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Substitution Reactions of Oxalato Complex Ions. XI. Kinetics of the Anation of Aquopentaamminecobalt(III) Ion by Oxalate in Aqueous Acidic Solution[1,2]

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The title reaction has been studied in the temperature range 50–80°, with the acidity range from pH 7.5 up to 1.0 *M*, and with oxalate concentrations between 0.04 and 0.45 *M*. It goes essentially to completion even at the highest acidities in the presence of excess oxalate. Ion pairing is not significant between the complex ion and $H_2C_2O_4$ but is kinetically identifiable with $HC_2O_4^-$ and $C_2O_4^{2-}$, such that the rate expression becomes as shown in eq 4. The essentially temperature-independent ion-pair formation constants for bioxalate and oxalate ions are $Q_1 = 1.8\ M^{-1}$ and $Q_2 = 9.2\ M^{-1}$, respectively. The rate constants at 70° for anation by $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ are $k_0 = 1.5 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$, $k_1 = 4.9 \times 10^{-4}\ \text{sec}^{-1}$, and $k_2 = 4.0 \times 10^{-4}\ \text{sec}^{-1}$. The corresponding temperature parameters are $\Delta H^\ddagger = 14.3 \pm 1.7$, 22.4 ± 2.1, and 24.8 ± 1.8 kcal/mol, respectively, and $\Delta S^\ddagger = -35.0 \pm 4.8$, -8.6 ± 6.3, and -2.1 ± 5.4 cal/(deg mol), respectively. On the basis of the contrast in temperature parameters and a study of the solvent D_2O effect, it is concluded that the mechanism for $H_2C_2O_4$ addition may not be of the conventional water–ligand dissociative type which appears to be the mechanism for the two ionic oxalate species.

Introduction

Previous papers in this series have reported studies of the anation by oxalate of the diaquobis(ethylenediamine)cobalt(III) ion in acidic[3] and neutral or basic[4] solution. These reactions take place by means of a two-step mechanism in which there is first replacement of one aquo ligand by oxalate, followed by release of the second aquo ligand as chelation of the metal ion by oxalate occurs. Similar results have recently been reported for oxalate anation of the diaquoethylenediaminediacetatocobalt(III) analog.[5] In order to throw more light on the nature of the intimate mechanism of the first water-replacement step, we have in the present study examined the kinetics of the reaction with oxalate of aquopentaamminecobalt(III) ion, in which system chelation of the metal ion by the entering ligand does not occur. This contrasts with the behavior of the aquopentaamminechromium(III) analog, where the final product is the tetraammineoxalato species, made possible by the elimination of an ammonia ligand in the ring-closure step.[6] A further significant feature of our work is that it adds a new dimension to the study of $Co(NH_3)_5H_2O^{3+}$ anation in that the reaction has been studied over a wide enough pH range to encompass all possible acidic and basic forms of each reactant species and involves a bifunctional anion. While there has been a long-standing interest in the mechanism of $Co(NH_3)_5H_2O^{3+}$ anation,[7,8] nearly all previous studies have involved monodentate entering ligands over a limited range of acidity. Another interest we have in this study is to determine whether conditions exist such that anation of aquopentaamminecobalt(III) by oxalate can proceed by direct addition of the entering ligand to the oxygen atom of the aquo ligand such as is now known to occur in the formation reaction of carbonatopentaamminecobalt(III) complex.[9] Finally, it has proved to be instructive to relate our findings to earlier studies[10,11] of the aquation equilibration in acidic aqueous solutions of the species $Co(NH_3)_5C_2O_4H^{2+}$.

Table I. Spectral Data for Aquopentaammine- and Oxalatopentaamminecobalt(III) Complexes

Complex ion	λ_{max}, nm	ϵ_{max}	Ref
$Co(NH_3)_5H_2O^{3+}$	487	41.7	*a*
	491	48.6	*b*
	491	49.0	*c*
	491	49.0	This work[d]
$Co(NH_3)_5C_2O_4H^{2+}$	507	74.0	*e*
	507	74.1	*a*
	505	73.0 (pH <2.5)	This work[f]
	505	74.5 (pH 5.0)	This work[f]
	505	76.0 (pH 7.5)	This work[f]

