chemical reaction $S^{--} + 2Fe^{+++} \longrightarrow S^{\circ} + 2Fe^{++}$. It was impossible to verify this quantitatively because of restrictions in the analytical procedures.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

AZIDO-CARBONDISULFIDE. I. FORMATION, PREPARATION AND GENERAL PROPERTIES[1]

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With Microscopical Studies by C. W. MASON

RECEIVED JULY 21, 1923

It was found by F. Sommer,[2] during an investigation of the properties of sodium azido-dithiocarbonate, that treatment of aqueous solutions of this salt with such oxidizing agents as ferric chloride, iodine in potassium iodide, and potassium permanganate, potassium dichromate, or ceric salts in sulfuric acid solution, results in the precipitation of an unstable white solid, surmised by him, from the method of its formation, to possess the formula $N_2—N—CS—S—S—CS—N—N_2$. No analysis was made of this compound, or study of its properties, aside from the observation that a sample of the insoluble needles, when heated under water, exploded violently at a temperature below 100°.

The formation of this substance, to which the name azido-carbondisulfide is provisionally assigned, has been repeatedly observed in this Laboratory[3] to take place when aqueous solutions of potassium trinitride and iodine are brought together under certain conditions in the presence of carbon disulfide. Azido-carbondisulfide has been shown to have an important catalytic effect upon the reaction between potassium trinitride and iodine, as does the related compound, potassium azido-dithiocarbonate. In fact, these two substances, the relationship between which is very similar to that between iodine and potassium iodide, behave in this reaction in the manner characteristic of what might be termed a *reciprocal catalytic pair.*[4]

Formation and Preparation.—The action of various oxidizing agents

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 4 under Heckscher Grant No. 4. For Articles 1, 2, and 3 see THIS JOURNAL, **44**, 2106, 2116, 2315 (1922). This paper was presented at the New Haven meeting of the American Chemical Society in April, 1923.

[2] Sommer, *Ber.*, **48**, 1833 (1915).

[3] Browne and Hoel, THIS JOURNAL, **44**, 2106 (1922).

[4] This term is intended to apply to any pair of chemical compounds that undergo repeated mutual conversion into each other while having their catalytic effect upon a given chemical reaction.

upon a 3% aqueous solution of potassium azido-dithiocarbonate has been investigated. Unless otherwise specified, a 1% solution of the oxidizing agent was gradually added in each case to 5 cc. of the azido-salt solution in a test-tube.

Hydrogen peroxide causes evolution of gas and produces a transitory, yellow-green color. The solution soon becomes turbid, and a considerable amount of azido-carbondisulfide is ultimately precipitated. Ozonized oxygen, when bubbled through the azido-salt solution, causes a slight evolution of gas. Potassium iodate and potassium chromate yield a small amount of precipitate after standing for several hours. With potassium persulfate, characteristic crystals of the azido-disulfide appear after a time. Mercuric chloride precipitates at once a heavy, white, crystalline substance, probably mercuric azido-dithiocarbonate, and later yields a fluffy, white precipitate of the azido-disulfide. In the presence of a slight excess of hydrochloric acid, ferric chloride first turns the solution red, and ultimately precipitates the azido-disulfide. Under similar conditions stannic chloride shows no action at first, but later forms a white precipitate. In the presence of sulfuric acid, potassium permanganate, solid manganese dioxide, solid cerium dioxide and sodium nitrite produce sooner or later the insoluble azido-disulfide, accompanied in the last case by evolution of considerable gas and appearance of a temporary brown color in the solution. Chlorine, bromine and iodine yield at once an abundant precipitate of the azido-disulfide.

Electrolysis of an approximately 20% solution of potassium azido-dithiocarbonate between a rotating platinum anode of 30 sq. cm. total area and a stationary platinum cathode enclosed in a parchment thimble, with anode current density of 18.6 amp./sq. dm., resulted in the formation of relatively large amounts of azido-carbondisulfide, small particles of which occasionally exploded, under the solution, at or near the anode, with a sharp, crackling noise.

