[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

NITRO-AMINOGUANIDINE

BY ROSS PHILLIPS AND JOHN F. WILLIAMS

RECEIVED MAY 11, 1928 PUBLISHED SEPTEMBER 5, 1928

Nitroguanidine, $HN{=}C(NH_2)NHNO_2$, was first prepared by Jousselin[1] by dissolving guanidine nitrate in concentrated sulfuric acid, when the compound separated upon dilution with water. More recently several articles[2] have appeared concerning this compound. It is used principally as an explosive. Thiele[2a] prepared nitrosoguanidine as well as aminoguanidine, $HN{=}C(NH_2)NHNH_2$, by reduction of nitroguanidine. Hofmann and Stollé[3] and also Pellizzari and co-workers[4] prepared diaminoguanidine hydrochloride, $HN{=}C(NHNH_2)_2{\cdot}HCl$, by the action of cyanogen chloride on hydrazine in ethereal or aqueous solutions. Pellizzari and Gaiter[5] also prepared triaminoguanidine by treating guanidine or its mono- or diamino derivative with the calculated amount of hydrazine. This work was verified and a good yield of triaminoguanidine obtained by heating an alcoholic solution of guanidine nitrate and hydrazine at 100° for five hours.

Apparently nitro-aminoguanidine, $HN{=}C(NHNO_2)NHNH_2$, has never been prepared, as no reference to it was found in the literature. In 1920, while working on guanidine compounds, it was found that an interesting substance formed when nitroguanidine was heated with a solution of hydrazine. This substance is the subject of the present investigation.

Preparation of Nitro-aminoguanidine

The nitroguanidine used in this experiment was prepared by dissolving guanidine nitrate in concd. sulfuric acid, and pouring this solution into ice water. The crystals obtained were twice recrystallized from water.[2c,e]

Hydrazine sulfate, 32.53 g., was placed in a 2000-cc. Erlenmeyer flask with 200 cc. of distilled water and 500 cc. of *N* ammonia water. When the hydrazine sulfate had dissolved, 26 g. of nitroguanidine was added. The flask was then heated to 50–60°, during which time the nitroguanidine went into solution, nitrous oxide gas began to evolve and the reaction liquor turned to an orange-red color. In about one hour at the above temperature, gas ceased to form and the liquor was rapidly evaporated to about one-third its volume. On cooling, a white crystalline powder separated which was filtered off, washed with cold water and dried in the air; yield, 13.1 g. This was purified by dissolving in boiling water containing decolorizing carbon, and filtering. Upon chill-

[1] (a) Jousselin, *Compt. rend.*, **88**, 1087 (1879); (b) Pellizzari, *Gazz. chim. ital.*, **21**, II, 405 (1891).

[2] (a) Thiele, *Ann.*, **270**, 1 (1892); (b) Boehringer and Söhne, *J. Chem. Soc.*, (Abs.), **90**, 637 (1906), D. R. P. 167,637; (c) Ewan and Young, *J. Soc. Chem. Ind.*, **40**, 109 (1921), (d) Davis, THIS JOURNAL, **44**, 868 (1922); (e) *ibid.*, **47**, 1063 (1925); (f) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

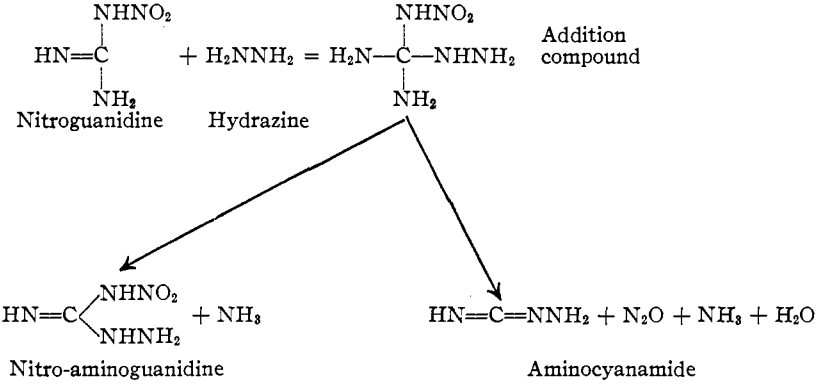
[3] Hofmann and Stollé, *Ber.*, **37**, 4524 (1904).

[4] Pellizzari and Cantoni, *Gazz. chim. ital.*, **35**, I, 291 (1905).

