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The Reaction of Nitrous Acid with Nitroaminoguanidine

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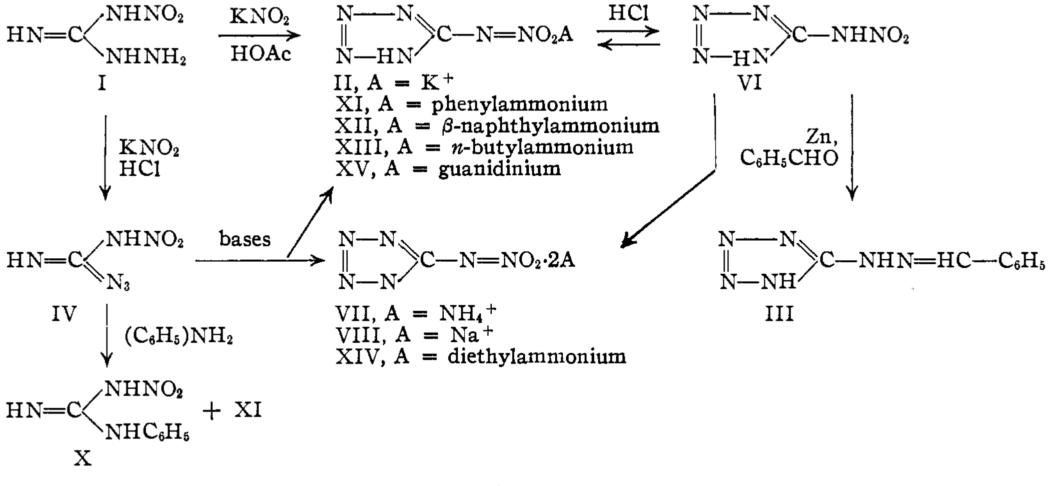
The reaction of nitrous acid with nitroaminoguanidine in neutral, weak acid and strong acid media is described with reference to the isolation, proof of structure and chemical and physical properties of the products obtained in the several reactions. In strong acid media, nitroguanyl azide is produced in excellent yield. The cyclization of nitroguanyl azide with inorganic and organic bases is described and the previous erroneous interpretation of its reaction with ammonium hydroxide corrected. In neutral and weak acid media the alkali salt of 5-nitroaminotetrazole is the sole product. The isolation of 5-nitroaminotetrazole is described and its physical and chemical properties are reported.

The reaction of nitrous acid with nitroaminoguanidine (I) in strong acid media and some of the reactions of the chief product, nitroguanyl azide (IV), have been described by O'Connor and coworkers.[2] The present paper[3] offers additional evidence as to the nature of some of these products, outlines a method for preparing nitroguanyl azide in better yield and describes several new derivatives of the azide.

In hydrochloric acid solution the reaction of nitroaminoguanidine (I) with nitrous acid gives nitroguanyl azide (IV) in yields as high as 77%, the lower yields reported by O'Connor[2] being ascribed to impure starting material and to overheating during the reaction.

In neutral and acetic acid solution the only isolable product is potassium 5-nitroaminotetrazole (II) which can also be prepared from nitroguanyl azide (IV) by the action of potassium acetate in alcoholic solution, alcoholic potassium hydroxide or aqueous potassium cyanide. The structure of the tetrazole (II) was confirmed by reduction to 5-hydrazinotetrazole and isolation of this product as the known[4] benzal derivative (III).



The liberation of 5-nitroaminotetrazole (VI) from its potassium salt (II) yields a fine crystalline substance which is very sensitive to shock and pressure. Small quantities detonate with great shattering force, accordingly it must be handled with caution and only in small quantities. Its water solutions display strong acid properties. On reaction with ammonium hydroxide it yields the same diammonium salt (VII) as obtained on reaction of nitroguanyl azide with ammonium hydroxide. This latter reaction was reported by O'Connor to lead to the formation of 5-nitroaminotetrazole. O'Connor's product could not be obtained by duplicating his published procedure.

Impact sensitivity measurements on nitroguanyl azide indicate that it is quite sensitive to shock; accordingly it should be handled with caution and in small amounts. While it exhibits a sharp melting point it may be caused to explode by heating rapidly well beyond the fusion point. On heating slowly above the melting point it undergoes gaseous decomposition and deposits a solid material. When heated in high boiling petroleum ether, it also undergoes gaseous decomposition. The same phenomenon is exhibited when the compound is heated in chloroform solution. Furthermore, an ether- and chloroform-insoluble but water soluble substance is thus formed. This latter material has not yet been subjected to detailed investigation.