The method finally selected for the preparation of azido-carbondisulfide involves the following procedure.

Five cc. of the clear, concentrated solution of potassium azido-dithiocarbonate, obtained by filtering the liquid resulting from interaction of 6 g. of potassium trinitride and 6 g. of carbon disulfide in 25 cc. of water, is diluted with 50 cc. of water. Normal iodine solution in potassium iodide is added drop by drop, with continual stirring, until complete precipitation of the azido-disulfide has been effected. The slightest excess of free iodine must be avoided, however, as iodine appears to be adsorbed by the disulfide, and can be removed from it by washing only with some difficulty. If an excess of iodine be inadvertently added this may be reduced by addition of the requisite amount of a dilute solution of the azido-salt. The possible formation of an intermediate product such as iodine azido-dithiocarbonate, $ISCSN_3$, will be considered in a later investigation.

The precipitated azido-disulfide is washed in a Büchner funnel with cold water until free from soluble material, and is partially dried by suction. Small portions are carefully spread upon a porous plate with the aid of a bone spatula, avoiding tapping or undue pressure, and are finally stored in a desiccator over phosphorus pentoxide, kept at 10° or lower, to minimize spontaneous decomposition.

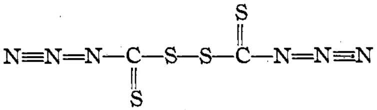
Analysis.—Sulfur was determined in the thoroughly dried crystals of azido-carbondisulfide by oxidizing weighed samples with concd. nitric acid and bromine, and weighing the sulfur in the form of barium sulfate.

Analyses. Subs., 0.2251, 0.2002: $BaSO_4$, 0.8911, 0.7943. Calc. for $(SCSN_3)_2$: S, 54.27. Found: 54.37, 54.49.

Nitrogen was determined by combustion of the azido-disulfide in the manner already employed for potassium azido-dithiocarbonate.[5]

Analyses. Subs., 0.0567, 0.1890: N_2, 16.12 cc. (0.02016 g.), 53.83 cc. (0.06733 g.). Calc. for $(SCSN_3)_2$: N, 35.57. Found: 35.56, 35.62.

These results point toward the formula suggested by Sommer for this compound and, in connection with the data concerning its decomposition submitted below, tend to confirm the following structure.



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

Properties.—Azido-carbondisulfide is a white, crystalline solid, soluble to the extent of about 3 parts in 10,000 of water at 25°. It is very unstable, and is distinctly more sensitive to impact and to heat than is potassium azido-dithiocarbonate. Explosions have frequently occurred at various stages of its preparation and investigation. These explosions result in the liberation of much heat, with more smoke but less flame than is characteristic of explosions of the azido-dithiocarbonate.

Three consecutive attempts to effect the slow, quantitative decomposition of weighed samples of the dry azido-disulfide, varying from about 0.06 to 0.17 g. in weight, by careful heating in a glass tube connected with a nitrometer, and immersed in a water-bath, resulted in violent explosions, in the first case at 54°, and in the second and third at 50°. Qualitative proof of the evolution of nitrogen and of the presence of thiocyanates in the residue and in the water above the mercury in the nitrometer tube was nevertheless obtained in the second experiment.

In a fourth experiment, 0.1097 g. of azido-carbondisulfide was held at 40° for 3 hours, with the result that 20.54 cc. (corr.) or 0.02569 g. of nitrogen, corresponding to 3.95 atoms of nitrogen per molecule of the disulfide, was liberated. Continued heating for a number of hours to an ultimate temperature of 60° increased the volume to 20.83 cc. (corr.) corresponding to 0.02605 g. of nitrogen, or 4.005 atoms of nitrogen per molecule of the compound.

