per quantum of light energy. The comparability of the two reactions in this regard is, therefore, in good measure established.

Between the researches here presented in their modified form and the photochemical investigations of the same chemical reaction by Bodenstein and Dux, a considerable degree of parallelism is quite evident. Any theory that aims to represent the facts of the one must evidently suggest, also, explanation of the other. The hypothesis originally put forward by Bodenstein to account for the kinetics of the photochemical reaction covers equally well the facts obtained from this radioactive study. It has, however, excited from many quarters a considerable amount of criticism, which has called for a reconsideration of the original theory. The conclusions to which such reconsideration has led will form the subject of another communication elsewhere by Professor Bodenstein, to whom is due in large part whatever material gain in knowledge the investigations herein recorded have yielded.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE OXIDATION OF HYDRAZINE. VII.

THE ALLEGED ROLE OF NITROUS ACID IN THE FORMATION OF HYDRONITRIC ACID.[1]

BY A. W. BROWNE AND O. R. OVERMAN.

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In a series of investigations[2] conducted in this laboratory, the behavior of a number of oxidizing agents toward hydrazine in aqueous solution, and usually in the presence of sulfuric acid, has been studied. On the basis of the results obtained it was found possible to classify the oxidizing agents provisionally into three groups comprising those substances that oxidize hydrazine at the boiling temperature in the presence of sulfuric acid:

(*a*) with formation of fairly large amounts of hydronitric acid and ammonia;

(*b*) with formation of little or no hydronitric acid, but large amounts of ammonia;

(*c*) with formation of little or no hydronitric acid and ammonia. Hy-

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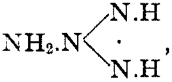
[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by O. R. Overman in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. The experimental work was completed in June, 1915.

A typewritten copy of the original thesis will be found in the files of the Cornell University Library.

[2] Browne, THIS JOURNAL, **27**, 551–5 (1905); Browne and Shetterly, *Ibid.*, **29**, 1305–12 (1907); **30**, 53–63 (1908); **31**, 221–37, 783–99 (1909); Hale and Redfield, **33**, 1353–62 (1911); Hale and Nunez, **33**, 1555–63 (1911).

drogen peroxide, potassium chlorate, and potassium persulfate were found to be typical of the first group; potassium permanganate, manganese dioxide, and hydrated ferric oxide of the second group; and potassium iodate, mercuric oxide, and mercuric chloride of the third group.

From the list of substances thus studied and classified, all of the oxidizing agents that contain nitrogen, such as, for example, nitrous acid,[1] or its salts,[2] and esters,[3] nitrogen trichloride,[4] and nitric acid[5] have been excluded. It has been shown previously by other investigators that various substances of this sort react with hydrazine under proper conditions yielding hydronitric acid. The nitrogen coupling involved in the transformation of hydrazine into hydronitric acid by means of such reactions, has hitherto been explained on the assumption that a more or less direct condensation of the oxidizing agent with the hydrazine takes place, as a result of which the nitrogen of the oxidizing agent, in certain cases at least or under certain conditions in a given case, probably participates in the synthesis of the N_3 group. In view of the very high yields of hydronitric acid obtained by Thiele and by Stollé[6] by the action of alkyl nitrites upon hydrazine hydrate in alcoholic solution, it is obvious that the nitrogen of the oxidizing agent in this case participates quantitatively in the synthesis of the N_3 group. In the opinion of the authors, however, there is much reason to doubt whether or not in aqueous solution nitrous acid behaves solely in this way. The presence of nitrous oxide and of ammonia[7] among the products of the interaction of nitrous acid and hydrazine in aqueous solution seems to indicate that a considerable part, at least, of the nitrous acid may behave after the fashion of certain oxidizing agents containing no nitrogen.

It has long been the contention of the authors and their co-workers, that the formation of hydronitric acid and ammonia in fairly large amounts from hydrazine by the action, in sulfuric acid solution, of oxidizing agents of the first class containing no nitrogen is to be explained by the initial formation of intermediate condensation products such as "buzylene," $HN:N.NH.NH_2$, or "aminotriimide,"  $NH_2.N<\begin{matrix}N.H\\ \cdot\\ N.H\end{matrix}$, which subsequently

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[1] Curtius, *Ber.*, **26**, 1263 (1893).

[2] Angeli, *Atti accad. Lincei*, [5] **2**, I, 569 (1893); *Chem. Centr.*, **1893**, II, 559; Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876 (1897); *Chem. Centr.*, **1897**, II, 1093; De Girard and de Saporta, *Bull. soc. chim.*, [3] **31**, 905–7 (1904). See also Rimini, *Atti accad. Lincei*, [5] **14**, I, 386–92 (1905); *Chem. Centr.*, **1905**, I, 1546; E. Francke, *Ber.*, **38**, 4102 (1905).

[3] Thiele, *Ber.*, **41**, 2681–3, 2806–11 (1908); Stollé, *Ibid.*, 41, 2811–13 (1908).

[4] Tanatar, *Ibid.*, **32**, 1399 (1899).

[5] Sabanejeff and Dengin, *Z. anorg. Chem.*, 20, 21 (1899).