Nitroguanyl azide is reduced to nitroguanidine (V) by hydrogen sulfide, a characteristic reaction of azides. Nitroguanyl azide reacts with aniline, β-naphthylamine, *n*-butylamine and diethylamine to give the corresponding alkyl or aryl ammonium salts of 5-nitroaminotetrazole which may also be obtained from 5-nitroaminotetrazole and the amines (XI, XII, XIII and XIV). In the case of the re-

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[1] Quaker Oats Company, Chicago, Illinois.

[2] T. E. O'Connor, G. Fleming and J. Reilly, *J. Soc. Chem. Ind.* (*London*), **68**, 309 (1949).

[3] The work on the reaction of nitrous acid with nitroaminoguanidine in strong acid media describing the isolation and structure proof of nitroguanyl azide (IV) was previously submitted for publication to THIS JOURNAL, and accepted on April 17, 1950. It was withdrawn from publication when the authors became aware of O'Connor, *et al.*[2] through *C. A.*, **44**, 3443 (1950).

[4] J. Thiele and H. Ingle, *Ann.*, **287**, 244 (1895).

action with aniline, N-phenyl-N′-nitroguanidine was also isolated and identified. In aqueous solution the monobasic salts of 5-nitroaminotetrazole (II, XI, XII and XIII) display slightly acidic properties, while the dibasic salts (VII and XIV) yield neutral solutions. In contrast to the explosive properties of 5-nitroaminotetrazole its amines salts are innocuous and have reproducible decomposition points.

Experimental[5]

The nitroaminoguanidine, prepared by a modification[6] of the method of Phillips and Williams[7] and recrystallized twice from water, melted with explosive decomposition at 190–191°. *Anal.* Calcd. for $C_2H_5N_5O_2$: N, 58.81. Found: N, 58.30.

Reaction of Nitroaminoguanidine with Nitrous Acid. A. In Neutral Solution.—A solution of 1.70 g. (0.02 mole) of potassium nitrite in 10 ml. of water and 2.38 g. (0.02 mole) of nitroaminoguanidine partially dissolved in 25 ml. of water at 70° were mixed, maintained[8] at 70° until solution was complete (about 15 minutes) and then rapidly chilled. The filtered product weighed 2.22 g. (66.1%) and evaporation of the filtrate gave 0.95 g. (28.3%) more of crude product. The impure first crop was recrystallized twice from water (decolorizing carbon), giving about 1.3 g. of pure potassium 5-nitroaminotetrazole as almost colorless plates. The compound explodes with a purple flash when dropped on a hot bar at about 220°.

Anal. Calcd. for $CHKN_6O_2$: N, 49.98. Found: N, 49.84.

B. **In Acetic Acid.**—A mixture of 1.90 g. (0.021 mole) of potassium nitrite, 2.38 g. (0.02 mole) of nitroaminoguanidine and 1.32 g. (0.022 mole) of glacial acetic acid in water was let stand for 24 hours, solution requiring about 2 hours and separation of the product beginning shortly thereafter. The yield of crude product was 2.72 g. (81%). Recrystallization of the product gave 1.6 g. (60%) of pure potassium 5-nitroaminotetrazole.

C. **In Hydrochloric Acid.**—By duplicating the procedure of O'Connor,[2] 5.95 g. of nitroaminoguanidine gave a 67% yield of slightly yellowish nitroguanyl azide melting at 78–79° with decomposition. No nitroguanidine was obtained, indicating that O'Connor used impure starting material. The method outlined in the following paragraph gives a better yield of the azide.[9]

An ice-cold solution of 23.4 g. (0.275 mole) of potassium nitrite in 100 ml. of water was added with stirring to 27.3 g. (0.25 mole) of nitroaminoguanidine in 23.6 ml. of concentrated hydrochloric acid (37%) and 250 ml. of water, keeping the temperature of the mixture below 20°. The mixture was then allowed to come to room temperature, filtered and spontaneously evaporated. The solid residue was extracted with three 100-ml. portions of anhydrous ether. The ether extract, filtered and evaporated at room temperature, gave 24.6 g. (77%) of practically colorless nitroguanyl azide melting at 79° with decomposition. For analysis, the azide was twice recrystallized from benzene, giving fine white needles melting at 79° with decomposition.

