for tetraiodonickelate(II). This explanation is consistent with the observation that in molten salt systems, iodide is incapable of forming octahedral nickel(II) complexes while bromide does so with considerably more difficulty than chloride, which already prefers the tetrahedral geometry.[11,12]

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Substitution Reactions of Oxalato Complex Ions. VIII. The Kinetics of the Anation Reaction of Diaquobis(ethylenediamine)cobalt(III) Ion by Oxalate in Acidic Aqueous Solution[1]

By P. M. Brown and G. M. Harris

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The reaction appears to proceed by a typical SN1 ion-pairing mechanism. The rate-limiting water dissociation reaction has a rate constant, k_0, very similar in magnitude and temperature dependence to that for water exchange under comparable conditions. The association constants for the reactant pairs $Co(en)_2(H_2O)_2^{3+}$–$H_2C_2O_4$ and $Co(en)_2(H_2O)_2^{3+}$–$HC_2O_4^-$ are 11 and 100, respectively, at 50°. These values are several times greater than predicted by simple point-charge interaction theory, as might be expected for large-ion systems amenable to hydrogen-bonding effects. The constant k_0 is increased more or less linearly by a factor of about 4 when the "inert" nitrate salt concentration is increased from zero to 3 *M*. This is typical of a nonspecific medium effect in this kind of reaction.

The water replacement reactions of various anionic nucleophiles with stable aquo cations are believed by many researchers to involve the prior establishment of an ion-pairing associative equilibrium between the reacting species. This is followed by ligand–water rate-determining dissociation, whereupon the nearby nucleophile slips into the position vacated by the leaving water molecule. Typical examples are afforded by the series of anation reactions symbolized by

$$Co(NH_3)_5(H_2O)^{3+} + X^{n-} \longrightarrow Co(NH_3)_5X^{(3-n)+} + H_2O$$

where X^{n-} may be SO_4^{2-}, $H_2PO_4^-$, Cl^-, SCN^-, etc.[2] Only two similar studies of the ion $Co(en)_2(H_2O)_2^{3+}$ have thus far been reported—those of anation by sulfate[3a] and by phosphate.[3b] In these cases, the expected SN1 ion-pairing mechanism also appears to be applicable, as suggested by the near equivalence of the ligand–water isotopic exchange rates and the limiting anation rates at high anion concentration. Study of the reaction of $Co(en)_2(H_2O)_2^{3+}$ with oxalate offers another interesting possibility, since rapid and complete chelation is involved in formation of the final product.[4] The question thus arises as to what limits the rate of the substitution—water dissociation or chelation of monodentate oxalate. Of further significance is the fact that the product cation, $Co(en)_2C_2O_4^+$, is completely stable in strongly acidic solution,[5] unlike several analogous cobaltammine oxychelates (such as with SO_4^{2-}, CO_3^{2-}, PO_4^{3-}), all of which aquate readily in strong acid. Thus, in the present study it has been possible to observe "anation" by the uncharged species $H_2C_2O_4$ as well as by ionic oxalate. The investigation is also of interest relative to the recently reported[6] reaction of ionic oxalate with the complex anion $Cr(C_2O_4)_2(H_2O)_2^-$. For this process, the question of preequilibration of the reactants is somewhat controversial, since both are negatively charged. In the present study, conventional ion association is possible, but the data indicate considerable reinforcement of this process by factors which are probably independent of ionic charge. The reactant association mechanism assumed in the interpretation of the anation of bis(oxalato)diaquochromium(III) anion by oxalate is thus offered indirect support.

Experimental Section

cis-$Co(en)_2(H_2O)_2(NO_3)_3 \cdot CH_3OH$ was prepared and crystallized from methanol solution by the procedure of Dwyer, Sargeson, and Reid.[7] The results of a commercial analysis[8] follow. *Anal.* Calcd for *cis*-$Co(en)_2(H_2O)_2(NO_3)_3 \cdot CH_3OH$: C, 13.86; H, 5.58; N, 22.63; Co, 13.60. Found: C, 13.86; H, 5.70; N, 23.18; Co, 13.35. Aqueous solutions of the product gave extinction coefficients which compared well with those reported by Bjerrum and Rasmussen.[9] To test for possible impurities which might catalyze the reaction, the material was also prepared by the method described by Tong and Yankwich.[10] Observed reactivity data for the two different materials agreed within experimental error. All other reagents were commercial

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(1) Part VII: H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).

(2) C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967).