[6] *Loc. cit.*

[7] Francke, *Loc. cit.* See also THIS JOURNAL, **31**, 783–99 (1909), p. 792, footnote 6.

decompose with formation of hydronitric acid and ammonia. The two stages of the reaction may be expressed by the following equations:

$$2N_2H_4 + 2O = N_4H_4 + 2H_2O$$
$$N_4H_4 = HN_3 + NH_3$$

In support of this hypothesis may be cited the following facts: Diazobenzenimide and aniline may be obtained[1] by the oxidation of phenylhydrazine under certain conditions. Similar products are obtainable[2] by the decomposition of certain buzylenes in accordance with the equations:

$$R_INH.NH.N{:}N.R_{II} = R_IN_3 + R_{II}NH_2$$
$$R_INH.NH.N{:}N.R_{II} = R_{II}N_3 + R_INH_2$$

Diazobenzenimide may be formed by the oxidation of phenylhydrazine[3] with hydrogen peroxide.[4]

From a consideration of the analogy between hydroxylamine and hydrazine in their behavior toward oxidizing agents, A. Angeli[5] has independently formulated an explanation of the formation of hydronitric acid as an oxidation product of hydrazine which is essentially similar to that just presented. In the opinion of Angeli the oxidation of hydroxylamine results in the formation of the unstable intermediate product "nitroxyl" which polymerizes to hyponitrous acid. This decomposes, yielding nitrous oxide and water. The entire process may be considered to take place in accordance with the following scheme:

$$\begin{matrix} H_2N.OH \\ \\ H_2N.OH \end{matrix} \longrightarrow \begin{matrix} NOH \\ \\ NOH \end{matrix} \longrightarrow \begin{matrix} NOH \\ \| \\ NOH \end{matrix} = \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>O + H_2O$$

In the case of hydrazine it is the opinion of Angeli that "diimide" is formed during the first stage of the reaction and at once polymerizes to form "tetrazone," which then decomposes, yielding hydronitric acid and ammonia. The progress of the reaction may be indicated as follows:

$$\begin{matrix} H_2N.NH_2 \\ \\ H_2N.NH_2 \end{matrix} \longrightarrow \begin{matrix} HN{:}NH \\ \\ HN{:}NH \end{matrix} \longrightarrow \begin{matrix} N.NH_2 \\ \| \\ N.NH_2 \end{matrix} = \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>NH + NH_3$$

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[1] E. Fischer, *Ber.*, 10, 1336 (1877).

[2] Curtius, *Ibid.*, 29, 759–83 (1896), p. 781. See also Wohl and Schiff, *Ibid.*, 33, 2741–58 (1900).

[3] Wurster, *Ibid.*, 20, 2631–3 (1887).

[4] From the fact that ammonia, as well as hydronitric acid, is obtained as a product of the oxidation of hydrazine with hydrogen peroxide it would seem very probable that not only diazobenzenimide but also aniline should be formed by the action of hydrogen peroxide upon phenylhydrazine.

[5] *Atti accad. Lincei*, [5] 19, II, 94–101 (1910), p. 99. This article was not published until about one year after the appearance of the fourth article in the present series of investigations on the oxidation of hydrazine (This Journal, 31, 783–99 (1909)), in which a detailed discussion of the theory here reviewed was presented. Inasmuch as no reference was made in the article of Angeli to the theory advanced by Browne and Shetterly, it is to be assumed that his conclusions were reached independently.

From this brief statement it will be at once recognized that the theory stated by Angeli is identical with that previously advanced by Browne and Shetterly, in that the formation of hydronitric acid and ammonia by the oxidation of hydrazine is explained on the assumption that intermediate condensation products of the nature of higher hydronitrogens are formed. One point of difference, however, lies in the fact that Angeli believes this intermediate product to be "tetrazone," while Browne and Shetterly have, for the reasons cited above, assumed it to be "buzylene" (or perhaps "aminotriimide"). This would seem to be justified by the fact that the derivatives of "tetrazone" yield on decomposition nitrogen and the derivatives of ammonia, while the derivatives of "buzylene" yield on decomposition the derivatives of both hydronitric acid and ammonia.

A second point of difference between the two statements of the theory lies in the assumption of Angeli that the product of the first stage of the reaction necessarily is "diimide." The authors are more inclined to believe with Browne and Shetterly that the initial product might take either the form $H_2N.N:$ or $HN^{\cdot}.N^{\cdot}H$, according as two hydrogen atoms joined to the same or to different nitrogen atoms were first removed. Polymerization of two of the unsymmetrical residues would obviously yield "tetrazone," while polymerization of two of the symmetrical residues would be expected to yield "tetrimide." The formation of "aminotriimide" would take place by the union of one symmetrical with one unsymmetrical residue. The symmetrical residues might, of course, spontaneously take the form of "diimide" but it is difficult to see how two of these "diimide" molecules could polymerize to form "tetrazone" as assumed by Angeli.

The final stage of the reaction as the result of which ammonia and hydronitric acid are obtained from the intermediate condensation product, may simply consist in an intramolecular rearrangement of this product with formation of the empirically isomeric compound,[1] ammonium trinitride, which at once in acid solution yields an ammonium salt and free hydronitric acid.

[1] There is some reason to suppose that isomeric or perhaps tautomeric forms of ammonium trinitride may be capable of existence. In the course of an investigation completed in this laboratory some months ago, but still unpublished, Mr. F. Friedrichs discovered that ammonium trinitride forms three ammonates with the respective formulas $NH_4N_3.NH_3$, $NH_4N_3.2NH_3$, and $NH_4N_3.4NH_3$. It was found that while either the monammonate or the diammonate could be readily obtained under proper conditions, neither one could be directly prepared from the other by addition or removal of ammonia; or in other words, that no inversion point at which the diammonate was transformed into the monammonate could be located although the inversion of each of the compounds into anammonous ammonium trinitride and saturated solution was readily observable. These facts may possibly point toward the existence of at least two modifications of ammonium trinitride. Efforts to separate the two forms

In explanation of the behavior of oxidizing agents of the second class, such as potassium permanganate, manganese dioxide, and ferric oxide toward hydrazine in sulfuric acid solution, it has been assumed by the authors that varying amounts of some such intermediate condensation product as "tetrazone," $H_2N.N:N.NH_2$, are formed and are subsequently decomposed, yielding nitrogen and ammonia in accordance, perhaps, with the equations:

$$2N_2H_4 + 2O = N_4H_4 + 2H_2O$$
$$N_4H_4 + H_2O = N_2 + 2NH_3 + O$$

The reactions expressed by these equations may be regarded as strictly analogous with the formation of the tetrazones[1] by the oxidation with mercuric oxide of the unsymmetrical secondary hydrazines and with their decomposition in acid solution.[2]

Oxidizing agents of the third class, such as potassium iodate, mercuric oxide, and mercuric chloride, which ordinarily do not yield appreciable amounts of either hydronitric acid or ammonia, in all probability do not yield intermediate condensation products of the type presumably formed by the action of oxidizing agents of the first and second classes. The residues obtained as the initial product of the oxidation probably undergo complete oxidation to nitrogen and water before they have had time to polymerize, or in any event even if polymerization should be effected the more complex molecules must themselves be completely oxidized before they have had time to decompose into hydronitric acid and ammonia.

