine, "The Reduction of Hydronitric Acid. I. A Preliminary Note on the Structure of Hydronitric Acid," THIS JOURNAL, **34**, 385 (1912).

states that it dissolves metals with an evolution of hydrogen.[1] Metallic compounds in which the metal exists at a lower of two possible valences, reacted with the acid and it became an oxidizing agent, giving rise to ammonia and nitrogen as reduction products. Certain oxidizable non-metallic compounds interacted with the acid and afforded as the products of the reaction, again, nitrogen and ammonia, and the negative element of the reducing agent in a higher state of oxidation.

It was found also that the acid acted as a depolarizer. Certain metals lying near the bottom of the electrochemical series, it is recalled, do not displace the hydrogen of acids, it may be said, because of the large difference between the electrode potentials of those metals and hydrogen. The reaction may be regarded as a reversible one, the reverse action taking place at a much greater rate than the direct one. A substance capable of reducing the active mass of the hydrogen—a depolarizer—prevents the reverse action and enables the direct action to proceed to completion. In the presence of the depolarizer, hydronitric acid, hydrochloric acid dissolved platinum.[2] Ammonia and nitrogen were among the reduction products.

When one examines the behavior of hydronitric acid in the reactions mentioned and attempts to bring it into line with that of other inorganic acids under like conditions, he is impressed at once with the parallelism between the chemical properties of this acid and those of nitric acid. This analogy is brought out when a comparison is made of the equations representing the reactions of the two acids with the respective reducing agents, as follows:

$$\left\{\begin{array}{ll}(1) & M^\circ + 3HN_3 = M^{II}N_6 + N_2 + NH_3 \\ (2) & 3M^\circ + 8HNO_3 = 3M^{II}(NO_3)_2 + 2NO + 4H_2O\text{[3]}\end{array}\right.$$

$$\left\{\begin{array}{ll}(3) & M_2^IO + 5HN_3 = 2M^{II}N_6 + N_2 + NH_3 + H_2O\text{[4]} \\ (4) & 3M_2^IO + 14HNO_3 = 6M^{II}(NO_3)_2 + 2NO + 7H_2O\end{array}\right.$$

$$\left\{\begin{array}{ll}(5) & 2H_2S + 2HN_3 = S_2 + 2N_2 + 2NH_3 \\ (6) & 6H_2S + 4HNO_3 = 3S_2 + 4NO + 8H_2O\end{array}\right.$$

$$\left\{\begin{array}{ll}(7) & Pt + 2HN_3 + 4HCl = PtCl_4 + 2N_2 + 2NH_3 \\ (8) & 3Pt + 4HNO_3 + 12HCl = 3PtCl_4 + 4NO + 8H_2O\end{array}\right.$$

An inspection of the first two equations brings out the following points

---

[1] While the study of the reduction of hydronitric acid was made by the writer during the academic year 1910–11, the details of the experiments yet remain to be published.

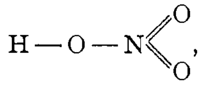
[2] Curtius and Radenhausen (*Ber.*, **23**, 3023) have observed that the action of hydronitric acid on gold and silver apparently results in their solution.

[3] While it is recognized that other products may, and do, result from the action of nitric acid on metals, those represented in the above expression are the most typical.

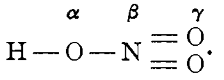
[4] Two reactions are represented by this equation, one the action of an acid on an oxide to form a salt and water, and the other, the oxidation of the metal to a higher valence.

of similarity: In neither reaction is hydrogen evolved. In both cases a portion of the acid radicle appears as a gaseous product, in one instance consisting chemically of a nitrogen atom united to a nitrogen atom, and in the other a nitrogen atom united to an oxygen atom. In the one case ammonia results, and in the other the strictly analogous substance, water, is produced. That the same analogy holds as strictly throughout the series, is quite evident without further elaboration.

Kindred elements in analogous situations in molecules lead to analogous reactions. The display of analogous chemical properties by two compounds likewise is to be taken as evidence of analogous structures—from which it follows that hydronitric acid must have a structure comparable to that of its analog, nitric acid.

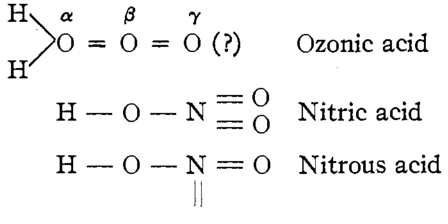
Since hydronitric acid is lacking in oxygen it must be assumed that the positions occupied by oxygen in nitric acid are occupied by nitrogen in hydronitric acid. Such a structure is expressed by the formula, $H - N = N \equiv N$, already derived from a theoretical consideration of the dehydration of secondary ammonium orthonitrate. This formulation, it may be seen, is strictly parallel to the formula,  $H - O - N\begin{smallmatrix}\diagup\!\!\!\!= O\\ \diagdown\!\!\!\!= O\end{smallmatrix}$, commonly accepted as representing the structure of nitric acid. In the one instance a pentavalent nitrogen, the nucleus of the molecule, is united to nitrogen, and in the other, to the kindred element, oxygen. In the one instance, the acid hydrogen is united to nitrogen, forming an imide group, and in the other, to oxygen, constituting an analogous hydroxyl group.

