Vol. XXVI. [JUNE, 1904.] No. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.

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Received March 28, 1904.

THE following paper contains: I. A brief historical review of the work published up to the present time upon hydronitric acid and the inorganic trinitrides; II. An experimental study of (A) the method of W. Wislicenus for preparing hydronitric acid, (B) the composition of certain inorganic trinitrides, (C) a method for the detection of hydronitric acid and inorganic trinitrides, and (D) the reaction between hydronitric acid and potassium permanganate in the presence of sulphuric acid.

I. HISTORICAL.

Under this head will be considered (1) the methods of preparing hydronitric acid, (2) the inorganic compounds of hydronitric acid and the methods of preparing them, and (3) the properties and reactions of hydronitric acid and the inorganic trinitrides. The organic derivatives will be considered in the present work only in so far as they are of interest in the preparation of the acid.

At the outset it may be well to discuss the question of nomenclature. A variety of names for the acid and its derivatives have been used by English and American investigators and writers.

The name *azoimide* has, perhaps, been most frequently used to designate the acid. This has the disadvantage of neither expressing the acid character of the compound, nor indicating its close analogy to the halogen hydracids. Among other names which have been used are *hydrazoic acid*,[1] *triazoic acid*[2] (derivatives called respectively *azides* and *triazoates*), *hydronitrous acid*,[3] *hydrogen nitride*,[4] and *nitrogen hydride*.[5]

In the publications from this laboratory the term hydronitric acid has been employed for the following reasons:

In English usage the prefix "hydro" connotes the absence of oxygen, and acids bearing this prefix have also the termination "ic." The name employed is derived from nitrogen instead of azote, for the reason that while both are of Greek origin, nitrogen is distinctly a word of English usage, while azote is still to be regarded as a foreign word that has not yet received adoption into our language. Following the analogy between the term hydronitric acid and the names of the halogen acids, such as hydrochloric acid, the salts of hydronitric acid would normally be termed nitrides, but a distinct group of nitrides, of which potassium nitride, K_3N, may be cited as an example, has long been known. Consequently the term "trinitride" was adopted to distinguish the salts of hydronitric acid from this other group of nitrides, and the termination "ide" is employed to show that the compounds contain no oxygen. In further recognition of the analogy between the trinitrides and halides, it is suggested that the ring of three nitrogen atoms be called the nitrine group and that the hypothetical compound, $(N_3)_2$, analogous to the chlorine, bromine or iodine molecule, be called nitrine.

(1) METHODS FOR PREPARING HYDRONITRIC ACID.

The methods employed by various investigators in the preparation of hydronitric acid may be classified under five heads:

(*a*) Methods involving the action of a compound containing a chain of two nitrogen atoms united to *positive* atoms or radicals, upon a compound containing a single nitrogen atom united to *negative* atoms or radicals.

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[1] *J. Chem. Soc.* (London), **77**, 705.

[2] H. C. Jones: "Principles of Inorganic Chemistry," p. 208. The Macmillan Company, New York. 1903.

[3] "Principles of Chemistry," Vol. I, Mendeléeff. 2nd English edition by Kamensky and Lawson, p. 265. Longmans, Green and Company. London, 1897.

[4] *J. Chem. Soc.* (London), **60**, I, 56, 524.

[5] *Ibid.*, **60**, I, 394.

(*b*) Methods involving the action of a compound containing a chain of two nitrogen atoms united to *negative* atoms or radicals, upon a compound containing a single nitrogen atom united to positive atoms or radicals.

(*c*) Methods involving the simultaneous oxidation of two compounds, one of which contains a chain of two nitrogen atoms, the other a single nitrogen atom, and both of which are united to *positive* atoms.

(*d*) Methods involving the decomposition of a compound containing a chain of three or more nitrogen atoms.

(*e*) Methods involving the hydrolysis of aromatic derivatives of hydronitric acid.

A possible new class of methods, which has received as yet no experimental attention, is the converse of (*c*). This class will include methods involving simultaneous reduction of two compounds, one of which contains a chain of two nitrogen atoms, the other a single nitrogen atom, and both of which are united to negative atoms.

(*a*) The reactions involved in the methods under this head may, in their simplest form, be expressed by the typical equation

$$NH_2.NH_2 + NO_2H = HN_3 + 2H_2O.$$

The now classical experiments which led Curtius,[1] in 1890, to the discovery of hydronitric acid consisted in the preparation of benzoyltrinitride by the action of nitrous acid upon benzoylhydrazine.

By saponifying the benzoyltrinitride with sodium hydroxide he obtained sodium trinitride from which he was able to prepare free hydronitric acid by distillation with sulphuric acid.

Subsequently he used, instead of sodium hydroxide, sodium ethylate[2] and alcoholic ammonia.[3]

In 1893 Curtius[4] found that a dilute aqueous solution of hydronitric acid could be obtained by leading the red gases, evolved from a mixture of nitric acid and arsenic trioxide, into a dilute ice-cold solution of hydrazine hydrate, or by adding the blue solution obtained by condensing the red gases upon ice. This method he considered particularly adapted for lecture-room purposes.

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[1] *Ber. d. chem. Ges.*, **23**, 3023.

[2] *Ibid.*, **24**, 3341.

[3] *Ibid.*, **29**, 759.

[4] *Ibid.*, **26**, 1263.

At about the same time Angeli[1] prepared silver trinitride by adding a solution of hydrazine sulphate to a cold saturated solution of silver nitrite.

Dennstedt and Göhlich,[2] in 1897, described the preparation of hydronitric acid by the interaction of hydrazine sulphate and potassium nitrite.

In 1899 Sabanejeff and Dengin[3] found that by gently heating in a test-tube a mixture of 1.5 grams of hydrazine sulphate and 4 cc. of nitric acid (density 1.3), they could obtain hydronitric acid as one of the reaction products. The yield amounted to from 10 to 12 per cent. of the hydrazine sulphate used. The method is recommended by its author as an especially available one for lecture-room work.

In the same year, Tanatar[4] devised a method for preparing hydronitric acid by the action of nitrogen trichloride upon hydrazine.

(*b*) The reaction typical of this class of methods may be expressed by the equation

$$NH_3 + N_2O = HN_3 + H_2O.$$

W. Wislicenus[5] stated in 1892 that he was unable to prepare the acid by direct union of the two substances, but that its sodium salt could be obtained by passing dry nitrous oxide over sodium amide heated to a temperature of between 150° and 250°.

A detailed experimental study of the method of Wislicenus will be found below.

(*c*) The typical reaction for this class of methods is expressed by the equation

$$NH_2.NH_2 + NH_2OH + 2O = HN_3 + 3H_2O.$$

In 1902 Tanatar[6] found that when a molecular mixture of hydrazine and hydroxylamine salts was oxidized in acid solution by bromine water, permanganic acid, lead dioxide or red lead, a small quantity of hydronitric acid was invariably formed. With hydrogen peroxide a yield of 24.3 per cent., and with chromic acid a yield of 29.27 per cent. was obtained.

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[1] *Attid. Reale Accad.* (5), **2**. 1. 569; *Centrbl.*, **2**, 559 (1893).

[2] *Chem. Ztg.*, **21**, 876.

[3] *Ztschr. anorg. Chem.*, **20**, 21.

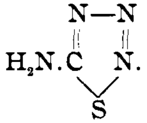
[4] *Ber. d. chem. Ges.*, **32**, 1399.

[5] *Ibid.*, **25**, 2084.

[6] *Ber. d. chem. Ges.*, **35**, 1810.

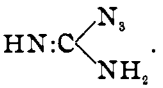
(*d*) In 1892 Thiele[1] obtained hydronitric acid by decomposing the salts of diazoguanidine.

Freund and Schander[2] obtained hydronitric acid by the action of an alkali upon aminotriazsulphol,



It will be seen that both methods thus far considered under this head may be looked upon as involving the decomposition of compounds that are derivatives of the hypothetical compound of hydrogen and nitrogen, $NH_2.H:NH$.

In the opinion of Hantzsch and Vagt,[3] however, the so-called diazoguanidine is not to be regarded as a real diazo compound, but as a trinitride with this structure:



$$HN:C\begin{matrix} N_3 \\ NH_2 \end{matrix}.$$

The method of Angeli, given above, might be regarded as a member of this class of methods if the possible formation of the intermediate product is considered of any importance.

In 1893 Curtius[4] found that by the action of certain diazo-compounds upon hydrazine or certain of its primary substitution products he in all probability obtained derivatives of the hypothetical compound of hydrogen and nitrogen, $NH_2.NH.N:NH$, which he called buzylene.

(*e*) Methods of obtaining hydronitric acid by the hydrolysis of aromatic trinitrides are perhaps not of the same theoretical interest as those described above, as the former start from compounds already containing the nitrine group, and prepared by some other method. Work done upon the subject has, however, brought out still further the interesting analogy between the trinitrides and the chlorides, by showing that the replaceability of the nitrine group, as well as of the chlorine atom, is increased by the introduction of certain groups into the benzene ring.

