3. The effects of 36 other inorganic salts, acids and bases have been studied. Salts and oxides of elements of the transition series had various degrees of promoting power. All alkalies accelerated the reaction. Mineral acids had little effect.

4. The effect of some substances on the promoting power of ferrous chloride was examined. Large amounts of hydrochloric acid diminished its effectiveness. Sodium nitrate and sodium chloride had very little effect on the acceleration produced by the ferrous chloride, but the latter caused the reaction to proceed slowly beyond the alcohol stage to the hydrocarbon. Sodium nitrite caused a large increase in the induction time and slightly repressed the main part of the reaction.

5. Whether a promoter was present or not, and regardless of the nature of the promoter, the first product of the reduction of the aldehydes appeared always to be almost exclusively the corresponding primary alcohol. The formation of hydrocarbon was sometimes observed as a subsequent reaction, but it was always very slow.

6. Hypotheses which might account for the mechanism of the promoter effects observed are discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

TWO FORMS OF NITROGUANIDINE[1]

BY TENNEY L. DAVIS, AVERY A. ASHDOWN AND HENRY R. COUCH

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Nitroguanidine exists in two forms, both agreeing with published descriptions in being "asbestos-like," but differing in their appearance and crystal habit, and being definitely distinguished as different by their indices of refraction.

α-Nitroguanidine appears invariably to be produced when guanidine nitrate is dissolved in concd. sulfuric acid and the solution is poured into water. It has been prepared in this Laboratory more than 200 times by that procedure. It crystallizes from water in long, thin, flat, flexible, lustrous needles which resemble phthalic anhydride; $N_\alpha = 1.518$, N_β a little greater than 1.668, N_γ greater than 1.768, double refraction 0.250.

β-Nitroguanidine is produced in variable amount, usually along with some of the alpha compound, by the nitration of the mixture of guanidine sulfate and ammonium sulfate which results from the hydrolysis of dicyanodiamide by sulfuric acid. After many experiments at different con-

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[1] This experimentation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. The assistance of Professor Charles H. Warren in the crystallographic work is gratefully acknowledged.

centrations, temperatures, etc., we have found a procedure which in more than 30 trials has yielded exclusively the beta compound. It crystallizes from water in fern-like clusters of small, thin, elongated plates; N_α = 1.525; N_β could not be determined because of the difficulty of getting the thin crystal to stand upon its narrow face, N_γ = 1.710, double refraction 0.185.

Both forms in water solution have the molecular weight of anhydrous nitroguanidine, as determined by the ebullioscopic method with the apparatus of Cottrell, Washburn and Spencer;[2] calcd., 104; found, α-, 103.2, β-, 102.4. Both give up the nitro group quantitatively in the nitrometer.

Calcd.: nitro-group N, 13.46. Found: α—, 13.32, 13.44; β—, 13.49, 13.32.

Both melt with decomposition at 232° if the temperature of the melting-point bath is raised with moderate slowness, but, as is usual with substances which decompose on melting, the melting point varies with the rate of heating and melting points varying from 220° to 250° have been obtained with both compounds. Both give the tests for nitroguanidine which are described below. They yield nitrosoguanidine of identical physical properties and are convertible into identical benzal-aminoguanidine nitrate which melts, after recrystallization from alcohol or from water to constancy of melting point, at 161.5–161.6° (corr.).

Neither form can be converted into the other by solution in water, and the two forms may be separated by fractional crystallization from this solvent. They appear to differ slightly in their solubility in water, the two solubility curves lying close together but apparently crossing each other at about 25°, where the solubility is about 4.4 g. per liter, and again at about 100°, where the solubility is about 82.5 g. per liter. Between these temperatures the beta form appears to be more soluble. The promptness with which the substances crystallize from a warm, saturated solution and their decomposition, with the production of ammonia, on long continued contact with warm water have made it impossible to obtain the desired precise data relative to solubility in water.

Neither substance appears to be an *aci* form or a stronger *pseudo* acid than the other, for they have essentially the same solubility in 0.1 *N* potassium hydroxide solution. Neither is altered by recrystallization from glacial acetic acid or from ammonia water. They yield identical nitrates and hydrochlorides, and these salts on recrystallization from water yield only α-nitroguanidine. When either compound is dissolved in concd. sulfuric acid and the solution is poured into water, α-nitroguanidine is precipitated.

Experiments

Preparation of Alpha-Nitroguanidine.—Four hundred g. of guanidine nitrate was added in small portions at a time to 500 cc. of concd. sulfuric

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[2] Spencer, This Journal, **43**, 301 (1921).

acid (d., 1.84) while the mixture was stirred with a thermometer and its temperature was kept below 25°. The guanidine nitrate dissolved to form a slightly milky solution. This was poured into 3 liters of ice water, and the mixture was allowed to stand, with chilling, until precipitation and crystallization were complete. The product, collected on a filter, rinsed with water for the removal of sulfuric acid, and recrystallized from water, yielded 252 g. of α-nitroguanidine, or 73.9% of the calculated amount.