[5] Pellizzari and Gaiter, *ibid.*, **44**, 72 (1914); Gaiter, *ibid.*, **45**, I, 450 (1915).

ing the filtrate a pure crystalline powder formed. Changes in the above procedure were tried but no better yield was obtained.

Repeated yields of approximately 50% were obtained, which would seem to indicate the following reaction.



No indication of aminocyanamide (which is perhaps decomposed in the reaction liquor) was obtained. Nitro-aminoguanidine and ammonia were formed in the quantities indicated above and nitrous oxide came off freely.

Analysis of Nitro-aminoguanidine

The analysis of nitro-aminoguanidine presented a difficulty not easily met. The standard processes for the determination of nitrogen, such as the modified Kjeldahl, nitrometer and alkaline fusion methods, failed to yield the nitrogen expected. The following procedure proved successful.

One five-hundredth mole, 0.2383 g., was dissolved in 2 cc. of 1:1 sodium hydroxide solution and washed into a nitrometer with 3 cc. of water. Two grams of cupric sulfate dissolved in 4 cc. hot water was next introduced. Gas immediately formed and slowly subsided. The nitrometer bulb was now cautiously and later vigorously heated with steam for two hours. On cooling the gas measured 70.2 cc. at 0°. There was then carefully introduced 10 cc. of concd. sulfuric acid, and after gently mixing there still remained an insoluble copper precipitate. The nitrometer bulb was again heated with steam for one hour and cooled. The gas now measured 96.7 cc. at 22° and at 741 mm. and was then analyzed. The liquid remaining in the nitrometer measured 18 cc. and was reserved for a separate analysis. By passing aliquot portions of the gas into Hempel gas pipets containing, respectively, 1:1 sodium hydroxide, cuprous chloride and alkaline pyrogallol solutions, a shrinkage with the first indicated that 9% of the gas was carbon dioxide, while no shrinkage in the remaining solutions showed the absence of carbon monoxide and oxygen. A small portion mixed with air failed to give a brown coloration showing the absence of nitric oxide. The gas consisted of a mixture of nitrogen and nitrous oxide, the latter as shown by the splinter-glow test, and its solubility in alcohol indicated approximately one volume of nitrous oxide to three volumes of nitrogen. This residual mixture of 88.0 cc. of gas was calculated as nitrogen by substitution in the Dumas formula

$$V_0 = \frac{V(B - W)}{760} \times \frac{273}{273\,t}$$

$$88.0 \text{ cc.} \times \frac{732}{760} \times \frac{273}{295} \times 0.00125 = 0.09787 \text{ grams of nitrogen}$$

This represented about 70% of the calculated quantity of nitrogen.

The liquid remaining in the nitrometer was analyzed by the Gunning modification of the Kjeldahl method[6] and 0.0421 g. of nitrogen obtained in the form of ammonia: nitrogen as gas, 0.09787 g.; nitrogen as NH_3, 0.04210 g.; nitrogen found, 0.13997 g.; calcd., 0.14008.

Properties of Nitro-aminoguanidine

Nitro-aminoguanidine is a white, crystalline powder belonging to the monoclinic system; soluble in water to the extent of 0.34% at 20° and 3.0% at 70°; insoluble in most organic solvents. It dissolves readily in caustic alkali solutions with the formation of a yellow color, does not evolve ammonia when this solution is boiled but loses its identity after standing for several hours in the caustic alkaline solution. It melts accompanied by explosion at about 190°. It reduces solutions of permanganate and dichromate, Nessler's reagent and ammoniacal silver nitrate in the cold. With the latter reagent gas is evolved and metallic silver is precipitated, along with an explosive silver compound.

Similarly, it reduces Fehling's solution with the formation of an explosive copper compound. With nickel solutions interesting and characteristic reactions occur. If to a solution of nitro-aminoguanidine containing caustic alkali a trace or more of a nickel salt is added, an intense deep blue color develops and lasts for fifteen to twenty minutes. This test can be made to detect as little as 0.0002 mg. of nickel. Cobalt and a number of other metals failed to give this test. In the absence of caustic alkali, however, and in the presence of ammonia, nitro-aminoguanidine will yield, with solutions of nickel, a fawn colored nickel precipitate which will be described later. Like nitroguanidine it may be ground in a mortar without detonation, but differs from the former when heated near a flame on an iron spatula. Each separate particle of nitro-aminoguanidine explodes as it becomes ignited by the flame, leaving a yellow, insoluble residue. It condenses with aldehydes and ketones, as will be described.

