

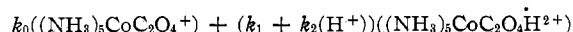
CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

Equilibrium and Kinetic Behavior of $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ in Aqueous Solution

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The acid dissociation constant for $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$, the aquation equilibrium constant, and the rates of aquation have been measured, all at $\mu = 1.00$. The acid dissociation constant has the value 8.8×10^{-3} at 25° ; at 70° , the value $1.7 \pm 0.3 \times 10^{-2}$ is indicated. Aquation proceeds by three parallel paths



The values of k_0 , k_1 , and k_2 at 25° are $1.5 \times 10^{-8} \text{ sec}^{-1}$, $2.2 \times 10^{-8} \text{ sec}^{-1}$, and $19.5 \times 10^{-8} M^{-1} \text{ sec}^{-1}$, and the corresponding values of ΔH^* are 26.2 ± 1 , 28.4 ± 1 , and $22.7 \pm 1 \text{ kcal mole}^{-1}$.

The studies we embarked on several years ago to measure the rate of oxygen exchange between oxalato-pentaamminecobalt(III) and the solvent¹ water necessitated knowing what the equilibrium behavior and the aquation rate of this ion are. In this paper we report the results of the experiments we have done to measure the affinity of the bound oxalate for H^+ , of the pentaamminecobalt(III) for oxalate ion, and the rate at which the aquation equilibrium is established.

Experimental Section

Preparation and Analysis of the Oxalato-pentaamminecobalt(III) Complex.—The salt $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}](\text{ClO}_4)_2$ was prepared as described by Saffir and Taube.² To determine the oxalate content, the complex was hydrolyzed in alkaline solution. The cobalt oxide which formed was separated by filtration and the oxalate was determined by standard permanganate titration.³ The salt was analyzed for ClO_4^- by the method described by Hunt⁴ and for nitrogen content by the Kjeldahl method.⁵ The results of the analyses were: $\text{C}_2\text{O}_4^{2-}$, 20.33%; ClO_4^- , 45.90%; N, 16.20%, to be compared to 20.37%, 46.04%, and 16.21%, respectively, as theoretical values. The molar extinction coefficient of the ion $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ at $507 \text{ m}\mu$ was found to be 74.0, to be compared to the value of 74.1 reported by Tsuchida.⁶

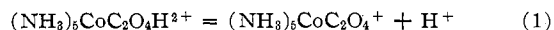
Procedure.—The spectrophotometric measurements were made on a Cary Model 14 recording spectrophotometer equipped with a thermostated cell compartment.

The solutions used for the determinations of the acid dissociation constant of $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ were made up from the component ones stored at $25.0 \pm 0.05^\circ$ until temperature equilibrium was reached, and readings of the optical densities were made in the thermostated cell compartment. Since measurements were made on the shoulder of an intense absorption band (at wavelengths of 270 and 210 $\text{m}\mu$), control of temperature during the measurements of optical density was essential.

The studies of the rate of acid hydrolysis of $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ were done by placing the solutions in volumetric flasks which were immersed in a thermostat, the temperature of which was controlled to $\pm 0.05^\circ$. In the experiments carried out at 25° the reagents were mixed at room temperature before placing the final solution in the thermostat. At 25° the hydrolysis is slow enough for this procedure to be suitable. In the experiments conducted at higher temperatures, $45 \pm 0.1^\circ$ and $70 \pm 0.2^\circ$, the reagent solutions were kept in the thermostat before mixing them until the temperature of the experiment was reached. Samples were withdrawn at various times and cooled down rapidly to room temperature, and the absorption was determined at $500 \text{ m}\mu$.

The equilibrium constant for the reaction between $(\text{NH}_3)_5\text{CoOH}_3^{3+}$ and $\text{H}_2\text{C}_2\text{O}_4$ was determined by placing the reagent solutions in sealed ampoules of approximately 50-ml capacity. These ampoules were kept in a thermostat at the desired temperature, until the equilibrium was reached. Sealed ampoules were used to avoid variations in the concentration of the solution due to evaporation, a serious consideration, especially in the experiments carried out at 45 and 70° . The concentrations of the aquo and oxalato complexes at equilibrium were determined by analyzing the solutions spectrophotometrically at $500 \text{ m}\mu$, immediately after they were cooled down to room temperature.