Anal. Calcd. for $CH_2N_6O_2$: C, 9.23; H, 1.55; N, 64.62. Found: C, 9.22; H, 1.67; N, 64.31.

Benzaltetrazolyl Hydrazone.—About 4 g. of zinc dust was added in small portions to an ice-cold solution of 1.68 g. of potassium 5-nitroaminotetrazole in 20 ml. of 1:1 hydrochloric acid. The mixture was then permitted to come to room temperature, filtered and treated with benzaldehyde until precipitation stopped. Purification of the crude product gave 0.4 g. of pure hydrazone, identified by a mixed melting point with an authentic specimen.[4]

5-Nitroaminotetrazole.—A mixture of 3.36 g. (0.02 mole) of potassium 5-nitroaminotetrazole, 25 ml. of water and 10 ml. of 1:1 hydrochloric acid was heated gently until solution was complete, then chilled and filtered. Evaporation of the filtrate gave a second crop of product. The ether solution obtained by triturating the product gave 1.23 g. (50%) of crude 5-nitroaminotetrazole. The tetrazole was purified by dissolving it in a small volume of warm dioxane, adding a large volume of dry benzene and then chilling the solution. The purified product separates as fine white crystals which explode with an orange flash at about 140°.

Anal. Calcd. for $CH_2N_6O_2$: N, 64.62. Found: N, 64.12.

Reduction of Nitroguanyl Azide with Hydrogen Sulfide.—A solution of 0.65 g. (0.005 mole) of the azide in 35 ml. of water was treated with hydrogen sulfide for 30 minutes. The mixture was then heated, filtered and the filtrate cooled. On cooling there was obtained 0.47 g. (90%) of crude nitroguanidine. Recrystallization of the product from hot water gave about 80% of the calculated amount of nitroguanidine as long, white needles.

Diammonium 5-Nitroaminotetrazole.—A solution of 0.5 g. of nitroguanyl azide in 10 ml. of water to which 10 ml. of 0.5 *N* ammonium hydroxide was added was refluxed until the odor of ammonia could not be detected (about 2 hours). Evaporation to 10 ml. and refrigeration for two weeks gave only 0.01 g. of solid. Successive concentrations of the filtrate gave a total yield of 0.58 g. of product which melted at about 220° and exploded shortly thereafter. Analysis showed the product to be diammonium 5-nitroaminotetrazole.

Anal. Calcd. for $CH_8N_8O_2$: C, 7.32; H, 4.91; N, 68.27. Found: C, 7.64; H, 4.48; N, 67.63.

Diammonium 5-nitroaminotetrazole was also prepared by heating 5-nitroaminotetrazole and ammonium hydroxide on a steam-bath and then chilling the mixture. The salt crystallized as short needles, melting at 220–221° and exploding at slightly higher temperatures. The yield of diammonium 5-nitroaminotetrazole from 0.2 g. (0.00154 mole) of 5-nitroaminotetrazole was 87.3%.

When treated with dilute sodium hydroxide solution, ammonia is liberated. Acidification with hydrochloric acid and extraction with ether gives 5-nitroaminotetrazole.

Guanidinium 5-Nitroaminotetrazole.—A suspension of 11.0 g. of guanidine carbonate in 50 ml. of water was treated with 15 ml. of glacial acetic acid. The resulting solution was heated to 50°, filtered from a small amount of insoluble material and slurried with 9.4 g. (0.079 mole) of nitroaminoguanidine. A solution of 10 g. (0.094 mole) of guanidine nitrite in 30 ml. of water was added all at once. There was an immediate reaction and warming, followed by complete solution of the nitroaminoguanidine. White platelets soon began to separate. The mixture was stirred for one hour at room temperature, after which it was cooled to 0°. The solid was removed by filtration and washed with two 25-ml. portions of cold water. The yield of product was 11.2 g. (75%) and the melting point was 224° with decomposition. One recrystallization raised the melting point to 225–226°.

