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AZIDO-DITHIOCARBONIC ACID

IV. AMMONIUM AND TETRAMETHYLAMMONIUM AZIDO-DITHIOCARBONATES; TETRAMETHYLAMMONIUM THIOCYANATE[1,2]

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WITH MICROSCOPICAL STUDIES BY C. W. MASON

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In view of the peculiar photosensitivity of the rubidium and cesium azido-dithiocarbonates,[1c] it has been thought probable that the tetramethylammonium salt might, like these compounds, show a reversible color change under the influence of light. The chief objective of the present investigation has therefore been the isolation and description of this substance, which should be of interest in any event from the fact that it contains a strongly electropositive radical, or "synthetic metal" in combination with a strongly electronegative radical of the halogenoid type. For the sake of comparison, the hitherto unknown ammonium azido-dithiocarbonate has also been prepared, as well as the tetramethylammonium thiocyanate, the principal product of the thermal decomposition of tetramethylammonium azido-dithiocarbonate.

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[1] For the earlier articles of this series see (a) Smith and Wilcoxon with Browne, THIS JOURNAL, **45**, 2604 (1923); (b) Browne and Smith, *ibid.*, **47**, 2698 (1925); (c) Browne and Audrieth, *ibid.*, **49**, 917 (1927).

[2] 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 3 under Heckscher Grant No. 60. For Articles 1 and 2, see (a) THIS JOURNAL, **45**, 2604 (1923); (b) **47**, 1916 (1925). For articles 1, 2, 3 and 4 under Heckscher Grant No. 4, see (c) *ibid.*, **44**, 2106 (1922); (d) **44**, 2116 (1922); (e) **44**, 2315 (1922); (f) **45**, 2541 (1923).

Ammonium Azido-dithiocarbonate[3]

NH_4SCSN_3

This compound may be obtained (1) by neutralization of free azido-dithiocarbonic acid[1a] with ammonium hydroxide in aqueous solution, (2) by prolonged treatment of ammonium trinitride in aqueous solution with carbon disulfide under conditions prescribed for use in the synthesis of the potassium salt,[2e] and (3) by bubbling ammonia gas through an ethereal solution of the azido-acid. The third procedure, which is similar to the method used by Browne and Houlehan[4] in preparing ammonium trinitride, was adjudged the most satisfactory for the present investigation.

The ammonium radical was determined in the usual way after distillation of the ammonia from alkaline solution into standard sulfuric acid. The azido-dithiocarbonate radical was determined by the modified Volhard method recommended by Browne and Smith.[1b]

Anal. (a) Subs., 0.6584, 0.7965: NH_4, 0.0864, 0.1063. Calcd. for NH_4SCSN_3: NH_4, 13.25. Found: 13.12, 13.35. (b) Subs., 0.3097, 0.1733: $SCSN_3$, 0.2694, 0.1505. Calcd. for NH_4SCSN_3: $SCSN_3$, 86.8. Found: 87.0, 86.8.

Ammonium azido-dithiocarbonate is a white, crystalline, non-deliquescent solid, readily soluble in water, methyl or ethyl alcohol, and acetone, somewhat soluble in ether, but practically insoluble in benzene and xylene.

Heated in a Thiele melting-point tube the ammonium salt assumes at 90° a reddish-orange color, RO–O on the Milton Bradley Standard.[5] Decomposition becomes perceptible at about 110°, and the substance melts with evolution of gas at about 120°. The residue was found to consist of ammonium thiocyanate and sulfur, indicating that the reaction proceeds in accordance with the equation $NH_4SCSN_3 = NH_4SCN + S + N_2$. Larger samples have been found to decompose suddenly, with a puff, between 115 and 120°.

Samples composed of larger crystals obtained by the second method were invariably found to decrepitate vigorously between 80 and 100° as a result of the presence of occluded nitrogen formed during prior thermal decomposition. When such crystals are dissolved in water the presence of these occluded gases becomes manifest.

On exposure to direct sunlight the salt undergoes coloration, within a few minutes, to a very light orange tint, OT2 on the Milton Bradley Standard.[5] A partial reversal of this color change takes place very slowly in the dark.

When strongly heated on an asbestos board, the salt suddenly decomposes with considerable flame and a puff of smoke. An attempt to effect a molecular rearrangement of the salt by heating a sample in a sealed tube resulted in a violent explosion.

Under the microscope, ammonium azido-dithiocarbonate is seen to form crystals that are mostly thick, six-sided tablets of varying proportions. The parallel or symmetrical extinction exhibited in more than one position, together with the crystal forms present, indicate that the substance very probably is orthorhombic. The terminal angle of the truncated rhomb-shaped crystals is about 120°. Numerous forms are represented on well-developed crystals: 001, 100, 010, 111, 211, 110, and probably other forms as well, may be recognized. The index of refraction is about 1.9 for vibrations

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[3] The authors would express, herewith, their appreciation of the assistance rendered by Mr. G. G. Parker, of this Laboratory, in connection with a part of the experimental work upon this substance.

[4] Browne and Houlehan, This Journal, 33, 1742 (1911).