(3) (a) C. G. Barraclough and R. S. Murray, *J. Chem. Soc.*, 7047 (1965); (b) S. F. Lincoln, R. S. Murray, and D. R. Stranks, Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz, Switzerland, Sept 1966, p 357.

(4) No evidence has previously been presented for anything but the fleeting existence of aquooxalato complexes of the type Co(bidentate ligand)$_2$-$(C_2O_4)(H_2O)^+$.

(5) Part III: S. Sheel, D. T. Meloon, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962).

(6) Part VI: H. Kelm and G. M. Harris, *ibid.*, **6**, 706 (1967).

(7) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).

(8) Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

(9) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(10) J. Y. Tong and P. E. Yankwich, *J. Am. Chem. Soc.*, **80**, 2664 (1958).

products of good quality and were used without further purification.

Reaction rates were determined by optical density measurements at 500 mμ, where a substantial difference exists in the spectra of the species $Co(en)_2(OH_2)_2^{3+}$ and $Co(en)_2C_2O_4^+$ (see Figure 1). A Beckman DU spectrophotometer fitted with a temperature-controlled 1-cm cell compartment was used. The complex concentration was fixed at 5.81×10^{-3} *M* in all of the experiments reported, a value which gives the convenient optical density range of about 0.45–0.70 in the rate measurements. The ionic strength was controlled by addition of the requisite amounts of nitric acid and potassium nitrate, and oxalate was added in the form of oxalic acid. In the runs in which the oxalate concentration greatly exceeded that of the complex, first-order kinetics[11] was well obeyed over several half-times of reaction. At the lower oxalate concentrations, the rate constants were obtainable from the initial slopes of the plots, which were linear at least up to 1 half-time.

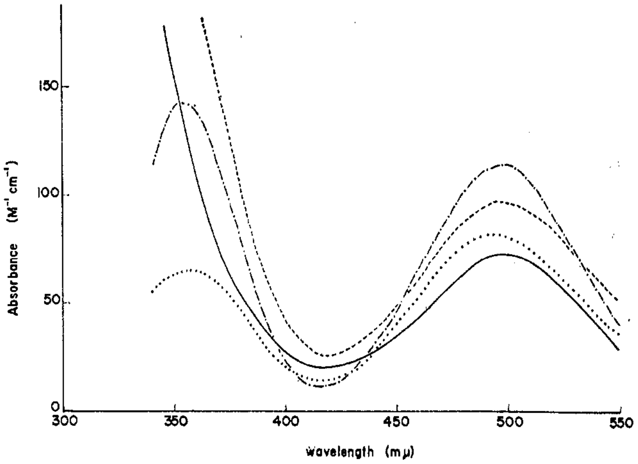

Figure 1.—Spectra of the significant compounds: — · — ·, $Co(en)_2C_2O_4^+$; · · · ·, $Co(en)_2(OH_2)_2^{3+}$; ———, $Co(NH_3)_5C_2O_4^+$; – – – –, intermediate obtained in low-acidity equation of $Co(en)_2C_2O_4^+$.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR REACTION OF THE $Co(en)_2(H_2O)_2^{3+}$ ION WITH OXALATE AT IONIC STRENGTH 2.0 *M*

(Oxalate), *M*	(HNO_3), *M* 0.10	0.50	1.00	2.00
	10^5k, sec^{-1}			
		(a) 40°		
0.012	1.31	0.84	0.76	0.66
0.015	1.59	0.98	0.83	...
0.020	1.82	1.28	1.09	...
0.030	2.18	1.57	1.47	1.27
0.060	2.63	2.37	2.32	1.98
0.12	...	...	2.85	2.78
0.24	...	...	...	3.35
		(b) 50°		
0.012	4.75	2.68^a	2.27	1.86^a
0.015	5.45	3.18^c	2.60^a	2.18
0.020	6.56	4.02	...	2.83
0.030	7.42	5.54^a	4.43^b	3.75
0.060	9.08	7.66^a	6.74^a	5.98
0.12	...	9.62	9.28^a	7.85
0.24	...	...	11.42	10.38
		(c) 60°		
0.012	12.3	7.03	5.61	4.15
0.015	14.0	9.03^a	7.12	...
0.020	19.2	10.9	8.37	...
0.030	24.3	14.0^a	11.9	9.25
0.060	31.0	21.2^b	19.5	16.5
0.12	...	...	27.4	25.3
0.24	...	...	...	33.2

^{a} Mean of two runs. ^{b} Mean of three runs. ^{c} Mean of four runs.

