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

Azido-dithiocarbonic Acid. VII. Conductivity of the Azido-dithiocarbonate Ion[1]

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In the effort properly to classify azido-dithiocarbonic acid, $HSCSN_3$, within the group of acids, and more specifically to compare it with the other halogenoid[3] hydracids and with the halogen hydracids, a study of the electrical conductivity of sodium and potassium azido-dithiocarbonates in aqueous solution has been undertaken, and a determination of the equivalent conductivity at infinite dilution of the azido-dithiocarbonate ion, $SCSN_3^-$, has been made. The apparent dissociation constant of the acid has been calculated from its electrical conductivity, and further evidence concerning the strength of the free acid has been obtained by potentiometric titration, and by determination of its freezing point depression in aqueous solution.

Preparation of Materials

In view of the comparative facility with which the azido-dithiocarbonates, and more particularly the free azido-dithiocarbonic acid, undergo appreciable decomposition in aqueous solution even at ordinary temperature, it was not considered imperative to prepare water of extreme purity, or to use quartz instead of glass cells,[4] since the error inherent in the observations made upon these substances is undoubtedly of a magnitude higher than that attributable to impurities in the water. The distilled water used had a specific conductance of from 1.3 to 2.3×10^{-6} mhos.

Samples of the solid azido-dithiocarbonic acid, prepared according to the method described by Smith and Wilcoxon with Browne,[5] were dissolved in distilled water, and were either diluted to the desired concentrations for the determination of the conductivity of the free acid, or exactly neutralized with an aqueous solution of either sodium hydroxide free from carbonates,[6] or of potassium hydroxide prepared by dilution of a saturated solution that had been allowed to stand until solid impurities had subsided. Azido-dithiocarbonic acid was freshly prepared for each series of measurements, and was used immediately, in order to minimize the error due to the tendency of the acid and its salts to undergo spontaneous decomposition. The concentrations of the solutions of sodium and potassium azido-dithiocarbonates were determined by titration with standard solutions of silver nitrate and ammonium thiocyanate according to the method of Browne and Smith.[7] The concentrations of the solutions of the acid were determined in the same manner, or in certain cases weighed amounts of the acid, dried over phosphoric anhydride *in vacuo*, were dissolved in the required amount of water. In measuring the cell constants (Kahlbaum) potassium chloride, twice recrystallized from water and dried at low red heat, was used.

Apparatus

In determining the specific conductances of the various solutions, errors in observation introduced in the ordinary arrangement of the apparatus by the capacity effects between the telephone and the body of the observer, were eliminated by use of a modification of the "Wagner" earth connection. In order to eliminate capacity effects in the solutions of high conductance a special mica condenser replaced the ordinary air condenser.[8] The alternating current was obtained from a high frequency generator adjusted to 1000 cycles and 30 volts. The solutions under observation were held at a temperature of 25 ± 0.01°. The Ostwald dipping electrode type of cell with platinum electrodes was used. All of the cell constants were based on the assumption that the specific conductance of a 0.02 *N* solution of potassium chloride (volume method) at 25° is 0.002768 mhos. The conductance of water was subtracted from the observed values when this exceeded the experimental error.

For the potentiometric titration of the free azido-dithiocarbonic acid, the Bunker type of hydrogen electrode was employed. The depressions of the freezing point of water caused by the addition of known amounts of azido-dithiocarbonic acid were determined with the familiar Beckmann thermometer and apparatus.

Equivalent Conductivity of the $SCSN_3^-$ Ion

The specific conductances, κ, of the solutions of sodium azido-dithiocarbonate and potassium azido-dithiocarbonate of the various concentrations were determined directly at 25° and the

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(3) The term "*halogenoid*" has been used in this Laboratory to designate *any univalent chemical aggregate composed of two or more electronegative atoms, which shows in the free state certain characteristics of the free halogens, and which combines with hydrogen to form an acid, and with silver to form a salt insoluble in water*. The group of halogenoid hydracids includes such compounds as hydrocyanic, hydronitric, thiocyanic, and azido-dithiocarbonic acids. The term "*pseudo-halogen*" has been suggested for this class of substances by Birckenbach and Kellermann, *Ber.*, **58**, 786 (1925).

(4) (a) Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922); (b) Parker, *ibid.*, **45**, 2017 (1923).

(5) Smith, Wilcoxon and Browne, *ibid.*, **45**, 2605 (1923).

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

(7) Browne and Smith, *ibid.*, **47**, 2700 (1925).