In a recent article, the theory of intermediate condensation products, reviewed in the preceding paragraphs has been adversely criticized by Sommer,[3] who has presented an alternative hypothesis which, in his opinion, is less complicated and is in closer accord with the facts.

From the viewpoint of this hypothesis the oxidation of hydrazine by means of oxidizing agents such as hydrogen peroxide and potassium persulfate, which yield fairly large amounts of hydronitric acid and ammonia, may be considered to proceed in the following stages: (1) formation of ammonia as the initial oxidation product of hydrazine, (2) oxidation of the ammonia with formation of nitrous acid, (3) interaction of the nitrous acid with the excess of unchanged hydrazine with formation of hydrazine nitrite, (4) decomposition of the hydrazine nitrite, which proceeds in two

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by fractional sublimation did not, however, meet with success. In this connection it is interesting to note that Mendeléeff (*Ber.*, **23**, 3464–72 (1890)), predicted the transformation of ammonium trinitride into an isomeric form. Further experiments will be performed in this laboratory with a view to obtaining the isomers of ammonium trinitride.

[1] See, for example, E. Fischer, *Ann.*, **199**, 281–332 (1879).

[2] Renouf, *Ber.*, **13**, 2169–74 (1880).

[3] *Z. anorg. Chem.*, **86**, 71–87 (1914).

concurrent reactions, one of which yields nitrous oxide, ammonia and water and the other hydronitric acid and water.

The formation of ammonia from hydrazine can indeed be readily accomplished as pointed out by Sommer. It is possible to obtain ammonia, for example, (1) by catalytic decomposition[1] of hydrazine, (2) by reduction[2] of hydrazine, and (3) by oxidation of hydrazine. The formation of ammonia by the third of these methods, which alone is of particular importance in the present discussion, has been repeatedly observed in this laboratory as a result of numerous reactions between hydrazine and the various oxidizing agents studied. In fact, no instance of the formation of hydronitric acid as a product of the oxidation of hydrazine without the simultaneous formation of ammonia[3] has yet been recorded in this laboratory.

The ease with which ammonia may be experimentally obtained from hydrazine by various methods, however, affords no assurance that the mechanism of the reactions involved is necessarily simple. While the mechanism of the formation of ammonia and nitrogen by catalysis (which could be regarded as analogous with the formation of water and oxygen by the catalytic decomposition of hydrogen peroxide) or by reduction of hydrazine may be relatively simple, that of the formation of ammonia, which is normally to be considered a reduction product of hydrazine, as an *oxidation* product of hydrazine may well be more complicated. The splitting apart of the nitrogen atoms in the hydrazine molecule by oxidation, in the face of their strong tendency to escape in the form of molecular nitrogen, presents, to the minds of the authors at least, very nearly if not quite as difficult a problem as does the nitrogen coupling involved in the formation of hydronitric acid under these conditions. The authors find it impossible, then, to agree with Sommer that "seine Bildung über das Tetrazon zu erklären, erscheint daher sehr gezwungen." On the basis of their present knowledge of the subject the authors are unable to formulate an explanation of the formation of ammonia more satisfactory than that involving (1) the splitting off of one molecule of this substance from an unstable intermediate condensation product containing a chain of four nitrogen atoms, such as "buzylene" or "aminotriimide" the remaining three atoms of which would in either case retain

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[1] Tanatar, *Z. physik. Chem.*, 40, 475–80 (1902); 41, 37–42 (1902); A. Purgotti and L. Zanichelli, *Gazz. chim. ital.*, 34, I, 57–87 (1904).

[2] W. T. Cooke, *J. Chem. Soc.*, 19, 213 (1903).

[3] In the earliest investigation of the interaction of hydrogen peroxide and hydrazine sulfate conducted in this laboratory (THIS JOURNAL, 27, 551–5 (1905)), no attempt was made to detect ammonia in the products of the reaction. Later work upon the same reaction, however, showed conclusively that hydrogen peroxide was no exception to the general rule, but that large amounts of ammonia were formed during its interaction with hydrazine sulfate. See THIS JOURNAL, 31, 221–237 (1909), p. 231.

one hydrogen forming hydronitric acid, or (2) the splitting off of two molecules of ammonia by hydrolysis from a molecule of "tetrazone," in which case the remaining nitrogen would appear in the form of molecular nitrogen.

In view of these considerations it would seem fair to conclude that, unless Sommer can suggest a new and simpler explanation of the formation of ammonia as an oxidation product of hydrazine, his adoption of this reaction as the first stage in the process of obtaining hydronitric acid by the oxidation of hydrazine would seem to complicate, rather than to simplify, the issue.

The formation of nitrous acid by oxidation of ammonia can be effected under proper conditions. The literature of the oxidation of ammonia is very extensive. Among the investigators that have given attention to the oxidation of ammonia in aqueous solution may be mentioned the following: Loew[1] found that blue hydrated copper oxide in strong ammonium hydroxide solution oxidizes the ammonia to nitrous acid. Traube and Biltz[2] electrolyzed a solution containing ammonia, sodium hydroxide, and copper hydroxide, and found that nitrites and nitrates were formed. Müller and Spitzer[3] observed the formation of nitrites when a solution of ammonia and an alkali was electrolyzed in the presence of copper hydroxide or with an iron anode. When no alkali was present, however, a nitrite which had been added to the electrolyte was destroyed and large amounts of gaseous nitrogen were evolved. When an acid or neutral solution of ammonium sulfate was electrolyzed with a platinum anode, ammonium persulfate and hydrogen were formed. Kempf[4] allowed a solution of ammonium persulfate in a dilute solution of silver sulfate in sulfuric acid to stand at room temperature. Nitric acid was formed. In the absence of silver salts this oxidation did not take place. Levi and Migliorni[5] heated alkaline and neutral solutions of ammonium persulfate. Part of the ammonia was oxidized to nitric acid. Herschkowitsch[6] obtained nitrous acid and nitric acid by the action of potassium permanganate upon a neutral or an alkaline solution of ammonium sulfate. Brochet and Boiteau[7] electrolyzed an ammoniacal solution of ammonium carbonate and noted the formation of nitrates. Alexjew[8] electrolyzed a solution of ammonium sulfate using an anode of lead peroxide. In acid solution nitrous oxide and in alkaline solution nitrogen was formed. Reitlinger[9]

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[1] *J. prakt. Chem.*, [2] **18**, 298 (1878).