[a] R. Tsuchiya, *Bull. Chem. Soc. Jap.*, **35**, 666 (1962). [b] Reference 7. [c] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968). [d] The figure quoted is for the aquo ion, the p*K* of which is 6.6 at 25°.[9] At higher pH's a shift in the peak and an increase in absorbance take place as deprotonation to form the $Co(NH_3)_5OH^{2+}$ ion occurs, such that λ_{max} and ϵ_{max} have the values 497 and 57.6 at pH 7.7: S. Ficner, unpublished work in the laboratory. [e] Reference 10. [f] The variation of ϵ_{max} between 73.0 and 76.0 presumably results from the deprotonation of $Co(NH_3)_5C_2O_4H^{2+}$. The p*K* of this cation at 25° is close to 2.[10,13]

Experimental Section

The complexes $[Co(NH_3)_5H_2O](ClO_4)_3$ and $[Co(NH_3)_5(HC_2O_4)](ClO_4)_2$ were prepared by standard procedures,[12,13] and purified by recrystallization. Chemical analysis[14] confirmed the purity, as did a comparison with published visible absorption spectral data, as shown in Table I. The anation reaction was followed at 497 nm where the decrease in absorbance on aquation of the oxalato complex is nearly 35% up to pH 4.5, though reduced to about 25% at pH 7.5. (see footnote *d* to Table I). The ionic strength was maintained at 1.0 *M* with KNO_3, since a perchlorate medium limits the solubility of oxalate salt. Blank experiments indicated that nitrate ion did not in any identifiable way compete with oxalate anation.[15] The rate studies were made by batch-sampling techniques in a thermostat controlled to ±0.1°. The aquo complex ion concentration was 0.010

Table II. Observed Rate Constant (10^5k_{obsd}, sec^{-1}) for Anation as a Function of pH and Oxalate Concentration at Various Temperatures

		Total Oxalate Concentration, *M*												
Temp, °C	pH	0.45	0.40	0.35	0.30	0.25	0.20	0.16	0.15	0.12	0.10	0.08	0.05	0.04
50	7.5						2.5	2.4		2.0		1.7		1.1
	7.0						2.5	2.2		1.9		1.6		1.0
	6.5						2.8	2.3		2.2		1.8		1.2
	6.0						2.4	2.2		1.9		1.5		0.9
	5.5						2.9	2.5		2.3		1.7		1.3
	4.5						2.9	2.5		2.1		1.5		1.0
	4.0				3.2	3.1	2.7		1.9		1.8			
	3.5				2.8	2.4	2.1		1.7		1.3			
	2.5				2.1	1.8	1.6		1.3		0.9			
60	7.5						6.8	6.5		5.7		4.7		3.2
	4.5						9.3	9.2		8.0		5.2		3.8
	3.0						7.6	6.5		6.1		4.7		3.6
	2.5				5.9	5.5	5.0		3.7		2.7			
	2.0				5.4	4.5	4.1		3.0		2.2			
	1.0	4.1		4.1		3.4			2.2				0.77	
	0.52	4.2		4.0		2.4			1.5				0.62	
	0.22	4.5		3.2		2.8			1.7				0.52	
	0.00	4.4		3.0		2.0			1.3				0.45	
70	7.5						24.5	23.9		20.8		17.4		12.0
	4.5						28.8	26.0		22.0		15.0		9.7
	2.5				16.2	15.6	12.3		10.9		7.1			
	1.00	14.0	14.6	12.6	11.6	9.4	6.6		6.4		4.0		2.5	
	1.00[a]	12.8		12.1		8.9			5.4				2.1	
	0.70	10.7	10.1	9.9	8.2	6.9	6.3		5.4		3.7		2.2	
	0.52	12.4	10.3	9.0	8.6	7.1	5.9		4.7		3.5		1.8	
	0.52[a]	11.0		8.5		6.1			4.4				1.4	
	0.30	9.0	9.6	7.7	7.0	5.8	4.8		3.9		3.2		1.7	
	0.22	10.6	9.7	7.6	7.0	6.7	4.7		3.5		2.1		1.3	
	0.22[a]	8.0		7.3		5.3			3.0				1.3	
	0.15	9.6	9.2	7.8	7.1	5.7	4.0		3.8		1.7		1.1	
	0.10	8.1	8.2	7.5	6.2	5.5	3.8		4.2		2.4		1.4	
	0.10[a]	8.6		6.8		5.9			3.9				1.6	
	0.00	8.6	7.9	7.3	5.8	4.3	3.4		2.5		2.3		1.6	
	0.00[a]	8.2		6.8		5.6			3.1				1.7	
80	1.00	36.6		26.2		22.0			15.3				6.4	
	0.52	26.8		20.2		16.9			11.6				3.6	
	0.22	18.0		16.8		8.0			7.8				3.5	
	0.10	16.1		14.1		9.9			7.1				3.3	
	0.00	15.1		12.9		10.2			6.5				2.9	

[a] Concentration of complex 0.015 *M*. In all other runs, concentration of complex is 0.010 *M*.