The Acid Dissociation Constant for $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$.—The dissociation of protons from the bound oxalate, reaction 1, takes



place much more rapidly than does dissociation of the bound oxalate, and therefore the acid dissociation of the complex can be studied by quite direct means. The spectrum of the oxalato complex in the wavelength region of the charge-transfer band

(1) R. B. Jordan, C. Andrade, and H. Taube, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, Akadémiai Kiadó (Publishing House of the Hungarian Academy of Sciences), Budapest, 1965, pp 381-394.

(2) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

(3) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p 52.

(4) J. P. Hunt, Ph.D. Dissertation, University of Chicago, 1960.

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 536.

(6) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).

responds sensitively to the dissociation process, and the spectrophotometric method of determining the dissociation constant was selected as being convenient and accurate. The extinction coefficients of the limiting forms $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ and $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$ were determined in strongly acidic and basic solutions, respectively, and the distribution of Co(III) between these forms at intermediate acidities was determined by comparing the optical densities with those of the complexes in the limiting forms. Table I shows the results of the spectrophotometric investigations at 25° and at $\mu = 1.00$ which yield for K_1 , under these conditions, $8.8 \pm 0.4 \times 10^{-3}$.

TABLE I

THE ACID DISSOCIATION CONSTANT FOR $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ (Co(III)) = 0.010 M; $\mu = 1.0$ except for expt at 2.0 M HClO_4 ; measurements at $\mu = 270 \text{ m}\mu$; temp $25.0 \pm 0.05^\circ$

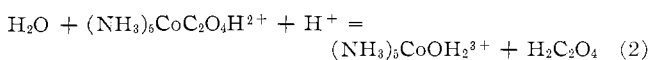
[HClO_4], M	[NaOH], M	k_1	k_2	K_1
2.00	None	647	10.0	...
1.00	None	648	10.0	...
0.0100	None	952	6.20	8.5×10^{-3}
0.0050	None	1028	5.26	8.8×10^{-3}
0.0000 ^a	None	1132	3.96	9.2×10^{-3}
None	0.01	1449
None	0.05	1449
None	0.10	1444

^a (H^+) is fixed by the stoichiometric concentration of $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}](\text{ClO}_4)_2$.

To minimize the effects of hydrolysis, the measurements of optical density were made immediately after mixing the solutions. This is particularly important in alkaline media because there the results can be vitiated by the formation of insoluble products.

Direct spectrophotometric determinations of K_1 were not made at other temperatures but, as is shown in the next section, the results on the rate of aquation as a function of acidity yield for K_1 at 70° and $\mu = 1.0$ the value $1.7 \pm 0.3 \times 10^{-2}$.

Aquation of $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ in Acid Solution.—The course of the reaction



was followed spectrophotometrically. At high (HClO_4) at the concentration of complex used, $2 \times 10^{-3} \text{ M}$, and with no added oxalate, reaction 2 goes essentially to completion. The half-times for the aquation under such conditions were determined from plots of $\log [(\text{OD})_t - (\text{OD})_\infty]$ vs. time where $(\text{OD})_\infty$ is the calculated value of optical density corresponding to complete aquation. When the concentration of HClO_4 is low, the reaction stops short of completion, and for experiments under such conditions, the measurement of the rate was based on data for partial completion, 10% or less. The values of specific rate k' recorded in Table II thus correspond to the rate of the forward reaction for all conditions. The specific rate k' is defined by

$$-d \ln \frac{[T]}{dt} = k'$$

where $[T]$ represents the total oxalato complex whether in the form $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$ or $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$.

The form of the variation of k' with the concentration of mineral acid is shown for the data at 70° in Figure 1. At high concentration of acid, the dominant form of the Co(III)-oxalato complex is $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$; under these conditions the variation of rate with acidity is straightforward, there apparently being a term in the rate law first order in (H^+) and another which is zero order in acid. At low (H^+) , the rate falls off from that which is required by the relationship described, undoubtedly because $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ is converted to $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$, which aquates at a lower rate than does $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$. The rate of aquation of $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$ is by no means zero, however. This conclusion is suggested by the fact that the rate at zero acid is finite and is borne out by the detailed analysis of

