

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Azido-dithiocarbonic Acid. VIII. Guanidine Trinitride and Azido-dithiocarbonate¹

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Guanidine Trinitride, $\text{HNC}(\text{NH}_2)_2 \cdot \text{HN}_3$

Preparation.—It was found possible to prepare guanidine trinitride by interaction of (1) guanidine hydrochloride and silver trinitride, (2) guanidine sulfate and barium trinitride, and (3) guanidine carbonate and hydronitric acid. The third method, which yields 90% of the purified final product, was adjudged the best.

To 5 g. of guanidine carbonate dissolved in about 50 cc. of water 3.5% aqueous hydronitric acid was added until effervescence ceased. The solution was evaporated nearly to dryness over the steam-bath, and was allowed to cool, with the result that a crystalline mass of guanidine trinitride was obtained. This product was recrystallized from water, washed with small amounts of ice water and placed in a vacuum desiccator over phosphorus pentoxide.

Anal. Total nitrogen was determined by the method of Dumas, and the trinitride group by that of Raschig. Calcd. for $\text{HNC}(\text{NH}_2)_2 \cdot \text{HN}_3$: C, 11.70; H, 5.90; N (total), 82.40; N_3 , 40.99. Found: C, 12.03, 11.64; H, 5.81, 5.97; N (total), 82.5, 82.45; N_3 , 41.25.

Properties.—Guanidine trinitride crystallizes from aqueous solution in the form of long, colorless prisms (m. p. 93.5°) that deliquesce slowly under ordinary atmospheric conditions. At 20°, 100 g. of water will dissolve 159.2 g. of the salt, which is also somewhat soluble in the following liquids, listed in the order of decreasing solvent action: 80% ethanol, acetone, methanol, absolute ethanol and ether. It is not appreciably soluble in chloroform, benzene, carbon disulfide or carbon tetrachloride.

Aqueous solutions respond to the ferric chloride test² for the trinitride ion, and yield hydrogen trinitride vapor when acidified. In aqueous solution at 40° the trinitride ion discharges upon the carbon disulfide molecule, with formation of the azido-dithiocarbonate ion: $\text{N}_3^- + \text{CS}_2 \rightarrow \text{SCSN}_3^-$. This reaction takes place in conformity with the general behavior of inorganic trinitrides in aqueous solution toward carbon disulfide.³ The organic trinitrides do not condense directly with carbon disulfide to form the corresponding azido-dithiocarbonates.^{1a}

**Guanidine Azido-dithiocarbonate,
 $\text{HNC}(\text{NH}_2)_2 \cdot \text{HSCSN}_3$**

Preparation.—Two methods were employed in the preparation of guanidine azido-dithiocarbonate.

(1) For the earlier articles of this series see (a) *THIS JOURNAL*, **45**, 2604 (1923); (b) **47**, 2698 (1925); (c) **49**, 917 (1927); (d) **49**, 2129 (1927); (e) **52**, 1928, (f) 2806 (1930); (g) **56**, 1116 (1934). The experimental work recorded in the current article was carried out by Dr. Craik as a part of an informal "minor" during the period of his incumbency as Commonwealth Fund Fellow at Cornell University, and Mr. Berger as a part of his "Senior Research."²

(2) Browne, *ibid.*, **37**, 531 (1909).

(3) See, for example, Browne and Hoel, *ibid.*, (a) **44**, 2106, (b) 2315 (1922); (c) Currier with Browne, *ibid.*, **44**, 2849 (1922); also *Refs. 1(e) and 1(d)*.

(1) Freshly prepared solid azido-dithiocarbonic acid,^{1a} still moist, was added to an aqueous solution of guanidine carbonate until no further evolution of gas was observed to take place. The slightly turbid liquid was filtered, and the filtrate concentrated *in vacuo* over phosphorus pentoxide. The resulting sirupy supersaturated solution, when vigorously stirred with a glass rod, yielded slightly yellowish crystals to the amount of about 60% of the theoretical yield. By recrystallizing this product from water, pure colorless crystals were obtained.

(2) To a solution prepared by dissolving 2 g. of guanidine trinitride in 25 cc. of water was added 2 cc. of carefully purified carbon disulfide. The reacting mixture was held at 40° in a tightly-stoppered 100-cc. bottle for sixty hours. At the end of this period portions of the solution failed to respond to the iodine test^{3b} for unchanged trinitride ion. After filtration, concentration of the filtrate *in vacuo*, and recrystallization of the solid product had been effected, the purified substance was stored *in vacuo* at a temperature below 10°.

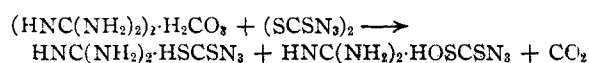
Anal. Total nitrogen was determined by the method of Dumas, sulfur with the aid of the Parr bomb, and the azido-dithiocarbonate radical according to the procedure of Volhard.^{1b} Calcd. for $\text{HNC}(\text{NH}_2)_2 \cdot \text{HSCSN}_3$: C, 13.47; H, 3.40; N (total), 47.19; S, 35.94; SCSN_3 , 66.3. Found: C, 13.6, 13.6; H, 3.7, 3.6; N, 47.3, 47.5; S, 35.99, 35.90; SCSN_3 , 65.8.