Table III. Rate Parameters for Anation of Aquopentaamminecobalt(III) Ion by Oxalate

	50°	60°	70°	80°
10^5k_0, M^{-1} sec^{-1}	3.5[a]	6.6	15	23
10^5k_1, sec^{-1}	6.1	18	49	130[a]
Q_1, M^{-1}	1.8	1.8	1.8	1.8[a]
10^5k_2, sec^{-1}	4.0	12.5	40	115[a]
Q_2, M^{-1}	9.2	9.2	9.2	9.2[a]
10^5k_{ex},[b] sec^{-1}	20	71	235	730

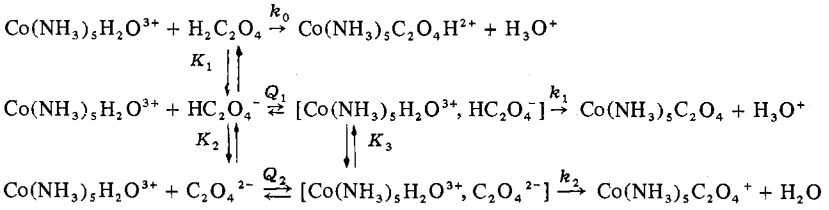
[a] Extrapolated values using the tabulated temperature parameters. [b] Rate constant for water exchange calculated from the data of H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

M in most cases, with a few runs at 0.015 *M*. The spectral changes during reaction were recorded either on a Cary Model 15 spectrophotometer or on a Beckman Model DU instrument with a Gilford Model 220 digital readout attachment. The acidities were attained by additions of HNO_3. Acid concentrations were established volumetrically down to 0.1 *M* and at lower values were measured by means of a Beckman Research Model pH meter. No added buffer was needed since the oxalate solution provided adequate self-buffering up to pH 4.5 and the reaction was independent of pH above that value. All chemicals used were of reagent grade and the laboratory-distilled water was further purified by passage through a mixed-bed ion-exchange column.

Each reaction mixture was sampled over a period of about 2 half-lives, and the data were plotted on the assumption that anation was complete; *i.e.*, the final absorbance was assumed to be that of pure oxalato complex ion of equivalent concentration. Such pseudo-first-order plots were linear for a considerable fraction of the reaction period as expected from the favorable equilibrium constant for aquo ligand displacement.[15] This enabled accurate determination of the experimental rate constants from the slope of the initial straight-line portions of the curves.

Results and Discussion

Studies were made of the variation in the observed initial rate constant k_{obsd} as a function of total oxalate concentration and $[H^+]$ at 50, 60, 70, and 80°. The major portion of the data was obtained at 70°, and plots of k_{obsd} *vs.* $[oxalate]_t$ at a number of acidities are presented in Figure 1. It is noted that in the most acidic solution the plot is linear, while curvature becomes apparent at pH 1 and above. Also, there appears to be little variation in k_{obsd} with acidity above pH 4.5, a fact better confirmed by more comprehensive data in



$$\begin{tikzcd}[column sep=small] Co(NH_3)_5H_2O^{3+} + H_2C_2O_4 \arrow[r, "k_0"] \arrow[d, shift left, "K_1"] & Co(NH_3)_5C_2O_4H^{2+} + H_3O^+ \quad (1) & & \\ Co(NH_3)_5H_2O^{3+} + HC_2O_4^- \arrow[u, shift left] \arrow[r, shift left, "Q_1"] \arrow[d, shift left, "K_2"] & {[Co(NH_3)_5H_2O^{3+}, HC_2O_4^-]} \arrow[l, shift left] \arrow[r, "k_1"] \arrow[d, shift left, "K_3"] & Co(NH_3)_5C_2O_4 + H_3O^+ \quad (2) \\ Co(NH_3)_5H_2O^{3+} + C_2O_4^{2-} \arrow[u, shift left] \arrow[r, shift left, "Q_2"] & {[Co(NH_3)_5H_2O^{3+}, C_2O_4^{2-}]} \arrow[l, shift left] \arrow[u, shift left] \arrow[r, "k_2"] & Co(NH_3)_5C_2O_4^+ + H_2O \quad (3) \end{tikzcd}$$