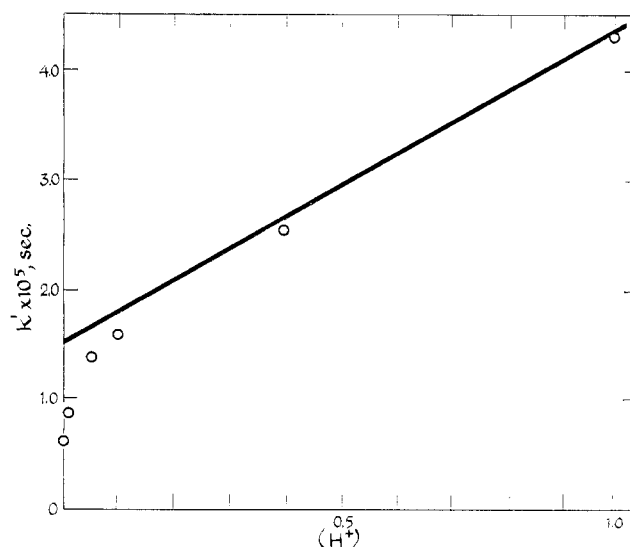


Figure 1.—The variation of rate of aquation with acidity at 70°. The experimental values of k' are plotted against the concentration of (H^+) , which except for the points at lowest acidity is within 1% of that expected from the perchloric acid added. The line has been drawn assuming that all the oxalato complex is present in the form $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$, using the specific rates deduced below for the k_1 and k_2 paths and assuming that only these paths contribute. The need for invoking appreciable acid dissociation for the complex is apparent from the falling off of the experimental points from the line at low acid; the need for a k_0 path is equally apparent from the nonzero intercept at $(\text{H}^+) = 0$.

TABLE II

RATES OF AQUATION OF $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ $[T] = 2 \times 10^{-3} \text{ M}$; $\mu = 1.00$

[HClO_4] added, M	$k' \times 10^5, \text{ sec}^{-1}$		
	25°	45°	70°
0.00	0.163	2.80	64.5
0.010	0.203	...	99.0
0.050	138
0.100	0.380	...	169
0.200	...	9.63	...
0.40	1.00	15.0	253
1.00	...	26.0	423

the data at low acid, which shows clearly that at zero added acid the rate is in excess of that expected for the ion $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$.

The points at 0.40 and 1.00 M acid for the data at 70° define the coefficients k_1 and k_2 in the general rate law

$$\frac{-d[T]}{dt} = k_0((\text{NH}_3)_5\text{CoC}_2\text{O}_4^+) + k_1((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}) + k_2((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+})(\text{H}^+)$$

With k_1 and k_2 thus determined, the data at low acid can be treated to yield values of k_0 and of K_1 . Iteration leads to improved values of k_1 and k_2 and these to improved values of K_1 and k_0 . $K_1 = 1.7 \pm 0.3 \times 10^{-2}$ at 70° was settled on as giving the best agreement with the experimental data. The value of K_1 at 25° was measured independently, and the data obtained at 25° are readily treated to yield k_0 , k_1 , and k_2 for that temperature. The data at 45° are least complete, too incomplete to lead to a dependable value of K_1 at that temperature. At the lowest acidity, the complex exists largely in the deprotonated form and the bulk of the reaction proceeds by the k_0 path, so the value of k_0 is relatively insensitive to the value chosen for K_1 . At acidities of 0.2 M and above, most of the complex exists in the acid form, and the data are again insensitive to the value of K_1 . To treat the data at 45°, K_1 was chosen as 1.2×10^{-2} , which is the value expected if $\log K_1$ is linear in $1/T$ in the temperature range 25–70°.

The parameters k_0 , k_1 , and k_2 selected for 25, 45, and 70° are,

TABLE III
 ANALYSIS OF DATA ON THE RATES OF AQUATION

Temp, °C	[HClO ₄] added, M	(H ⁺), M	Fraction of complex in acid form	Fraction of reaction by		$k' \times 10^7$ calcd	$k' \times 10^7$ obsd
				k_0 path	k_1 path		
25	0.000	0.00168	0.160	0.778	0.214	0.164	0.163
25	0.0100	0.0109	0.553	0.332	0.592	0.205	0.203
25	0.100	0.100	0.919	0.035	0.510	0.395	0.380
25	0.400	0.400	0.978	0.003	0.219	0.980	0.997
45	0.000	0.00175	0.127	0.735	0.264	2.80	2.80
45	0.200	0.200	0.943	0.014	0.560	9.75	9.63
45	0.400	0.400	0.978	0.005	0.394	14.1	15.0
45	1.00	1.00	0.988	0.001	0.208	27.4	26.0
70	0.000	0.00181	0.095	0.784	0.216	63.0	64.5
70	0.010	0.0112	0.400	0.354	0.645	93.	89.
70	0.050	0.0505	0.748	0.100	0.806	139.	139.
70	0.100	0.100	0.854	0.050	0.800	161.	159.
70	0.400	0.400	0.959	0.008	0.568	254	253
70	1.00	1.00	0.983	0.002	0.348	425	422