Preparation of Beta-Nitroguanidine.—To 20 g. of dicyanodiamide in a 300cc. round-bottom flask under a reflux condenser was added 25 cc. of 61% aqueous sulfuric acid. The mixture evolved heat and frothed considerably with the evolution of gas. When the first vigorous reaction had subsided, the material was heated for two hours in an oil-bath at 140°. The reaction product, chilled in a freezing mixture, was treated with ice-cold nitrating acid prepared by mixing 20 cc. of fuming nitric acid (d., 1.567 at 28°) with 10 cc. of concd. sulfuric acid (d., 1.84). After the evolution of red fumes had stopped, the mixture was heated for one hour in boiling water, cooled, and poured into 300 cc. of constantly stirred cracked ice and water. The precipitate, collected on a filter, rinsed with water for the removal of acid, and recrystallized from water, yielded 6.0 g. of β-nitroguanidine, or 24.5% of the calculated amount.

Salts of Nitroguanidine.—When either form of nitroguanidine is dissolved in hot, concd. nitric acid and allowed to crystallize, apparently identical nitrates are deposited in thick rhomb-shaped prisms; m. p., 147°, with decomposition. They lose nitric acid slowly in the air and yield α-nitroguanidine when recrystallized from water.

By recrystallization of either form from concd. hydrochloric acid, apparently identical hydrochlorides are obtained, crystallizing in needles. The crystals lose hydrogen chloride rapidly in the air, and show the melting point of nitroguanidine. If recrystallized from water, they yield the alpha compound.

It was not possible to isolate the sulfates from concd. sulfuric acid, as that acid attacks nitroguanidine. Both forms were dissolved in concd. sulfuric acid, and the solutions deposited α-nitroguanidine when they were diluted.

Solubility in Alkali.—Six-g. samples of each form of nitroguanidine were introduced into glass-stoppered bottles, 250 cc. of N potassium hydroxide solution was added, and the mixtures were agitated in the thermostat at 25° for 24 hours. At the end of this time it was found that the solutions smelled of ammonia and there was a pressure in the bottles due to the gas which had been liberated. The remaining nitroguanidine was collected, washed with 10 cc. of cold, distilled water, dried, and weighed. It was found that 3.052 g. of α- and 3.072 g. of β-nitroguanidine had dissolved.

Tests for Nitroguanidine.—We have tried various test-tube reactions of nitroguanidine and have found none which distinguish between the two forms. The two described below are reliable qualitative tests for nitroguanidine.

A. To 0.01 g. of nitroguanidine in 4 cc. of cold water were added 2 drops of saturated ferrous ammonium sulfate solution, then 1 cc. of 6 *N* sodium hydroxide solution, and the mixture was allowed to stand for two minutes. When the mixture was filtered, the filtrate was fuchsin-colored[3] and faded to colorless on standing for half an hour. Stronger solutions gave a stronger and more lasting color.

B. To 0.1 g. of nitroguanidine were added 5 cc. of water and 1 cc. of 50% acetic acid, and the mixture was warmed at 40° to 50° until everything dissolved. One g. of zinc dust was added, and the tube was set aside in a beaker of cold water for 15 minutes. After filtering, 1 cc. of 6% copper sulfate solution was added; the solution became intensely blue and, on boiling, gave off gas, became turbid, and presently deposited a precipitate of metallic copper. *Or*, after filtering, 1 cc. of saturated silver acetate solution (2 g. of silver acetate, 2 cc. of glacial acetic acid, diluted to 100 cc., warmed, filtered, and allowed to cool) was added; on boiling the solution a precipitate of metallic silver was deposited.

Nitrosoguanidine gives both of these tests, but its physical properties are such that there is no possibility of confounding it with nitroguanidine. The second test depends upon the reducing properties of aminoguanidine which are exceptional in that the substance precipitates metallic copper and metallic silver in the presence of free acetic acid.

Summary

Two forms of nitroguanidine are described, together with a method for the preparation of each.

They are distinguished by their indices of refraction, and differ greatly in crystal habit and slightly in solubility in water.

The beta form is converted to the alpha form by the action of strong mineral acids; otherwise there appears to be no chemical difference between the two, for they show the same reactions and yield identical derivatives.

CAMBRIDGE A, MASSACHUSETTS

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[3] Jousselin [*Compt. rend.*, **88**, 815 (1879)] obtained this color by digesting nitrosoguanidine with water and reduced iron at 40°. Thiele [*Ann.*, **270**, 21 (1892)] obtained it by treating nitroguanidine with sodium hydroxide solution and feathered zinc and then with a solution of ferrous salt. It now appears that Thiele's reduction of nitroguanidine is unnecessary in this test.