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[1] *Ann. Chem.* (Liebig), **270**, 1.

[2] *Ber. d. chem. Ges.*, **29**, 2500.

[3] *Ann. Chem.* (Liebig), **314**, 339.

[4] *Ber. d. chem. Ges.*, **26**, 1263.

As illustrative of methods of this class, the work of Nölting and Grandmougin[1] and of Nölting, Grandmougin and Michel[2] may be cited.

Later Michel[3] extended the experiments of the above-mentioned investigators and confirmed the conclusion already indicated by them, that aromatic trinitrides containing negative radicals in the ortho or para position may be hydrolyzed by the action of alcoholic potassium hydroxide, while the meta substitution products do not so react.

In so far as any attempt has been made by different authors to compare the above methods for preparing hydronitric acid on the basis of practical utility, the almost unanimous verdict seems to be that the method of Wislicenus is on the whole the most satisfactory. One reviewer[4] speaks of the nitrogen trichloride method of Tanatar as the one next to be preferred.

(2) INORGANIC COMPOUNDS OF HYDRONITRIC ACID.

In 1890 Curtius[5] briefly described the trinitrides of silver (AgN_3), mercury (Hg_2N_6), and barium (BaN_6). He also mentioned the existence of the ferrous, cuprous, sodium, and ammonium trinitrides. In 1891[6] he further described some of the same compounds, and also the trinitrides of lead and diammonium ($N_2H_5N_3$).

In 1896 Dennis and Doan[7] prepared thallous trinitride (TlN_3), and thallous-thallic trinitride ($TlN_3.TlN_9$).

In 1898 Dennis and Benedict,[8] in the course of a general investigation upon the trinitrides of the alkali and alkaline earth metals, prepared the trinitrides of lithium ($LiN_3.H_2O$), sodium, potassium (KN_3), rubidium (RbN_3), and caesium (CsN_3), and the trinitrides of calcium (CaN_6), strontium (SrN_6), and barium ($BaN_6.H_2O$).

In the same year Curtius and Rissom[9] prepared the following compounds: Ammonium, lithium (LiN_3), sodium, potassium, rubidium, caesium, thallium, calcium, strontium, barium, diam-

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[1] *Ber. d. chem. Ges.*, **24**, 2546.

[2] *Ibid.*, **25**, 3328.

[3] *Moniteur scientifique* (4), **7**, II. 749

[4] Harden : *J. Chem. Soc.* (London). **76**, II. 479.

[5] *Ber. d. chem. Ges.*. **23**, 3023.

[6] *Ibid.*, **24**, 3341.

[7] This Journal, **18**, 970.

[8] *Ibid.*, **20**, 225 ; *Ztschr. anorg. Chem.*, **17**, 18.

[9] *J. prakt. Chem.* (2), **58**, 261.

monium, cadmium (CdN_6), pyridine cadmium ($((C_5H_5N)_2N_6Cd)$), and cupric (CuN_6) trinitrides; also basic trinitrides of zinc (ZnN_3OH ?), manganese (MnN_3OH), nickel (NiN_3OH ?), cobalt (CoN_3OH), and chromium (ratio $3Cr:2N_3$); and double trinitrides of cobalt and potassium ($CoN_6.KN_3$), cobalt and ammonium ($CoN_6.N_4H_4$), and of nickel and potassium ($NiN_6.Kn_3$?). He did not succeed in isolating the trinitrides of magnesium, beryllium, iron, aluminum, platinum and gold.

In 1900 Curtius and Darapsky,[1] in continuation of the work just described, made a further study of the behavior of aluminum, iron and chromium toward hydronitric acid. They found that solutions of alums of these elements reacted with sodium trinitride in a manner similar to that described for thorium by Dennis and Kortright,[2] and by Dennis[3] who found that thorium is quantitatively precipitated from solution by the addition of potassium trinitride on boiling. These three elements, as well as the thorium, separate under this treatment in the form of hydroxides. A new basic trinitride of chromium (ratio, $Cr:N_3$) was prepared. Zirconium was found to be precipitated quantitatively as hydroxide, even in the cold, by the addition of sodium trinitride to a solution of zirconium sulphate. With yttrium, lanthanum, cerium and didymium they obtained basic salts in which two nitrine groups were joined to each atom of the element in question. By boiling a solution of uranyl nitrate after treatment with sodium trinitride they effected a quantitative separation of uranyl hydroxide. Using the method of precipitation with alcohol and ether, they confirmed the results of Curtius and Rissom by preparing the basic trinitride of manganese, and also prepared the neutral trinitride of nickel ($NiN_6 + aq$). Attempts were made to isolate the trinitrides of arsenic and antimony, but without success.

In 1900 Hantzsch[4] prepared a trinitride of iodine (IN_3) by the action of a solution of iodine in benzene or ether upon silver trinitride.

A crystallographic study of several of the inorganic trinitrides was made by Gill[5] and by Rosenbusch.[6]

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[1] *J. prakt. Chem.* (2), **61**, 408.

[2] Dennis and Kortright: *Ztschr. anorg. Chem.*, **6**, 35; *Am. Chem. J.*, **16**, 79.

[3] Dennis: This Journal, **18**, 947.

[4] *Ber. d. chem. Ges.*, **33**, 522.

[5] This Journal, **20**, 225; **18**, 970; *Ztschr. anorg. Chem.*, **17**, 18.

[6] *J. prakt. Chem.*, **58**, 261; *Z. Krystall.*, **33**, 99.

Curtius and his students have prepared a large number of the compounds of hydronitric acid with organic acids. The compound carbonyl trinitride (carbazide), $CO(N_3)_2$, is of especial interest to the inorganic chemist because of its analogy to carbonyl chloride. Curtius[1] prepared this compound by the action of sodium nitrite upon the hydrochloric acid salt of carbonyl hydrazide, $CO(NH.NH_2.HCl)_2$. Pommerehne[2] has prepared several compounds of hydronitric acid with organic bases. For information with respect to these compounds, and for further details concerning the inorganic compounds mentioned above, the reader is referred to the original papers, or to the recent work of Dr. Leopold Spiegel, "Der Stickstoff und seine wichtigsten Verbindungen."

(3) PROPERTIES AND REACTIONS OF HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.

The properties of anhydrous hydronitric acid have been described by Curtius and Radenhausen.[3] They have also described[4] the action of a 7 per cent. aqueous solution of the acid upon different metals. It acts upon metallic iron, zinc, copper, aluminum, and magnesium with vigorous evolution of hydrogen, while a more concentrated solution appears to attack even gold and silver. Curtius and Rissom[5] found that in aqueous solution the acid is very slowly decomposed by boiling with moderately dilute mineral acids, but remains unchanged on boiling with pure water. During distillation practically all of the acid comes over with the first quarter of the liquid, leaving behind a very dilute solution, which distils unchanged. Aqueous solutions of the acid, even when very dilute, may be kept in stoppered glass bottles indefinitely without decomposition. In concentrated aqueous solution it is, however, dangerously explosive.[6]

Ostwald determined by measuring the electrical conductivity of hydronitric acid that it was slightly stronger than acetic acid. His experimental data seem to be inaccessible. Two other investigators almost simultaneously repeated his work. Hantzsch[7] found that the conductivity increased with the temperature.

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[1] *Ber. d. chem. Ges.*, **27**, 2684.
[2] *Arch. Pharm.*, **236**, 479
[3] *J. prakt. Chem.*, (2). **43**, 207.
[4] *Ber. d. chem. Ges.*, **23**, 3023.
[5] *J. prakt. Chem.* (2), **58**, 261.
[6] Curtius: *Ber. d. chem. Ges.*, **23**, 3023.
[7] *Ibid.*, **32**, 3066.

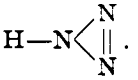
West[1] measured the conductivity of the acid and of its sodium salt. He finds the strength of the acid at 25° to be slightly greater than that of acetic acid, and about one-seventieth that of hydrochloric acid.

In 1895 Peratoner and Oddo[2] examined the gaseous products obtained by the decomposition of certain compounds of hydronitric acid in the hope of finding argon in case this should be polymeric nitrogen. Only traces of argon were found, coming probably from the air dissolved in the solutions.

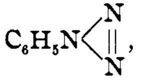
This subject was further studied by Szarvasy.[3]

See also Peratoner and Oddo.[4]

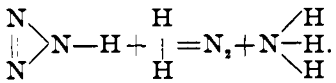
With regard to the structure of hydronitric acid, three lines of evidence tend to support the current belief that the compound contains a closed ring composed of three nitrogen atoms, and has the structural formula



(1) Fischer[5] showed that phenyltrinitride (diazobenzenimide) has the structure



which had already been suggested by Kekulé.[6] And from this, by the saponification with alcoholic potassium hydroxide of an appropriate substitution product (see reference to Nölting's work above), potassium trinitride is obtained. (2) Dennis and Doan[7] found that the decomposition of thallous trinitride in a current of hydrogen yielded both ammonia and nitrogen, which may be expressed



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[1] *J. Chem. Soc.* (London). **77**, 705.