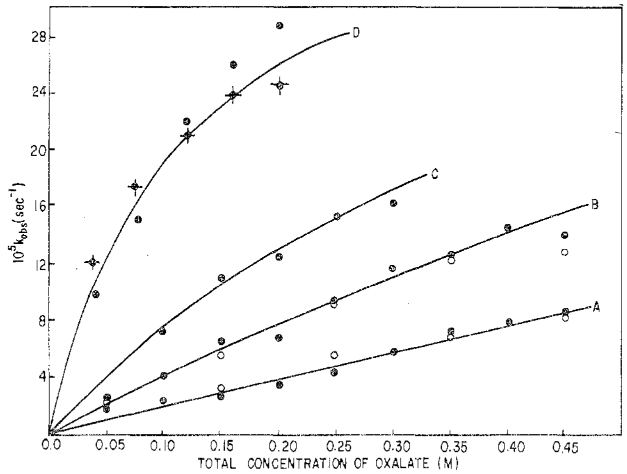


Figure 1. Variation of rate of anation of $Co(NH_3)_5H_2O^{3+}$ by oxalate as a function of reactant concentration and acidity at 70°: curve A, pH 0.0; curve B, pH 1.0; curve C, pH 2.5; curve D, pH 4.5 (●), 7.5 (✦); filled circles, [complex] = 0.010 *M*; open circles, [complex] = 0.015 *M*.

this pH range obtained at 50° (see Table II). The curvature in the k_{obsd} plots at pH 2.5, where the oxalate species[16] is about 95% $HC_2O_4^-$, and at pH 4.5 and above, where the oxalate species is almost totally $C_2O_4^{2-}$, suggest an ion-pair intermediate type of mechanism in these instances, as previously proposed for $Co(en)_2(H_2O)_2^{3+}$ anation.[3] By contrast, in the strongly acid solutions, the linearity of the plot suggests simple second-order kinetics for anation of $Co(NH_3)_5H_2O^{3+}$ by $H_2C_2O_4$. A mechanism of reaction consistent with these considerations is given in eq 1–3. The observed rate constant of anation in excess oxalate at fixed $[H^+]$ will then be given by eq 4.[17,18]

$$k_{obsd} = \frac{-d \ln [Co(NH_3)_5H_2O^{3+}]}{dt} = k_0[H_2C_2O_4] + \frac{k_1Q_1[HC_2O_4^-]}{1 + Q_1[HC_2O_4^-]} + \frac{k_2Q_2[C_2O_4^{2-}]}{1 + Q_2[C_2O_4^{2-}]} \tag{4}$$

The data of Table II were fitted at each temperature by the following procedure. The pH ≥4.5 data were plotted in the double reciprocal form $1/k_{obsd}$ *vs.* 1/[oxalate], which yielded good straight lines. In this pH range, all anation is occurring by reaction 3 so only the third term on the right of eq 4 is operative. A linear regression analysis of these plots therefore yields values for the intercept $1/k_2$ and the slope $1/k_2Q_2$, and thus of k_2 and Q_2 separately. Similarly, at pH 2.5, the double-reciprocal-plot technique yields values for k_1 and Q_1, since at this acidity, the contributions to anation by $H_2C_2O_4$ and $C_2O_4^{2-}$ may be neglected. The high-acidity data (pH ≤1) were then fitted by means of a computer program[19] to the rate equation modified for the absence of $C_2O_4^{2-}$, *viz.*

$$k_{obsd} = k_0[H_2C_2O_4] + \frac{k_1Q_1[HC_2O_4^-]}{1 + Q_1[HC_2O_4^-]} \tag{5}$$

This was accomplished by "floating" the value for k_0, utilizing the known values of k_1 and Q_1 and the experimental figures for k_{obsd}, $[H_2C_2O_4]$, and $[HC_2O_4^-]$ (the latter two being calculated from total [oxalate], $[H^+]$, and K_1). This procedure provided an excellent fit to the data, as is illustrated by the curves plotted in Figure 1. The values of the various rate parameters, all of which are within a ±10% standard deviation limit, are recorded in Table III.

