Summary

1. The apparatus employed and precautions observed in carrying out conductivity measurements with trimethylsulfonium iodide and triethylsulfonium bromide between concentrations of 0.04 and 1.2 millimoles per liter are described. The measurements were carried out in a quartz cell. The solutions were made up by weight to an error of less than 0.05%. Water was used having a specific conductance of the order of 0.1×10^{-6}.

2. Values at round concentrations have been interpolated from the results upon trimethylsulfonium iodide and triethylsulfonium bromide.

3. Extrapolation of the results, on the assumption that the mass action is approached as a limiting form at infinite dilution, gives a value of Λ_∞ for trimethylsulfonium iodide, 127.49, and for triethylsulfonium bromide, 113.49.

4. Assuming that the value of Λ_∞ at 25° of the iodide ion is 76.12 and that of the bromide ion 77.44, then values of 51.36 and 36.05 for the Λ_∞ of the trimethyl- and triethylsulfonium ions respectively, are obtained.

5. This is the first paper of a series of investigations on the mobility of the -onium ions. The investigation as well as other researches, such as the effect of -onium ions on the potential of lipoid-water interfaces, have been undertaken in this Laboratory with the hope of obtaining an explanation of the mechanism of physiological activity.

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

AZIDO-CARBONDISULFIDE. II. REACTION OF AZIDO-CARBONDISULFIDE AND OF FREE THIOCYANOGEN WITH HYDROGEN TRINITRIDE (HYDRONITRIC ACID) IN CERTAIN NON-AQUEOUS SOLVENTS[1]

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In connection with an extended series of investigations in the field of the halogenoids and the halogenoid hydracids, certain reactions of these compounds toward each other, or toward other substances, including the halogens and the halogen hydracids, have been studied. The various reactions to be considered may for convenience be classified under seven headings, as follows. Interaction of (1) a halogenoid and a halogen,

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(2) a halogenoid hydracid and a halogen, (3) a halogenoid and a halogen hydracid, (4) a halogenoid and a halogenoid hydracid, (5) two halogenoids, (6) a halogenoid hydracid and a halogen hydracid and (7) two halogenoid hydracids.

(1) The action of cyanogen upon chlorine has been investigated by Serullas,[2] and that of thiocyanogen by Kaufmann and Liepe.[3] (2) Serullas also studied the behavior of hydrocyanic acid toward chlorine. Raschig[4] acidified a solution containing equimolecular quantities of sodium trinitride and sodium hypochlorite, obtaining chloro-azide, ClN_3, which was no doubt formed as a product of the interaction of hydronitric acid and nascent chlorine. The oxidation of hydronitric acid by iodine in the presence of suitable catalysts has been utilized as an analytical method by Raschig[5] and by Sommer and Pincas.[6] (3) Söderbäck[7] has prepared two hydrochlorides of thiocyanogen by treatment of non-aqueous solutions of hydrogen chloride with the free halogenoid. (4) Cyanogen has been found by Oliveri-Mandalà and Passalacqua[8] to act upon a 40% aqueous solution of hydronitric acid, with the formation of cyanotetrazole and of *bis*-tetrazole. (5) Thiocyanogen in non-aqueous solution has been found in this Laboratory to accelerate greatly the rate of decomposition of the new halogenoid, azido-carbondisulfide. (6) Curtius and Rissom[9] have observed that hydronitric acid is slowly decomposed in boiling aqueous solutions of hydrochloric acid. Dennis and Isham[10] have studied the interaction of anhydrous hydrogen trinitride and hydrogen chloride vapors. The nitridizing action of hydronitric acid toward hydrochloric acid has been reported by Turrentine,[11] and toward hydriodic acid by Browne and Hoel.[12] (7) Dimroth and Fester[13] have synthesized tetrazole by heating an alcoholic solution of hydrogen trinitride and hydrogen cyanide. The investigations reported in the present article deal with the reaction of each of the new halogenoids, azido-carbondisulfide and thiocyanogen, with the halogenoid hydracid hydrogen trinitride. These reactions come within the scope of the fourth heading in the classification just outlined.

[2] Serullas, *Ann. chim. phys.*, **35**, 299 (1827).

[3] Kaufmann and Liepe, *Ber.*, **57**, 923 (1924).

[4] Raschig, *Ber.*, **41**, 4194 (1908).

