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

AZIDO-CARBONDISULFIDE. IV. PREPARATION AND PROPERTIES OF THE NEW INTER-HALOGENOID, CYANOGEN AZIDO-DITHIOCARBONATE[1,2]

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Among the recent accessions to the list of halogen-halogenoids probably capable of existence are bromine azide,[3] thiocyanogen monochloride and trichloride,[4] chlorine azido-dithiocarbonate,[5] and the mono-bromine and tri-bromine azido-dithiocarbonates.[5] A new method for the preparation of cyanogen selenocyanate, a substance included within the smaller group of inter-halogenoids, has been described.[6]

The somewhat wide-spread attention devoted at present to compounds of this type finds justification not merely in the inherent scientific interest to be found in each of these substances, but also in the contribution made by each of them to the gradually extending chemical series of electronegative substances comprising both the halogens and the halogenoids or "pseudo-halogens."[7] The present article deals with the formation, preparation, properties and behavior of a new inter-halogenoid, cyanogen azido-dithiocarbonate.

Formation and Preparation.—Cyanogen azido-dithiocarbonate is formed under appropriate conditions by interaction either of negative cyanide and positive azido-dithiocarbonate radicals, or of positive cyanide and negative azido-dithiocarbonate radicals.

Mercuric cyanide, for example, either in the solid state or in aqueous solution, reacts with azido-carbondisulfide in ether, alcohol or acetone in accordance with the equation

$$Hg(CN)_2 + 2(SCSN_3)_2 = Hg(SCSN_3)_2 + 2CN{\cdot}SCSN_3 \qquad (1)$$

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[2] Manuscript received April 11, 1929.

[3] Spencer, *J. Chem. Soc.*, **127,** 216 (1925).

[4] Kaufmann and Liepe, *Ber.*, **57,** 923 (1924); Lecher and Joseph, *ibid.*, **59,** 2603 (1926).

[5] Gardner and Browne, THIS JOURNAL, **49,** 2759 (1927).

[6] Kaufmann and Kögler, *Ber.*, **59,** 178 (1926). See also Verneuil, *Ann. chim. phys.*, [6] **9,** 326 (1886).

[7] Birckenbach and Kellermann, *Ber.*, **58,** 786, 2377 (1925).

Three grams of slightly moist azido-carbondisulfide, prepared by the method of Browne, Hoel, Smith and Swezey,[1i] was dissolved in acetone and 1.8 g. of finely powdered mercuric cyanide was added to the solution. After prolonged agitation of the reacting mixture, pearly flakes[8] of mercuric azidodithiocarbonate, found under the microscope to consist of thin, hexagonal plates, were precipitated. The solid was removed by filtration, the filtrate evaporated to dryness and the residue extracted with ether. The extract yielded, on evaporation, a white solid identical in crystallographic and chemical properties with cyanogen azido-dithiocarbonate as prepared by the second method. The difficulty of obtaining the product free from traces of mercury, and the smallness of the yields produced have led to the choice of the alternative method.

To 50 cc. of a cold aqueous solution that contained about 3 g. of sodium azido-dithiocarbonate was added 2.4 g. of freshly prepared cyanogen bromide dissolved in 20 cc. of ether. After the reacting mixture, cooled in the ice-bath, had been shaken for a few minutes, a finely crystalline solid appeared in the aqueous layer. This was filtered on a Büchner funnel, washed with cold water and partially dried by suction. Desiccation was completed over phosphorus pentoxide in the ice chest. The yield of cyanogen azido-dithiocarbonate amounted to about 85% of the theoretical, calculated on the basis of the equation[9]

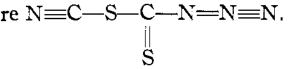
$$\mathrm{CNBr + KSCSN_3 = KBr + CN{\cdot}SCSN_3} \qquad (2)$$

Analysis.—Sulfur was determined by oxidizing the substance with sodium peroxide in the Parr bomb and weighing the sulfur as barium sulfate. Nitrogen was determined by the Dumas method as modified in this Laboratory for use in analyzing potassium azido-dithiocarbonate.[1h]

Anal. (a) Subs., 0.1055, 0.1307: $BaSO_4$, 0.3410, 0.4225. Calcd. for $CN{\cdot}SCSN_3$: S, 44.47. Found: S, 44.39, 44.40. (b) Subs., 0.1914, 0.1778: N_2, 59.96 cc. (0.0751 g.), 55.23 cc. (0.0692 g.). Calcd. for $CN{\cdot}SCSN_3$: N, 38.87. Found: N, 38.86, 39.19.

