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

AZIDO-DITHIOCARBONIC ACID. II. METHODS FOR THE DETERMINATION OF THE AZIDO-DITHIOCARBONATE RADICAL, $SCSN_3$[1]

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As a preliminary to the preparation and systematic investigation of an extended series of compounds of the new halogenoid-hydracid azido-dithiocarbonic acid, $HSCSN_3$, it has been deemed essential to devise methods for the rapid and accurate determination of the azido-dithiocarbonate radical to replace the more tedious method of ultimate analysis by combustion used for the most part in the earlier work.[2] The possible methods considered involve, respectively, (1) titration of the free acid with standard alkali, using methyl red as indicator; (2) quantitative precipitation of the free acid or its salts as the insoluble silver azido-dithiocarbonate, $AgSCSN_3$, which is preferably weighed directly, under conditions that minimize the danger of explosion and afford protection to the operator, inasmuch as quantitative conversion of this compound into silver chloride is not readily accomplished; (3) titration with standard silver nitrate solution in conformity with the procedure of Gay-Lussac;[3] (4) treatment with a measured excess of standard silver nitrate solution and subsequent determination of the excess of silver remaining in the filtrate by titration, according to the method of Volhard,[4] with standard ammonium thiocyanate solution, using ferric alum as indicator; and (5) titration with a standard solution of iodine in ethyl alcohol.

Determination of Free Azido-dithiocarbonic Acid by Titration with Standard Alkali

It has been shown that azido-dithiocarbonic acid is rather highly dissociated in aqueous solution, and that it is comparable in strength to sulfuric acid. Solutions of the free acid may therefore be readily titrated with standard alkali. Methyl red is to be preferred as indicator, although

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[2] (a) Sommer, *Ber.*, **48,** 1833 (1915). (b) Browne and Hoel, THIS JOURNAL, **44,** 2106, 2315 (1922). (c) Currier with Browne, *ibid.*, **44,** 2849 (1922). (d) Browne, Hoel, Smith and Swezey, *ibid.*, **45,** 2541 (1923). (e) Smith and Wilcoxon with Browne, *ibid.*, **45,** 2604 (1923). (f) Wilcoxon, McKinney and Browne, *ibid.*, **47,** 1916 (1925).

[3] Fresenius-Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, New York, **1904,** vol. 1, p. 342.

[4] Volhard, *J. prakt. Chem.*, [2] **9,** 217 (1874).

methyl orange may be used for solutions containing at least 0.5% of the acid.

The tendency of azido-dithiocarbonic acid to decompose spontaneously at ordinary temperatures, either in the dry state or in aqueous solution, in accordance with the equation, $HSCSN_3 = HSCN + S + N_2$, makes it imperative to proceed with the analysis as promptly as possible after the samples have been prepared and weighed. The acid may, however, be stored in the dark for several hours at 0° or at lower temperatures, without significant loss in weight.

Samples of azido-dithiocarbonic acid prepared by the usual method[5] and dried over phosphoric anhydride for 12 hours at 0° in a vacuum desiccator were weighed and were then dissolved in 100 cc. of water. Titration was effected in the presence of methyl red with an approximately 0.05 *N* solution of sodium hydroxide prepared from metallic sodium[6] to insure freedom from carbonates. A typical series of results is recorded in Table I.

TABLE I

DATA OBTAINED BY TITRATION WITH ALKALI

$HSCSN_3$, taken, g.	0.1656	0.2686	0.2273	0.2035	0.2607	0.1225
found, g.	.1651	.2683	.2268	.2034	.2604	.1221
Error, %	.30	.20	.25	.05	.14	.34

The slight deficit in acid found in each case is probably attributable either to the presence of traces of moisture in the samples, which were of necessity dried at a low temperature, or to a slight decomposition of the acid itself during the period of drying. This reaction must have been accompanied, however, by a liberation of traces of thiocyanic acid in the form of vapor, or by the precipitation of this compound in polymerized form; for if this acid product of the putative decomposition were entirely retained in soluble form in the solid sample, as a consequence of adsorption, for example, no error would result, unless the decomposition took place prior to the weighing of the sample, in which case the slight error due to this cause would be positive, instead of negative.