[5] Raschig, *Ber.*, **48**, 2088 (1915).

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

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

[8] Oliveri-Mandalà and Passalacqua, *Gazz. chim. ital.*, **41** (II), 430 (1911); **43**, (II), 465 (1913).

[9] Curtius and Rissom, *J. prakt. Chem.*, [2] **58**, 261 (1898).

[10] Dennis and Isham, THIS JOURNAL, **29**, 31 (1907).

[11] Turrentine, *ibid.*, **34**, 385 (1912).

[12] Browne and Hoel, *ibid.*, **44**, 2116 (1922).

[13] Dimroth and Fester, *Ber.*, **43**, 2219 (1910).

Reaction of Azido-carbondisulfide with Hydrogen Trinitride

Preparation of Materials.—The azido-carbondisulfide was prepared in the manner described in the first article of the current series,[14] except that the sodium salt of azido-dithiocarbonic acid was used instead of the potassium salt. This was obtained by interaction of recrystallized sodium trinitride and purified carbon disulfide in a tightly-corked bottle immersed in a constant-temperature-bath held at 40°, and agitated vigorously by means of an efficient shaking device.

The ether used as a solvent for the reagents was prepared by allowing Kahlbaum's anhydrous ether (distilled over sodium) to remain in contact with freshly cut sodium for a week and then distilling the liquid from the metal.

Anhydrous hydrogen trinitride was prepared with the aid of an apparatus similar to that used by Browne and Lundell,[15] and was transferred in the liquid state to the solvent by the procedure followed in the work of McKinney and Houck with Browne.[16] This procedure has been found very convenient for the rapid preparation of anhydrous solutions of hydrogen trinitride of known concentration in various organic solvents. All usual precautions were, of course, taken to protect the operators from danger due to possible explosions.

Details of Experiments.—When dry azido-carbondisulfide is introduced into ethereal hydrogen trinitride, a rather vigorous reaction, accompanied by an evolution of nitrogen, takes place at once. The solution gradually assumes a yellow color, due in part at least to the liberation of sulfur, and a white precipitate slowly accumulates, while the azido-carbondisulfide disappears. The presence of free thiocyanogen in the ethereal liquid at this stage of the reaction is clearly attested by its ability to impart to the skin, or to a piece of filter paper, a reddish color which later turns yellow, to form black cupric thiocyanate from white cuprous thiocyanate, and to oxidize metallic iron or ferrous sulfate with the formation of red ferric thiocyanate, soluble in ether.[17] Control experiments with ethereal solutions of hydrogen trinitride containing no thiocyanogen have shown that hydrogen trinitride, although itself a nitridizing agent, does not interfere in these tests for free thiocyanogen under the prevailing conditions.

The liberation of nitrogen gas continues steadily for a period of from two to three hours, at the end of which time all of the azido-carbondisulfide has undergone decomposition, and the solution no longer contains free thiocyanogen. A notable feature of the reaction is the large ratio of nitrogen evolved to azido-carbondisulfide employed, indicating the participation of a relatively large amount of hydrogen trinitride in the process.

After the reaction had gone to completion the precipitate was subjected to qualitative examination under the microscope, with the result that the presence of the ammonium, thiocyanate and trinitride groups was established. Azido-dithiocarbonates were absent, showing that the decomposition of the disulfide was complete. The ethereal filtrate contained free sulfur in considerable quantities.

In a typical experiment, 1 g. of azido-carbondisulfide was added in small portions to 200 cc. of a 3% ethereal solution of hydrogen trinitride. The total nitrogen in the solid product was determined by combustion with copper oxide according to the method of Dumas.

Anal. Subs., 0.0535, 0.0502: N_2, 34.2 cc. (0.0429 g.), 32.2 cc. (0.0403 g.). Calcd. for 77.4% NH_4SCN and 21.8% NH_4N_3: N, 80.27. Found: 80.17, 80.28.

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[14] Browne, Hoel, Smith and Swezey, Ref. 1 e.

[15] Browne and Lundell, This Journal, **31**, 435 (1909).

[16] To be submitted for publication in the near future.

[17] In connection with the identification of free thiocyanogen, see Söderbäck, Ref. 7, p. 229; Kerstein and Hoffmann, *Ber.*, **57**, 491 (1924).