[2] *Gazz. chim. ital.*, **25**, II, 13: *Chem. Centrbl.*, **95**, 2, 864.

[3] *J. Chem. Soc.* (London), **77**, 603.

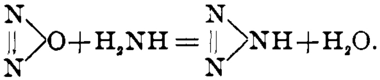
[4] *Gazz. chim. ital.*, **30**, II, 95: *Chem. Centrbl.*, II, 660 (1900).

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

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

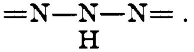
[7] This Journal, **18**, 970.

(3) Erdmann[1] suggests that the formation of hydronitric acid by the method of Wislicenus is proof of its structure.



$$\left.\begin{matrix}N\\ \|\\ N\end{matrix}\right>O+H_2NH=\left.\begin{matrix}N\\ \|\\ N\end{matrix}\right>NH+H_2O.$$

In opposition to the foregoing is the belief of Armstrong,[2] based upon a study of the optical properties of the acid, that it may be an unsaturated compound with the formula



$$=N-\underset{H}{N}-N=.$$

Mendeléeff[3] regards hydronitric acid as being theoretically derived from secondary ammonium orthonitrate, by the abstraction of 4 molecules of water, as follows:

$$H(NH_4)_2NO_4-4H_2O=HN_3.$$

From the corresponding primary salt, nitrous oxide is considered to be derived, and ammonium trinitride from the tertiary salt by a similar theoretical process. It may not be out of place to mention here that orthonitric acid, predicted years ago by Mendeléeff, has recently been made by Erdmann.[4]

Berthelot and Matignon,[5] and Bach[6] have almost simultaneously determined the thermochemical data for hydronitric acid.

Details concerning the explosive character of the salts of hydronitric acid will be found in the articles of Curtius, Dennis and Benedict, Dennis and Doan, and Berthelot and Vieille.[7]

Hydronitric acid and its salts have a pronounced toxic effect upon living organisms. When the fumes of the acid are inhaled, even in very small amounts, they produce a characteristic headache and dizziness. The effect upon certain mammals of the subcutaneous injection of small doses of the sodium salt, is the production of spasms, and symptoms of heart and lung paralysis.[8] In the case of bacterial life, growth is prevented.[8, 9]

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[1] *Lehrbuch. d. anorg. Chem.*, 2te Auf.. p. 190.

[2] *Chem. News*, **67**, 153.

[3] "Principles of Chemistry" (2nd Eng. ed.), Vol. I. p. 267.

[4] *Ztschr. anorg. Chem.*, **32**, 431.

[5] *Compt. rend.*, **113**, 672.

[6] *Ztschr. phys. Chem.*. **9**, 241.

[7] *Ann. chim. phys.* (7). **2**, 339.

[8] Loew : *Ber. d. chem. Ges.*. **24**, 2947.

[9] Schattenfroh : *Arch. für Hyg.*, **27**, 231.

II. EXPERIMENTAL.

(A) A STUDY OF THE WISLICENUS[1] METHOD FOR PREPARING HYDRONITRIC ACID.

The hydronitric acid used in this investigation, as well as in the earlier ones carried on in this laboratory, has been made entirely by the Wislicenus method, and several years ago a careful examination of this process was begun with a view to ascertaining the conditions most favorable to a high percentage yield, especially when the sodium amide and sodium trinitride were prepared on a somewhat large scale. In describing our results, it may be well to classify the experiments under (*a*) The Preparation of Sodium Amide, (*b*) The Preparation of Sodium Trinitride from Sodium Amide, and (*c*) The Preparation of Hydronitric Acid from Sodium Trinitride.

(*a*) *The Preparation of Sodium Amide.*

Sodium amide was discovered about the year 1808 by Gay-Lussac and Thenard[2] during an investigation of the properties and reactions of the then newly discovered metals, potassium and sodium. Fifty years later it was subjected to further scrutiny by Beilstein and Geuther.[3] In 1892, W. Wislicenus[4] first used it as a source of hydronitric acid, as stated above. And finally, in 1894, Titherley[5] prepared it in large quantities, and carefully studied its composition and many of its properties.

In the work here to be described, attention has been paid to the following considerations involved in the preparation of the compound: (1) The action of molten sodium upon vessels of different materials; (2) construction of safe and convenient apparatus for enclosing the vessel containing the molten sodium; (3) necessary precautions to be employed in obtaining ammonia and sodium of sufficient purity; (4) means of securing good contact between the reacting substances; (5) the influence of temperature upon the nature of the product; and (6) method of analyzing the product. These points will be considered in detail.

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[1] *Ber. d. chem. Ges.*, **25**, 2084 (1892).

[2] *Recherches Physico-chimiques*, **1**, 337.

[3] *Ann. Chem.* (Liebig). **108**, 88 (1858).

[4] *Ber. d. chem. Ges.*, **25**, 2084 (1892).

[5] *J. Chem. Soc.* (London), **65**, 504 (1894): **71**, 460.

(1) The durability of vessels of different materials was tested in the course of several preliminary experiments in which were used a porcelain boat, a platinum boat, a tube of hard, thick glass, a silver crucible and a nickel crucible. In each case several grams of sodium were heated in the vessel under examination to a temperature of from 250° to 300°, in a current of ammonia, for about four hours. It was found that the interior of the porcelain boat had completely lost its glaze, and had assumed a dark brown color, presumably due to the presence of free silicon liberated by the action of the sodium. The action upon the platinum boat was so marked that the amide obtained left, on treatment with water, a soft, spongy mass of platinum which retained the shape of the original product, and showed, under the microscope, a peculiar foliated structure. The glass tube stood the test surprisingly well. The surface, where it had come into direct contact with the molten sodium, was clouded to some extent, but the walls had not been eaten away appreciably. The silver crucible was acted upon to such an extent that the product firmly adhered to it on solidification, and showed a residue of numerous little spangles of silver when treated with water. When the sodium amide was prepared in a nickel crucible, however, the metal suffered no appreciable injury. The amide, after it had cooled, was easily removable by tapping the crucible and gently pressing its sides.

These results are not entirely in accord with those obtained by Titherley,[1] who concluded that "platinum is only slowly corroded, but after a few weeks' constant use the metal becomes friable and much corroded." In his later experiments he used a silver boat, saying that "the amide is practically without action on the metal." For preparing the amide on a large scale he suggests the use of a polished iron retort. This material, however, is open to serious objection. In the early experiments in this laboratory, dating back as far as 1895, a polished iron crucible was used in the preparation of the sodium amide, and the amide was then heated in a current of nitrous oxide in a second iron crucible to convert it into the trinitride. On dissolving the product of the second reaction in water and acidifying the solution with sulphuric acid a heavy blue precipitate resulted. This was found

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[1] *J. Chem. Soc.* (London), **65**, 504 (1894).

to be essentially Prussian blue. On distilling off the hydronitric acid from this acidified solution the distillate was found to contain hydrocyanic acid as well. It was at first suspected that the carbon necessary to the formation of this hydrocyanic acid came from the kerosene in which the metallic sodium had been kept. To avoid the presence of this element, large pieces of sodium 9 inches long by 3 inches in diameter were procured and after fully half an inch of the end had been cut off a core of sodium, not over 1.5 inches in diameter, was cut from the middle of the stick. The use of this material in the preparation of fresh samples of sodium amide in iron crucibles diminished the amounts of hydrocyanic acid and cyanides that were formed, but did not lead to the total avoidance of these products. It was then suspected that the carbide of iron present in the iron of the crucible might be attacked by the molten sodium and furnish the cyanogen. To test this supposition, fresh portions of the amide were prepared in crucibles made of nickel that was free from carbon, and no indication of the formation of either Prussian blue or hydrocyanic acid was obtained upon examination of the products. This formation of hydrocyanic acid, when iron vessels were used, has been pointed out by Szarvasy,[1] who did not attempt to avoid the formation of cyanides, but separated the sodium cyanide from the sodium trinitride by treating the mixture with alcohol, the sodium cyanide remaining in solution. In all of the later work in this laboratory the sodium amide and the sodium trinitride have been prepared in nickel dishes 5 inches in diameter with perpendicular sides 3 inches high. As a result of long-continued use these dishes show signs of being somewhat attacked by the sodium, but the polishing of the dish with fine sea-sand before each run prevents any perceptible action upon it during the course of a single experiment.

(2) In the above examination of the action of sodium on the material of the container the porcelain and platinum boats were heated in combustion tubing, the small silver and nickel crucibles in vertical glass tubes 2.5 inches in diameter and sealed at one end, while the large crucibles were heated in a perpendicular iron tube 3.5 inches in diameter and closed at each end with a heavy screw cap, the upper cap being perforated for the entrance and exit of the gases. For preparing the sodium amide in large

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[1] *J. Chem. Soc.* (London), 77. 603 (1900).

amounts in the 5-inch nickel dishes above-mentioned a special container was necessary, and after many experiments with different devices the apparatus shown in Fig. 1 was finally adopted.