Anal. Calcd. for $C_2H_7N_9O_2$: C, 12.70; H, 3.73; N, 66.65. Found: C, 12.79; H, 3.76; N, 66.46.

Conversion of Nitroguanyl Azide to Potassium 5-Nitroaminotetrazole.—In each of the three conversions which follow, the salt product was identified by analysis, explosion with characteristic color at 140° and/or conversion to 5-nitroaminotetrazole.

A. **With Potassium Acetate.**—The addition of a solution of 0.56 g. (0.005 mole) of potassium acetate in 10 ml. of ethanol containing a few drops of water to a solution of 0.65 g. (0.005 mole) of nitroguanyl azide in 10 ml. of ethanol resulted in the instantaneous, quantitative precipitation of potassium 5-nitroaminotetrazole.

B. **With Potassium Hydroxide.**—Potassium 5-nitroaminotetrazole, 0.58 g. (69.1%), was obtained as a white precipitate by chilling a solution of 0.65 g. (0.005 mole) of nitroguanyl azide in 10 ml. of 50% aqueous ethanol mixed with 0.28 g. (0.005 mole) of potassium hydroxide dissolved in 10 ml. of 50% aqueous ethanol.

C. **With Potassium Cyanide.**—A solution containing 1.0 g. (0.015 mole) of potassium cyanide in 10 ml. of water and

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[5] Melting points are uncorrected and were determined on a Dennis bar. Micro analyses were by Micro-Tech Laboratories, Skokie, Illinois.

[6] R. A. Henry, R. C. Makosky and G. B. L. Smith, THIS JOURNAL, **73**, 474 (1951).

[7] R. Phillips and J. F. Williams, *ibid.*, **50**, 2465 (1928).

[8] The reaction required several days when carried out at room temperature and yielded 2.51 g. of crude potassium 5-nitroaminotetrazole containing unreacted material. A minimum of three crystallizations was required before a good nitrogen analysis was obtained.

[9] O'Connor[2] reported the formation of two products for the reaction, *viz.*, nitroguanidine (20%) and nitroguanyl azide (30%).

1.5 g. (0.0115 mole) of nitroguanyl azide in 15 ml. of water was heated to 60° on the steam-bath, cooled in an ice-bath and then left at room temperature until the solvent evaporated. The residual solid was stirred with 5 ml. of water and filtered, giving 1.21 g. (62.3%) of potassium 5-nitroaminotetrazole.

Reaction of Nitroguanyl Azide with Amines. A. Aniline.—A solution of 4.8 g. (0.05 mole) of freshly distilled aniline in 10 ml. of ethanol was added to a solution of 6.5 g. (0.05 mole) of nitroguanyl azide in 50 ml. of ethanol. The mixture turned yellow, then red-orange, and after three hours began to deposit small plates. After standing overnight, filtration gave 4.81 g. of solid product. Spontaneous evaporation of the filtrate gave another 4.83 g. of solid, 2.66 g. of which was soluble in water and was, after isolation, combined with the first crop of crystals.

The water insoluble residue, 2.0 g., was crystallized from aqueous ethanol and then from absolute ethanol, giving fine white needles, melting at 152–155°. This compound was identified as N-phenyl-N′-nitroguanidine by analysis and by comparison with an authentic specimen prepared by the method of McKay and Wright[10]; yield 20%.

The water soluble product phenylammonium 5-nitroaminotetrazole, 7.47 g. (67%), was recrystallized from absolute ethanol, giving large lustrous plates which decompose without melting at about 160°. This substance soluble in water and hot ethanol, insoluble in the common organic solvents, gives a weakly acid reaction in water solution, liberates aniline when treated with dilute sodium hydroxide and liberates 5-nitroaminotetrazole when treated with dilute sulfuric acid. It also results from the addition of aniline to an absolute ether solution of 5-nitroaminotetrazole.

Anal. Calcd. for $C_7H_9N_7O_2$: C, 37.67; H, 4.06; N, 43.93. Found: C, 37.88; H, 4.28; N, 44.20.

B. **β-Naphthylamine.**—Application of the procedure described in A, using 2.86 g. (0.02 mole) of β-naphthylamine and 2.6 g. (0.02 mole) of nitroguanyl azide, gave a 75% yield of crude β-naphthylammonium 5-nitroaminotetrazole. This salt is rather insoluble in the common solvents, including water, but can be recrystallized from an acetone–water mixture (one drop of water to one ml. of acetone), giving thin white plates which decompose without melting at 175–177°.