[2] *Ber.*, **37**, 3130 (1904).

[3] *Ibid.*, **38**, 778 (1905); *Z. Elektrochemie*, **11**, 917 (1905).

[4] *Ber.*, **38**, 3966–71 (1905); see also *Ibid.*, **38**, 3972–4 (1905).

[5] *Gazz. chim. ital.*, [2] **38**, 10 (1908); *C. A.*, **2**, 2912 (1908).

[6] *Z. physik. Chem.*, **65**, 93 (1908).

[7] *Bull. soc. chim. de France*, [4] **5**, 667 (1909).

[8] *Jour. Russ. Phys.-Chem.*, **41**, 1155 (1909); *Chem. Zentr.*, **1910**, I, 403.

[9] *Z. Elektrochem.*, **20**, 261 (1914).

obtained nitrous acid in a solution of ammonium hydroxide and sodium hydroxide by electrolytic oxidation. Scagliarini and Casali[1] observed anodic oxidation of ammonia in an acid medium in the presence of silver salts. Nitric acid but no nitrous acid was produced.

From the foregoing citations it will be seen that the formation of nitrous acid and even of nitric acid by the chemical or by the electrochemical oxidation of ammonia in neutral or alkaline solution has repeatedly been effected. Up to the present, however, no evidence of the formation of these substances by the oxidation of ammonia in acid solution has been found by the authors, with the exception of that furnished by the work of Kempf[2] and of Scagliarini and Casali,[2] who obtained nitric (but no nitrous acid) by the oxidation of ammonia in acid solution *in the presence of silver salts.* In connection with his investigation of the oxidation of ammonia both in alkaline and in acid solution in the presence and in the absence of silver sulfate Kempf makes the following statement:

> "Bei Abwesenheit eines Silbersalzes ist dagegen eine Persulfatlösung nicht im Stande, gebundenes Ammoniak in schwefelsaurer Lösung zu Salpetersäure zu oxidieren. Es kommt diese energische Oxydationswirkung, die der von den Salpeterbacterien ausgeübten ganz analog ist, also nur dem Silberperoxyd zu, nicht der Ueberschwefelsäure oder den aus ihr leicht entstehenden, anderen oxydierenden Agentien: dem Ozon, der Caro'schen Säure oder dem Wasserstoffsuperoxyd."

Among the conclusions drawn by Kempf as a result of his work are the following:

> (1) "Alkalipersulfat oxydirt in schwefelsaurer Lösung bei Gegenwart von Silbersulfat Ammoniumsalze schon bei gewöhnlicher Temperatur nahezu quantitativ zu Salpetersäure, (2) Bei Abwesenheit von Silbersalzen tritt diese Oxydation nicht ein."

Two references to the literature of nitrous acid were made by Sommer in support of his contention that the oxidation of hydrazine under the conditions prevailing in the experiments of Browne and Shetterly yields nitrous acid as a product of the alleged second stage of the reaction. The first reference is to a report of the work of Weith and Weber,[3] the entire text of which is as follows:

> "Die HH. Verfasser haben dagegen constatirt, dass Wasserstoffsuperoxyd und Ammoniak mit einander reichlich salpetrige Säure gaben, wodurch die Entstehung der salpetrigen Säure in der Natur eine einfache Erklärung findet."

This meager statement, which contains no information whatever concerning the conditions under which the experiment was performed, as, for example, whether the ammonia used was in the gaseous form, or was in acid, neutral or alkaline solution, has apparently been accepted by Sommer as a corroboration of his theory. The second reference is to the work of Kempf[2] who has made an explicit statement, which has already been quoted above, to the effect that in the absence of a silver salt neither

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[1] *Atti accad. Lincei,* 21, II, 726 (1913); *C. A.,* 7, 1457 (1913).

[2] *Loc. cit.*

[3] *Ber.,* 7, 1745 (1874).

persulfuric acid nor hydrogen peroxide oxidizes combined ammonia in sulfuric acid solution to nitric acid.

The reliability of the well-known Kjeldahl method[1] and its numerous modifications for the determination of nitrogen further attests the improbability of the formation of volatile nitrogen acids by the oxidation of ammonia in strongly acid solution. Powerful oxidizing agents are often used in connection with the determination of nitrogen by this method. Krüger[2] added a small excess of potassium dichromate to the mixture of the substance containing nitrogen with sulfuric acid in the digestion flask. The nitrogen determination was found to be accurate. In the determination of nitrogen in nitro and nitroso compounds[3] the compound was first reduced by heating with stannous chloride to form the amido-derivatives and then the oxidation was carried on with potassium dichromate. Dakin[4] used potassium persulfate to oxidize the organic matter rapidly and completely without loss of nitrogen. Milbauer[5] determined nitrogen in phenylhydrazine and in various hydrazones and osazones. The substances were first reduced with nascent hydrogen from zinc dust and sulfuric acid. In the case of phenylhydrazine the reduction was expressed by the following equation:

$$C_6H_5NH.NH_2 + 2H = C_6H_5NH_2 + NH_3$$

Potassium persulfate was then added and the mixture was digested. The determination of nitrogen was accurate.