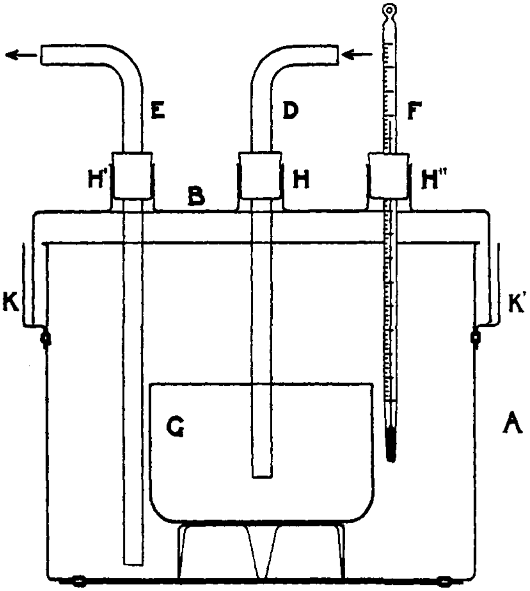

Fig. 1.

The can A is of sheet iron and is provided with a double bottom and with a grooved top, K K′, into which fits the cover B. This has three tubular openings, H, H′, H″, for rubber stoppers holding respectively the inlet tube for ammonia D, the outlet tube E, and the thermometer F. The nickel dish G stands upon a little tripod which prevents direct contact between the dish and the highly heated bottom. No solder was used in making the can. All joints were fastened with rivets. After the cover has been placed in the grooved top, the outside annular space is tightly packed with asbestos and sand. The can is placed upon a thick iron plate, and heated with a triple burner.

(3) The ammonia used in several of the earlier experiments was prepared from ammonium chloride purified according to the method of Stas.[1] A saturated solution of the ordinary "C. P."

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[1] Stas: "Untersuchungen über die Gesetze der chemischen Proportionen," German translation by Aronstein, p. 49.

salt was boiled with one-tenth its volume of concentrated nitric acid until chlorine was no longer evolved. The crystals that separated on cooling were redissolved, and similarly evaporated with a smaller amount of acid. The crystals thus obtained were dried and mixed with twice their weight of calcium hydroxide. The mixture was then placed in a seamless copper bottle, was moistened with a little water and was heated. By this means freedom from pyridine bases was insured. Comparative tests, however, in which other conditions were kept constant showed this extreme precaution to be unnecessary, and consequently ordinary "C. P." ammonium chloride was commonly employed. The ammonia was dried by passing it through a long chain of tubes containing fused sodium hydroxide and soda-lime. It was not found necessary to use a tube containing metallic sodium, as suggested by Titherley.

The sodium used in the experiments was cut from the center of large sticks of the metal for the reason already mentioned. In handling the sodium, care was taken to warm all apparatus with which it was to be brought into contact, in order to drive off the film of moisture that is present at ordinary temperatures.

(4) To test the effect of greatly increasing the surface of contact between the reacting substances, two simultaneous experiments were conducted at the same temperature (about 250°). In one the ammonia was allowed to pass, as usual, over the surface of the molten sodium, while in the other it was led beneath the surface of the molten sodium through a hard glass tube. The results of the analysis of the products obtained by these two different treatments are given in Table I.

TABLE I.

	Time of action. Hours.	Per cent. nitrogen.		Per cent. sodium.	
		Found.	Theory.	Found.	Theory.
Surface contact only	4½	31.0	35.9	61.2	59.0
Ammonia bubbling through the molten sodium	1	35.3		59.4	

These results show that when the ammonia passes through the molten sodium rather than over its surface, the formation of the amide is much accelerated. one hour's treatment by the bubbling process yielding a product of greater purity than four and one-half hours of treatment by surface contact. At the beginning of the experiment, after the sodium has become molten, the tube is submerged until it almost reaches the bottom of the dish. Then, from time to time, as the action proceeds, the tube is slightly raised, to avoid unnecessarily stirring up the amide, which sinks to the bottom as it is formed Finally, when only a small globule of the metal remains, the tube is raised out of the liquid during the remainder of the treatment. No very perceptible error seems to be introduced by the slight action of the sodium upon the hard glass tube through which the ammonia is led. A tube of pure nickel, however, would undoubtedly be preferable to one of glass.

(5) The rapidity of action of the ammonia upon the molten sodium was found to increase with the temperature, as was to be expected. But at temperatures much above 350° (which was the temperature found on the whole to give the best practical results) there seemed to be some loss of the product by sublimation. This was noted also by Titherley, who worked chiefly between temperatures of 300° and 400°. At temperatures below 250°, on the other hand, rather curious results were obtained in our work. Although in every case the reaction seemed to have been completed, analysis invariably showed too low a percentage of nitrogen, and too high a percentage of sodium. Moreover, the deficit of nitrogen and excess of sodium showed a tendency to increase as the temperature became lower. At first this was attributed to the possible presence of uncombined sodium dissolved in the amide; but when pieces of the product were thrown upon water beneath an inverted glass tube filled with water, no hydrogen was liberated.

In Table II are given the results of three experiments conducted at different temperatures in the neighborhood of the temperature limit below which apparently a good product cannot be obtained. In the second and third of these experiments, about 100 grams of sodium were employed in each case, while in the first a somewhat smaller amount was used. The method of bubbling was used in each case, and the reaction was allowed to proceed to completion.

TABLE II.

Per cent. of	Theory for $NaNH_2$.	No. 1. (250°)	No. 2. (240°)	No. 3. (200°)
Sodium	59.0	59·4	61.4	71.2
Nitrogen	35·9	35·3	33·6	23·4

It would appear from the foregoing results that at a temperature below 250° a satisfactory product is not obtained.

(6) Method of analyzing the amide. Beilstein and Geuther[1] made analyses of the compound by dissolving weighed samples in dilute hydrochloric acid in a long-necked flask, evaporating the solution to dryness and determining the ratio between the amounts of sodium chloride and ammonium chloride formed.

Titherley[2] in one series of experiments attempted to determine the yield of sodium amide by ascertaining the ratio between the weight of sodium taken and that of the product formed. In his second series he obtained the ratio between the increase in weight due to the change of sodium into amide and the weight of hydrogen evolved. In his experiments very satisfactory results were obtained by the use of this method, because, no doubt, of the extreme precautions he had taken to exclude air and moisture from the apparatus. For general use. however, the method used in his first series, at least, is open to the objection that it would fail to show even a considerable error due to the action of air or moisture upon the sodium, for the reason that the molecular weights of $NaNH_2$,$NaO(= \frac{1}{2}Na_2O_2)$ and NaOH are nearly the same.

It is evident that definite information concerning the yield of sodium amide can be obtained only by determining the percentages of both nitrogen and sodium in the product. To accomplish this a weighed portion of the product was placed in a Kjeldahl flask provided with a Reitmeier bulb and a dropping funnel. Water was introduced through the dropping funnel, and the ammonia set free by the decomposition of the sodium amide was distilled off into standard hydrochloric acid, the excess of acid being then determined by titrating back with standard sodium hydroxide, using methyl orange as the indicator. To insure complete removal of the ammonia, the solution in the Kjeldahl flask was carefully evaporated to dryness, redissolved in fresh water and again evaporated to dryness. The percentage of sodium was determined by titrating the residue of sodium hydroxide in the flask with standard hydrochloric acid. This method was used in obtaining the results given in Tables I and II.

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[1] *Ann. Chem.* (Liebig). **108**, 88 (1858).

[2] *J. Chem. Soc.* (London). **65**, 504 (1894).

(b) The Preparation of Sodium Trinitride from Sodium Amide.

In his original work upon the method, W. Wislicenus[1] prepared sodium trinitride by passing nitrous oxide over sodium amide heated to a temperature of between 150° and 250°. He obtained a yield equal to 50 per cent. of the theory called for by the equation $2NaNH_2 + N_2O = NaOH + NaN_3 + NH_3$.

Szarvasy[2] worked between the temperatures of 190° and 220° and obtained a yield of 56 per cent.

In the early work done in this laboratory the temperature varied between 210° and 225°. As the thermometer was usually from 1 to 3 inches above the nickel dish in the iron can, the actual temperature of the amide was probably somewhat higher. In one experiment the attempt was made to bring the bulb very close to the surface of the amide. As a result, the bulb broke during the course of the experiment probably because it came in contact with the molten amide, and the mercury upon dropping into the amide caused a violent explosion that completely wrecked the apparatus. The best method of securing accurate temperature measurement in this work would probably be to encase the thermometer bulb in a polished nickel tube, closed at the lower end, and then submerge it in the molten amide. In our later work, however, the thermometer was simply placed outside the nickel dish within the can, so the bulb was on a level with the amide.