Tests for Nitro-aminoguanidine

Although the above-described nickel test is characteristic, other tests for the compound may be mentioned. Davis and others[2e] give qualitative tests for nitroguanidine. The first is based upon the purple color which develops when a few drops of sodium hydroxide solution is added to a solution of nitroguanidine containing a little ferrous sulfate. The second test depends upon the reduction of copper or silver acetates by the re-

[6] "Methods of Analysis," A. O. A. C., **1925**, p. 9.

duced nitroguanidine, that is, the aminoguanidine formed when nitroguanidine is treated with zinc dust in acetic acid solution.

We found that nitro-aminoguanidine gives both these tests. In fact, in the second test, it reacts more energetically than does nitroguanidine. A simple qualitative test for nitro-aminoguanidine was found to be as follows. When 2 mg. or more is dissolved in warm, concd. sulfuric acid, gas is evolved and a light green solution develops and lasts. When a few drops of a 5% ferrous sulfate solution is added, the color changes to a cherry red. Nitroguanidine, nitro-urea and hydrazine do not give this test.

Reactions of Nitro-aminoguanidine

A. Reactions with Aldehydes and Ketones

When aldehydes or ketones were added to a saturated solution of nitro-aminoguanidine, crystalline precipitates formed. For example, the formaldehyde reaction took place as follows. To about 10 cc. of a warm saturated solution of nitro-aminoguanidine there was added 4 to 5 drops of 37% formaldehyde solution. Upon standing and cooling, long needles of the condensation product formed, the reaction taking place, perhaps, in the following manner

$$HN{=}C\begin{matrix}NHNO_2\\NHNH_2\end{matrix} + HCHO = HN{=}C\begin{matrix}NHNO_2\\NHN{:}CH_2\end{matrix} + H_2O$$

Similar hydrazones were obtained with acetaldehyde, citral, benzaldehyde and vanillin. The aromatic aldehyde hydrazones were nearly insoluble in water while the aliphatic hydrazones were somewhat soluble in water.

Ketones yielded in a similar manner their corresponding products and white, needle-like crystals were obtained with acetone, methylethyl ketone, diethyl ketone and pyruvic acid, $CH_3COCOOH$. The general reaction with ketones is expected to take place as follows

$$HN{=}C\begin{matrix}NHNO_2\\NHNH_2\end{matrix} + RR'CO = HN{=}C\begin{matrix}NHNO_2\\NHN{=}C\begin{matrix}R\\R'\end{matrix}\end{matrix} + H_2O$$

These condensation products with aldehydes and ketones were observed, when dried, to detonate when ignited. This was not the case when similar compounds of diaminoguanidine (the benzaldehyde compound was prepared and examined) were ignited. This property of detonation was considered evidence that the nitro group is retained in the former case. Also, the property of nitro-aminoguanidine of forming condensation products with aldehydes and ketones was considered evidence of the presence of a hydrazine group. Indication of the reduction of the nitro group in the benzaldehyde hydrazone was obtained. This compound was suspended in water slightly acidified with hydrochloric acid and zinc dust was added. After standing for two hours at room temperature, the solution was filtered and on evaporation the fitrate gave abundant crystals of a hydro-

chloride which did not detonate. Nitro-aminoguanidine did not yield insoluble, crystalline hydrazones with glucose, fructose, galactose or arabinose.

B. Reactions with Metals

The composition of the explosive compounds of silver and copper with nitro-aminoguanidine has not been determined. They differ from the nickel compound in that they are formed during the decomposition of nitro-aminoguanidine, while the nickel compound is in the nature of an addition product.

Preparation of Nickel Nitro-aminoguanidine

Five cc. of nickel sulfate solution, containing 0.093 g. of metallic nickel, was placed in a 250cc. beaker and diluted with 100 cc. of hot water. Five cc. of *N* ammonia water was added, followed immediately by a solution of 0.5 g. of nitro-aminoguanidine dissolved in 50 cc. of hot water. The precipitate formed was boiled gently for fifteen to twenty minutes, filtered through a weighed crucible, washed with hot water and dried at 110°. The weight became constant in three hours, giving 0.4955 grams of the compound. The filtrate was evaporated and a delicate test made for the presence of nickel but none was found. Since the solution of nickel sulfate used contained a known amount of nickel (electrolytically determined) and all of it was shown to have reacted, the precipitate contained 18.75% Ni; calcd. for $NiO[HN{=}C(NHNO_2)NHNH_2]_2$, 18.76%. The filtrate, after the removal of the nickel compound, was found to have 0.225 g. of ammonium sulfate together with the excess of nitro-aminoguanidine.