This formula assures hydronitric acid a position in the family of inorganic acids to whose names *hydro-* is not prefixed. From a comparison of the structures of these various acids, additional evidence of the reasonableness of the proposed new structure for hydronitric acid may be obtained. It is seen that in the acidic radicles of all these compounds there are three positions which, for the sake of elaboration, may be designated the α, β, and γ positions, respectively:



$$\overset{\alpha}{H - O} - \overset{\beta}{N} \overset{\gamma}{\begin{smallmatrix}= O\\ = O\end{smallmatrix}}.$$

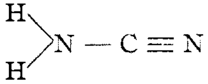
In this series one finds the various negative elements occupying in turn the various positions to form the respective acids, as follows:



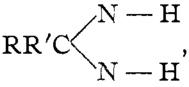
$$\begin{matrix} H \\ H \end{matrix}\!\!>\overset{\alpha}{O} = \overset{\beta}{O} = \overset{\gamma}{O}\ (?) \quad \text{Ozonic acid}$$

$$H - O - N\begin{smallmatrix}= O\\ = O\end{smallmatrix} \quad \text{Nitric acid}$$

$$H - O - \underset{\|}{N} = O \quad \text{Nitrous acid}$$

$H-O-C\equiv N$	Cyanic acid
$H-N=C=O$	Isocyanic acid[1]
$H-S-C\equiv N$	Thiocyanic acid
$H-N=C=S$[2]	Isothiocyanic acid
 $\begin{matrix}H\\H\end{matrix}\!\!>\!N-C\equiv N$	Cyanamidic acid
$H-N=N\equiv N$	Hydronitric acid

Assuming the correctness of the structures here given, it is seen that oxygen may occupy any of the three positions and in ozonic acid occupies all three at the same time. Sulfur is found in the α-position in thiocyanic acid and in the γ-position in the isothiocyanic acid. Carbon shows less mobility. Nitrogen, finally, is found in the α-position in isothiocyanic acid in the γ-position in cyanic acid and in the β-position in the fulminates. In cyanamides, it occurs simultaneously in both the α- and the γ-positions. In hydronitric acid it appears simultaneously in all three positions.

Since the announcement by the writer of his conception of the chain structure of the trinitride radicle, but before its publication in the form of a journal article,[3] Thiele[4] announced his derivation of the same structure. Thiele's deductions were based on certain experiments which showed that the condensation products of hydrazine with ketones, instead of being hydrazi-compounds,  $RR'C\!<\!\begin{matrix}N-H\\N-H\end{matrix}$, are in fact hydrazones, $RR'C=N-N=H_2$. The oxidation of the latter leads to the formation of diazo-compounds with such ease as to justify the conclusion that the hydrazones contain an open chain rather than a ring structure. Other arguments are advanced by this author, all of which are attacked by Forster,[5] who fails, however, to bring to his assistance any experimental evidence whatever and bases his arguments entirely on what appear as probabilities.

Franklin, in his interesting work on the ammonia system of acids, bases and salts,[6] frequently has referred to the amides of the respective acids as ammono-acids and has shown that the amides in their relation to ammonia are strictly analogous to the acids in their relation to water. In its bearing

---

[1] The position of the nitrogen in cyanic and isocyanic acids appears to be in some doubt.

[2] The structure assigned to mustard oils.

[3] Turrentine, *Loc. cit.*

[4] *Ber.*, **44**, 2522 (1911).

[5] "Structure of the Azoimide Nucleus," *Trans. 8th Intern. Congr. Appl. Chem.*, **6**, 108 (1912).

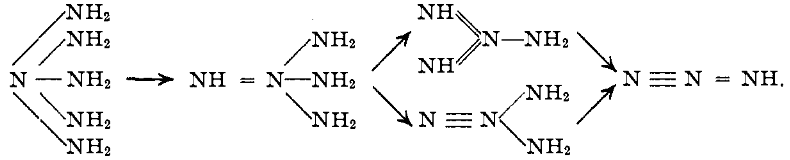
[6] *Am. Chem. J.*, **21**, 8 (1899).

on the matter under discussion in the present paper, the following quotation from Franklin[1] is of especial interest:

"More perfect analogs of the aquo acids, however, would be compounds entirely devoid of oxygen, and in which all the functions of oxygen in the aquo acids are performed by nitrogen.

"If, after the familiar manner, acetic acid, carbonic acid, and nitric acid, and their anhydrides are assumed to be derived from the normal acids of the respective formulas, $CH_3C(OH)_3$, $C(OH)_4$, and $N(OH)_5$ by successive dehydration, the formulas for strictly analogous ammono acids and their anammonides may be deduced from the hypothetical ammono acids of the formulas, $CH_3C(NH_2)_3$, $C(NH_2)_4$ and $N(NH_2)_5$.*****

"Normal ammono nitric acid and its deammonation products [are then represented] by the formulas



"The indicated successive deammonation of nitrogen pentamide is especially interesting in view of the fact that the formula of the final product is identical with that recently proposed********for hydronitric acid. The experimental work*****shows very clearly the analogy between hydronitric acid and nitric acid as acids, respectively, of the ammonia and water systems, and proves to a practical certainty the correctness of the formula $HN=N\equiv N$ for hydronitric acid."

[Contribution from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 97.]

ON THE RELATION BETWEEN THE CONDUCTANCE AND THE VISCOSITY OF ELECTROLYTIC SOLUTIONS AND ITS BEARING ON THE THEORY OF THESE SOLUTIONS.

By Charles A. Kraus.

Received October 11, 1913.

1. Introduction.[2]

That the conductance of an electrolytic solution is dependent on its viscosity was first suggested by G. Wiedemann(1)[3] in 1856. The ex-

---

[1] "The Organic Acid Amides and their Metallic Derivatives as Acids and Salts of the Ammonia System of Acids, Bases and Salts," *Trans. 8th Intern. Congr. Appl. Chem.*, 6, 119 (1912).

[2] This investigation was assisted by a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington. I wish to express my indebtedness for this assistance whereby the completion of this work was made possible.

[3] References to earlier papers will be found in the collected list of references at the end of this paper.