Azido-carbondisulfide undergoes gradual spontaneous decomposition at ordinary room temperatures, with liberation of nitrogen, and formation of a solid residue probably consisting of a mixture of free sulfur and polymeric thiocyanogen,[6] in accordance with the equation

$$(SCSN_3)_2 = 2N_2 + 2S + (SCN)_2 \qquad (1)$$

A freshly prepared sample of the azido-disulfide weighing 0.1145 g. was placed in the nitrometer tube, which was immersed in a thermostatic

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[5] Browne and Hoel, THIS JOURNAL, **44**, 2315 (1922).

[6] Söderbäck, *Ann.*, **419**, 217 (1919).

bath and held at 25° under close observation for a period of 72 consecutive hours. The volume of nitrogen evolved was read at intervals of 1 or 2 hours. The data obtained are shown in Figs. 1 and 2.

These curves show clearly that the velocity of the decomposition, which has hitherto undergone a remarkably regular acceleration, begins to decrease as soon as two atoms, or $^1/_2$ of the available nitrogen, has been evolved. This may indicate that the decomposition of azido-carbondisulfide takes place in two stages, with initial formation of an inter-halogenoid substance, azido-carbondisulfide thiocyanate, intermediate in composition between azido-carbondisulfide itself, and dithiocyanogen, in accordance with the equation

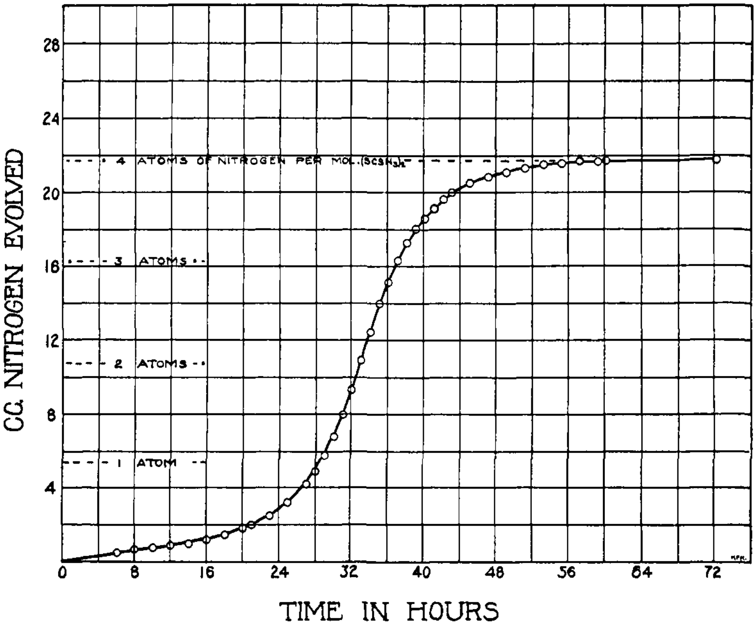

Fig. 1

$$(SCSN_3)_2 = N_2 + S + SCSN_3.SCN \qquad (2)$$

This intermediate product may then decompose more slowly, during the second stage of the reaction, as expressed by the equation

$$SCSN_3.SCN = N_2 + S + (SCN)_2 \qquad (3)$$

During the decomposition of azido-carbondisulfide a very noteworthy change of color gradually takes place. In one experiment, typical of the many that have been performed, a sample of the pure white compound, after standing at room temperature (about 25°) for 23 hours, assumed a very light yellow color, YT2 on the Milton Bradley Standard.[7] After

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

successive time intervals further changes in color resulted as follows: 4 hours, YT1; 16, OY; $3^{1}/_{2}$, YO; $3^{1}/_{2}$, O; 2, RO; $15^{1}/_{2}$, RO–OS1; 7, OS1. The dark orange color thus attained, after a total period of nearly 75 hours, remains unchanged for an indefinite length of time. This series of changes seems to be in no way dependent upon the degree of illumination to which the material is subjected. One sample, exposed for some time to direct (July) sunlight, showed changes in color identical with those of a sample kept in a dark cupboard. The rate of change, however, varies directly with the temperature.