In this way fairly accurate measurements were possible.

The yields of sodium trinitride obtained in the early work here were very low, seldom rising above 5 per cent. of the theory, even when the amide used was of a high-grade of purity. Consequently, some years ago Mr. Edward Hirshfield undertook, in this laboratory, a careful study of the process and found that the low yield was not attributable either to leakage of air or moisture into the apparatus, or to the catalytic action of the nickel crucible.

Mr. Hirshfield then noticed that small portions of the product adhering to the bottom of the inlet tube were of an appearance quite different from that of the rest of the mass, and showed a percentage of sodium trinitride in one case equal to 79 per cent. of theory, while the main mass showed no more than 2 per cent. This at once suggested a consideration of the influence of temperature upon the reaction. The product scraped from the inlet

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[1] *Ber. d. chem. Ges.*, **25**, 2084

[2] *J. Chem. Soc.* (London), **77**, 603.

tube had undoubtedly been formed at a lower temperature than that to which the contents of the crucible had been subjected. It had a crumbly appearance, as though it had solidified as soon as formed, while the contents of the crucible gave the appearance of having been perfectly fused.

A series of four experiments was now conducted in which, to facilitate observation and to enable quick regulation of temperature, a long combustion tube, bent upwards at the ends, was used. In each case a quantity of the amide, broken into small pieces, was introduced into the tube, which was then cautiously heated in a combustion furnace until the amide was in a state of perfect fusion. As anticipated, the greenish liquid began slowly to change to a white solid, the transformation beginning at the end of the tube nearest the nitrous oxide generator and proceeding toward the other end. If during the process any portion of the tube became slightly overheated, there would result a violent rush of gas and a local ignition confined to the limited area that has been overheated. This could instantly be checked by shutting off the supply of nitrous oxide. The results of these four experiments are shown in Table III. In Nos. 1, 2, and 3 several local ignitions were observed to take place. In No. 4 their occurrence was prevented by regulating the temperature with extreme care.

TABLE III.

	Grams AgCl per gram product.	Percentage yield of NaN_3.
1	1.0086	74.0
2	1.1177	82.0
3	0.9405	69.0
4	1.2376	90.8

The results of these experiments seem to show that the low yield in the previous runs was due probably to the secondary reaction between nitrous oxide and sodium trinitride, this action taking place with almost explosive violence at temperatures above a certain limit and to some slight extent perhaps even at comparatively low temperatures.

To further test this assumption, Mr. Hirshfield conducted several experiments upon weighed amounts of carefully prepared sodium trinitride. In each case the substance was placed in a porcelain boat and introduced into a combustion tube as close as possible to the bulb of the thermometer. Heated for one hour in a current of nitrous oxide to a temperature of between 200° and 205°, the sodium trinitride remained unchanged in appearance except that it became slightly darker. Analysis showed, however, that it had lost about 5 per cent. of its nitrogen. In another experiment the temperature was gradually raised. Before fusion could take place there was a bright ignition, accompanied by a violent rush of gas. A small amount of metallic sodium sublimed along the walls of the tube, and the boat, which had been considerably attacked during the experiment, was found to contain a white substance, soluble in water, and yielding fumes of nitrogen peroxide on acidification with sulphuric acid. In the next experiment care was taken to free the nitrous oxide from any of the higher oxides of nitrogen that it might contain by passing it though a strong solution of potassium hydroxide. Notwithstanding this precaution, acidification of the product with sulphuric acid gave the same result as before. Tests for hyponitrites gave negative results. The product was finally decided to contain sodium nitrite, which was probably formed in accordance with the equation

$$NaN_3 + 2N_2O = NaNO_2 + 3N_2.$$

When heated in a current of pure nitrogen, sodium trinitride was decomposed before it reached its melting-point. The process of decomposition was accompanied by a violent evolution of gas, but by no ignition. Only metallic sodium remained in the boat.

As a consequence of these experimental results the temperature of 190° was adopted by the authors for the conversion of sodium amide into sodium trinitride. The temperature may be allowed to vary 3° or 4° from this point without materially influencing the result.

In the hope of shortening the process by increasing the surface of contact between the reacting substances, as was done in the preparation of sodium amide, the attempt was made to bubble the nitrous oxide through the molten amide. Two experiments convinced us that this could not be done without stoppage of the inlet tube, due to the formation there of the solid products of the reaction.

To determine the percentage yield of sodium trinitride, the product is dissolved in considerable water barely acidified with sulphuric acid and made up to a known volume. In measured portions of this solution the hydronitric acid is then determined by the method of Dennis.[1] This consists in precipitating the hydronitric acid with silver nitrate, collecting the silver trinitride upon a hardened filter, washing with cold water until the wash-water gives no reaction for silver, dissolving the precipitate upon the filter with dilute, hot nitric acid, adding hydrochloric acid to the solution thus obtained and collecting and weighing the resulting silver chloride. This method was used in obtaining the results given in Table III. Curtius[2] determined hydronitric acid by distilling the substance to be analyzed with sulphuric acid, and catching the distillate in a measured excess of tenth-normal potassium hydroxide solution. Other volatile acids must, of course, be absent. West[3] modified the method of Curtius by using a measured excess of tenth-normal sulphuric acid to drive off the hydronitric acid from the solution of (say) its sodium salt. The amount of sulphuric acid used was then determined by titrating back with tenth-normal sodium hydroxide. Here, again, no volatile acid other than hydronitric acid may be present.

(*c*) *The Preparation of Hydronitric Acid from Sodium Trinitride.*

To prepare free hydronitric acid the aqueous solution of the mixture of sodium hydroxide and sodium trinitride obtained by the action of nitrous oxide upon sodium amide is placed in a distilling flask and a few drops of litmus solution are added. A separatory funnel is then inserted in the neck of the flask and the side tube is connected with a condenser, and the condenser with a receiving flask containing a little water. The solution is then heated nearly to boiling and sulphuric acid (1 : 1) is slowly introduced through the separatory funnel until the acid is in excess. Distillation is continued as long as the distillate gives the reaction for hydronitric acid with silver nitrate.

SUMMARY.

For the convenience of the reader the method for the preparation of hydronitric acid that has finally been adopted as the result of our examination of the process may be summarized as follows:

One hundred grams of metallic sodium are placed in a nickel dish and heated in the iron can, previously described, to a tem-

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[1] This Journal, 18, 947 (1896).

[2] Curtius and Rissom: *J. prakt. Chem.* (2), 58, 261.

[3] *J. Chem. Soc.* (London), 77, 705.

perature of about 350° in a current of pure ammonia gas, that is first dried by passing it through soda-lime and fused sodium hydroxide. During this process the temperature must not be allowed to fall below 250°. The inlet tube, through which the ammonia enters, is pushed down beneath the surface of the sodium as soon as that metal melts so that the gas may bubble up through the liquid. When the reaction is nearly complete (from five to seven hours) the inlet tube is raised out of the liquid. The flow of ammonia gas should be steady to prevent the rise of sodium in the inlet tube. In any case it is well to guard against the danger due to sudden stoppage by providing the inlet tube at some point outside of the iron can with a perpendicular side tube dipping into mercury. The end of the reaction is shown by the absence of hydrogen in the gas escaping from the can. Hydrogen in this escaping gas may be detected by collecting the gas in a test-tube by displacement, closing the tube with the thumb and immersing the mouth of the tube in water to absorb the ammonia, and then bringing the residual gas in the test-tube into contact with a flame. When no inflammable gas is present in the tube, the operation may be regarded as complete. The apparatus is then allowed to cool nearly to the temperature of the room. It has been found inadvisable to treat all of this product in one operation with nitrous oxide because of the tendency to "creep," shown by the sodium trinitride. Consequently, about three-fourths of the sodium amide resulting from the above operation is removed and placed in a desiccator over metallic sodium.