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

parallel, and 1.7+ for vibrations perpendicular, to the long diagonal of the rhomb-shaped forms. Double refraction is strong; the interference figure is biaxial, but the axial angle is so large that the acute bisectrix and the sign of double refraction cannot be determined with certainty. The axial plane is parallel to the short diagonal of the rhomb-shaped forms.

Tetramethylammonium Azido-dithiocarbonate $N(CH_3)_4SCSN_3$

Three methods for the preparation of this substance have been studied: (1) neutralization of free azido-dithiocarbonic acid with tetramethylammonium hydroxide in aqueous solution, (2) double decomposition of barium azido-dithiocarbonate and tetramethylammonium sulfate, and (3) digestion of an aqueous solution of tetramethylammonium trinitride, a compound first prepared in this Laboratory by Friedlander,[6] with an amount of carbon disulfide slightly in excess of that required by the equation $N(CH_3)_4N_3 + CS_2 = N(CH_3)_4SCSN_3$. The third method, carried out under the conditions specified by Browne and Hoel,[2e] was found most satisfactory for use in the current investigation.

Nitrogen was determined by the Dumas method, and the azido-dithiocarbonate radical by the modified Volhard procedure.[1b]

Anal. (a) Subs., 0.1164, 0.1054: N_2 (corr.), 26.9, 24.2 cc. Calcd. for $N(CH_3)_4SCSN_3$: N_2, 29.1. Found: 28.9, 28.7. (b) Subs., 0.2217, 0.2220: $SCSN_3$, 0.1362, 0.1360. Calcd. for $N(CH_3)_4SCSN_3$: $SCSN_3$, 61.5. Found: 61.4, 61.3.

The tetramethylammonium salt crystallizes from aqueous solution in the form of large, white tablets, which may be purified by recrystallization from warm alcohol. The addition of ether to an alcoholic solution results in the precipitation of the salt in a voluminous, finely divided mass. The compound is readily soluble in water, fairly soluble in either methyl alcohol or acetone, slightly soluble in ether, and insoluble in carbon tetrachloride, carbon disulfide and chloroform.

The salt does not explode when struck with a hammer. When thrown upon the hot plate, or heated directly in the Bunsen flame, it suddenly decomposes with a puff. Heated gently, the substance always yields the characteristic odor of trimethylamine, which indicates that the primary decomposition of the substance may involve its dissociation into the tertiary amine and methyl azido-dithiocarbonate, in accordance with the equation $N(CH_3)_4SCSN_3 = N(CH_3)_3 + CH_3SCSN_3$.

In the melting-point tube the substance apparently undergoes fusion at 95–98°, assuming at the same time a dark green color. The color change is usually followed by a sudden puff indicative of complete decomposition. Like all other azido-dithiocarbonates thus far studied the tetramethylammonium salt gradually decomposes, even at room temperature, with formation of the thiocyanate, sulfur and nitrogen. In aqueous solution the negative ion resists decomposition for a time, and only after several hours of vigorous boiling fails to respond to the usual qualitative tests.

On exposure at room temperature to direct sunlight the white salt in a few minutes assumes a light orange color, OT1 on the Milton Bradley Standard.[5] In the dark this effect undergoes a gradual reversal which takes place more slowly than in the case of the cesium salt.[1c] Further work on the photosensitivity of the tetramethylammonium salt and of various other azido-dithiocarbonates and related compounds is now in progress.

Under the microscope the salt is seen to crystallize from aqueous solution in the form of rectangular tablets and stout prisms with beveled long edges. Some crystals show parallel extinction and give biaxial interference figures. They are optically positive, with 2V rather small, the axial plane being parallel to the elongation of the tablets, and

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[6] Friedlander, THIS JOURNAL, 40, 1945 (1918).

the acute bisectrix perpendicular to their principal plane. Other crystals, lying on one of the beveling faces, give oblique dispersed extinction and somewhat anomalous polarization colors. The maximum extinction angle observed is about 40° for the position corresponding to an edge view of the elongated tablets. Some end views were observed and these showed parallel extinction. The optical properties and symmetry of the crystals point to their being in the monoclinic system.

Tetramethylammonium Thiocyanate $N(CH_3)_4SCN$

In connection with a study of the power of solution and ionization of various nonaqueous solvents towards binary salts, Walden[7] prepared tetramethylammonium thiocyanate (1) by heating methyl thiocyanate with a solution of trimethylamine. During the current research this method has been compared with two others, by which the salt is obtainable either (2) by prolonged boiling of an aqueous solution of tetramethylammonium azido-dithiocarbonate, until quantitative decomposition into the thiocyanate has occurred, or (3) by bringing together tetramethylammonium trinitride[6] and carbon disulfide in alcoholic solution and boiling under the reflux condenser until the reaction has proceeded to completion.[8] The third method was found most convenient. Four cc. of carbon disulfide was dissolved in 50 cc. of absolute alcohol, and 5 g. of tetramethylammonium trinitride was added little by little to the boiling solution, which was refluxed until qualitative tests indicated the absence of trinitrides and azido-dithiocarbonates. After the solution had been concentrated and cooled, the thiocyanate was recrystallized from alcohol and obtained in the form of glistening white needles.