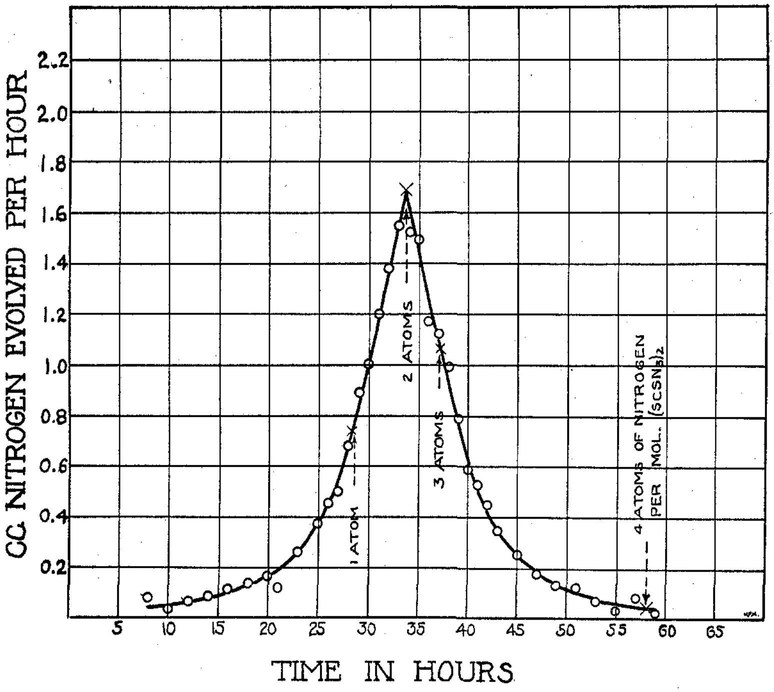

Fig. 2

Under the microscope, crystals of the freshly prepared azido-carbondisulfide are seen to be colorless, and of tabular prismatic to acicular habit. For this reason end views are not obtainable. All prismatic views exhibit parallel extinction and fairly strong double refraction. The lower index of refraction corresponds to vibrations parallel to the elongation of the crystals. The mean index of refraction cannot readily be determined, on account of the solubility of the crystals in the various immersion liquids (essential oils), but it is estimated at about 1.8. The crystals show faces corresponding to the prism, bipyramid of a different order, and rarely the basal pinacoid. Tabular crystals, 6-sided in outline, exhibit terminal angles of about 138°. Asymmetric forms are frequent, particularly those in which 2 or 4 of the pyramid faces are not developed, giving rise to 5-sided or to trapezoidal outlines. At the ends of the crystals V-shaped markings are frequent. The habit and all observable optical properties lead to the classification of the crystals in the tetragonal or in the orthorhombic system.

When newly precipitated, dry azido-carbondisulfide is allowed to decompose at room temperature on a microscope slide, the crystals show surface corrosion after about 24 hours, and are coated with a yellow, viscous substance. Gas evolution takes place coincidently with a progressive corrosion or decomposition of the crystals from the surface inward, and not infrequently an isolated crystal is seen at this stage to be almost completely decomposed, a fragment remaining for a time imprisoned in the center of the viscous, amber liquid. Starting again at the outside, the decomposition product gradually becomes more viscous and also grows darker in color, yielding, in about 48 hours, after further evolution of gas, a reddish-orange, brittle, amorphous, vesicular mass, particles of which may retain something of the form of the original crystals. The final product, as seen by transmitted light, is of a somewhat greenish-yellow appearance in thin layers, while in thicker layers it is of a reddish-orange tint.

When a dried sample of the azido-disulfide is heated on a microscope slide it explodes, leaving an oily, viscous, yellow residue, apparently identical with the product of partial decomposition at room temperature. In case the detonation has been effected in such a way as to avoid heating of the slide, as by touching the sample for an instant with a hot platinum rod or wire, or by quickly passing a flame over it, the resulting liquid is of a very pale yellow color, and remains for some time entirely free from gas bubbles. If, on the other hand, the slide is heated, transformation of the yellow product into the usual brittle, vesicular mass, which would be formed in any event after the lapse of some time, soon takes place with comparatively rapid evolution of gas.