Determinations of the molecular weight in benzene were made by the cryoscopic method. Subs., 0.4042, 0.5015, 0.4560: solvent, 26.87, 23.73, 17.58; ΔT, 0.535°, 0.810°, 0.929°. Calcd. for $CN{\cdot}SCSN_3$: mol. wt., 144. Found: 144, 130, 140.

On the basis of these results, cyanogen azido-dithiocarbonate is believed to possess the structure



$$\mathrm{N{\equiv}C{-}S{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}N{=}N{\equiv}N.}$$

Properties.—Cyanogen azido-dithiocarbonate is a white, crystalline solid, soluble in water at 0° to the extent of about 1.5 g. per liter, and more soluble in various organic

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[8] The precipitate was identified, by an extended series of qualitative tests, with mercuric azido-dithiocarbonate, a very explosive compound which, with various other heavy metal salts of azido-dithiocarbonic acid, has been isolated, analyzed and studied in this Laboratory.

[9] The use of cyanogen bromide in this reaction, and in the preparation of cyanazide [(a) Darzens, *Compt. rend.*, **154,** 1232 (1912)], suggests the general applicability of this reagent in the formation of other interhalogenoids. It has been found in this Laboratory that cyanogen thiocyanate (sulfur dicyanide), for example, may be formed by the interaction of an ethereal solution of cyanogen bromide and an aqueous solution of potassium thiocyanate, as expressed by the equation $\mathrm{CNBr + KSCN = CN{\cdot}SCN + KBr}$. This interhalogenoid, which has been prepared previously by other methods [(b) Linnemann, *Ann.*, **120,** 36 (1861); (c) Söderbäck, *ibid.*, **419,** 217 (1919); (d) Schneider, *J. prakt. Chem.*, [2] **32,** 187 (1885)] was obtained in relatively small yields in the form of a crystalline substance which melts at 62°, volatilizes readily and possesses the overpowering odor characteristic of the cyanogen halides.

solvents. It is distinctly less unstable than azido-carbondisulfide,[11] and unlike this substance is insensitive to mechanical impact.

When prepared by the second method, the substance possesses a barely perceptible odor, suggesting that of cyanogen and the cyanides. In finely divided form the solid has a decided sternutatory effect. If prepared in contact with organic solvents, many of which tend to catalyze its decomposition, it has a more pronounced odor, somewhat resembling that of cyanogen iodide, and undoubtedly due to the presence of cyanogen thiocyanate, the principal product of its decomposition.

In the Bunsen flame small samples of the interhalogenoid decompose with a scarcely audible puff, and a violet flash. When heated in a somewhat restricted space, as in an open test-tube, larger quantities invariably explode with a fairly sharp detonation at 65–70 °. An interesting sequel to each of these explosions was the liberation of a heavy, dark orange vapor, of an odor comparable with that of thiocyanogen and also with that of cyanogen thiocyanate. Very small samples heated in the Thiele melting-point tube withstand somewhat higher temperatures. At 60 ° the samples assume a yellowish tint, which deepens with rising temperature, until at 80.5–81 ° fusion takes place with decomposition and formation of a yellowish-orange (YO-O on the Milton Bradley Standard)[10] residue.