The trinitride nitrogen in the solid was determined by the method of Raschig,[18] which consists in the measurement of the nitrogen liberated on treatment of the sample with iodine in the presence of a small crystal of sodium thiosulfate.

Anal. Subs., 0.1002, 0.1090: N_2, 43.6 cc. (0.0545 g.), 47.2 cc. (0.0590 g.). Calcd. for 77.4% NH_4SCN and 21.8% NH_4N_3: N, 54.16. Found: 54.17, 54.37.

The qualitative and quantitative results obtained indicate that the solid reaction product is essentially a mixture of ammonium thiocyanate and ammonium trinitride. The fact that the percentages of these substances do not quite reach a total of 100 is probably attributable to the slight volatility of ammonium trinitride, which renders difficult its analysis by the Dumas method, as already noted by Curtius.[19] Control experiments have shown that the presence of thiocyanates does not interfere in the determination of trinitrides by Raschig's method.

In view of the surprisingly large volume of gas liberated when even small amounts of the solid reagent were introduced into ethereal hydrogen trinitride, a determination of the molecular ratio of nitrogen evolved to azido-carbondisulfide used, became of interest.

A series of three quantitative determinations of this ratio was made with the aid of a specially designed nitrometer.[20] This consisted of an evolution cell of about 10 cc. capacity connected through a long absorption tube filled with alcohol (which served to remove hydrogen trinitride and ether vapor from the gas) with a jacketed Hempel buret. The alcohol vapor, together with residual traces of hydrogen trinitride and ether, was removed by passing the gas into a pipet containing a dilute solution of sodium hydroxide, prior to the usual analysis and final measurement. The gas was found in every case to be pure nitrogen. The procedure consisted in introducing a weighed sample of azido-carbondisulfide into the evolution cell, which was then completely filled with a 5% ethereal solution of hydrogen trinitride. The reaction was complete after about three hours and the results were as follows.

Anal. Subs. $(SCSN_3)_2$, 0.0749, 0.0677, 0.0688: N_2, 97.21, 90.92, 90.33 cc. Molecular ratio $(SCSN_3)_2$:N_2: 1:13.7, 1:14.1, 1:13.8.

These ratios are in fair agreement with the equation

$$(SCSN_3)_2 + 8HN_3 = 2NH_4SCN + 2S + 13N_2 \qquad (1)$$

Azido-carbondisulfide has been shown by earlier work[21] in this Laboratory to decompose with liberation of nitrogen, sulfur and thiocyanogen.

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

The free halogenoid $(SCN)_2$ may be expected to oxidize hydrogen trinitride, the hydracid of a weaker halogenoid, yielding thiocyanic acid and triatomic nitrogen, which undergoes immediate transformation into ordinary diatomic nitrogen.

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[18] Raschig, "Schwefel- und Stickstoff-Studien," Verlag Chemie, G.m.b.H., Leipzig-Berlin, **1924,** p. 201.

[19] Curtius, *Ber.*, **24,** 3397 (1891). A modification of the Dumas method applicable to the analysis of volatile nitrogen compounds has been described by Dennis and Isham, Ref. 10, p. 18.

[20] The experimental work on this topic has been performed in this Laboratory by Mr. P. O. Blackmore, to whom the authors wish to express their appreciation.

[21] Ref. 1 e, p. 2543.

$$(SCN)_2 + 2HN_3 = 2HSCN + 3N_2 \quad (3)$$

The thiocyanic acid should then react with hydrogen trinitride as does hydrochloric acid,[9,10,11] with evolution of nitrogen and formation of the ammonium salt,

$$HSCN + 3HN_3 = NH_4SCN + 4N_2 \quad (4)$$

By doubling Equation 4, and adding together 2, 3 and 4, which represent consecutive stages of the reaction under investigation, Equation 1 is obtained.

The apparent importance of the role played in the reaction by the transitory product, free thiocyanogen, has led to a separate investigation of the behavior of this halogenoid toward hydrogen trinitride.

Reaction of Free Thiocyanogen with Hydrogen Trinitride

Ethereal solutions of free thiocyanogen were prepared by treating suspensions of dry lead thiocyanate in ether with slightly less than the calculated amount of bromine.[22] In view of the tendency of thiocyanogen to precipitate in polymerized form from ether, it was found necessary to use freshly prepared solutions of this reagent. This tendency varies greatly with the nature of the solvent. It has been found, for example, that solutions of the halogenoid in monobromobenzene may be kept in the ice box for a week without appreciable loss of strength.