respectively: $1.52 \times 10^{-8} \text{ sec}^{-1}$, $2.20 \times 10^{-8} \text{ sec}^{-1}$, and $19.5 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$; $2.36 \times 10^{-7} \text{ sec}^{-1}$, $5.8 \times 10^{-7} \text{ sec}^{-1}$, and $22.0 \times 10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$; $5.5 \times 10^{-6} \text{ sec}^{-1}$, $15.1 \times 10^{-6} \text{ sec}^{-1}$, and $27.8 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$. In Table III, the values of k' calculated using these parameters are shown in comparison to those observed. Table III serves also to describe the composition of the solutions and the contribution to the total reaction by each of the various paths.

In Table IV are summarized the values of ΔH^* and ΔS^* which were calculated from the specific rates at the three temperatures of experiment.

 TABLE IV
 ACTIVATION PARAMETERS FOR AQUATION OF $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$
 CALCULATED FROM $k_n = \frac{kT}{p} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$

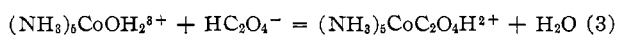
	$10^8 \times k_n$ at 25°	ΔH^* , kcal mole ⁻¹	ΔS^* , eu
k_0	1.52	26.2 ± 1	-5
k_1	2.20	28.4 ± 1	1
k_2	19.5	22.7 ± 1	-14

Equilibrium between Oxalatopentaammine- and Aquopentaamminecobalt(III) Complexes.—A spectrophotometric study of the equilibrium quotient for reaction 2 was made at 45 ± 0.1 and $70 \pm 0.20^\circ$. The experiments were done at 1.00 M HClO₄ and the concentration of H₂C₂O₄ was high compared to that of the Co(III) complex. The dominant forms of oxalate under these conditions are therefore those shown in eq 2. The starting reaction mixtures contained pure aquopentaammine complex with different concentrations of H₂C₂O₄. The relative amounts of the oxalato and aquo complexes were determined by measuring the optical densities of the solutions at 500 m μ ; at this wavelength the two forms have usefully different values of extinction coefficients.

The half-lives estimated for the approach to equilibrium were 6.5 days and 15 hr at 45 and 70°, respectively. Accordingly, the solutions were kept at 45 and 70° for 42 and 12 days, respectively, before the optical densities were read. The ratio $((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+})/((\text{NH}_3)_5\text{CoOH}_2^{3+})$ at equilibrium is obtained by comparing the final optical density to those expected for the pure oxalato and aquo forms. Since the values of (H⁺) and (H₂C₂O₄) are known, the equilibrium quotient K_2 for reaction 2 can be calculated.

The results of the experiments on the determination of the values of K_2 are summarized in Table V.

The equilibrium quotient for reaction 3 has been determined



at 25° by Tsuchiya⁷ at ionic strengths ranging from 0.015 to 0.22. Because of the differences between the ionic strength

 TABLE V
 THE EQUILIBRIUM QUOTIENT K_2 FOR THE REACTION^a
 $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+} + \text{H}_2\text{O} + \text{H}^+ \rightleftharpoons (\text{NH}_3)_5\text{CoOH}_2^{3+} + \text{H}_2\text{C}_2\text{O}_4$

Temp, °C	[H ₂ C ₂ O ₄], M	OD ^b	OD _{ox} - OD	OD - OD _a	K_2
45	0.10	0.530	0.169	0.059	0.286
45	0.20	0.566	0.133	0.090	0.295
70	0.05	0.511	0.188	0.039	0.241
70	0.10	0.539	0.160	0.067	0.239

^a (HClO₄) = 1.00 m; μ calculated as 1.01; the concentration of aquo complex was $2 \times 10^{-3} \text{ M}$. ^b OD, OD_{ox}, and OD_a represent, respectively, the optical densities of the solutions containing the equilibrium mixture, the pure oxalate, and the pure aquo forms.