The iron can containing the remainder of the sodium amide in the nickel dish is now connected with an apparatus furnishing dry nitrous oxide, the arrangement being that shown in Fig. 2. This gas is made by heating ammonium nitrate. The ammonium nitrate is contained in the flask *A* resting on an iron plate and heated by a single Bunsen burner. The outlet tube *B* slopes downward and carries a two-way stop-cock, *C*, and the branch tube *D*, and at the end is bent down and inserted in a test-tube, *E*. The branch tube *D* is about 30 cm. long and is immersed to the depth of not more than one centimeter in mercury that stands in the bottom of the small cylinder *F*. This arrangement serves to collect in *F* water that may flow down the side tube *D* and furnishes also a safety-valve for the release of pressure when-

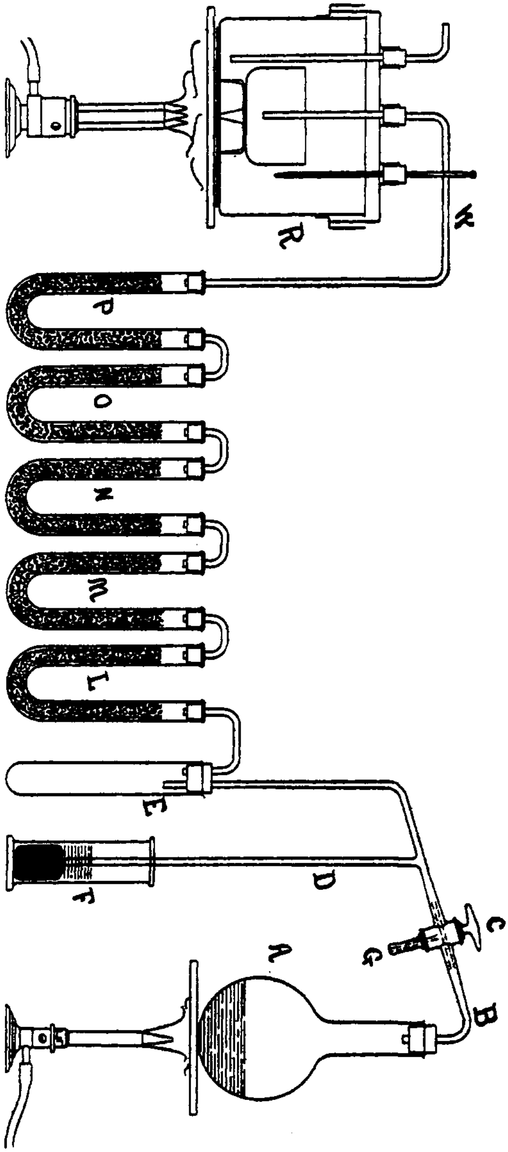

Fig. 2.

ever stoppage occurs in the tube *W*. The object of this device is to catch most of the water evolved in the decomposition of the ammonium nitrate, preventing, on the one hand, the passage of the large amount of moisture into the drying agents beyond, and on the other hand, the return flow of the condensed moisture into the flask *A*. During the operation the two-way stop-cock *C* stands in such a position that the flask communicates with the drying agents beyond. Whenever it is desired to stop the flow of nitrous oxide through the apparatus the stop-cock is turned to such a position as allows the escape of the gas through its lower end. The test-tube E serves to collect the condensed water that may have passed beyond the side arm *D*. The outlet tube from *E* is connected with U-tubes *L M* containing soda-lime, and beyond these are three U-tubes *N O P* containing fused sodium hydroxide. The gas then enters the inlet tube *W* of the apparatus *R*, which has already been shown in Fig. 1.

The generation of the nitrous oxide is now begun and when all air has been displaced from the apparatus the iron can is heated to a temperature of 190°. In this part of the operation the gas is not bubbled through the molten amide because the product is solid and would cause stoppage of the tube. The conversion of the 25 grams of sodium amide takes about five hours. The end of the reaction is indicated by the absence of ammonia in the gas escaping from the outlet tube of the can. When the conversion is complete, the flame under the can is extinguished and the contents of the nickel dish is allowed to cool in a current of nitrous oxide. The cold product, consisting of a mixture of sodium trinitride and sodium hydroxide is then dissolved in water. Hydronitric acid is distilled off in the manner previously described.

If the process has been properly conducted, no gas will be evolved when the final product is dissolved in water.

(B) THE COMPOSITION OF CERTAIN INORGANIC TRINITRIDES.

Lithium Trinitride and Barium Trinitride.—In the course of the investigation by Dennis and Doan[1] upon the compounds of thallium a large amount of pure hydronitric acid had been prepared by a modification of the Wislicenus method, but no systematic study of the compounds of the acid with inorganic

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[1] This Journal, **18**, 970.

bases was entered upon because of the expressed reservation of of this field by Curtius[1] in 1891. When, however, seven years had elapsed without the appearance of any publication by Curtius on the inorganic trinitrides, it was thought that this branch of the field might, without discourtesy to the discoverer of hydronitric acid, be regarded as open to other investigators. Consequently, there appeared in 1898 an investigation carried on in this laboratory by Dennis and Benedict[2] upon the salts of hydronitric acid. Curtius, however, had evidently considered that his reservation of this field was a perpetual one, for, in an article with Rissom[3] upon the inorganic trinitrides, published shortly after the appearance of the investigation by Dennis and Benedict, he courteously refers to their work in the following words: "In neuester Zeit, nach dem Abschlusse unserer Untersuchungen haben Dennis und Benedict mitgetheilt, dass sie das Bedürfniss gefühlt haben, 'ein systematisches Studium der Verbindungen der Stickstoffwasserstoffsäure' zu beginnen und in einer Abhandlung die Resultate mitgetheilt,[4] welche sie bei der Untersuchung der Elemente der Alkali- und Erd-alkalimetalle erhielten."

Dennis and Benedict prepared the trinitrides of lithium, sodium, potassium, rubidium, and cesium by dissolving the respective hydroxides in hydronitric acid and the trinitrides of calcium, strontium, and barium by dissolving the respective oxides in hydronitric acid. They stated that all of these compounds crystallized without water of crystallization, except those of lithium and barium, to the first of which they assign the formula $LiN_3.H_2O$, and to the second $BaN_6.H_2O$. Curtius and Rissom, in the article above quoted, state that all of these trinitrides are without water of crystallization and advance in proof of that statement analyses of lithium trinitride and barium trinitride that show fairly good agreement with the results calculated for the anhydrous salts. Before making their analyses, however, they dried the lithium trinitride over sulphuric acid to constant weight. They did the same with the barium salt, but analyzed also an air-dried sample of that compound and claim that the analyses of both products showed that barium trinitride is free from water of crystalliza-

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[1] *J. prakt. Chem.*, **43**, 208.

[2] This Journal, **20**, 225; *Ztschr. anorg. Chem.*, **17**, 18.

[3] *J. prakt. Chem.*, **58**, 261 (1898).

[4] *Ztschr. anorg. Chem.*, **17**, 18.

tion. Dennis and Benedict had no intention of giving the impression that they considered it impossible to dehydrate the trinitrides of lithium and barium by long-continued drying over concentrated sulphuric acid, nor did they suppose that analyses of salts dried in this manner would give a correct idea of the composition of those compounds as they separate from solution. To make sure, however, that water of crystallization is present in the two salts in question, Mr. J. H. Pettit prepared, in this laboratory, fresh portions of the trinitrides of barium and lithium, drying these samples in air between sheets of filter-paper, and then over night in a desiccator containing calcium chloride. His analyses gave the following results:

TABLE IV.

	Calculated for		Found.	
	LiN_3. Per cent.	$LiN_3.H_2O$. Per cent.	I. Per cent.	II. Per cent.
Li	14.29	10.46	10.82	10.88
	BaN_6. Per cent.	BaN_6H_2O. Per cent.	I. Per cent.	II. Per cent.
Ba	61.96	57.32	57.16	57.31

To ascertain whether the air-dried, hydrated barium trinitride would lose water of crystallization on standing over sulphuric acid, 0.2429 gram of the air-dried salt was allowed to stand for two months in a desiccator containing sulphuric acid. The amount of water contained in the above-mentioned weight of $BaN_6.H_2O$ is 0.0184 gram. The salt lost, on standing, over the sulphuric acid 0.0182.

The above analyses confirm the statement of Dennis and Benedict that lithium trinitride and barium trinitride, as crystallized from aqueous solutions, contain each 1 molecule of water of crystallization.

Silver Trinitride.—Curtius[1] states that silver trinitride is insoluble in water and dilute acids. Both of these statements are incorrect. As pointed out by Dennis,[2] silver trinitride is soluble in dilute, hot nitric acid, and recent experiments by the authors have shown that the compound is also somewhat soluble in boiling water (about 0.1 gram in 1 liter of water), and that it crys-

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[1] *Ber. d. chem. Ges.*, **23**, 3023 (1890).

[2] This Journal, **18**, 947 (1896).

tallizes in minute needles from this solution. This crystalline form of silver trinitride has already been mentioned by Angeli.[1]

(C) A METHOD FOR THE DETECTION OF HYDRONITRIC ACID AND THE INORGANIC TRINITRIDES.

In 1898 Curtius and Rissom[2] called attention to the deep red coloration produced either indirectly by shaking in air a solution of ferrous ammonium sulphate which had been treated with sodium trinitride, or directly by treating a ferric chloride solution with the same substance. From the red solution, boiling caused the precipitation of all of the iron as ferric hydroxide, and caused the red color entirely to disappear. Even in the cold they found the color faded gradually, and that a precipitate containing a basic ferric trinitride appeared. In a parenthetical clause they suggested that the production of this red color was a "charakteristische Reaktion auf Stickstoffwasserstoff und auf Eisenoxydsalze."