Further support of the efficacy of this analysis is provided by the available equilibration data for the reaction

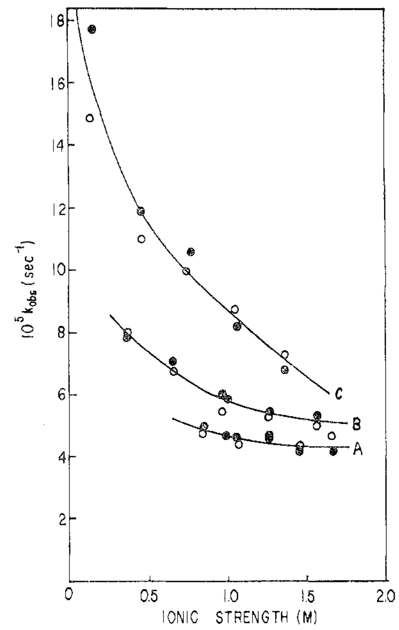


Figure 2. Variation of rate of anation of $Co(NH_3)_5H_2O^{3+}$ (concentration 0.010 *M*) by oxalate (total concentration 0.25 *M*) at 70° and various acidities as a function of ionic strength: curve A, $[H^+]$ = 0.6 *M*; curve B, $[H^+]$ = 0.3 *M*; curve C, $[H^+]$ = 0.1 *M*; filled circles, KNO_3 as neutral salt; open circles, $LiNO_3$ as neutral salt.

$$Co(NH_3)_5C_2O_4H^{2+} + H_3O^+ \underset{k_r}{\overset{k_f}{\rightleftarrows}} Co(NH_3)_5H_2O^{3+} + H_2C_2O_4 \tag{6}$$

At 70° in 1 *M* $HClO_4$, the equilibrium constant *K* for this reaction is reported[10] to be 0.24, along with a value[10,11] for k_f of 28 × 10^{-6} M^{-1} sec^{-1}. Our value for k_r (k_0 in our system) is 15 × 10^{-5} M^{-1} sec^{-1} at 70°, whence $K = k_f/k_r = 0.19$, in satisfactory agreement with the published figure. We have in fact redetermined[20] this equilibrium constant at 70° in the same perchlorate medium and obtained a value of 0.16, also in good agreement with the rate constant ratio estimate.

We obtained some data concerning the effect of ionic strength on the anation reaction in both KNO_3 and $LiNO_3$ media. These results are presented in Figure 2. They show the expected increase of ionic strength effect on the reaction as the uncharged entering species $H_2C_2O_4$ is replaced by $HC_2O_4^-$ as the acidity is reduced. However, the limited ionic strength range accessible in the high-acid runs and the complexity of the mechanism at the lower acidities (see eq 5) prevent other than the qualitative observation concerning the effect already stated.

In Table IV are presented the conventional transition-state theory temperature parameters for the rate constants recorded in Table III, together with their standard deviations as deduced by least-squares analysis.[21] One notes that the parameters for k_1 and k_2 are identical within experimental error suggesting near identity of the respective transition states. This seems logical since the cyclic nature of the equilibria described by K_2, Q_1, K_3, and Q_2 requires that $K_3 \approx 5K_2$. This increased acidity of the ion-paired $HC_2O_4^-$ over that of the unpaired bioxalate ion would tend to promote similarity between the k_1 and k_2 transition states, in that the proton in the first case would tend not to be involved intimately in transition-state geometry. As is also evident from Table IV, a corresponding similarity has been previously observed for the reactions of $H_2C_2O_4$ and $HC_2O_4^-$ with *cis*-$Co(en)_2(H_2O)_2^{3+}$ (en = ethylenediamine) and for the reactions of $HC_2O_4^-$ and $C_2O_4^{2-}$ with either *cis*-$Co(EDDA)(H_2O)_2^+$ (EDDA = ethylenediaminediacetate) or $Cr(NH_3)_5H_2O^{3+}$. It has been previously pointed out[3,7,8] that the rate constants for the rate-determining

Table IV. Temperature Parameters of Various Substitution Reactions of Cobalt(III) Complexes