The precipitate is insoluble in hot or cold water and organic solvents. It dissolves in caustic alkali solutions with the formation of an intense deep blue color. It is decomposed by sulfuric acid with the formation of a toxic gas. It explodes with a flash when placed in a flame but may be heated in a test-tube to 220° without detonation. It explodes mildly when struck with a hammer.

It would seem that nitro-aminoguanidine may serve as a reagent for nickel determination, having the advantage over dimethylglyoxime of being water soluble.

Reduction of Nitro-aminoguanidine

If the new compound has the structure assigned, then it should yield diaminoguanidine on reduction, as follows

$$HN{=}C\begin{matrix}NHNO_2\\NHNH_2\end{matrix} + 3H_2 = HN{=}C\begin{matrix}NHNH_2\\NHNH_2\end{matrix} + 2H_2O$$

This was actually found to be the case.

The experiment was made in the following manner: 1.19 g. of nitro-aminoguanidine was mixed with 7 g. of zinc dust and cracked ice in a 200cc. cylinder. There was then slowly introduced with stirring 50 cc. of 10% acetic acid solution. The temperature was kept below 10° by repeated additions of ice. After stirring for one hour, the solution was allowed to reach room temperature and then filtered. The zinc was removed from the filtrate by hydrogen sulfide, and after the removal of the zinc sulfide the solution was evaporated on the steam-bath with the aid of a current of air. When the excess of acetic acid was evaporated, the residue was dissolved in a little water and the

calculated amount of hydrochloric acid, 20 cc. of $N/2$, added. After again evaporating to dryness, a slight excess of hydrochloric acid was added to insure complete removal of acetic acid. The dried residue was next extracted with hot alcohol, filtered and upon cooling in the ice box crystals were obtained; weight 0.75 g., 60% yield. They were again recrystallized from alcohol, dried and examined; melted with decomposition at 176°. Hofmann reported 174°; Pellizzari, 185°.

Anal. Calcd. for HCl: 29.0. Found: 28.90.

The nitrate was prepared from the hydrochloride by double decomposition with silver nitrate (in excess of nitric acid) and recrystallized from alcohol. The slightly impure crystals melted from 140–144°. Pellizzari reported 143°. These salts of diaminoguanidine agreed with those reported by Hofmann and Pellizzari by forming yellow radiating needles with picric acid, reduced ammoniacal silver nitrate in the cold and also solutions of gold, platinic and cupric salts, and with benzaldehyde they formed crystalline condensation products in the cold.

The benzaldehyde compound with diaminoguanidine, dibenzylidenediaminoguanidine, was prepared as follows. To a solution of diaminoguanidine hydrochloride there was added an excess of benzaldehyde and, after stirring, a white precipitate formed. The reaction took place in the following manner

$$HN{=}C\begin{matrix}NHNH_2\\NHNH_2\end{matrix}\cdot HCl + 2OHCC_6H_5 = HN{=}C\begin{matrix}NHN{=}CHC_6H_5\\NHN{=}CHC_6H_5\end{matrix}\cdot HCl + 2H_2O$$

The excess benzaldehyde was removed with ether, the crystals were washed with water, dissolved in sodium carbonate solution and extracted with ether. After the ether was evaporated the residue was recrystallized from alcohol and yellow crystals of dibenzylidenediaminoguanidine were obtained, m. p. 178° (corr.); reported by Hofmann 176°; by Pellizzari, 180°. The base was insoluble in water but soluble in alcohol. The hydrochloride of dibenzylidenediaminoguanidine was prepared from the base and when recrystallized from alcohol yielded fine, cotton-like, nearly white crystals, m. p. 230°; reported by Hofmann, 232°; by Pellizzari, 230°. This sums up the evidence showing the reduction of nitro-aminoguanidine to diaminoguanidine.

It is likely that the new compound, nitro-aminoguanidine, in addition to being useful in analytical chemistry with reference to nickel, aldehydes and ketones, may also find use in the chemistry of explosives.

The assistance of Professor E. Raymond Riegel is gratefully acknowledged.

Summary

1. The preparation of nitro-aminoguanidine is described as well as its analysis, properties and reactions.

2. Its structure is indicated by its method of preparation, its power to form hydrazones, its yielding the characteristic purple color with alkaline ferrous sulfate, its reduction to diaminoguanidine and, finally, its analysis for nitrogen.

3. Crystalline compounds with aldehydes and ketones were prepared.

4. The compound nickel nitro-aminoguanidine is described, which may lead to a new qualitative and quantitative test for nickel.

5. A special procedure for nitrogen determination is given.

BUFFALO, NEW YORK