In 1900 Curtius and Darapsky[3] again commented upon the blood-red coloration, produced this time by the action of sodium trinitride upon ferric ammonium sulphate in sufficiently strong solution. The colored solution they again found to deposit a brown basic ferric trinitride, that appeared at once, if the solution was dilute, but only after some time, if it was concentrated.

It has been found, on experimenting with the substances in this laboratory, that by observing the simple precaution of keeping the ferric compound in excess, the red coloration produced by the action of hydronitric acid or an inorganic trinitride will last indefinitely, even in very dilute solutions. If, for example, a ferric chloride solution of any desired strength is treated with hydronitric acid or the solution of a trinitride (also of any desired strength) up to the point only where the brown precipitate at first formed, is redissolved when the solution is shaken up, then the coloration produced will last for weeks. The color may vary, according to the strength of the solutions used, from a light reddish brown to a blood-red color so deep that the solution, even in thin layers, appears almost black. In very concentrated solutions the odor of hydronitric acid may be perceived.

The action of an excess of the ferric salt in preventing the spontaneous precipitation of ferric hydroxide or a basic ferric

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[1] *Atti. R. Accad. dei Lincei Roma* (5), **2**, I, 569 (1893).

[2] *J. prakt. Chem.* (2), **58**, 261.

[3] *Ibid.* (2), **61**, 408.

trinitride from a solution of ferric trinitride is probably to be explained on the ground that the precipitation occurs as the result of hydrolysis, and that this is prevented by the addition of a salt with a common ion, which forces back the dissociation of the ferric trinitride.

This characteristic behavior of a ferric salt toward the trinitrides has been of considerable use in this laboratory in testing residues and old solutions for hydronitric acid. It would also be of value in experimental work upon new methods of preparing the acid. In order to insure the perfect reliability of the test, a study has been made of some of the properties, physical and chemical, of the solution of ferric trinitride.

The color of the solution is remarkably similar to that of a solution of ferric sulphocyanate. When the color intensity of the two is about the same, the eye, even with the aid of the spectroscope, can find no difference between them. The color intensity of both solutions rapidly diminishes on dilution with water, that of the ferric sulphocyanate, however, fading more rapidly than the color due to the ferric trinitride, as was ascertained by a series of careful experiments conducted with a Duboscq colorimeter. These facts may be readily explained on the assumption that the color is in each case characteristic of the undissociated compound. Increasing the dilution would then not merely distribute the colored bodies throughout a greater space, but would also, by increasing the dissociation, diminish their total number. Thus, diluting a given solution with its own volume of water would reduce the color to less than one-half its former intensity. Moreover, since sulphocyanic acid is a much stronger acid than hydronitric,[1] its salts will be dissociated to a greater extent for a given concentration. Therefore dilution of a given solution of ferric sulphocyanate should cause a greater loss of color than similar dilution of a solution of ferric trinitride of the same concentration.

Concerning the sensitiveness of the ferric chloride test for trinitrides it may be said that if one part by weight of N_3 be present in 100,000 parts of water, the addition of a little ferric chloride solution, insufficient in itself to produce any perceptible coloration, will, by the formation of ferric trinitride, produce a quite distinct color, which may be clearly seen by looking down through

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[1] *J. prakt. Chem.* (2), **32**, 300 (1885).

the test-tube at a white background. Of course in dealing with such weak solutions it is necessary to take care not to mistake the color of the ferric chloride solution itself for that of the trinitride. The danger may easily be avoided by adding the same amount of ferric chloride solution as that used in the test, to a volume of water equal to that of the solution to be tested.

With respect to the general applicability of the test it may be said that many representative inorganic trinitrides have been tested, including the potassium, sodium, barium, calcium, strontium, mercuric, cadmium, nickel, etc., etc., as well as even the comparatively insoluble lead, silver and mercurous compounds. In every case the characteristic red coloration has been quickly produced. Even in pyridine solution dry silver trinitride and ferric chloride act in the same way.

Dilute mineral acids (preferably hydrochloric acid), discharge the color of ferric trinitride, but do not materially affect the color of ferric sulphocyanate. On the other hand, mercuric chloride discharges the color of ferric sulphocyanate more readily than it does that of ferric trinitride. By the aid of these reactions sulphocyanates and trinitrides may be identified even when both are present.

(D) THE REACTION BETWEEN HYDRONITRIC ACID AND POTASSIUM PERMANGANATE IN THE PRESENCE OF SULPHURIC ACID.

It seemed reasonable to suppose that hydronitric acid might be quantitatively determined by titration with potassium permanganate, and that the reaction would proceed according to the following equation:

$$2KMnO_4 + 10HN_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 15N_2.$$

Preliminary experiments showed, however, that the amount of permanganate necessary for the oxidation of the hydronitric acid was considerably higher than that called for in the above equation, and the experiments described in this chapter were undertaken with a view to ascertaining the exact nature of the reaction.

The attempt was first made to determine the ratio between hydronitric acid and potassium permanganate in presence of sulphuric acid by ordinary methods of titration. An approximately tenth-normal solution of potassium permanganate was accordingly standardized with ammonium ferrous sulphate. A dilute solution of hydronitric acid was standardized by precipitation of measured volumes with silver nitrate, evaporation of the washed precipitate with hydrochloric acid, and weighing as silver chloride.

Titrations were made by the following methods: (In each case sulphuric acid was added in sufficient quantity to keep the solution quite strongly acid throughout the experiment.) (1) By adding a measured amount of hydronitric acid to a measured excess of potassium permanganate, (*a*) at room temperature (20°), and (*b*) at a temperature of 45°. The excess of permanganate was subsequently determined by back titration with standard ammonium ferrous sulphate solution. (2) By gradually adding hydronitric acid to a measured amount of permanganate until the color was just destroyed. (3) By adding hydronitric acid in slight excess to a measured amount of permanganate and then adding more permanganate, drop by drop, until the faintest discernible permanent coloration was produced. In each case the reaction took place only after the lapse of several minutes. Raising the temperature hastened the reaction to some extent, and apparently had no other effect. At temperatures much above that of the room it was considered advisable to keep the reacting substances in a stoppered flask provided with a U-tube containing silver nitrate solution, in order to detect any loss of hydronitric acid during the titration. No loss was found to have occurred in any of the experiments. The results of the titrations are given in Table V.

TABLE V.

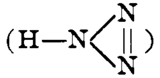
Number of experiment.	Number of different titrations made.	Ratio of molecules of HN_3 to one molecule of $KMnO_4$.	
		Extremes.	Average.
1*a*	5	2.12–2.22	2.18
1*b*	6	2.10–2.29	2.21
2	10	2.11–2.39	2.25
3	5	2.40–2.60	2.47

Average from tue twenty-six titrations, 2.27

From the foregoing results it will be seen that this method of ascertaining the ratio between the two reacting substances is rather unsatisfactory. Both the variations within a given series of titrations and the variations of the averages of different series seem to be outside the limits of experimental error. The difficulty is no doubt due to the impossibility of securing a definite end-point, owing to the extreme slowness of the reaction toward the end of the titration. It is probably also due, in some degree, to a tendency on the part of the reacting substances to unite in different proportions under different conditions, as when, for example, one or the other may temporarily or locally be in excess during the titration. Further reason for this view will be seen later. The method employed in the first experiment was found to be doubly unreliable because of the fact that when hydronitric acid is added to potassium permanganate in excess, there are thrown down oxides of manganese of varying composition which are insoluble alike in sulphuric and hydronitric acids. (This is true even when there is a considerable excess of sulphuric acid present in the solution during the titration.)

The titration experiments were now discontinued, and a qualitative study made of the reaction products formed. The solution obtained by allowing a slight excess of hydronitric acid to act upon a quantity of potassium permanganate solution in the presence of sulphuric acid and then destroying the excess of hydronitric acid by adding permanganate drop by drop, until the characteristic color was just discernible, was examined as follows. It was not considered necessary to look for free N_3 among the reaction products, for it does not seem reasonable to suppose, with Dennstedt and Göhlich,[1] that the monovalent nitrine group, similar in so many respects to the chlorine atom, could exist alone, even if the hydrogen atom could be removed from hydronitric acid without breaking it up. There would probably be immediate union of two such groups, as suggested by other investigators,[2] to form a compound, $(N_3)_2$, which we have called nitrine, analogous to the chlorine molecule. It was, however, theoretically possible that during the oxidation of the hydronitric acid certain oxyacids might have been formed, analogous to the oxyacids of chlorine. To show the analogy the following list is given:

$(H—Cl)$



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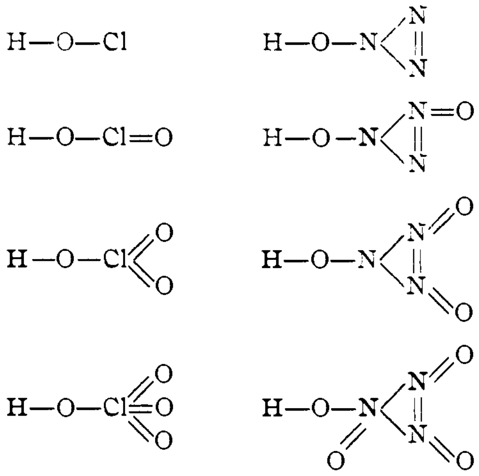
[1] *Chem. Ztg.*, **21**, 876.