Nitrogen was determined by the Dumas method, and thiocyanogen was weighed as the silver salt.

Anal. (a) Subs., 0.1654, 0.1787: N_2 (corr.), 28.23, 30.45 cc. Calcd. for $N(CH_3)_4$-SCN: N_2, 21.2. Found: 21.35, 21.32. (b) Subs., 0.1933, 0.1847: AgSCN, 0.2413, 0.2310. Calcd. for $N(CH_3)_4SCN$: SCN, 43.9. Found: 43.7, 43.8.

Tetramethylammonium thiocyanate is fairly soluble in water and methyl alcohol, slightly soluble in ethyl alcohol and acetone, and insoluble in ether, chloroform, carbon disulfide and carbon tetrachloride.

When heated in the melting-point tube, the substance volatilizes at 304–305°. From the odor it is apparent that thermal dissociation into the tertiary amine and methyl thiocyanate readily takes place. By dry distillation a yellowish oil which boils at 132° (b. p. of CH_3SCN, 133°) is obtained.

Under the microscope the salt crystallizes in rectangular prisms with the long edges beveled, and in tabular crystals (flattened prisms). A few end views were obtainable, and these corresponded to the prismatic forms in symmetry and optical properties. The crystals exhibit parallel extinction in all positions, with moderately strong birefringence. They are biaxial, optically positive, with 2V rather small. The plane of the optic axis is parallel to the elongation of the tabular forms, and the acute bisectrix is perpendicular to their principal plane. The symmetry and optical properties indicate that the crystals are in the orthorhombic system.

Tetramethylammonium thiocyanate is empirically isomeric, not only with tetramethyl thio-urea,[9] but also with numerous other derivatives

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[7] Walden, *Z. Elektrochem.*, **27**, 34 (1921).

[8] Stollé [*Ber.*, **55**, 1289 (1922)] has shown that sodium trinitride and carbon disulfide react in boiling alcoholic solution to form sodium thiocyanate, free sulfur and nitrogen gas. The fact that sodium azido-dithiocarbonate was undoubtedly formed as an intermediate product seems to have escaped the notice of this investigator.

[9] Billeter, *Ber.*, **43**, 1853 (1910).

of thio-urea, including the *sym.*-diethyl,[10] *iso*butyl,[11] *sym.*-butyl,[12] normal butyl,[12] *d-sym.*-butyl,[13] methyl *sym.*-propyl,[14] α,α'-dimethyl-β-ethyl,[15] and *unsym.*-diethyl[16] thio-ureas. In the thought that the tetramethylammonium salt might undergo transformation into tetramethyl thio-urea, several preliminary experiments have been performed. No evidence of such a molecular rearrangement has thus far been obtained.

Summary

Two new compounds, ammonium azido-dithiocarbonate, NH_4SCSN_3, and tetramethylammonium azido-dithiocarbonate, $N(CH_3)_4SCSN_3$, have been prepared and described. Both are white, crystalline solids, fairly stable at room temperature, but decomposing rapidly, and under certain conditions explosively, when heated. Both undergo a curious color change; the former when either heated or illuminated, the latter when illuminated at ordinary temperature.

Tetramethylammonium thiocyanate, a product of the thermal decomposition of the tetramethylammonium azido salt, has also been prepared and studied.

ITHACA, NEW YORK

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THE VOLUMETRIC DETERMINATION OF HYDRAZOIC ACID BY OXIDATION WITH CERIC SULFATE IN ACID SOLUTION

BY JEROME MARTIN

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Sommer and Pincas[1] developed a nitrometric method for determining hydrazoic acid which depends on its oxidation by a ceric salt in acid solution, and showed that the nitrogen evolved corresponds to the reaction $2Ce^{++++} + 2HN_3 = 3N_2 + 2Ce^{+++} + 2H^+$. In the present investigation an iodimetric method based on this reaction has been found to give satisfactory results. A measured quantity of a stock solution of ceric sulfate is added and the excess is determined iodimetrically. The writer is not aware of any other titration method which depends on the oxidation of hydrazoic acid.[2]

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[10] Hofmann, *Ber.*, **1**, 25 (1868).

[11] Hofmann and Reimer, *Ber.*, **3**, 755 (1870).

[12] Hofmann, *Ber.*, **7**, 508 (1874).

[13] Urban, *Arch. Pharm.*, **242**, 51 (1904), through *Chem. Zentr.*, **1904**, I, 997.

[14] Hecht, *Ber.*, **23**, 281 (1890).

[15] Billeter and von Pury, *Ber.*, **26**, 1681 (1893).

[16] Wallach, *Ber.*, **32**, 1872 (1899).

[1] Sommer and Pincas, *Ber.*, **48**, 1963 (1915).

[2] The volumetric method of West, *J. Chem. Soc.*, **77**, 705 (1900). Riegger [THIS JOURNAL, **33**, 1569 (1911)] depends on the distillation of hydrazoic acid and its titration with standard alkali.