Properties.—Guanidine azido-dithiocarbonate crystallizes from aqueous solution in the form of colorless prisms. Like the other inorganic compounds^{1a, 1d} of the azido acid, and unlike the alkyl and acyl derivatives^{1c} thus far studied, it is photosensitive. In the dark it may be stored at temperatures below 10° *in vacuo* over phosphorus pentoxide for days without appreciable decomposition. It was found to dissolve readily in water and in acetone, less readily in 95% ethanol and not appreciably in ether. Heated on platinum foil it decomposes rapidly, with evolution of much gas, but without detonation. In the capillary tube it decomposes at 88–90°. In aqueous solution the azido salt interacts with silver nitrate to form the insoluble silver azido-dithiocarbonate.^{1b, 1f}

Interaction of Guanidine Carbonate and Azido-carbon-disulfide.—Equivalent amounts of guanidine carbonate (1.80 g.) in aqueous, and azido-carbondisulfide (2.36 g.) in acetone, solution were brought together at room temperature. The resulting solution immediately assumed a greenish-yellow color, and a brisk evolution of gas took place. After five hours about 0.5 g. of free sulfur was recovered by filtration, and 1.75 g. of a crystalline solid identified as guanidine thiocyanate (m. p. 118°) was obtained from the filtrate.

The initial reaction that occurred is analogous with that of an alkali upon the halogenoid azido-carbondisulfide,⁴ and may be expressed by the equation

(4) Browne, Hoel, Smith and Swezey, *ibid.*, **45**, 2541 (1923).



The very unstable oxy-azido-dithiocarbonate quickly decomposes, with evolution of two-thirds of its azide nitrogen as gas (or one-third of the total nitrogen of the original azido-carbondisulfide used), deposition of sulfur and formation of the oxy-thiocyanate. This would tend to form the tri-oxy-thiocyanate, or chlorate analog.⁵

The guanidine azido-dithiocarbonate, on long standing, decomposes quantitatively, yielding nitrogen, sulfur and the thiocyanate. Five-sixths of the total original azido-dithiocarbonate is therefore converted into thiocyanate, while the remaining sixth yields the chlorate analog, guanidine tri-oxy-thiocyanate, or cyanosulfate, which hydrolyzes into the sulfate and cyanide.⁵

The amount of free sulfur recovered in this experiment corresponds to a yield of about 94% of the theoretical, while the guanidine thiocyanate, without correction for the amount unavoidably left in the mother liquor, corresponds to a yield of 83%. Nitrometric experiments upon samples of one-tenth the weight previously used led to the

⁵ Söderbäck, *Ann.*, **419**, 217 (1919).

conclusion that two atoms of nitrogen gas per mole of $(\text{SCSN}_3)_2$, or one-third of the total azide nitrogen, were liberated at once. This confirms the theory that the oxy-azido-dithiocarbonate undergoes very rapid decomposition under the prevailing conditions.

Summary

Guanidine trinitride, $\text{HNC}(\text{NH}_2)_2 \cdot \text{HN}_3$ (m. p. 93.5°), has been prepared by interaction, in aqueous solution, of (1) guanidine hydrochloride and silver trinitride, (2) guanidine sulfate and barium trinitride, and (3) guanidine carbonate and hydro-nitric acid.

Guanidine azido-dithiocarbonate, $\text{HNC}(\text{NH}_2)_2 \cdot \text{HSCSN}_3$ (dec. 88–90°), has been prepared by interaction in aqueous solution of (1) guanidine carbonate and azido-dithiocarbonic acid, and (2) guanidine trinitride and carbon disulfide.

Certain physical properties and chemical reactions of these salts have been studied, and a preliminary investigation of the reaction between guanidine carbonate and the free halogenoid, azido-carbondisulfide, has been made.

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The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XI. The Methylene Radical

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In this paper we shall describe some experiments in which we have proved that under certain conditions the methylene radical can be prepared by the thermal decomposition of diazomethane. When this compound is carried in a current of ether or butane at low pressures and is decomposed² at temperatures below about 550°, the fragments produced readily remove mirrors of tellurium, selenium, antimony and arsenic whereas zinc, cadmium, thallium, lead and bismuth mirrors are not removed.³ We analyzed the product formed by the combination of the fragments with metallic tellurium and found it to be a polymer of telluroformaldehyde $(\text{HCHTe})_n$; this is a red involatile solid which deposits on the

walls of the tube just beyond the tellurium mirror. Since methyl groups combine with metallic tellurium to form a red liquid, dimethyl ditelluride $\text{CH}_3\text{TeTeCH}_3$, which passes over into the liquid air trap, it is very easy to distinguish between the two radicals. We found the methylene group to be extremely reactive and to have a half life of the same order as that of the alkyl radicals, namely, of only a few thousandths of a second. It can be carried in a current of ether or butane under our conditions up to 600°; above this temperature but below the decomposition point of the carrier gas it disappears and is replaced by methyl groups.

Experimental

We have already pointed out that those metals which react with methyl radicals may be divided into two groups, one of which reacts with the methylene radical and the other not. We examined this effect in a more quantita-

(1) General Motors Co. Fellow, 1930–1934.

(2) A full description of the technique used is given in a paper by Rice, Johnston and Evering, *This Journal*, **54**, 3529 (1932). See also Rice and Glasebrook, *ibid.*, **55**, 4329 (1933), for a preliminary account of this work.

(3) Methyl radicals readily react with all these metals.