The yellow oil obtained as an intermediate product during the decomposition of azido-carbondisulfide is probably not identical with the amorphous thiocyanogen obtained, also in the form of a "clear, thick, yellow oil," by Söderbäck,[8] but may consist of a solution of still unchanged azido-carbondisulfide in thiocyanogen, or of an inter-halogenoid compound, $SCSN_3.SCN$, as suggested in an earlier paragraph, mixed with free sulfur. Except for the presence of this free sulfur, the dark orange (OS1), brittle, vesicular product finally obtained, after further spontaneous liberation of gas from the yellow oil, is probably identical, however, with Söderbäck's "brick-red, light substance" obtained when the yellow oil was gently heated in a vacuum, or with his spontaneously formed "yellow-brown or yellow-red resin."

The yellow oil obtained as an intermediate product, either by spontaneous decomposition at room temperature or by careful detonation of azido-carbondisulfide, has been found to have a marked catalytic effect upon the decomposition of the disulfide. Freshly prepared samples of the oil, when brought into contact with undecomposed portions of azido-

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[8] Ref. 6, p. 237.

carbondisulfide, start at once a decomposition at a rate apparently equal to the maximum velocity of spontaneous decomposition at the temperature chosen. After the oil has itself undergone the second stage of decomposition, with formation of the resinous product, it loses its catalytic power.

As a result of the vesicular and resinous character of the decomposition product considerable difficulty was experienced in effecting a quantitative separation of the free sulfur from the polymeric thiocyanogen. Three methods were investigated: (1) prolonged heating of the mixture to 125°, until no further vaporization of sulfur takes place; (2) extraction with carbon tetrachloride; and (3) extraction with carbon disulfide. The last method yielded the best results. A sample of the dark orange mixture, weighing 3.6486 g., was extracted with carbon disulfide in a Soxhlet apparatus for a period of 100 hours, after which further treatment effected the separation of no additional sulfur.

The percentage of sulfur contained in the residue was determined, with the following results.

Subs., 0.4980, 0.4997: $BaSO_4$, 2.0065, 2.0188. Calc. for $(SCN)_x$: S, 55.21. Found: 55.33, 55.48.

These data indicate that the residue was a fairly pure, polymerized thiocyanogen. Further work upon this product will be carried on, in order to determine its molecular weight, and to investigate its properties and reactions.

Behavior toward Non-Aqueous Liquids.—Azido-carbondisulfide is appreciably soluble in methyl alcohol, ethyl alcohol, diethyl ether, carbon tetrachloride and xylene. It is moderately soluble in benzene and in carbon disulfide, and more readily soluble in ethyl acetate and in acetone. A sample weighing 0.1180 g., for example, was easily taken up by 1.4 cc. of acetone.

Solutions of azido-carbondisulfide in these liquids undergo gradual spontaneous decomposition at room temperature, with deposition of solids ranging in color from yellow to dark orange (OS1) and resembling in composition the residue obtained by decomposition of the solid solute. In some instances a secondary product is formed, probably as a result of the action of the freshly liberated thiocyanogen, SCN or $(SCN)_2$, upon the solvent. The velocity of decomposition is very much greater in some cases than that of the dry solute.

Xylene solutions show a slow evolution of gas almost at once, assume a yellow color, and soon begin to deposit droplets of a yellow, viscous substance. The final product possesses an odor closely resembling that of scorched rubber. Acetone solutions yield a dark orange (OS1) residue possessing a strong odor of garlic.

Behavior toward Acids.—Dil. sulfuric acid (1:6) shows little or no action upon azido-carbondisulfide at room temperature. At 40° the solid slowly dissolves, and the resulting solution gradually becomes turbid owing to the liberation of sulfur. More concentrated acid (1:1) attacks the solid slowly even at room temperature, while the undiluted acid effects a more rapid reaction, accompanied by an appreciable evolution of gas.