Determination of the Azido-dithiocarbonate Radical by Weighing as $AgSCSN_3$ or as AgCl

Weighed samples of the pure, dry acid were in each case dissolved in about 200 cc. of water and were treated with a few drops of concd. nitric acid. A dilute solution of silver nitrate was then added, drop by drop, until precipitation was complete. The curdy, white precipitate[5] was allowed to settle for about one hour, was then filtered on a tared Gooch crucible and was dried in a vacuum over phosphorus pentoxide to constant weight.

Anal. Subs., 0.2015, 0.2000: $AgSCSN_3$, 0.3765, 0.3767. Found: $HSCSN_3$, 0.1985 (98.5%), 0.1986 (99.3%).

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[5] Ref. 2 e, p. 2605.

[6] Cornog, THIS JOURNAL, **43,** 2573 (1921).

In the attempt to duplicate for azido-dithiocarbonic acid the procedure first employed by Dennis and Isham[7] for hydronitric acid, involving the conversion of the silver salt into silver chloride, weighed samples of silver azido-dithiocarbonate, or samples obtained by quantitative precipitation from weighed amounts of the free acid were subjected to prolonged treatment with fuming nitric acid, with the result that solution was very slowly effected. After removal of the excess of nitric acid, silver chloride was precipitated in the usual manner.

Anal. Subs., $HSCSN_3$, 0.2340, 0.2015, 0.2000: AgCl, 0.2784, 0.2379, 0.2380. Found: $HSCSN_3$, 0.2315 (98.9%), 0.1978 (98.2%), 0.1979 (99.0%).

This method is subject to three inherent difficulties: (1) the extreme sensitivity of silver azido-dithiocarbonate, especially in the dry state, to either heat or impact; (2) the tendency shown by the salt to decompose gradually, in the manner characteristic of most azido-dithiocarbonates, even at ordinary temperatures; (3) the very great difficulty of effecting the solution of the silver salt as a preliminary to its conversion into a silver halide. The method is, therefore, not to be recommended as suitable for use under ordinary circumstances.

Determination of the Azido-dithiocarbonate Radical by Titration with Silver Nitrate Solution

Gay-Lussac Method.—Weighed samples of pure azido-dithiocarbonic acid were dissolved in 125–150 cc. of water. A few drops of concd. nitric acid were added and the solutions were titrated with 0.05 *N* silver nitrate solution, until the precipitated silver salt, on settling, left a perfectly clear, supernatant liquid. The end-point was found to be very sharp, as the solution in each case became clear after the final addition of a single drop of the precipitating agent.

Volhard Method.—Samples prepared as described in the preceding paragraph were treated with a measured excess of the standard silver nitrate solution. In order to insure complete precipitation of the silver salt, an excess of at least 10 cc. of the 0.05 *N* silver nitrate solution was invariably added, and the mixture was allowed to settle for at least two hours. The precipitated silver azido-dithiocarbonate was removed by filtration and the filtrate and wash water were treated with about 2 cc. of a 10% solution of ferric alum which contained one-fourth of its volume of nitric acid free from lower oxides of nitrogen. The excess of silver was then determined by titration against a standard solution of ammonium thiocyanate to the appearance of a permanent red coloration. It is also possible to titrate the excess of silver without previous removal of the precipitated silver salt. The results thus obtained, however, are usually somewhat low, owing to the fact that silver azido-dithiocarbonate is more soluble than silver thiocyanate. Determination of the solubility of the former salt in water at 25° by the conductivity method has led to the result 2.2×10^{-4} g. equiv. per liter.

The data obtained by the two procedures are compared in Table II.[8] The Volhard procedure has been followed in this Laboratory as the standard method for determining the azido-dithiocarbonate radical. It is obvious, however, that no method involving treatment with silver nitrate can be employed for this purpose in the presence of other halo-

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[7] Dennis and Isham, This Journal, 29, 18 (1907).

[8] Numerous preliminary determinations have been made in this Laboratory by Mr. George G. Parker, whose coöperation is hereby gratefully acknowledged by the authors.