Complex	Entering ligand	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)	Ref
$Co(NH_3)_5H_2O^{3+}$	$H_2C_2O_4$	14.3 ± 1.7	−35.0 ± 4.8	This work
$Co(NH_3)_5H_2O^{3+}$	$HC_2O_4^-$	22.4 ± 2.1	−8.6 ± 6.3	This work
$Co(NH_3)_5H_2O^{3+}$	$C_2O_4^{2-}$	24.8 ± 1.8	−2.1 ± 5.4	This work
$Co(NH_3)_5H_2O^{3+}$	$H_2{}^{18}O$	26.6 ± 0.3	6.7 ± 1.0	*a*
$Co(NH_3)_5H_2O^{3+}$	N_3^-	26.9 ± 1.3	5.4 ± 4.0	*b, c*
$Co(NH_3)_5OH_2{}^{3+}$	CO_2	15.3 ± 0.9	3.6 ± 0.3	*d*
cis-$Co(en)_2(H_2O)_2{}^{3+}$	$H_2C_2O_4$, $HC_2O_4^-$	24.8 ± 0.5	1.5 ± 1.5	*e*
α-*cis*-$Co(EDDA)(H_2O)_2{}^+$	$HC_2O_4^-$, $C_2O_4^{2-}$	28.4 ± 4.7	10.1 ± 14.9	*c, f, g*
cis-$Co(en)_2(H_2O)_2{}^{3+}$	$H_2{}^{18}O$	28.9 ± 2.3	15.1 ± 7.5	*c, h*
$Cr(NH_3)_5H_2O^{3+}$	$HC_2O_4^-$, $C_2O_4^{2-}$	26.4 ± 0.8	8.6 ± 0.4	*i, j*
$Cr(NH_3)_5H_2O$	$H_2{}^{18}O$	23.2 ± 0.5	0.0 ± 1.6	*k*

[a] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958). [b] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8**, 1604 (1969). [c] Redetermined from the published data so as to include standard deviations. [d] Reference 9. [e] Reference 3. [f] Reference 5. [g] The only observable product is the β-cis isomer. [h] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961). [i] Reference 6. [j] The only observable product is $Cr(NH_3)_4C_2O_4^+$. [k] T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, **94**, 8357 (1972).

ion-for-water interchange step in anation should be limited to values not greater than that for water exchange if metal–ligand bond fission is involved. The rate parameters recorded in Table IV show this to be in general true for the examples given. More specifically values for the water-exchange rate constant, k_{ex}, as determined by an oxygen-18-labeling procedure for the $Co(NH_3)_5H_2O^{3+}$ complex,[22] were calculated at the various temperatures of the present work and are included in Table III. It is seen that these values closely parallel those for k_1 and k_2, exceeding the latter constants by the frequently observed factor of between 4 and 6.[7] The k_0 values do not seem to conform to this pattern nearly so well, as is seen by converting them to first-order constants k'_0 by use of an "association factor" of $Q_0 = 0.5$ as obtained from conventional theory[23] and the relation $k'_0 = k_0/Q_0$. Because of the much smaller value of $\Delta H_0^{\ddagger}$ as compared to $\Delta H_1^{\ddagger}$ or $\Delta H_2^{\ddagger}$, the discrepancy between k'_0 and the other anation rate constants is magnified at the higher temperatures (see Table III).

The magnitudes of Q_1 and Q_2 are indicative of "normal" ion pairing since these values are within the range of expectation for the charge types involved in the given temperature range.[24] The ratio $Q_2/Q_1 \simeq 5$ is, nevertheless, somewhat greater than predicted for essentially electrostatic ion-pair systems since the factor Z_+Z_- only doubles in changing from $HC_2O_4^-$ to $C_2O_4^{2-}$. However, in the bioxalate ion, attachment in the ion pair may be blocked at the protonated end, giving the $C_2O_4^{2-}$ ion an additional advantage by a factor of 2, for a total of 4. Pairing between $H_2C_2O_4$ and the complex ion appears to be neglible in this system, in contrast with the *cis*-$Co(en)_2(H_2O)_2{}^{3+}$ system. For the latter, it was suggested that association of the reactants was greatly facilitated by the hydrogen-bonding possibilities with the two adjacent aquo ligands. It is noteworthy[4] that the ion $Co(en)_2(H_2O)(OH)^{2+}$ does not seem to exhibit the abnormal ability to associate with oxalate shown by the diaquo congener. This is partly perhaps because of the reduction in hydrogen-bonding possibilities and also may partly be due to the decreased proportion of cis isomer as compared to the trans at higher pH.[25]

Table V. Deuterium Solvent Isotope Effect on Oxalate Anation of the $Co(NH_3)_5H_2O^{3+}$ Ion