From the foregoing brief review of the literature it would appear that there is but little chance that nitrous acid could be formed under any ordinary conditions by the action of oxidizing agents upon ammonia in sulfuric acid solution. In order to ascertain positively, however, whether or not nitrous acid is formed under the particular conditions prevailing in the oxidation experiments of Browne and Shetterly, the authors have conducted an experimental investigation, the results of which will be discussed under the following headings: (1) materials used; (2) general procedure; (3) details of experiments; and (4) summary.

Materials Used.—The ammonium sulfate solution used in this investi-

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[1] It has occurred to the authors that the formation of ammonia by the action of oxidizing agents in strong sulfuric acid solution upon various nitrogenous substances may be in a sense analogous to the formation of water in the presence of concentrated sulfuric acid from the hydrogen and oxygen contained in various organic substances. If we look upon the charring of such substances by the action of concentrated sulfuric acid as essentially a process of dehydration effected by the strong acid, it may not be unreasonable to regard the formation of ammonia as a process of deammonation effected by the sulfuric acid after the organic molecules have been in part broken up by the oxidizing agent.

[2] *Ber.*, **27**, 609 (1894).

[3] Kruger, *Ibid.*, **27**, 1633 (1894).

[4] *J. Soc. Chem. Ind.*, **21**, 848 (1902).

[5] *Z. anal. Chem.*, **42**, 725 (1903).

gation contained 10.18 g. of the pure salt per liter and was thus of approximately equimolecular concentration with the 1% hydrazine sulfate solution employed in this laboratory in the oxidation of hydrazine. The various oxidizing agents were employed in the form and in the concentration used in these earlier experiments. The hydrogen peroxide solution was the ordinary 3% solution, 25 cc. of which, diluted with 50 cc. of distilled water, was used in each experiment. The potassium chlorate solution contained 9.423 g. per liter, while the solution of potassium permanganate contained 6.308 g. of this substance per liter. Potassium iodate was used in the form of a solution containing 16.458 g. per liter, while mercuric chloride was used in the form of its saturated solution of which 50 cc. were taken for each experiment. The insoluble, or difficultly soluble, oxidizing agents, including potassium persulfate, manganese dioxide, hydrated ferric oxide, and red mercuric oxide, were employed in the solid form.

The standard nitrite solution used in the experiments was of such concentration that 1 cc. contained 0.001 mg. of nitrogen in the form of potassium nitrite. The reagent employed in the detection of nitrous acid was a solution of α-naphthylamine and sulfanilic acid in 30% acetic acid.[1] The distilled water used throughout the entire investigation was shown by colorimetric tests made with this reagent to contain less than 0.005 part of nitrogen in the form of nitrous acid per million parts, that is, less than 0.005 mg. of nitrogen per liter.

General Procedure.—The apparatus employed in the experiments consisted of a liter distilling flask provided with a two-hole rubber stopper, through which passed the stem of a dropping funnel and a tube for the admission of a current of air. To the side arm of this flask was sealed a Reitmeier bulb, through which communication was established with a condenser. The receiver consisted of two 250 cc. Erlenmeyer flasks in series. The flask nearer to the condenser was connected to it by means of an adapter and contained at the outset 25 cc. of water, below the surface, of which dipped the lower end of the adapter. The second Erlenmeyer flask contained at the outset 10 cc. of water, into which dipped the end of the tube through which connection was established with the first flask.

In each of the experiments recorded in Tables I and II, 100 cc. of the ammonium sulfate solution were placed in the distilling flask, 50 cc. of concentrated sulfuric acid were added, and the resulting liquid was heated almost to the boiling point. The solution of the oxidizing agent was then added at the rate of about 40 drops per minute from a dropping funnel, the tip of which extended well below the surface of the liquid in the flask. In case the oxidizing agent was insoluble or difficultly soluble in water,

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[1] E. M. Chamot and H. W. Redfield, "The Analysis of Water for Household and Municipal Purposes," pp. 23, 24, and 38 (1911) Taylor and Carpenter, Ithaca, New York.

it was introduced into the flask in solid form, and 100 cc. of the ammonium sulfate solution were poured in upon it. Then, after the mixture had been heated almost to the boiling point, the sulfuric acid was added drop by drop below the surface of the liquid. The solution in the flask was kept, in either case, at a temperature just below the boiling point during the whole time necessary to add the solution of the oxidizing agent or the sulfuric acid. The temperature was then raised to the boiling point and 100 to 150 cc. of liquid were distilled over. Throughout the entire experiment a slow current of air that had been purified by passing through Friederichs' gas washing bottles containing, respectively, concentrated sulfuric acid and concentrated potassium hydroxide solution was either drawn or forced through the apparatus. This served to keep the mixture in the flask well stirred and to sweep any volatile products of the reaction over into the receiver. After the distillation had been discontinued the liquids in the two receiving flasks were mixed and the resulting mixture was tested for nitrous acid.

In Table I are recorded certain particulars concerning the individual experiments performed with the various oxidizing agents in the attempt to obtain nitrous acid by the oxidation of ammonia. These experiments were carried out in such a way as to duplicate so far as possible in every respect the conditions that prevailed in the experiments of Browne and Shetterly on the oxidation of hydrazine. That the nitrous acid if formed even in mere traces would promptly be carried over into the receiver was demonstrated by means of a blank experiment in which a small sample of the standard nitrite solution was used.

TABLE I.

No. of expt.	Cc. H_2SO_4.	Oxidizing agent.	Amount used.	No. of expt.	Cc. H_2SO_4.	Oxidizing agent.	Amount used.
1	50	H_2O_2	25 cc. 3% with 50 cc. water	9	5	MnO_2	1.6 g.
2	50	H_2O_2	25 cc. 3% with 50 cc. water	10	5	MnO_2	1.6 g.
3	50	H_2O_2	25 cc. 3% with 50 cc. water	11	10	MnO_2	1.6 g.
4	10	$KClO_3$	67 cc.	12	25	Fe_2O_3 hydrated	2.0 g.
5	50	$K_2S_2O_8$	4.183 g.	13	25	Fe_2O_3 hydrated	5.0 g.
6	50	$K_2S_2O_8$	4.183 g.	14	10	KIO_3	50 cc.
7	50	$KMnO_4$	65 cc. with 325 cc. water	15	10	KIO_3	50 cc.
8	50	$KMnO_4$	65 cc. with 325 cc. water	16	25	HgO (red)	10.0 g.
				17	25	HgO (red)	10.0 g.
				18	25	$HgCl_2$ sat. soln.	50 cc.
				19	25	$HgCl_2$ sat. soln.	100 cc.