Cyanogen azido-dithiocarbonate undergoes gradual spontaneous decomposition at room temperatures, with liberation of nitrogen and formation of a solid residue probably consisting of a mixture of free sulfur, polymerized thiocyanogen and cyanogen thiocyanate. This decomposition, which undoubtedly involves initial evolution of nitrogen, is believed to proceed subsequently in two different directions: (1) liberation of sulfur and formation of cyanogen thiocyanate, as expressed in Equation 3, and (2) liberation of thiocyanogen, in accordance with Equation 5. Both the cyanogen thiocyanate and the thiocyanogen evidently polymerize, as indicated in Equations 4 and 6.

$$\mathrm{CN{\cdot}SCSN_3 = N_2 + S + CN{\cdot}SCN} \qquad (3)$$

$$x\mathrm{CN{\cdot}SCN = (CN{\cdot}SCN)}_x \qquad (4)$$

$$\mathrm{CN{\cdot}SCSN_3 = N_2 + 2SCN} \qquad (5)$$

$$x\mathrm{SCN = (SCN)}_x \qquad (6)$$

The formation of a volatile product containing the thiocyanogen group was demonstrated by allowing a current of dry air that had passed over the solid to impinge upon filter paper moistened with ferric chloride solution. The characteristic red coloration soon appeared. The composition of the solid residue was determined by extraction with carbon disulfide, over a period of 150 hours, which accomplished complete removal of free sulfur, and analysis of the remaining solid, which was found to be intermediate in composition between thiocyanogen and cyanogen thiocyanate.

The velocity of decomposition of the interhalogenoid was measured in a series of nitrometric determinations conducted at room temperature (22.7°). In a typical experiment, of which the results are presented graphically in Fig. 1, a sample of cyanogen azido-dithiocarbonate weighing 0.3203 g. was placed in the nitrometer bulb. The volume of nitrogen liberated was read every twelve hours over a period of 1100 hours, during which a total of 51.7 cc. (corr.), corresponding to 1.016 mol of nitrogen per mol of the solid was evolved.

As the temperature is raised the velocity of decomposition undergoes marked acceleration. At 40 °, for example, complete decomposition takes place within eighty hours. In a typical experiment 0.5433 g. of the original solid yielded 86 cc. (corr.), or 1.019 mol of nitrogen. The results are depicted in Fig. 2.

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[10] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1st ed., **1905**, Vol. I, p. 232.

The concavity shown by the lower part of each curve toward the axis of ordinates indicates that the reaction is autocatalytic, and is therefore similar in type to the decomposition of azido-carbondisulfide.[11]

Pure white cyanogen azido-dithiocarbonate, after standing at room temperature for eighteen hours, takes on a light yellow color (YT2–YT1). After forty hours it assumes a very light orange-yellow tint (YT1–OYT2) and after forty-eight hours it attains its final color (Y–OY), which is intermediate between yellow and orange-yellow.[10]

Under the microscope the freshly prepared crystals are observed to consist of fine needles and thin prisms. These show parallel extinction and negative elongation, with fairly strong birefringence. The index of refraction for vibrations parallel to the long direction is 1.490; for vibrations transverse, between 1.7 and 1.8.

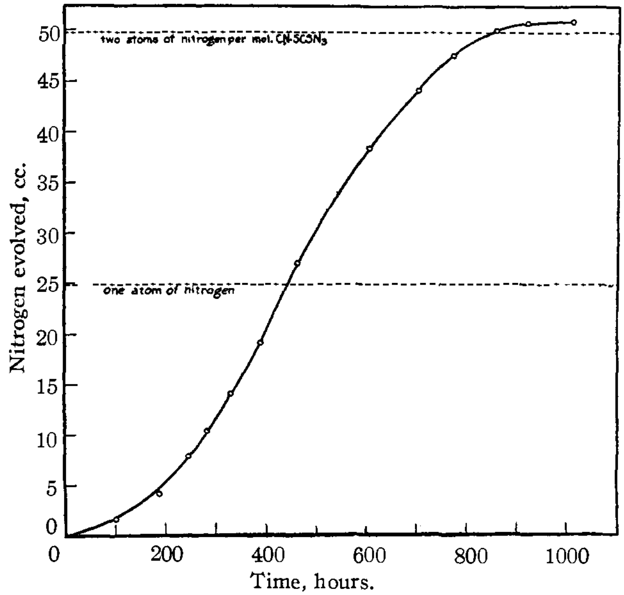

Fig. 1.—Nitrometric decomposition of cyanogen azido-dithiocarbonate at 22.7°.