[2] Curtius, Hantzsch and others.



In these compounds the nitrine group would show, according as none, one, two, or three of its nitrogen atoms became pentavalent, a monovalent, trivalent, pentavalent or heptavalent character, just as the chlorine atom is supposed to do.

To ascertain whether any such nitrogen acids were formed by the action of permanganate upon hydronitric acid, portions of the solution whose preparation was described in the first lines of the preceding paragraph were carefully distilled (*a*) at temperatures of 70° and 100°, respectively, at ordinary atmospheric pressure, and (*b*) at temperatures of 50° and 80°, respectively, at a pressure corresponding to 10 cm. of mercury. The vapors were in each case led into water containing a little phenolphthaleïn with just barely enough sodium hydroxide to redden it. In no case was the red color destroyed. The absence of nitric acid was still further established by the fact that the test with ferrous sulphate solution and concentrated sulphuric acid repeatedly gave negative results.

To show that none of the nitrogen had been changed to ammonia, or to some other nitrogen base, with consequent formation of ammonium sulphate or a sulphate of the base, a part of the solution was distilled with calcium hydroxide. The distillate gave no alkaline reaction.

From the foregoing experiments it was a legitimate inference that the hydrogen of the hydronitric acid had gone to form water, and that the nitrogen had been given off as gas, either as free nitrogen, or one of its non-acid-forming oxides.

During the titration experiments, described above, it had been observed that minute bubbles of the gas were slowly evolved as the decolorization took place. These were at first thought to be bubbles of hydronitric acid escaping from the solution as the result of the action of the sulphuric acid, until the use of stoppered flasks with U-tubes, containing silver nitrate solution, proved the contrary. Shaking the flask during the progress of the reaction, even after decolorization was complete, caused a comparatively brisk evolution of gas to take place.

The composition of the gas was determined qualitatively by collecting a quantity in a Hempel pipette, and treating it successively with the following series of reagents: Alcohol, water, caustic potash, alkaline pyrogallol, fuming sulphuric acid and cuprous chloride Contraction took place only after passing it through the alkaline pyrogallol. This indicated the presence of oxygen. The residues obtained by treating in this way gases evolved from reacting mixtures (of HN_3, $KMnO_4$, H_2SO_4) in which either the hydronitric acid or the potassium permanganate, respectively, was present in excess, showed no change in volume when mixed with either equal or double volumes of hydrogen, and subjected to the action of the electric spark in a Hempel explosion pipette. This showed quite conclusively that no oxides of nitrogen were present, a fact that already had seemed probable from the circumstance that no contraction had occurred in any case when the gas had been passed through alcohol or water. The residue, then, consisted of nitrogen.

To ascertain the quantitative composition of the gas under different conditions (*i. e.*, according as one or the other of the reacting substances was present in excess in the mixture from which the gas was evolved), portions were simply shaken with alkaline pyrogallol, and the volume measured before and after the operation.

It was found, in general, that when the permanganate was present in excess the percentage of oxygen in the gas mixtures evolved was not very constant. The insoluble higher oxide of manganese that appears under these conditions is, therefore, in all probability, of variable composition. While the results of a series of four experiments in which the permanganate was taken in excess vary in a way that seems to indicate that the ratio between the amounts of hydronitric acid and potassium permanganate entering into the reaction in different cases is not a constant one under these conditions, still the data accord fairly well with the amounts indicated in the equation

$$4KMnO_4 + 2H_2SO_4 + 8HN_3 = 2K_2SO_4 + 4MnO_2 + 6H_2O + 12N_2 + O_2.$$

This equation is not far from agreement with the results of titration given in Table V under the heads 1*a* and 1*b*. These results were also obtained with permanganate in excess.

When hydronitric acid was taken in excess, the results were more satisfactory. A series of experiments were made to determine the ratio of nitrogen evolved to permanganate reduced, when hydronitric acid was in excess. The composition of the gas evolved was found to be 92 per cent. nitrogen (by volume) and 8 per cent. oxygen. Knorre and Arndt,[1] in somewhat similar work on the oxidation of hydroxylamine by various agents, devised a special form of apparatus to serve the double purpose of measuring the gas evolved and preserving it free from air or other gases for subsequent analysis. In our work, however, this was not necessary, as the gas mixture, evolved under certain conditions in a Hempel pipette, was analyzed separately, without making any effort to measure the total volume. The total volume of gas evolved from a measured amount of the same reacting mixture, under similar conditions, was then measured in an ordinary Lunge nitrometer. To ascertain the amount of nitrogen evolved, the volume of oxygen, calculated from the results of analysis, was subtracted from the total volume. In using the nitrometer care was taken to immerse the evolution bottle in a constant temperature-bath before each reading. During the reaction the bottle was frequently shaken to facilitate evolution of the gas. To test whether any appreciable quantity of the gases remained in solution, additional experiments were performed in which a small Erlenmeyer flask was substituted for the evolution bottle. One of the reacting substances was placed in the flask, and the other in a small test-tube standing upright within the flask. By inclining the flask, the two solutions were mixed.

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[1] *Ber. d. chem. Ges.*, **33.** 30 (1900).

After the reaction was complete, the solution was heated nearly to boiling, and then permitted to cool down to the initial temperature. The volume of gas evolved was not appreciably greater than when the evolution bottle was used and the solution not boiled. Therefore no appreciable amount of gas had remained in solution.

In Table VI are given the results of a series of experiments showing the ratio, as obtained above, between nitrogen evolved and permanganate reduced when hydronitric acid is in excess.

TABLE VI.

Number of experiment.	Cubic centimeters $KMnO_4$ taken.	Cubic centimeters gas evolved.	Cubic centimeters nitrogen evolved.	Molecules N_2 per molecule $KMnO_4$.
1.	24.6	24.7	22.7	4.54
2.	25.0	25.1	23.1	4.56
3.	24.5	24.7	22.7	4.56
4.	24.7	24.1	22.2	4.44
5.	22.4	22.2	20.4	4.49
6.	20.2	20.1	18.5	4.51
			Average,	4.52

From these results it will be seen that when hydronitric acid is in excess the ratio potassium permanganate : hydronitric acid is smaller than when the permanganate is in excess; that is, in the former case a given amount of permanganate will act upon more hydronitric acid than in the latter case. This conclusion is also indicated in a rough way by the results given in Table V, where we find the ratio to have smaller values when potassium permanganate is in excess than when equivalent amounts are taken, or when hydronitric acid is virtually in excess. The following equation best represents the results given in Table VI:

$$2KMnO_4 + 6HN_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 6H_2O + 9N_2 + O_2.$$

To obtain a further check upon this equation the ratio between potassium permanganate and hydronitric acid (the latter in excess) was determined by adding a measured amount of a standardized solution of the former to a measured excess of the latter, and determining the excess of hydronitric acid by precipitation with silver nitrate in the usual way, after the reaction had taken place. The results of the two experiments performed are given in Table VII.

TABLE VII.

Number of experiment.	Cubic centimeters $KMnO_4$ taken.	Cubic centimeters HN_3 taken.	Cubic centimeters HN_3 oxidized.	Molecules HN_3 per molecule $KMnO_4$.
1	24.6	49.0	17.2	3.08
2	25.0	48.8	16.7	2.94
				Average 3.01

These results show close agreement with those given in Table VI, and point toward the same equation. Moreover, by combining the results of Table VI and VII it may be proved that under the conditions of the experiments no polymeric nitrogen is evolved, for if 1 molecule of permanganate oxidizes 3 molecules of hydronitric acid, as indicated by Table VII, causing the evolution of 4.5 molecules of nitrogen gas, as indicated in Table VI, then for each molecule of hydronitric acid oxidized there are produced 1.5 molecules of nitrogen. Hence all the nitrogen of the acid appears as diatomic nitrogen. A density determination, made according to the method of Dumas, confirmed this conclusion.

Only one experimental fact is not in close accord with the above equation. Upon inspection of the equation it will be seen that in the mixture of gases evolved during the progress of the reaction there should be 10 per cent. (by volume) of oxygen and 90 per cent. of nitrogen. Experimentally, however, the mixture was found to contain about 8 per cent. of oxygen and 92 of nitrogen. No explanation of the error has been found, but it is not to be considered as sufficiently serious to cast doubt upon the validity of the equation as given above.

It is apparent from the results of these experiments upon the reaction between hydronitric acid and potassium permanganate that the latter agent can not be used for the accurate quantitative determination of the acid. The results are of theoretical interest, however, because of the light that they appear to throw upon the structure of potassium permanganate, a subject that will be discussed by the authors in a later paper.

CORNELL UNIVERSITY.
March, 1904.