In no experiment were appreciable amounts of nitrous acid obtained. In several instances, it is true, traces of the acid were detected but never more than the almost infinitesimal amount present in the distilled water used. Some difficulty was experienced in the case of hydrogen peroxide and potassium chlorate, owing to the tendency for hydrogen peroxide and chlorine, respectively, to distil over into the receiver. Tests were made in all cases for nitric acid by the ferrous sulfate method, but in no case was any indication of the presence of this acid obtained.

In a second series of experiments the solution in the distilling flask, after the distillation had taken place, was in each case made alkaline and the ammonia was distilled into standard sulfuric acid. The details of these experiments, in which three oxidizing agents of the first class have been used, are given in Table II.

TABLE II.

No. of expt.	Cc. H_2SO_4.	Oxidizing agent.	Amount used.	Ammonia taken (g).	Ammonia found (g).	Percentage loss of NH_3.
20	50	H_2O_2	25 cc. 3% 50 cc. water	0.2624	0.2607	0.64
21	50	H_2O_2	25 cc. 3% 50 cc. water	0.2624	0.2612	0.46
22	10	$KClO_3$	67 cc.	0.2624	0.2593	1.18
23	10	$KClO_3$	67 cc.	0.2624	0.2586	1.45
24	10	$KClO_3$	67 cc.	0.2624	0.2604	0.76
25	50	$K_2S_2O_8$	4.183 g.	0.2624	0.2615	0.34

From these experiments the conclusion may be drawn that ammonia is practically unaffected by treatment with hydrogen peroxide, potassium chlorate, and potassium persulfate in sulfuric acid solution. The largest amount of ammonia lost in any case (Expt. 23) amounted to 1.45%. Even if this had been quantitatively converted to nitrous or to nitric acid, the quantities of these substances thus formed would not, under the most favorable conditions, produce more than a small fraction of the hydronitric acid normally obtained by the oxidation of hydrazine with any one of the three oxidizing agents under consideration. Moreover, the possibility, or at any rate the probability, of the conversion of ammonia even in small amounts to nitrous or to nitric acid under the prevailing conditions, is virtually excluded by the experiments recorded in Table I.

It might possibly be contended that the influence of the unoxidized excess of hydrazine present in each experiment on the actual oxidation of hydrazine until the oxidation was nearly complete, might in some way favor the formation of nitrous acid by oxidation of ammonia; for example, by furnishing a means for the very rapid disposal of the nitrous acid as soon as it is formed. If this be at all reasonable, and if the Sommer theory be correct, it is to be expected that the addition of ammonia to the reacting mixture should tend to increase the yield of hydronitric acid obtained, both by supplying material from which nitrous acid could be formed, and by sparing a corresponding amount of hydrazine for participation in the later stages of the reaction.

In case, however, the Sommer theory is not tenable, and the theory propounded by Browne and Shetterly is to be given credence, it would scarcely be expected that an increase in the yield of hydronitric acid should be obtained by the addition of ammonia to the reacting mixture. On the other hand, it is even possible that, by increasing the active mass of ammonia, the decomposition of the intermediate condensation products (which yield, as stated above, either hydronitric acid and ammonia, or ammonia and nitrogen) might be retarded. This would result either in permitting their complete oxidation to nitrogen and water by the oxidizing agent, or even in facilitating their preservation in the unchanged condition in the residual liquid.

In order to ascertain the effect of adding ammonia to the reacting mixture of hydrazine sulfate and hydrogen peroxide in sulfuric acid solution three preliminary experiments have been performed. These experiments (the details of which are given in Table III) were performed under conditions exactly similar, except for the addition of ammonia, to those prevailing in the experiments described below (in Table IV) and in those described in the earlier articles of this series. The ammonia was added in the form used in the preceding series of experiments, namely, in the form of a solution of ammonium sulfate containing 10.18 g. per liter. In each case the volume of this solution taken was about one-half that of the hydrazine sulfate solution. This proportion was chosen in order that in the event of the quantitative oxidation of the ammonia to nitrous acid there would be formed one molecule of this acid for each molecule of hydrazine.

The procedure consisted in mixing the hydrazine sulfate and ammonium sulfate solutions with sulfuric acid in the usual distillation flask and then slowly introducing the hydrogen peroxide as before. The receiver contained, in place of pure water, 5 cc. of a 10% solution of silver nitrate, 2 cc. of a 10% solution of sodium acetate, and 35 cc. of distilled water. After the oxidizing agent had been added (at the rate of about 40 drops per minute) the solution was boiled until all of the hydronitric acid had been distilled into the receiver. The precipitated silver trinitride was then washed by decantation and was finally collected upon an asbestos filter in a tared Gooch crucible. The crucible with the precipitate was thoroughly dried in an evacuated desiccator over concentrated sulfuric acid and was weighed. The results were as follows:

TABLE III.