obtaining in his experiments and ours, the comparison of the results which follows is of limited validity. From a plot of $\log K_3$ vs. $\sqrt{\mu}$, Tsuchiya obtained a relation for K_3 as a function of μ which has a minimum at about $\sqrt{\mu} = 0.52$ and then rises again with almost the same curvature beyond this value of $\sqrt{\mu}$.

$$\log K_3 = 3.79\mu - 3.95\sqrt{\mu} + 3.43$$

Using this equation for extrapolation to $\mu = 1.0$ yields 2.1×10^{-2} for K_3 (but with the standard state of H₂O as the liquid). The values for K_2 obtained in our experiments at 45 and 70°, $\mu = 1.01$, on extrapolation to 25° together with an estimate of the dissociation constant⁸ of H₂C₂O₄ at $\mu = 1.0$ lead to a value of 3.4×10^{-2} for K_3 , in reasonable agreement with the other value. Other studies⁹ on the variation of the equilibrium quotient with μ suggest that the behavior assumed for the variation of K_3 with μ is not out of line.

From a plot of $1/T$ against $\ln K_2$, ΔH_2 is estimated as 2.2 kcal and ΔS_2 as 5 eu.

Discussion

It is of interest to compare the value of the acid dissociation constant measured for $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ with the corresponding constants in related systems. The large effect of the positive charge on the metal ion center is clear from the comparisons in Table VI, which show that in this particular case the effect of the metal ion approaches that of the proton. Where

(7) R. Tsuchiya, *Bull. Chem. Soc. Japan*, **35**, 666 (1962). Note that Tsuchiya uses 55.5 for the activity of water in his values of equilibrium constants.

(8) Estimated by using 5.5×10^{-2} as K_1 for H₂C₂O₄ at $\mu = 0$ and assuming that 1 M HClO₄ changes K_1 for H₂C₂O₄ to the same extent that 1 M LiCl changes K_0 for HOAc. Values of K_0 for HOAc as a function of μ are given by H. S. Harned and F. C. Hickey, *J. Am. Chem. Soc.*, **59**, 1284 (1937).

(9) E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

TABLE VI

	$^{-}\text{O}_2\text{CO}_2\text{H}^{\text{a}}$	$\text{HO}_2\text{CCO}_2\text{H}^{\text{b}}$	$(\text{NH}_3)_5\text{CoO}_2\text{CCO}_2\text{H}^{2+}$
K_{D}	5.4×10^{-5}	6×10^{-2}	8.8×10^{-3}
μ	0	Low	1.0

^a G. D. Pinching and R. G. Bates, *J. Res. Natl. Bur. Std.*, **40**, 405 (1948). ^b G. Kortüm, W. Vogel, and K. Andrussov, "Dissociation Constants of Organic Acids in Aqueous Solutions," Butterworths, London, 1961, p 249.

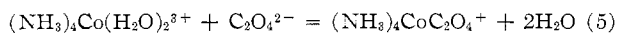
the influence of the acidity promoting groups is exerted through fewer bonds, the effect of H^+ is much greater than that of the tripositive center, e.g., note the K_{D} values: H_2O , 2×10^{-16} ; H_3O^+ , 56; $(\text{NH}_3)_5\text{CoOH}_2^{3+}$, 10^{-6} . For $[(\text{NH}_3)_5\text{CoO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}]^{2+}$, the dissociation constant at $\mu = 1.0$ and 25° as determined¹⁰ by potentiometric titration using a glass electrode is 1.4×10^{-4} ; for succinic acid at $\mu = 0$, $K_{\text{D}} = 5 \times 10^{-5}$. As might be expected, the effect of the highly charged metal ion falls off less rapidly as the number of intervening bonds increases than does that of H.

If it is assumed that the affinity of $(\text{NH}_3)_4\text{H}_2\text{OC}(\text{OH})_2^{3+}$ for $\text{C}_2\text{O}_4^{2-}$ in the monodentate form is the same as that of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$, Tsuchiya's results¹¹ on the affinity of aminocobalt(III) for oxalate in the chelate form and ours on the affinity of the bound oxalate for H^+ can be used to estimate the equilibrium constant for the ring closure reaction

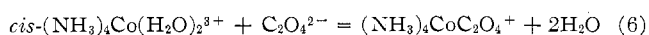


The assumption we feel is not bad, and in any event no worse than those which must be made in bringing data at differing ionic strengths together.