[Acid], M	Solvent	[Oxalate], M	$10^5 k_{obsd}$,[a] sec^{-1}	$10^5 k$/[oxalate], $M^{-1}\ sec^{-1}$
1.0	H_2O	0.20	4.3	21.5
1.0	H_2O	0.30	6.3	20.9
1.0	H_2O	0.40	8.4	21.1
				Av 21.2
1.0	D_2O	0.20	3.2	15.9
1.0	D_2O	0.30	4.3	14.4
1.0	D_2O	0.40	6.1	15.3
				Av 15.2
0.1	H_2O	0.20	7.9	39.4
0.1	H_2O	0.30	12.2	40.7
0.1	H_2O	0.40	14.8	36.9
				Av 39.0
0.1	D_2O	0.20	6.9	34.4
0.1	D_2O	0.30	10.2	33.8
0.1	D_2O	0.40	13.2	33.1
				Av 33.8

$10^5 k_0^{H} = 18\ M^{-1}\ sec^{-1}$ $10^5 k_1^{H} Q_1^{H} = 74\ M^{-1}\ sec^{-1}$
$10^5 k_0^{D} = 13\ M^{-1}\ sec^{-1}$ $10^5 k_1^{D} Q_1^{D} = 130\ M^{-1}\ sec^{-1}$

[a] Each rate constant is the average of two runs.

We have already mentioned the contrasting magnitudes of k_0 and its temperature parameters as compared to the corresponding constants for the other two reactions under study. One might explain the large difference between $\Delta S_0^{\ddagger}$ and $\Delta S_1^{\ddagger}$ on the basis of simple encounter control theory,[26] which would predict an increase in $\Delta S_1^{\ddagger}$ over $\Delta S_0^{\ddagger}$ of about 30 eu as is observed. This reasoning would, however, suggest an additional 30-eu increase for ΔS_2, not the small differential observed. As regards enthalpy of activation, an increase of $\Delta H_1^{\ddagger}$ or $\Delta H_2^{\ddagger}$ over $\Delta H_0^{\ddagger}$ is theoretically logical but the large differential observed here (about 8 kcal/mol) is well beyond expectation. It was therefore of interest to us to explore the possibility that anation by $H_2C_2O_4$ proceeds by an entirely different mechanism than it does by either $HC_2O_4^-$ or $C_2O_4^{2-}$. In conventional aquo ligand replacement, the original metal–oxygen bond is severed and a new one is made to the substituting ligand, in our case oxalate. With oxalic acid, it might be that the water substitution occurs indirectly by carbon–oxygen bond formation. This would be closely analagous to the formation of carbonatopentaamminecobalt(III) ion by direct addition of CO_2 to the aquo species.[9] The best test of such a concept would be by oxygen-18-tracer experiments. Unfortunately, in our system the relatively rapid exchange of $H_2{}^{18}O$ with $Co(NH_3)_5H_2O^{3+}$, as discussed above, prevents use of the oxygen-tracer technique for any other purpose. However, some anation experiments were performed by our usual procedure in which the rate of reaction in D_2O was compared to that in H_2O under otherwise identical conditions. The assumption made is that a substantial contrast in mechanism could well lead to a substantial contrast in solvent isotope effect. The results of this study are given in Table V. The estimates for k_0 and k_1Q_1 are made by using an approximate form of eq 5

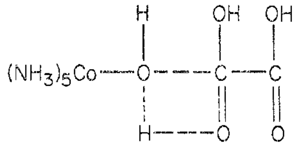
$$k_{obsd} = k_0[H_2C_2O_4] + k_1Q_1[HC_2O_4^-] \tag{7}$$

In terms of total oxalate concentration and K_1^{H}, the first acid dissociation constant of $H_2C_2O_4$, eq 7 for the H_2O system may be written

$$k_{obsd}^{H}/[oxalate]_t = k_0^{H} + (k_1^{H}Q_1^{H} - k_0^{H})\left(\frac{K_1^{H}}{h + K_1^{H}}\right) \tag{8}$$

A value for K_1^D, the applicable dissociation constant in the D_2O medium, is readily estimated by well-established criteria[27] to be 0.022, as compared to $K_1^H = 0.06$. Values for the constants k_0 and k_1Q_1 for each medium can thus be calculated and are included in Table V. It is noted that k_0^H and $k_1^HQ_1^H$ are in reasonable agreement with our more accurately determined values of Table III. The values of the isotope effects are $k_0^H/k_0^D = 1.4$ and $k_1^HQ_1^H/k_1^DQ_1^D = 0.6$. The contrast in these ratios could be ascribed to a large increase in Q_1 in D_2O as compared to that in H_2O, but recent data[28] suggest that ion-pairing constants are rather insensitive to replacement of the normal solvent by heavy water. The ratio k_0^H/k_0^D is in keeping with the concept that fission of a bond to a proton is at least partially significant in the rate-determining step for $H_2C_2O_4$ addition. For the anation by $HC_2O_4^-$, it appears that the rate-determining step is *faster* in D_2O. This rate-determining step is identified with Co---OH_2 bond fission, which could well be slower than that for Co---OD_2 because of the decreased stability of this bond which results from the known lower acidity of D_2O relative to H_2O. However, at present there are no confirming experimental data of the type needed, such as a measurement of the rate of water exchange with an aquo complex ion in D_2O as compared to that in H_2O.