Hydrochloric acid reacts with azido-carbondisulfide somewhat more readily than does sulfuric acid, with liberation of sulfur and evolution of gas. The residual solution obtained when concd. acid was used as the solvent was found to contain thiocyanates as well as an oxidizing agent capable of liberating iodine from a solution of sodium iodide. This action is attributable either to free chlorine, to thiocyanogen, or to an inter-halogen-halogenoid compound such as chlorine azido-dithiocarbonate, $ClSCSN_3$, or chlorine thiocyanate, $ClSCN$.

Nitric acid in corresponding concentrations behaves in much the same way as hydrochloric acid, except that no precipitation of sulfur takes place. Acetic acid reacts somewhat less vigorously than the mineral acids, although the concd. acid promptly dissolves the solid azido-disulfide at room temperature, yielding a solution that is clear at first, but that becomes turbid after a time.

Behavior toward Alkalies.—Azido-carbondisulfide reacts at once with solutions of potassium hydroxide, yielding a clear, greenish-yellow solution. At room temperatures the liberation of small amounts of gas takes place immediately, and is followed by a very slow, long-continued evolution of gas as the unstable product is gradually decomposed. At low temperatures no perceptible evolution of gas occurs. For example, when about 3 cc. of a 10 *N* solution of potassium hydroxide was treated at —10° with the solid halogenoid, the usual greenish-yellow solution was formed, without liberation of gas. The reaction, in its initial stage, probably takes place in accordance with the equation

$$(SCSN_3)_2 + 2\,KOH = KSCSN_3 + KOSCSN_3 \qquad (4)$$

with formation of potassium azido-dithiocarbonate and potassium azido-oxydithiocarbonate, respectively, analogous to the chloride and hypochlorite formed by interaction of free chlorine and potassium hydroxide. Acidification of the greenish-yellow solution with dil. sulfuric acid in slight excess causes the precipitation of azido-carbondisulfide, as follows.

$$KSCSN_3 + KOSCSN_3 + H_2SO_4 = K_2SO_4 + (SCSN_3)_2 + H_2O \qquad (5)$$

This corresponds to the liberation of chlorine by acidification of a solution containing a chloride and a hypochlorite. The filtrate obtained on removal of the solid halogenoid was found to contain relatively large amounts of the azido-salt. This was shown by the abundant precipitation of azido-carbondisulfide that took place on addition of a solution of iodine, and by the vigorous catalytic action exerted by even a minute amount of the filtrate upon the reaction between iodine and potassium trinitride.[9] These point toward the conclusion that at least a part of the azido-dithiocarbonate, or hypochlorite analog, has undergone transformation to a derivative containing a larger amount of oxygen, such as the azido-trioxydithiocarbonate, or chlorate analog, as expressed by the equation

$$3\ KOSCSN_3 = 2\ KSCSN_3 + KO_3SCSN_3 \qquad (6)$$

This chlorate analog may be regarded as a derivative of sulfuric acid obtained by replacement of an hydroxyl by the azido-thiocarbonyl group, CSN_3. On this assumption, the compound might easily hydrolyze in aqueous solution, especially after acidification with hydrochloric acid, yielding free sulfuric acid as one product. The presence of sulfuric acid in considerable amount has been established experimentally by repeated examination of the solutions obtained by interaction of azido-carbondisulfide and potassium hydroxide.[10] It is of course possible that the appearance of sulfuric acid may be due partly or wholly to the formation of potassium oxythiocyanate, KOSCN, by decomposition of the azido-oxydithiocarbonate, and subsequent transformation of this hypochlorite analog of the thiocyanogen series to the chlorate analog, KO_3SCN, which in acid solution should hydrolyze, yielding sulfuric and hydrocyanic acids. Söderbäck,[11] while apparently overlooking the analogy between cyanosulfuric and chloric acids, has demonstrated the formation of sulfuric and hydrocyanic acids as products of the hydrolysis of free thiocyanogen. The absence of hydrocyanic acid from the products of hydrolysis of azido-carbondisulfide, however, points toward the conclusion that the sulfuric acid is not in this case formed by way of the thiocyanogen derivatives, but that the new halogenoid probably forms its own series of oxyacids.