Table II

Data Obtained by Titration with Silver Nitrate Solution

$HSCSN_3$ taken, g.	$HSCSN_3$ found, g. Gay-Lussac	Error %	$HSCSN_3$ found, g. Volhard	Error %
0.1255	0.1244	−0.88	0.1256	+0.08
.1785	.1774	−0.62	.1784	− .06
.1402	.1384	−1.28	.1397	− .36
.1330	.1321	−0.68	.1328	− .15
.1575	.1570	−0.32	.1574	− .06
.0889	.0878	−1.24	.0883	− .68

genoid ions or of halogen ions. This method is preferable to the acidimetric method in all cases except those in which the sample consists of the free acid, for the reason that no convenient analytical method for the quantitative liberation of azido-dithiocarbonic acid from its salts has yet been devised.

Attempt to Determine the Azido-dithiocarbonate Radical by Titration with a Standard Solution of Iodine

The relative insolubility of the free halogenoid azido-carbondisulfide, $(SCSN_3)_2$, in water, in contrast with the comparative solubility of the other halogenoids and of the halogens, has led to the thought that this characteristic property might serve as the basis for a method of detecting and determining the azido-dithiocarbonate radical in the presence of other radicals of its class.

The formation of a white, microcrystalline precipitate on treatment of azido-dithiocarbonates in aqueous solution with iodine has repeatedly served in this Laboratory as a means of identifying these substances. The appearance of the crystals under the microscope offers a ready confirmation of the qualitative test.

The problem of adapting this reaction to the quantitative determination of the radical under investigation, however, has been complicated by the tendency of the azido-carbondisulfide, especially at the moment of liberation as the nascent $SCSN_3$ radical, to undergo hydrolysis.

An extended series of experiments on this topic[9] has led to the conclusion that hydrolysis may in large measure be prevented by the addition of tartaric acid, or of certain other substances, to the solution to be analyzed. The use of a standard solution of alcoholic iodine is preferable to that of the aqueous iodine-potassium iodide solution, since by this means the concentration of the iodide ion is kept at a minimum. The end-point is determined as usual with the aid of starch as indicator.

Summary

Various possible methods for determining the azido-dithiocarbonate radical, $SCSN_3$, have been investigated. These include (1) titration of

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[9] These experiments have been performed chiefly by Mr. S. Haber, to whom the authors take pleasure in expressing their gratitude.

free azido-dithiocarbonic acid against standard alkali, with methyl red as indicator; (2) gravimetric determination as silver azido-dithiocarbonate, or as silver chloride; (3) titration with standard silver nitrate solution after the method of either Gay-Lussac or Volhard; (4) titration with standard alcoholic iodine.

Of these, the Volhard method is the one adjudged best for use under ordinary circumstances.

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TERNARY SYSTEMS. III. SILVER PERCHLORATE, TOLUENE AND WATER

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Silver perchlorate, toluene and water give rise to equilibria resembling in many respects those found in the case of the same salt with benzene and water.[2] These resemblances include the formation of a single molecular compound between silver perchlorate and the organic component, $AgClO_4.C_7H_8$; further, systems consisting of three co-existent liquid phases occur, in this instance over a much wider temperature range; and finally, there is a clearly indicated submerged binodal curve for two liquid phases composed of the three components which fails to appear in any of the three 2-component systems.

The Binary System; Silver Perchlorate and Toluene

The ternary system under investigation may be regarded as made up from the three binary systems which can be derived from the three components. Silver perchlorate and water have previously been investigated.[2] Water and toluene proved to be a difficult system to study because of the extremely low mutual solubility of these substances; the only new information as to this pair is the fact that the solubility of water in toluene is too low to be measured by the delicate method described later in this paper and is therefore not more than a few hundredths of a per cent., markedly lower than the value of 0.07% found for water in benzene[3] at 25°. The third pair, however, has been studied over the temperature range —73.5° to +75°.

The silver perchlorate used was prepared from silver nitrate, from which hydrous silver oxide was precipitated by sodium hydroxide and dissolved in 60% perchloric acid.

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[1] The material of this paper was presented by Frederick W. Miller, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1923.

[2] Hill, THIS JOURNAL, **44**, 1163 (1922).

[3] Hill, *ibid.*, **45**, 1143 (1923).