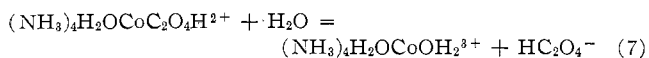
Tsuchiya, *et al.*,¹¹ report $K = 2 \times 10^6$ for the reaction



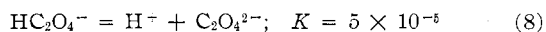
at 25° and $\mu = 0$. Introducing the measurement¹² of the *cis-trans* equilibrium constant, we find $K = 10^7$ for the reaction



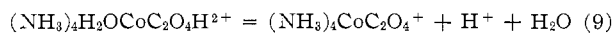
Let K for



be the same as it is for the pentaammine, namely 0.02 at 25° and $\mu = 0$. Adding to reactions 6 and 7 the following¹³



We find for



$K = 10$ ($\mu = 0$). The equilibrium represented by reaction 9 will not be strongly ionic strength dependent. If we assume that K for reaction 9 is unchanged at $\mu = 1.0$, using our value for the dissociation constant of

(10) D. Bearcroft, unpublished observations.

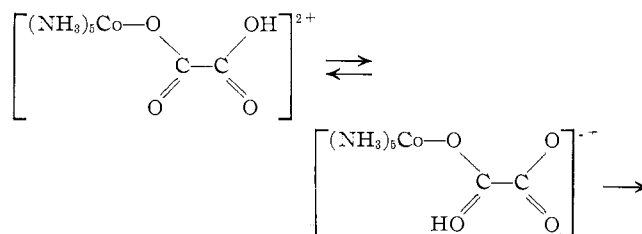
(11) M. Mori, R. Tsuchiya, and E. Matsuda, *Bull. Chem. Soc. Japan*, **34**, 1761 (1961). It should be noted that the authors chose the standard state for H_2O not as the liquid but a 1 M solution. Their computations of free energies of formation of some of the complexes must therefore be used with caution. For the equilibrium constant we quote, the standard state for water is the pure liquid.

(12) R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59**, 298 (1955).

(13) See footnote a of Table VI.

the binoxalate complex we find that K for reaction 4 at $\mu = 1.0$ and 25° is 10^3 . The constants for reactions 4 and 9 seem to us remarkably low, but also the value reported as K for reaction 5 seems somewhat low. For Fe^{3+} and Mn^{3+} , the association constants¹⁴ lie between 10^9 and 10^{10} ; even allowing for *cis-trans* isomerism, a factor of only *ca.* 5, and the statistical factor, the disparity in the constants for Fe^{3+} and Mn^{3+} on the one hand and $(\text{NH}_3)_4\text{Co}(\text{H}_2\text{O})_2^{3+}$ amounts to a factor of 10 or greater.

Detailed discussion of the results on the rates of the aquation reactions will be deferred until the measurements of the rates of oxygen exchange for these complexes are published. One point, however, seems worthy of mention now: it is that there is a very small difference in rate for the aquation of $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}]^{2+}$ and $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4]^{2+}$. In view of the strong effect which H^+ has in accelerating the aquation of other carboxylato complexes, the difference in rate is so small as to be very striking. The specific rate observed for the aquation of $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}]^{2+}$ by the k_1 path, $1.5 \times 10^{-5} \text{ sec}^{-1}$ at 70° , is very close to the value reported¹⁵ for the aquation of $[(\text{NH}_3)_5\text{CoO}_2\text{CCF}_3]^{2+}$, 5.7×10^{-5} , also at 70° . The values of activation parameters, $\Delta H^* = 28 \text{ kcal mole}^{-1}$ for the former and $26 \text{ kcal mole}^{-1}$ for the latter, and $\Delta S^* = 1 \text{ eu}$ for the former and -2 eu for the latter, are also quite similar in magnitude. For the (H^+) dependent paths, the rates are also very similar, $2.8 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ for our system and $3 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ for that studied by Monacelli, *et al.* It is apparent from these comparisons that in the aquation of the binoxalate complex, the system does not avail itself of the opportunity it has for calling on a redistribution of the proton in the activated complex



This being so, it is less remarkable that k_0 and k_1 are so nearly alike for the oxalato complex.

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