[CONTRIBUTION NO. 26 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. II. Preparation and Properties of Nitrosoguanidine[1]

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Introduction

Nitrosoguanidine and aminoguanidine are formed by the reduction of nitroguanidine.[2] Nitrosoguanidine is a mixed ammonocarbonic–aquonitrous acid anammonide or anhydride, or a mixed ammonohydroxylamic carbonic acid and it is related to nitroguanidine as nitrous acid is to nitric acid.[1a] Thiele[2] has prepared nitrosoguanidine by reducing nitroguanidine in a solution of sulfuric acid with zinc. Reduction with zinc employing a solution of ammonium chloride has been used in this Laboratory for the preparation of nitrosoguanidine and has been found to be convenient and to give satisfactory yields. This paper describes the preparation and some of the general properties of this interesting substance.

Preparation

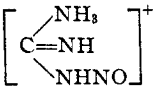
The reduction of nitroguanidine to nitrosoguanidine must be carried out so as to provide the following environmental conditions: (a) the reaction must be controlled so as to prevent the reduction proceeding beyond the nitroso stage; (b) dearrangement and hydrolysis must be minimized by controlling both the temperature and acidity of the solution; (c) nitrosoguanidine formed must be readily isolated without contamination with the reducing agent or with other substances formed by the reaction or present in the reaction system. With these conditions in mind the following method has been developed and has been used repeatedly by many workers.

Nitroguanidine[1b] (60 g.) is dissolved in 1 liter of boiling water and the nitroguanidine is precipitated in a finely divided form by violently agitating the solution while it is being rapidly chilled in an ice bath. Ammonium chloride (15 g. thus giving a concentration of 1.5%) is added to the solution and zinc powder (generally about 60 g.) is introduced at such a rate that the temperature of the reaction mixture is maintained below 50°. Samples of zinc dust vary widely in reducing activity so that the time of reduction and amount of zinc dust required must be established for each new sample of zinc. From twenty to forty minutes is usually sufficient for the reduction and when all the white nitroguanidine has been replaced by the yellow precipitate of nitrosoguanidine (nitroguanidine may be detected also by filtering 10 ml. of the mixture, treating the solid material with 5 ml. of hot ethanol, evaporating to half volume and cooling—white needles indicate the presence of nitroguanidine) ice is added to the reaction mixture and after cooling the solids are separated by filtration. Nitrosoguanidine is extracted from the mixture on the filter with 3–4 liters of water at 70° and recovered from the filtrate by chilling to 5° for half an hour. The product so obtained (98% nitrosoguanidine) is recrystallized from water (60–70°), washed with ethanol, ether and dried *in vacuo;* yield 40 to 60%.

Properties

Nitrosoguanidine is a yellow crystalline solid, individual crystals having a greenish cast by transmitted light and slightly pinkish by reflected light. Aqueous solutions are colored yellow and the intensity of this color is proportional to the concentration at constant temperature and *p*H between 6 and 10. At 10° the color intensity is 70% of that at 40° and at *p*H of 2 and 12 it is 80% of that at *p*H 7.[3] The solid detonates rather sharply at 161° and leaves only a slight amount of solid residue. It may be detonated on the open palm of the hand without any injury resulting. The following are the solubilities of nitrosoguanidine in grams per 100 g. of water at the several temperatures: 5°, 0.093; 15°, 0.118; 20°, 0.154; 25°, 0.185; 30°, 0.246; 40°, 0.365; 50°, 0.527; 72°, 1.22; 73°, 1.31. It is practically insoluble in diethyl ether and sparingly soluble in ethanol. In a slightly acidic solution a large excess of permanganate ion oxidizes nitrosoguanidine to nitroguanidine but in strongly acidic solutions nitric acid and guanidine are formed. In a solution of sodium hydroxide, permanganate ion is reduced to manganate ion and a gas is formed; further reduction yields acid permanganite ion while cyanamide and nitrate ion were identified.

Nitrosoguanidine is an ampholyte. It is dissolved to a greater extent in acidic and basic solution than in neutral solution and the isoelectric point is near *p*H 7.[3] The three forms present in aqueous solutions may be represented as follows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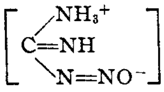
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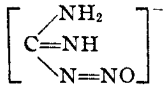
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This amphoteric character of nitrosoguanidine is of importance in connection with hydrolytic and

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[1] First article of series (a) Smith and Sabetta, THIS JOURNAL, **54**, 1034 (1932); see also (b) Smith, Sabetta and Steinbach, *Ind. Eng. Chem.*, **23**, 1124 (1931). This paper is based on the M.S. theses of Mr. Sabetta and Mr. Himmelfarb, the Polytechnic Institute of Brooklyn, 1931 and 1932.

