

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Polarographic Reduction of *cis*- and *trans*-Dinitrotetramminecobalt(III) Chloride in Chloride, Tartrate and Citrate Media

BY HENRY F. HOLTZCLAW, JR.

Polarographic reduction waves of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride in various concentrations of chloride, tartrate and citrate media are studied to discover effects of media upon the reductions. For both the *cis* and *trans* salts used in this work, the half-wave potentials for the first reduction step are displaced in a more negative direction and the diffusion current constants are decreased with increasing concentration of tartrate and citrate as media. Reductions are in all cases irreversible. The *cis* isomer is reduced more readily than the *trans* under all conditions tried.

Introduction

A method of distinguishing *cis* and *trans* forms of coordination compounds in solution by half-wave potential comparison would be highly useful. The papers of Willis, Friend, and Mellor¹ and of Laitinen, Bailar, Holtzclaw and Quagliano² make apparent the need for comparison of media first. The present paper studies the reduction of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride in the presence of chloride, tartrate and citrate media.

Experimental

Sargent Model XII and Model XXI polarographs were used with a cell of the type described by Lingane and Koltzoff.³ Oxygen-free nitrogen was passed through the cell before each electrolysis. The potentials of the dropping mercury electrode during electrolysis were measured against an external saturated calomel electrode by means of a standard potentiometer circuit. The pH of each cell solution was adjusted with a Beckman pH meter to 8.0 by means of addition of small quantities of sodium hydroxide or hydrochloric acid. Cell temperature was maintained at $25.0 \pm 0.1^\circ$ by means of a water thermostat. Reversibility of the electrode reactions was tested by determining the slopes of plots of $\log i/(i_d - i)$ vs. potential and calculating the n values. Half-wave potentials were taken from the logarithmic plots. The *cis* and *trans* salts of dinitrotetramminecobalt(III) chloride were prepared and tested by the method of Biltz and Biltz.⁴ Each solution for electrolysis was made fresh from the dry cobalt complex before use. Reagent grade materials were used throughout.

Results and Discussion

Lingane⁵ and Meites^{6,7} have discussed the effect of pH upon polarographic measurements of iron and copper, respectively, in tartrate and citrate media. Meites found that half-wave potentials of copper coordination compounds decrease with decreasing pH, corresponding to a shift from normal citrate to monohydrogen citrate at pH below 7.4. Exploratory measurements, in the present work, were made on solutions prepared without preliminary pH adjustment. Half-wave potentials obtained for these solutions, the pH of which varied generally within the range 7 to 8, compare closely with those reported in the data table for solutions in each of which the initial pH was adjusted to 8.0 immediately prior to the polarographic determination. Preliminary measurements made with *trans*-dinitrotetramminecobalt(III) chloride in 0.5

molar citrate indicate that half-wave potential is not affected significantly (within ± 10 mv.) when the initial pH of the solution is varied within the range 7.5 to 8.0. If change of pH at the electrode interface were a significant factor within the pH range studied, the effect upon half-wave potential should be greater than was actually observed when the initial pH of the solution was varied. No additional buffering agents were used for this reason and because the buffering agents themselves might cause an effect upon the half-wave potential and the diffusion current constant comparable to the effects of tartrate and citrate being studied in this paper.

Curves had no visible maxima. No maximum suppressors were used. Reduction was in each case irreversible as shown by the calculated n values. The second reduction step was not evaluated because of distorted limiting current regions for the second wave in tartrate and citrate media.

An examination of Table I shows that the *cis* isomer of dinitrotetramminecobalt(III) chloride is more readily reduced than the *trans* under all conditions tried. The unsymmetrical structure of the *cis* isomer with respect to charge of coordinated groups and the resulting possibility of greater

TABLE I

FIRST REDUCTION WAVE

0.001 molar dinitrotetramminecobalt(III) chloride; pH = 8.0; $m = 1.30$ mg./sec.; temperature = $25.0 \pm 0.1^\circ$

Supp. elect. Nature	Concn., M	Half-wave potential, $-E_{1/2}$ vs. S.C.E.	Slope	Calculated n values	i_d , μA	i , sec./drop	i_d/i , $m^2/i_d^{1/2}$
<i>cis</i> Isomer							
Potassium chloride	0.10	0.051	0.117	0.50	2.74	6.3	1.69
	.90	.122	.083	.71	2.72	6.3	1.68
Potassium sodium tartrate	.10	.058	.086	.69	2.94	6.3	1.82
	.50	.099	.080	.74	2.36	6.2	1.46
	.90	.120	.079	.75	2.28	6.2	1.41
Potassium citrate	.10	.101	.116	.51	2.82	5.9	1.76
	.50	.148	.099	.60	2.40	6.1	1.49
	.90	.167	.109	.54	2.00	6.3	1.23
<i>trans</i> Isomer							
Potassium chloride	0.10	0.216	0.128	0.46	2.88	6.2	1.78
	.90	.216	.111	.53	2.80	6.2	1.74
Potassium sodium tartrate	.10	.223	.077	.77	2.57	6.1	1.60
	.50	.241	.075	.79	2.50	5.9	1.56
	.90	.262	.077	.77	2.27	6.1	1.41
Potassium citrate	.10	.253	.080	.74	2.81	6.1	1.75
	.50	.267	.076	.78	2.34	5.9	1.46
	.90	.285	.094	.63	2.03	6.0	1.26

(1) J. B. Willis, J. A. Friend and D. P. Mellor, *THIS JOURNAL*, **67**, 1680 (1945).(2) H. A. Laitinen, J. C. Bailar, Jr., H. F. Holtzclaw, Jr., and J. V. Quagliano, *ibid.*, **70**, 2999 (1948).(3) J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).