(8) The authors take this opportunity to acknowledge with pleasure their indebtedness to Professor C. C. Murdock of the Department of Physics at Cornell University for his interest in this investigation, for his advice concerning the design of the apparatus, and for his kindness in loaning various pieces of equipment.

TABLE I

ELECTRICAL CONDUCTANCE OF $NaSCSN_3$ AND $KSCSN_3$ IN AQUEOUS SOLUTION

Φ	$\kappa \times 10^{-4}$	Λ
Sodium Azido-dithiocarbonate		
188,820	4.824	91.1
95,640	9.273	88.7
48,034	17.77	85.4
19,128	42.94	82.1
9564	81.54	78.0
4782	153.5	73.4
Potassium Azido-dithiocarbonate		
1,330,000	0.8565	113.9
532,000	2.159	114.9
266,000	4.236	112.7
133,000	8.332	110.8
53,200	20.30	108.0
26,600	39.40	104.8
13,300	76.07	101.2

equivalent conductivities, Λ, were calculated from the relation $\Phi\kappa = \Lambda$ where Φ is the number of ml. of solution which contains one equivalent of the solute. Typical sets of data are given in Table I. The equivalent conductivities at infinite dilution, Λ_∞, were found by extrapolating according to the method suggested by Noyes and Falk,[9] and data for concentrations from about 0.1 *N* to about 0.008 *N* were used for making these extrapolations, which are shown in Fig. 1. The equivalent conductivity at infinite dilution, Λ_∞, for $NaSCSN_3$ was 92.6 and for $KSCSN_3$ was 116.8. By subtracting the values of Λ_∞ for the Na^+ and K^+ ions[10] the values of Λ_∞ for the $SCSN_3^-$ ion are found to be, respectively, 41.4 and 42.0. The value accepted for the equivalent conductivity at infinite dilution of the azido-dithiocarbonate ion is the mean of these values, 41.7.

The unavoidable experimental error resulting from the instability of the compounds has been minimized by working with freshly prepared materials, and by making all observations as rapidly as was consistent with reasonable precision. The values given in the table have been repeatedly checked, and those used for extrapolation, although taken from a single series of measurements, actually represent an average of many observations. The value taken for the equivalent conductivity at 25° of the azido-dithiocarbonate ion is probably of a precision of 1%, and is certainly within 3% of the true value.

Conductivity of Azido-dithiocarbonic Acid

The early assumption[11] that free azido-dithiocarbonic acid is highly dissociated in aqueous solution has been confirmed by the present investigation. The specific conductances of two series of dilutions of the acid in aqueous solution have been determined, and from these data the apparent dissociation constant of the acid has been calculated by means of Ostwald's dilution law. The equivalent conductivity of the H^+ ion was taken as 350.[4a] The results of these measurements are given in Table II. The mean value of *K* from all of the observations is 2.14×10^{-2}. The concordance of these measurements over a region of tenfold dilution is interesting for a substance which belongs to the class of moderately strong electrolytes.

TABLE II

ELECTRICAL CONDUCTANCE OF $HSCSN_3$ IN AQUEOUS SOLUTION

Φ	$\kappa \times 10^{-3}$	Λ	K
50,000	5.144	257.2	2.5×10^{-2}
100,000	2.982	298.2	2.4×10^{-2}
200,000	1.634	326.8	2.1×10^{-2}
500,000	0.7085	354.2	1.7×10^{-2}
50,000	5.136	256.8	2.5×10^{-2}
100,000	2.957	295.7	2.3×10^{-2}
200,000	1.636	327.2	2.1×10^{-2}
500,000	0.7064	353.2	1.6×10^{-2}

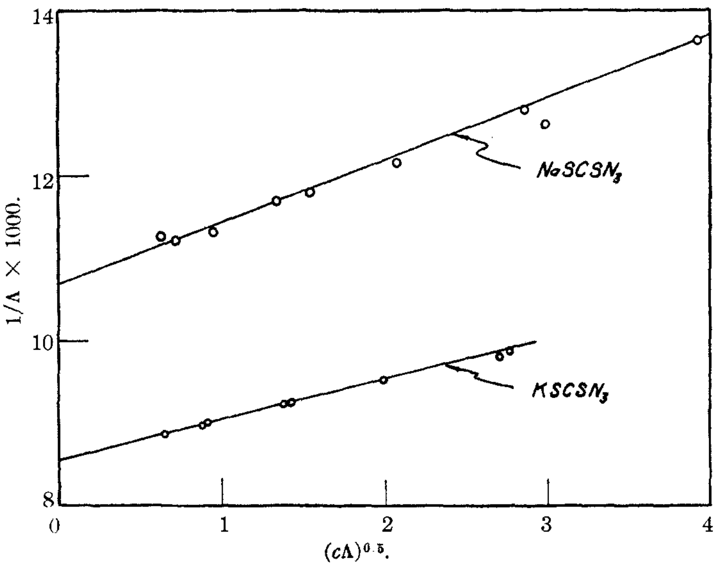

Fig. 1.—Extrapolations of limiting conductivities of sodium azido-dithiocarbonate and potassium azido-dithiocarbonate.