The substance crystallizes from xylene or benzene in prisms which are laterally elongated rhombic bipyramids, and in rhombs which correspond to the unit prism, basal pinacoid and macradome. These have acute angles of about 62°, and show symmetrical extinction. They are biaxial, negative, with 2V fairly large. The axial plane bisects the acute angle of the rhombs. The prisms show a very well-defined basal cleavage. The general habit of both prisms and rhombs is similar to that of ammonium perchlorate. The symmetry and the optical tests indicate that the crystals belong to the orthorhombic system.

On recrystallization from benzene the crystals "sweat" a yellow oil which is apparently insoluble in benzene. When touched with a hot wire under the microscope the crystals melt and evolve gas copiously. The melt is yellow and on cooling behaves as a supercooled liquid. Seeded with cyanogen azido-dithiocarbonate it solidifies almost completely, with a small amount of yellow oily material surrounding the crystals. The melt contains varying amounts of a brown, amorphous, isotropic, flocculent material, which does not appear to be a product of the decomposition at room temperature.

Solubility.—The solubility of cyanogen azido-dithiocarbonate at 0° in various non-aqueous solvents was determined by cooling solutions saturated at room temperatures in the ice-bath. After crystallization had occurred, 5-cc. samples of the supernatant liquid were in each case pipetted into weighed containers and the solvent was removed by evaporation. The results are presented in Table I.

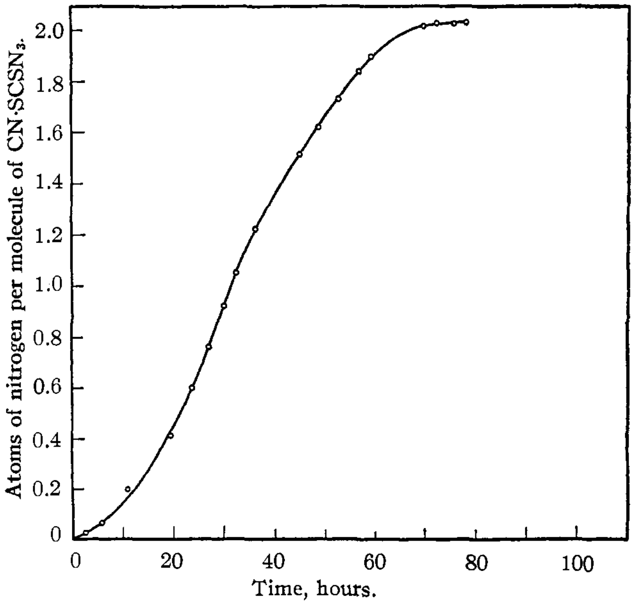

Fig. 2.—Nitrometric decomposition of cyanogen azido-dithiocarbonate at 40°.

Table I

Solubility of $CN\cdot SCSN_3$ in Various Solvents

Solvent	G. of solid per 100-cc. solution
Acetone	24.69
Ethyl acetate	13.19
Methanol	6.27
Chloroform	3.17
Ethanol	2.61
Ether	1.11
Carbon disulfide	0.29
Carbon tetrachloride	0.22
Water	0.15

All organic solvents tend to accelerate the decomposition of cyanogen azido-dithiocarbonate. For this reason the use of such solvents in the purification of the interhalogenoid is precluded. In chloroform and benzene solutions, for example, complete decomposition with formation of an orange-yellow (OY-O) solid takes place at room temperature in twelve hours. At 50° a copious evolution of gas begins at once and the solid product appears in about fifteen minutes, while the solvent retains a part of the cyanogen thiocyanate in solution.

Behavior toward Alkalies.—Cyanogen azido-dithiocarbonate dissolves readily and completely in aqueous solutions of sodium or potassium hydroxide, yielding a light greenish-yellow (GYT2–GY) solution. Immediate neutralization of such solutions at 0° with dilute acids results in a reprecipitation of part of the interhalogenoid. The presence of cyanide, thiocyanate, sulfate and azido-dithiocarbonate ions in the residual solution was demonstrated by appropriate tests. After a short time interval the formation of sulfide, sulfite, thiosulfate and ammonium ions was found to have occurred at room temperature. Nitrogen and carbon dioxide were evolved.