To sum up, we have shown that the rates of anation of $Co(NH_3)_5H_2O^{3+}$ ion by $HC_2O_4^-$ and $C_2O_4^{2-}$ ions conform to the established pattern for such reactions. This is clear from the comparisons made in Table IV, where one notes that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for all the representative anation and water-exchange reactions are within the range 26 ± 3 kcal/mol and 4 ± 10 eu, respectively. The noteworthy exception is the substitution by $H_2C_2O_4$ of the aquo ligand of the pentaammine species. While the *rate constants* do not differ greatly among the three types of oxalate within the temperature range studied, the temperature parameters are widely different for the fully protonated acid. Furthermore, though the rate of the $H_2C_2O_4$ reaction is much slower than that for CO_2 addition, this decrease is almost entirely ascribable to the change in $\Delta S^\ddagger$, which drops from +3.6 to −35 eu while $\Delta H^\ddagger$ is practically constant. Whether this is indicative of a parallelism between the mechanisms cannot be conclusively claimed on the basis of present evidence. A simple four-center transition state is readily visualized for the oxalic acid system, *viz.*



$$\begin{array}{ccccc} & H & & OH & OH \\ & | & & | & | \\ (NH_3)_5Co\text{—} & O & \text{- - -} & C\text{—} & C \\ & \vdots & & \| & \| \\ & H & \text{- - -} & O & O \end{array}$$

which can achieve oxalate addition without metal–oxygen bond cleavage. This concept is entirely analagous both to that proposed for the carbonato system[9] and for the recently reported formation reaction of pentaamminearsonatocobalt(III) ion,[29] in which the metal–oxygen bond is also known to remain unbroken. It is also consistent with the fact that reaction 6 appears to occur through cleavage of the carbon–oxygen bond,[30] unlike aquations at lower acidity where the "normal" Co–O bond rupture is the predominant reaction path.

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Registry No. $Co(NH_3)_5H_2O^{3+}$, 14403-82-8; $Co(NH_3)_5C_2O_4H^{2+}$, 19306-87-7; $H_2C_2O_4$, 144-62-7; $HC_2O_4^-$, 920-52-5; $C_2O_4^{2-}$, 338-70-5.

References and Notes

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(15) The equilibrium constant for oxalate complex formation is rather favorable even in strongly acid solution (see Discussion below and also ref 10), while that for the nitrato complex formation is very unfavorable (see ref 8).
(16) We have adopted values of $K_1 = 0.06$ and $K_2 = 2 \times 10^{-4}$ over the entire temperature range of our study (ionic strength 1.0 *M*). Some temperature variation is observed in these constants in the 50–80° range (see ref 3 and 6 and other references quoted therein) but it is not significant to our conclusions.
(17) The logical assumption is made that ion-pair equilibration is rapidly achieved and continuously maintained throughout the reaction.
(18) Above pH 7, the proportion of hydroxopentaamminecobalt(III) ion becomes appreciable, but, as noted earlier, this seems to have little effect on the anation rate characteristics. The assumption is therefore made that $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_5)OH^{2+}$ are kinetically indistinguishable in this system, in spite of the reduction in ionic charge. One might expect the latter fact to be reflected in a reduction in Q, but there is no evidence for this.
(19) We are indebted to Mr. S. Ficner of this laboratory for carrying out this analysis, utilizing a program provided by Dr. R. J. Buchacek (see ref 9, footnote 22).
(20) Sealed samples of aquo complex ion with known acid and oxalate concentration were thermostated at 70° for at least 10 half-lives before spectrophotometric determination of the final aquo:oxalato complex ratio. It was noted that in the presence of nitrate, spurious results were obtained, probably due to oxidation of oxalate by nitric acid. No such difficulty was experienced in perchlorate medium.
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