No. of expt.	Cc. H_2SO_4.	Cc. $N_2H_4.H_2SO_4$.	Cc. $(NH_4)_2SO_4$.	H_2O_2.	AgN_3 gram.
38	50	67	33	25 cc. 3% 50 cc. H_2O	0.0906
39	50	100	50	25 cc. 3% 50 cc. H_2O	0.1945
40	50	100	50	25 cc. 3% 50 cc. H_2O	0.1905

In Expt. 38 about one-third of the usual amount of hydrazine sulfate was replaced by an equimolecular quantity of ammonium sulfate. On the assumption that hydrazine might be quantitatively converted to ammonia and ammonia to nitrous acid, the yield of hydronitric acid obtainable under the conditions of Expt. 38 should be comparable with that from 100 cc. of the hydrazine solution in the absence of ammonia (See

Table IV). The actual yield obtained, however, was found to be less than half of this. Since it would scarcely be fair to draw conclusions from this experiment alone, Expts. 39 and 40, in each of which the full amount of hydrazine was used, were performed; but even in these cases the yields of silver trinitride were considerably lower than the average yield obtained when ammonium sulfate was absent. The average yield of silver trinitride obtained in the seven experiments on the oxidation of hydrazine by hydrogen peroxide in the absence of ammonia recorded in Table IV amounts to 0.2327 g. (max. 0.2468 g., min. 0.1891 g.). The results are entirely negative so far as any possible corroboration of the Sommer theory is concerned. The authors, however, do not venture to say, at the present stage of the work, that they afford distinct support to the theory of intermediate condensation products at present accepted in this laboratory. Further work on the influence of ammonium sulfate upon the yields of hydronitric acid and ammonia will be carried on, especially in the attempt to effect the isolation of the intermediate products by retarding their decomposition.[1]

Since the failure to demonstrate the oxidation of ammonia to nitrous acid in sulfuric acid solution is very unfavorable, if not quite fatal, to the main contention of the Sommer theory, there is no need of discussing in detail in the present article the final stages of the reaction between hydrazine and oxidizing agents that contain no nitrogen, as they have been assumed to take place by Sommer. It is of course true that nitrous acid, if present, would oxidize hydrazine in acid solution under proper conditions to hydronitric acid. The interaction of these substances has been investigated during the past few years by a number of workers. In the opinion of de Girard and de Saporta[2] the reaction takes place as follows:

$$N_2H_4 + 2HNO_2 = N_2 + 2NOH + 2H_2O$$

E. Francke[2] calls attention to the formation of nitrous oxide and ammonia in accordance with the equation

$$N_2H_4HNO_2 = NH_3 + N_2O + H_2O,$$

while Dey and Sen[3] believe that the reaction proceeds quantitatively in accordance with the equations

$$N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O.$$
$$N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O.$$

In the first of his "Studien über das Hydrazin und seine anorganischen Derivate"[4] Sommer attributes the formation of hydronitric acid to the

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[1] Various experiments of widely differing character are now in progress in this laboratory in connection with the search for the higher hydronitrogens.

[2] *Loc. cit.*

[3] *Z. anorg. Chem.*, **71**, 236–42 (1911); **74**, 52–4 (1912).

[4] *Ibid.*, **83**, 119–137 (1913), p. 134.

action of undissociated nitrous acid upon hydrazine ions, perhaps in accordance with the equation

$$N_2H_5^+ + HNO_2 = HN_3 + 2H_2O + H^+.$$

In his second article[1] he explains the simultaneous formation of hydronitric acid and ammonia as a result of the decomposition of hydrazine nitrite, which he believes to take place in two concurrent reactions, one of which yields nitrous oxide, ammonia, and water, and the other hydronitric acid and water.

The divergent conclusions reached by these investigators probably indicates that their experiments have been performed under different conditions. While not prepared, at the present writing, to formulate definitely their own views concerning the mechanism of the reaction, the authors will here simply reiterate the statement made sometime ago[2] to the effect that in aqueous solution one part of the nitrous acid may simply condense with the hydrazine to form hydronitric acid, while another part may decompose the hydrazine, after the manner of certain oxidizing agents containing no nitrogen, with formation of hydronitric acid and ammonia. This second process would, in the opinion of the authors, involve the formation of unstable intermediate condensation products, while the nitrous acid itself would probably undergo reduction to hyponitrous acid or nitrous oxide. Further work on this problem will be carried out in this laboratory in the near future with the especial object in view of comparing, over the widest possible range of conditions, the behavior of typical oxidizing agents containing no nitrogen with that of oxidizing agents containing nitrogen.

In order to obtain a comparison between the behavior of hydrogen peroxide and that of nitrous acid toward hydrazine under the usual conditions prevailing in the oxidation experiments, and especially from the viewpoint of the yields of hydronitric acid and ammonia, a preliminary series of experiments has been performed. The hydrogen peroxide used was a 3% solution which had been tested and found to be free from nitrites. The potassium nitrite solution contained 6.54 g. of the salt per liter and was thus of equimolecular concentration with the solution of hydrazine sulfate which contained 10.00 g. of $N_2H_4.H_2SO_4$ per liter. The apparatus employed was similar to that used in the preceding series of experiments. The procedure was, briefly, as follows: in each case 100 cc. of hydrazine sulfate solution together with 50 cc. of concentrated sulfuric acid were introduced into the distilling flask. This mixture was heated to boiling and the oxidizing agent was introduced well below the surface of the liquid at the rate of about 40 drops per minute. In the one case 25 cc. of 3% hydrogen peroxide diluted with 50 cc. of distilled water,

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[1] *Loc. cit.*

[2] THIS JOURNAL, 31, 783–99 (1909), p. 792, footnote 6.

and in the other 150 cc. of the solution of potassium nitrite were used, except in the case of Expts. 29 and 31, in which only 100 cc. were used. The reacting mixture was kept gently boiling throughout the addition of the oxidizing agent, and efficient stirring was effected by drawing a current of air through the liquid. The yields of hydronitric acid and ammonia were determined in the manner described above. In order to insure, so far as possible, the maintenance of similar conditions throughout the comparative study of the two reactions, the experiments in the two series, with the exception of Expts. 26 and 27 were carried out in parallel with the aid of two separate pieces of apparatus. The further details of the experiments are given in Table IV.

TABLE IV.