When ethereal solutions of free thiocyanogen and hydrogen trinitride are brought together, with the latter in excess, the resulting mixture, while remaining clear, assumes at once a fugitive, reddish-brown color. In a few moments this fades to a light yellow, and there ensues a copious evolution of gas (shown by analysis to be pure nitrogen), accompanied by the precipitation of a white solid. During this process a very noticeable rise of temperature occurs. The liberation of gas, rapid at first, gradually becomes slower, and continues for a period of about two hours.

The solid reaction product was filtered off, washed with anhydrous ether, dried and examined under the microscope. Evidence was obtained of the presence of the ammonium and thiocyanate groups, but not of the trinitride group. Quantitative determination of nitrogen by combustion with copper oxide yielded the following results.

Anal. Subs., 0.1003, 0.0984: N_2, 29.66 cc. (0.03710 g.), 29.06 cc. (0.03635 g.). Calcd. for NH_4SCN: N, 36.84. Found: 36.99, 36.95.

The molecular ratio of thiocyanogen used to ammonium thiocyanate formed was determined by allowing accurately weighed samples of an ethereal solution of thiocyanogen of known concentration to react with an excess of hydrogen trinitride in ether, and titrating the ammonium thiocyanate formed with silver nitrate by the Volhard method, after removal of the excess of ether and hydrogen trinitride by evaporation.

Anal. Subs. $(SCN)_2$: 0.0856, 0.2425: NH_4SCN, 0.1130, 0.3230. Molecular ratio $(SCN)_2$:2 NH_4SCN: 1:1.01, 1:1.02.

The ratio of thiocyanogen used to nitrogen gas evolved was determined with the following results.

Anal. Subs. $(SCN)_2$: 0.0374, 0.0372: N_2, 78.3 cc., 84.0 cc. Molecular ratio $(SCN)_2$:N_2: 1:10.45, 1:11.40.

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[22] Ref. 7, p. 228.

These results indicate that the reaction takes place in accordance with the equation

$$(SCN)_2 + 8HN_3 = 2NH_4SCN + 11N_2 \qquad (5)$$

The reaction in all probability proceeds in two stages, which may be expressed by Equations 3 and 4. By doubling Equation 4 and adding together 3 and 4, Equation 5 is obtained.

It is therefore evident that the halogenoids azido-carbondisulfide and thiocyanogen react in similar fashion with hydrogen trinitride in ethereal solution. This is no doubt ascribable to the fact that azido-carbondisulfide functions as a source of free thiocyanogen, and may indeed be regarded as thiocyanogen loosely combined with nitrogen and sulfur.

One difference between the two reactions is that ammonium trinitride is found in the solid product obtained from azido-carbondisulfide, and is not found in the product obtained when thiocyanogen is employed. This is probably a result of the relatively higher concentration of free thiocyanogen, and therefore also of thiocyanic acid in the reacting mixture in the latter case. In the former reaction, the thiocyanogen is liberated slowly and the concentration of thiocyanic acid is relatively low.

Summary

Azido-carbondisulfide reacts with hydrogen trinitride in ethereal solution in accordance with the equation, $(SCSN_3)_2 + 8HN_3 = 2NH_4SCN + 2S + 13N_2$. The reaction probably takes place in three principal stages: (1) decomposition of the disulfide, with the liberation of nitrogen, sulfur and thiocyanogen; (2) action of free thiocyanogen upon the hydrogen trinitride, with the formation of thiocyanic acid and triatomic nitrogen which undergoes transformation into ordinary molecular nitrogen; (3) interaction of thiocyanic acid and hydrogen trinitride to yield ammonium thiocyanate and nitrogen.

Free thiocyanogen reacts with hydrogen trinitride in ethereal solution as expressed by the equation, $(SCN)_2 + 8HN_3 = 2NH_4SCN + 11N_2$. The reaction presumably proceeds in two steps, identical with the second and third stages of the preceding reaction. This strongly supports the belief that free thiocyanogen is the active agent in the reaction with azido-carbondisulfide, which is thus found to be a convenient source of free thiocyanogen, and which may even be regarded as a labile combination of thiocyanogen with nitrogen and sulfur.

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