With solutions of sodium hydroxide, ammonium hydroxide, and sodium carbonate, azido-carbondisulfide was found to react as with a solution of potassium hydroxide, yielding the characteristic greenish-yellow solution.

Behavior toward Certain Oxidizing Agents and Reducing Agents.—Azido-carbondisulfide readily reduces potassium permanganate at room temperature in neutral, alkaline or acid solution. It reacts with potassium iodate in neutral and in acid, but apparently not in alkaline solution. A 3% solution of hydrogen peroxide slowly dissolves the disulfide, yield-

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[9] It has been found that potassium thiocyanate also has a marked catalytic effect upon the reaction between iodine and potassium trinitride, and it is thought that potassium thiocyanate and free thiocyanogen may, like potassium azido-dithiocarbonate and azido-carbondisulfide, constitute a reciprocal catalytic pair.

[10] The experimental work on this topic has been performed in this Laboratory by Mr. Frank Wilcoxon, who first called attention to the presence of sulfuric acid among the products of this reaction.

[11] Ref. 6, p. 294.

ing a solution which has the odor of hydrocyanic acid.[12] The reaction seems to take place less rapidly in the presence of dil. sulfuric acid. The greenish-yellow color of the dilute alkaline solution containing sodium hydroxide is discharged by hydrogen peroxide, with evolution of gas.

Successive portions of azido-carbondisulfide added to a fairly concentrated aqueous solution of hydriodic acid cause immediate liberation of iodine, the color of which soon disappears, owing to a secondary reaction that possibly results in the formation of iodine azido-dithiocarbonate or iodine thiocyanate. Dilute aqueous hydrazine hydrate dissolves the disulfide at once, with slow evolution of gas, yielding a solution which is at first colorless, but later assumes a light greenish-yellow color (GYT2), and deposits a light gelatinous precipitate. Five per cent. solutions of ferrous sulfate, stannous chloride, and oxalic acid show no appreciable immediate reducing action upon azido-carbondisulfide.

Further work upon many of the topics briefly mentioned in the present article is now in progress in this Laboratory, and will be made the subject of future communications.

Summary

Azido-carbondisulfide, $(SCSN_3)_2$, a new halogenoid substance, has been prepared by chemical or electrochemical oxidation of potassium azido-dithiocarbonate, $KSCSN_3$, and its composition has been established by analysis. It is a white, crystalline solid, very slightly soluble in water, but readily soluble in certain non-aqueous liquids, such as acetone and ethyl acetate. It is stable at 0°, but undergoes quantitative autocatalytic decomposition at room temperature, yielding polymeric thiocyanogen, sulfur and nitrogen gas.

A preliminary study has been made of the behavior of azido-carbondisulfide toward acids and alkalies, and toward certain oxidizing agents and reducing agents.

ITHACA, NEW YORK

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[12] Kastle and Smith [*Am. Chem. J.*, **32,** 376 (1904)] have shown that thiocyanic acid is oxidized by hydrogen peroxide, with formation of sulfuric acid and hydrocyanic acid, probably in accordance with the equation, $HSCN + 3H_2O_2 = HCN + H_2SO_4 + 2 H_2O$. The possible formation of cyano-sulfuric acid, the analog of chloric acid, as an intermediate product of this reaction, should be borne in mind. See also Bjerrum and Kirschner, *Kgl. Danske Vidensk. Selskab. Math. Medd.*, [8] V, No. 1, 76 pp. (1918); *C. A.*, **13,** 1057 (1919).