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(9) Noyes and Falk, THIS JOURNAL, **34**, 462 (1912).

(10) Ref. 9, p. 479.

(11) Ref. 5, p. 2606.

This dissociation constant is comparable with that of sulfuric acid, and therefore places azido-dithiocarbonic acid in the class of moderately strong acids.

The data obtained by potentiometric titration of the acid are presented graphically in Fig. 2.

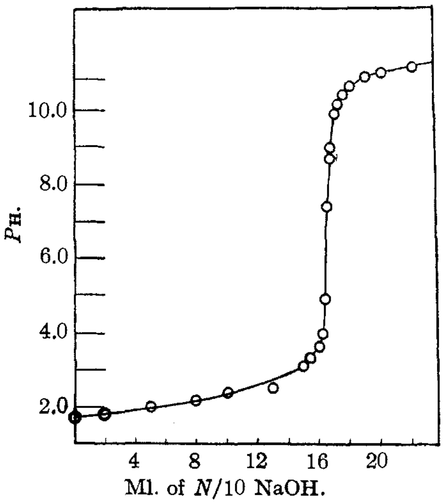

Fig. 2.—Potentiometric titration of azido-dithiocarbonic acid in aqueous solutions.

A sample of the free acid (0.1930 g.) was dissolved in 100 ml. of distilled water, and was titrated with 0.1 *N* sodium hydroxide. The vertical portion of the curve, representing equivalence of acid and base, lies between the *P*H values 3.5 and 9.5, and is therefore in close agreement with the corresponding portion of the curve for sulfuric acid.[12] Cryoscopic data of more concentrated aqueous solutions of the acid are given in Table III.

TABLE III

CRYOSCOPIC DATA FOR CONCENTRATED SOLUTIONS OF $HSCSN_3$

Φ	Δ	Mol. wt.	α
21,450	0.119	87.03	0.3695
14,950	.161	91.21	.3085
10,840	.217	95.20	.2520
8,756	.260	97.57	.2218

Summary

The electrical conductance of azido-dithiocarbonic acid, $HSCSN_3$, a halogenoid hydracid, in aqueous solution has been determined. These measurements place the compound in the class of the moderately strong acids. In the family of halogen and halogenoid hydracids, azido-dithiocarbonic acid is therefore to be placed above hydrofluoric, hydrocyanic and hydronitric acids and below hydrochloric, hydrobromic, hydriodic and (probably) thiocyanic acids. This conclusion has been confirmed by potentiometric titration of the azido acid which shows it to be comparable in strength with sulfuric acid, and also by cryoscopic determinations. The equivalent conductivity of the azido-dithiocarbonate ion $SCSN_3$, a halogenoid ion, has been established as 41.7 at 25°.

[12] Davis, Oakes and Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923).

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NOTE

Catalytic Decomposition of Lead Tetraphenyl

BY M. KOTON

Dull and Simons[1] have described the thermal decomposition of lead tetraphenyl which has also been studied in our laboratory.[2] The above authors state that at 252° the decomposition proceeds without the addition of catalyst. We, however, consider this (and it has been confirmed later on by experiments) to be a special case of the catalytic decomposition of lead tetraphenyl we are studying, in which case the metallic lead separated during the process acts as catalyst. With addition of lead the reaction proceeds at much lower temperatures.

Experiments have been carried out in small sealed glass tubes (5 cm. length) heated in a metallic bath with Wood's alloy. The temperature was allowed to vary in the range of about ±1–2°.

The lead tetraphenyl used in these experiments had a melting point of 223–225°. The metallic lead had been obtained by reducing lead oxide in a stream of hydrogen at a temperature of 150–180°.

In our experiments the decomposition of lead tetraphenyl began at higher temperatures compared with those of Dull and Simons, which possibly may be explained by the use of different experimental conditions.

In Run 6 newly prepared metallic lead was used which proved to be much more active than that used after standing during three weeks, as seen from Runs 4 and 5.

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[1] Dull and Simons, THIS JOURNAL, **55**, 4328 (1933).

[2] Koton, *Ber.*, **66**, 1213 (1933).