[2] Thiele, (a) *Ann.*, **270**, 1 (1892); (b) **273**, 133 (1893).

[3] Robertson, M.S. Thesis, Polytechnic Institute of Brooklyn, 1935.

dearrangement reactions of the substance in aqueous solutions. Guanidine and nitrous acid are formed in acidic aqueous solutions, nitrous acid having been recovered quantitatively and guanidine nitrate and picrate being isolated from the reaction solution. In neutral solution cyanamide and nitrogen are formed as Thiele[2] observed. In alkaline solutions carbon dioxide, ammonia, cyanamide and nitrogen have been detected.[4]

Measurements of velocity constants of the decomposition in acidic, neutral and basic solutions show that the reactions are all monomolecular or rather pseudo-monomolecular. The constants vary with the hydrogen-ion concentration in acid solution and with the hydroxyl-ion concentration in basic solution. The energy of activation in acidic and basic solutions is about 19,000 calories per mole and is probably somewhat higher in neutral solutions.[5]

Analytical Methods

Five methods for the determination of nitrosoguanidine are indicated from the studies of its properties and have been developed: (1) colorimetric; (2) estimation of nitrous acid formed by hydrolysis of nitrosoguanidine in a dilute solution of nitric acid; (3) titration with a standard solution of potassium permanganate; (4) weighing as silver nitrosoguanidine; (5) weighing silver chloride from the conversion of silver nitrosoguanidine. These methods have all been found to be of moderate precision and (3) which has been used in the routine establishment of the purity of nitrosoguanidine will be described in more detail.

A sample of nitrosoguanidine (approx. 0.2 g.) is dissolved in 100 ml. of 3 *M* sulfuric acid to which has been added about 2 g. of manganous sulfate. A standard solution of potassium permanganate (0.1 *N*) is added only as rapidly as the solution is decolorized and when about three-fourths of the nitrosoguanidine has been decomposed the reaction proceeds slowly. The end-point is taken when the pink color of permanganate ion persists for two minutes during which period the solution is violently agitated.

Analytical Results.—Method 2: Nitrosoguanidine taken: 0.1246, 0.1578, 0.1703, 0.1728 g. Found: 0.1250, 0.1576, 0.1708, 0.1735 g. Method 3: Nitrosoguanidine taken: 0.2000 g. (5 samples). Found: 0.2016, 0.1996, 0.2006, 0.2003, 0.1993 g. Method 4: Nitrosoguanidine taken: 0.1440, 0.2042, 0.1654 g. Found: 0.1447, 0.2046, 0.1653 g. Method 5: Nitrosoguanidine taken: 0.2332, 0.2449, 0.2830 g. Found: 0.2332, 0.2440, 0.2836 g.

Summary

A method for the preparation of nitrosoguanidine by reduction of nitroguanidine with zinc in a solution of ammonium chloride is proposed. Some of the characteristic physical and chemical properties of nitrosoguanidine are described. Five methods for the determination of nitrosoguanidine are suggested.

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[4] For suggestions regarding possible reactions see (a) Pellizzarri, *Atti accad. Lincei*, **30**, I, 171 (1921); (b) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

[5] These observations are based upon a large number of quantitative measurements under a variety of environmental conditions; see Ref. 3 and also Schmookler, B.S. Thesis, 1932; Weaver, B.S. Thesis, 1934, Polytechnic Institute of Brooklyn.

[CONTRIBUTION NO. 28 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. IV. Preparation of Nitrosoguanidine by Catalytic Hydrogenation

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Introduction

In this extended investigation of the reduction of nitroguanidine[1] catalytic hydrogenation to nitrosoguanidine has been accomplished over both the Adams platinum[2] and the Raney nickel catalysts.[3] These reactions may be used for the preparation of nitrosoguanidine, which is obtained in excellent yield and relatively high purity.

Method

Nitroguanidine[1a] (10.4 g.) is suspended in 150 ml. of water and 0.5 g. of Adams or 5 g. of Raney nickel catalyst is added. The reduction is carried out either at four atmospheres pressure using the Burgess–Parr apparatus[2] (p. 452) or at one atmosphere, in which case the hydrogen is introduced from a 100-ml. buret and the Burgess–Parr shaking equipment is employed. The reaction is discontinued when slightly more than one mole of hydrogen (2300 ml.) has been adsorbed. The contents of the reduction bottle are transferred to an Erlenmeyer flask and decolorizing charcoal is added. The solution is diluted to 700–800 ml., heated to 65° and then rapidly filtered. The filtrate is again treated

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[1] See (a) *Ind. Eng. Chem.*, **23**, 1124 (1931); (b) THIS JOURNAL, **54**, 1034 (1932); (c) **57**, 2478 (1935).

[2] Gilman, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York City, 1st ed., 1932, p. 53.

[3] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).