Anal. Calcd. for $C_{11}H_{11}N_7O_2$: C, 48.35; H, 4.06; N, 35.88. Found: C, 48.28; H, 4.20; N, 35.70.

C. ***n*-Butylamine.**—A solution of 1.46 g. (0.02 mole) of *n*-butylamine in 10 ml. of ethanol was added to a solution of 2.6 g. (0.02 mole) of nitroguanyl azide in 20 ml. of ethanol. An immediate temperature rise was noted. Spontaneous evaporation of the solution gave a mixture of crystals and oil which was washed with acetone. Recovery of a second crop of crystals from the acetone gave a total of 2.3 g. (79%) of *n*-butylammonium 5-nitroaminotetrazole. Recrystallization from hot 3:1 benzene–ethanol gave lustrous colorless plates decomposing at 161–163°. This salt is very soluble in water and alcohol and rather insoluble in the other common solvents.

Anal. Calcd. for $C_5H_{13}N_7O_2$: C, 29.55; H, 6.45; N, 48.25. Found: C, 29.60; H, 6.35; N, 48.55.

D. **Diethylamine.**—A solution of 1.46 g. of diethylamine in 10 ml. of ethanol was added to a solution of 2.6 g. of nitroguanyl azide in 20 ml. of ethanol. An immediate temperature rise was noted. Spontaneous evaporation of the solution gave 1.0 g. of crystals, after washing with ether, and an oil. The oil treated with an additional 1.46 g. of diethylamine in ethanol, gave another 4.0 g. of crystalline product. The total yield of di-(diethylammonium)-5-nitroaminotetrazole was about 90%. Recrystallization from warm 3:1 benzene–ethanol gave white needles melting at 105° with decomposition. This double salt is soluble in water and ethanol but not soluble in the common solvents. The salt was also synthesized in good yield by adding diethylamine to an absolute ether solution of 5-nitroaminotetrazole.

Anal. Calcd. for $C_9H_{24}N_8O_2$: C, 39.11; H, 8.75; N, 40.55. Found: C, 39.10; H, 8.84; N, 40.60.

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[10] A. F. McKay and G. F Wright, THIS JOURNAL, **69**, 3028 (1947).

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The Ultraviolet Absorption Spectra of 5-Nitroaminotetrazole and its Salts

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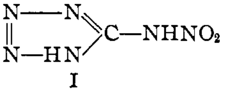
The ultraviolet absorption spectra for 5-nitroaminotetrazole and four of its salts have been studied in water solution. The free acid and its mono- and di-salts all have the same peak at 277 mμ. The removal of the first proton from the nitramide side chain of 5-nitroaminotetrazole yields an absorbing species similar in structure to the doubly charged anion. It is postulated that these species absorb at the same frequency. A zwitterion structure is proposed for nitroaminoguanidine and related substances.

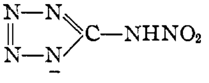
Introduction

In a previous communication[2] the preparation and properties of 5-nitroaminotetrazole (I) were described. I is an acidic substance combining

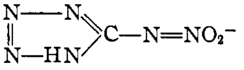


I

in a single compound the acidic properties of the tetrazole ring and the nitramide group. Well-defined crystalline mono- and di-acid salts of inorganic and organic bases are readily formed either by direct reaction with I or by isomerization of nitroguanyl azide with the desired base.[2] The interesting problem of determining the structure of the mono-acid salt arises, since the anion may have either the structure II or III.



II



III

It was suggested[2] that the mono-acid salts of I are in the *aci-nitro* form (III) on the basis of the comparative greater acidity of I with respect to tetrazoles which lacked the nitramine group. Evidence for either II or III was sought by a comparative ultraviolet absorption spectra study of I and its salts with other nitramides of the type of nitramide[3] and nitroaminoguanidine.

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[1] Quaker Oats Company, Chicago, Illinois.

[2] Lieber, Sherman, Henry and Cohen, THIS JOURNAL, **73**, 2327 (1951).

[3] R. N. Jones and G. D. Thorn, *Can. J. Research*, **B**, **27**, 830 (1949).