No. of expt.	Oxidizing agent.	AgN_3 obtained (g.).	Yield HN_3 (%).	NH_3 obtained (g.).	Yield NH_3 (%).
26	H_2O_2	0.2366	40.96	......	....
27	H_2O_2	0.2457	42.55	......	....
28	H_2O_2	0.2448	42.50	......	....
29	KNO_2	0.2026	35.15	......	....
30	H_2O_2	0.2468	42.85	0.03466	52.97
31	KNO_2	0.2592	45.00	0.01463	22.35
32	H_2O_2	0.2318	40.25	0.03401	51.97
33	KNO_2	0.3035	52.69	0.00898	13.73
34	H_2O_2	0.1891	32.82	0.03579	54.69
35	KNO_2	0.3117	54.12	0.01160	17.73
36	H_2O_2	0.2340	40.37	0.03349	51.17
37	KNO_2	0.2730	47.40	0.01039	15.88

In the foregoing table the yields of hydronitric acid and ammonia have been computed on the basis of the equation

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O.$$

The oxidation of hydrazine was complete in every case except in Expts. 29 and 31. Since the first six experiments were of a more or less preliminary character the results obtained in them have not been included in the average yields given below.

The average yield of silver trinitride obtained by the oxidation of hydrazine with hydrogen peroxide in Expts. 32, 34 and 36 is 0.2183 g., corresponding to 37.81% of hydronitric acid; the average yield of ammonia amounts to 0.03443 g., or 52.61%. The average yield of silver trinitride obtained by the interaction of potassium nitrite and hydrazine sulfate in Expts. 33, 35, and 37 is 0.2961 g., corresponding to 51.40% of hydronitric acid, while the average yield of ammonia is 0.01032 g., or 15.78%.

From these results it is apparent that the yields of hydronitric acid were distinctly larger and the yields of ammonia were distinctly smaller when nitrous acid was used than when hydrogen peroxide was taken as the oxidizing agent. This might well have been expected on the supposition that in the case of nitrous acid a part of the acid simply condenses with the hydrazine to form hydronitric acid and water, the nitrogen of the acid participating in the synthesis of the N_3 group, while another part acts as an oxidizing agent with formation of intermediate condensation products which finally decompose with formation of both hydronitric acid and ammonia.

In connection with his discussion of the relative merits of the two theories, Sommer has taken occasion to state that the reference made by Browne and Shetterly to analogous reactions from the field of organic chemistry scarcely suffices to strengthen their theory. In the opinion of the authors, however, one of the most interesting chapters in the investigation of the hydronitrogens and their inorganic derivatives is that dealing with the analogy between the reactions of these substances and the reactions of their respective organic derivatives. It is, of course, well known that both hydrazine and hydronitric acid were known in the form of their organic derivatives long before they were isolated by Curtius, and that a knowledge of the properties and reactions of the organic derivatives played a vitally important part in the work of effecting their isolation. The authors are, moreover, of the opinion that future developments in the field of the inorganic hydronitrogens and particularly the discovery of new hydronitrogens will probably take place to a large extent along lines that have already been marked out by the organic chemist.

Summary.

In the investigation that has been described in the foregoing pages it has been shown:

(1) That no indication of the formation of appreciable quantities of nitrous acid or of nitric acid could be obtained by treatment of ammonium sulfate in sulfuric acid solution with oxidizing agents such as hydrogen peroxide, potassium chlorate, potassium persulfate, potassium permanganate, hydrated ferric oxide, potassium iodate, mercuric oxide, and mercuric chloride, under the conditions prevailing in the earlier experiments of Browne and Shetterly on the oxidation of hydrazine.

(2) That ammonium sulfate in a solution strongly acid with sulfuric acid is but slightly affected by prolonged treatment with such oxidizing agents as hydrogen peroxide, potassium chlorate, and potassium persulfate at the boiling temperature.

(3) That the addition of ammonium sulfate to a reacting mixture of hydrazine sulfate, sulfuric acid, and hydrogen peroxide does not increase, but rather serves to decrease, the yields of hydronitric acid obtained.

(4) That potassium nitrite oxidizes hydrazine sulfate in sulfuric acid solution with formation under comparable conditions of larger yields of hydronitric acid and of much smaller yields of ammonia than are obtained by the action of hydrogen peroxide upon hydrazine sulfate.

(5) That, in view of the experimental results obtained and of various

other considerations, the theory advanced by F. Sommer in explanation of the formation of hydronitric acid and of ammonia by oxidation of hydrazine by means of oxidizing agents that contain no nitrogen is, in all probability, to be regarded as untenable.

ITHACA, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.

[SECOND PAPER.]

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In an earlier investigation on the atomic weight of neodymium by Baxter and Chapin,[1] the material examined was purified first by crystallization of the double ammonium nitrate and then by crystallization of the nitrate from concentrated nitric acid. The first process was found particularly successful in eliminating samarium, the second in freeing the neodymium from praseodymium. The fractions in the final series were converted to chloride, which, after very careful dehydration, was analyzed by comparison with silver, with the result that the atomic weight of neodymium was found to be 144.27 (Ag = 107.880).

During the purification of the neodymium material as described above, attempts were made to free the neodymium from its companions by other methods. One of these was the fractional crystallization of the chloride. This crystallization proceeds less readily than that of either the double nitrate or nitrate, and after the process had been carried on for ten series of crystallizations little evidence of separation could be observed. At the same time another portion of the original material was converted to nitrate and fractionally crystallized from concentrated nitric acid. As the chief impurity, praseodymium, seemed to accumulate rapidly in the more soluble fractions, the portion which had been crystallized as chloride also was converted to nitrate and fractionally crystallized from nitric acid. Fractional crystallization of these two portions was carried on separately for some time, for 75 series with one portion, for 76 with the other, then the two portions were combined and further crystallized in the same way. Both the least soluble and the most soluble fractions frequently were rejected, the least soluble fraction to eliminate samarium, gadolinium, etc., the most soluble to remove praseodymium, cerium and lanthanum, for Demarçay[2] has shown that the separation occurs in this order. The least soluble fraction was thus forty times dis-

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[1] *Proc. Amer. Acad.*, **46**, 213 (1911); THIS JOURNAL, **33**, 1; *Z. anorg. Chem.*, **70**, 1.

[2] *Compt. rend.*, **122**, 728 (1896); **130**, 1021 (1900).