(4) H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1909, p. 178.

(5) J. J. Lingane, *THIS JOURNAL*, **68**, 2448 (1946).(6) L. Meites, *ibid.*, **71**, 3269 (1949).(7) L. Meites, *ibid.*, **72**, 180 (1950).

orientation in the field around the dropping mercury electrode may be one contributing factor. An additional factor of probable significance is the greater thermodynamic stability of the *trans* isomer of many coordination compounds as compared with the corresponding *cis* isomer.

The half-wave potential for the first reduction wave becomes more negative and the diffusion current constant decreases with increasing concentrations of tartrate and of citrate. These trends, which hold true for both the *cis* and *trans* isomers, are in line with the postulate of Laitinen, Bailar, Holtzclaw and Quagliano² of a "super-

complex" of multivalent anions clustered about the central complex by electrostatic and ion-dipole attraction. An interesting observation for which an explanation is not readily apparent is the effect of increased chloride concentration upon the half-wave potential of the *cis* isomer but not upon that of the *trans*.

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The Ionization Constant of Sulfanilic Acid from 0 to 50° by Means of E.m.f. Measurements¹

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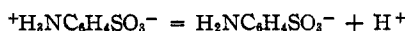
The ionization constant of sulfanilic acid has been determined from 0 to 50° by the use of cells without liquid junction. The equation $-\log K = 1143.71/T + 0.0023142T - 1.2979$ expresses the experimental data as a function of the temperature in the above temperature range with a standard deviation of 0.00063 in $-\log K$ for eleven experimental prints.

Introduction

The ionization constant of sulfanilic acid at a single temperature has been measured by several investigators and reported at four temperatures in one paper. All these investigations were carried out by means of conductivity measurements and modern methods of accounting for interionic attraction were not applied. These results are:

Investigator	$K \times 10^4$	$t, ^\circ\text{C.}$
Ostwald ²	5.81	25
Winkelblech ³	6.20	25
White and Jones ⁴	3.26	0
	3.93	6
	6.55	25
	8.20	35
Boyle ⁵	7.05	25
Stearn ⁶	7.05	21

Sulfanilic acid has been shown to exist in solution as the zwitterion by the dielectric constant data of Carr and Shutt⁷ and as may be concluded from the mere fact that it is a moderately weak acid. The ionization constant is that for the reaction



It is the object of this investigation to present accurate values of the ionization constant of sulfanilic acid determined over the temperature range 0 to 50° by the measurement of the electromotive force of cells without liquid junction following the general method developed by Harned and co-workers.⁸ The cells were of the type Pt, H₂/

HSu(m_1), NaSu(m_2), NaCl(m_3)/AgCl-Ag, in which HSu and NaSu are sulfanilic acid and its sodium salt and m_1 , m_2 and m_3 are weight molalities. The potential of this cell is given by

$$E = E^0 - \frac{2.3026RT}{F} \log m_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} \quad (1)$$

where E^0 is the molal electrode potential of the silver-silver chloride electrode which has been determined by Harned and Ehlers⁹ and where γ is an activity coefficient. By elimination of $m_{\text{H}^+} \gamma_{\text{H}^+}$ from equation (1) and the expression for the thermodynamic ionization constant

$$K = \frac{m_{\text{H}^+} m_{\text{Su}^-}}{m_{\text{HSu}}} \times \frac{\gamma_{\text{H}^+} \gamma_{\text{Su}^-}}{\gamma_{\text{HSu}}} \quad (2)$$

the following relation is found

$$\frac{(E - E^0)F}{2.3026RT} + \log \frac{m_{\text{HSu}} m_{\text{Cl}^-}}{m_{\text{Su}^-}} = -\log K - \log \frac{\gamma_{\text{HSu}} \gamma_{\text{Cl}^-}}{\gamma_{\text{Su}^-}} \quad (3)$$

The usual method of using equation (3) for the calculation of the ionization constant of weak acids, as, for example, in the case of acetic acid,¹⁰ is not suitable for sulfanilic acid since it involves a long series of successive approximations which converge slowly. Instead a procedure developed by Hamer¹¹ was used. First approximations to m_{H^+} , called m'^{H^+} , were calculated directly from (1) using the Debye-Hückel limiting law¹² to evaluate the activity coefficients. Then values of a first approximation to the ionization constant, K' , were calculated from (2), again using the limiting law and $m'^{\text{HSu}} = m_1 - m'^{\text{H}^+}$ and $m'^{\text{HSu}^-} = m_2 + m'^{\text{H}^+}$. The negative logarithms of these values were plotted vs. the ionic strength and extrapolated to $\mu = 0$. Using this value of K' , the limiting law and equation (2), second approximations to m_{H^+} ,

(1) Taken from the master's thesis of Richard O. MacLaren.
 (2) W. Ostwald, *Z. physik. Chem.*, **3**, 406 (1889).
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 (6) A. E. Stearn, *J. Gen. Physiol.*, **10**, 379 (1926).
 (7) W. Carr and W. J. Shutt, *Trans. Faraday Soc.*, **35**, 579 (1939).
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