Hydrolysis of cyanogen azido-dithiocarbonate may be considered to proceed in accordance with either Equation 7 or Equation 8.

$$CN{\cdot}SCSN_3 + 2KOH = KSCSN_3 + KOCN + H_2O \qquad (7)$$

$$CN{\cdot}SCSN_3 + 2KOH = KCN + KOSCSN_3 + H_2O \qquad (8)$$

The potassium azido-oxydithiocarbonate probably decomposes, with formation of the chlorate analog of azido-carbondisulfide, as described in an earlier article.[11] This in turn undergoes decomposition, yielding a variety of products.

An entirely similar hydrolysis of the interhalogenoid is effected more slowly by water in the absence of alkalies. The products formed comprise the various free acids, in place of the metallic salts yielded by hydrolysis in alkaline solution. A yellow solid, consisting chiefly of dithiocyanic acid and free sulfur is gradually deposited from the solution.

Ammonolysis.—When a current of ammonia gas is caused to impinge upon dry cyanogen azido-dithiocarbonate, explosive decomposition of the solid ensues at once. Bubbled through an ethereal solution of the interhalogenoid, ammonia precipitates a white solid consisting chiefly of ammonium azido-dithiocarbonate, contaminated with some ammonium thiocyanate. On evaporating the ethereal solution to dryness, a sticky, orange-colored residue was obtained, of which the aqueous extract was found to contain cyanamide. It is therefore highly probable that ammonolysis proceeds in accordance with the equation

$$CN{\cdot}SCSN_3 + 2NH_3 = NH_4SCSN_3 + NH_2CN \qquad (9)$$

Behavior toward Acids.—Cyanogen azido-dithiocarbonate dissolves completely, with decomposition accompanied by evolution of gas, in concentrated sulfuric, hydrochloric or nitric acid. In the case of sulfuric acid the reaction takes place with almost explosive violence. With hydrochloric acid the resulting solution, at first clear and colorless, ultimately grows turbid owing to the separation of free sulfur. Treated with potassium iodide, the solution liberates iodine, indicating the presence of free chlorine, thiocyanogen or one of the various possible halogen-halogenoid or interhalogenoid compounds. Dilute mineral acids react more slowly than the concentrated acids, but eventually effect complete solution of the interhalogenoid. Glacial acetic acid behaves like the dilute mineral acids except that a yellow-orange (Y–YO) solid is finally deposited.

Miscellaneous Reactions.—Cyanogen azido-dithiocarbonate slowly reduces potassium permanganate in dilute acid and neutral solutions. It does not react with potassium bromate. It is oxidized at least partially by hydrogen peroxide in alkaline solution, with formation of sulfate ion. It dissolves in stannous chloride solution with evolution of gas and formation of a light yellow (YT2–YT1) solution. It dissolves slowly in dilute solutions of hydrazine hydrate and reacts violently with concentrated solutions, yielding hydrogen sulfide and free thiocyanogen. It liberates iodine from solutions of potassium iodide in the presence of concentrated hydrochloric acid.

It is soluble in aqueous solutions of potassium azido-dithiocarbonate, with probable initial formation of a *polyhalogenoid* such as $KSCSN_3 \cdot CNSCSN_3$ or $KCN \cdot (SCSN_3)_2$, corresponding to the well-known polyhalides. The resulting solution smells strongly of cyanide, and after a time deposits solid azido-carbondisulfide

$$KSCSN_3 + CN \cdot SCSN_3 = KCN \cdot (SCSN_3)_2 \tag{10}$$

$$KCN \cdot (SCSN_3)_2 = KCN + (SCSN_3)_2 \tag{11}$$

Summary

Cyanogen azido-dithiocarbonate, $CNSCSN_3$, a new interhalogenoid, is formed by the interaction of azido-carbondisulfide and mercuric cyanide in acetone, but is best prepared by bringing together a cold, aqueous solution of sodium azido-dithiocarbonate and an ethereal solution of cyanogen bromide. It is a white, crystalline solid, slightly soluble in water, and more readily soluble in various non-aqueous liquids, especially acetone and ethyl acetate. It is stable at 0°, but undergoes a slow autocatalytic decomposition at room temperature, yielding thiocyanogen, cyanogen thiocyanate, sulfur and nitrogen.

The behavior of the interhalogenoid toward acids and alkalies, toward ammonia, and toward certain oxidizing and reducing agents has been studied.

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