TABLE II

EFFECT OF NITRATE ON THE RATE CONSTANTS FOR THE REACTION OF THE $Co(en)_2(H_2O)_2^{3+}$ ION WITH OXALATE IN 0.1 *M* HNO_3

(KNO_3), *M*	Ionic strength, *M*	10^5k, sec^{-1} 0.015 *M* oxalate 50°	0.015 *M* oxalate 60°	0.06 *M* oxalate 50°	0.06 *M* oxalate 60°	10^5k_0, sec^{-1} ^{a} 50°	60°
0.00	0.1	2.07	6.68	3.27	10.8	4.1	14
0.30	0.4	2.27	9.53	4.33	13.9	6.3	16
0.70	0.8	3.53	12.1	5.72	20.7	7.2	27
1.30	1.4	4.00	14.0	7.60	24.6	11	33
2.40	2.5	4.90	14.9	9.23	31.9	13	52
2.90	3.0	4.68	15.6	11.60	35.0	23	63

^{a} Obtained by extrapolation using the relation $1/k = (1/k_0) +$ [constant/(oxalate)] and the two sets of oxalate concentrations at each temperature. More precise values obtained at $I = 2.0$ *M* appear in Table III.

Results

In one series of experiments, the ionic strength was kept constant at 2.0 *M*, the oxalate concentration was varied over the range 0.012–0.24 *M*, and the nitric acid concentration was fixed at a number of values between 0.1 and 2 *M*. The temperature effect on the reaction was determined by running experiments at 40, 50, and 60°. The results of these studies appear in Table I. In a second set of data, the effect of varying the reaction medium is illustrated. Runs were made with oxalate concentrations of 0.015 and 0.06 *M*, in 0.1 *M* nitric acid, while varying the potassium nitrate concentration between zero and 2.9 *M*. These results, obtained at 50 and 60°, are presented in Table II.

Some preliminary experiments were performed at low acidity (pH 5.5), under which conditions a spectrophotometrically detectable intermediate appears, as shown in Figure 1. However, owing to the complexity of the system in this pH region,[12] the study was not pursued further at this time. Obviously, much more than spectrophotometric data are required to give the evidence needed to understand this phenomenon.

Discussion

The total reaction under the conditions specified for the data of Table I is given by the sum of the two processes

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(11) According to the relationship $-2.303 \log [(D_\infty - D_t)/(D_\infty - D_0)] = kt$, where k is the observed pseudo-first-order rate constant, obtainable from the slope of the conventional plot of the data. No spectral evidence appeared in the runs in acid solution for nitrato complexes or any other intermediate species.

(12) The following diaquocobaltic complex equilibria are significant at low acidities

$$Co(en)_2(H_2O)_2^{3+} \rightleftharpoons Co(en)_2(H_2O)(OH)^{2+} + H^+$$

$$Co(en)_2(H_2O)(OH)^{2+} \rightleftharpoons Co(en)_2(OH)_2^+ + H^+$$

the p*K*'s for the two reactions are,[9] respectively, 5.8 and 8.1 at 25° in 1 *M* $NaNO_3$. The decay of the observed intermediate is not instantaneous, resulting in the complication of a successive reaction system. *cis–trans* isomerization of the hydroxo species may also play a part in the process.

$$cis\text{-}Co(en)_2(H_2O)_2^{3+} + HC_2O_4^- \longrightarrow Co(en)_2C_2O_4^+ + H_3O^+ + H_2O \quad (1)$$

$$cis\text{-}Co(en)_2(H_2O)_2^{3+} + H_2C_2O_4 \longrightarrow Co(en)_2C_2O_4^+ + 2H_3O^+ \quad (2)$$

The assumption that only the *cis*-diaquo complex is involved is reasonable, since at equilibrium the *cis*:*trans* ratio is about 58 in strongly acidic solutions.[9] The water substitution goes essentially to completion, since the species $Co(en)_2C_2O_4^+$ is known to be completely stable in boiling 1 *M* acid.[5] Also, the equilibrium constant for oxalatotetraamminecobalt(III) ion formation from tetraamminediaquo is reported to be 10^7 under conditions of similar acidity.[13]

It is noted that the data of Table I cannot be fitted by simple second-order kinetics of the type $R = k$(complex)(oxalate) at any of the acidities recorded. However, it is found that a reciprocal plot of $1/k$ *vs.* $1/$(oxalate) at a given acidity does produce a linear relationship,[14] as is illustrated for the data at 50° in Figure 2. The most striking features of these plots are the existence of a common intercept at $(\text{oxalate}^{-1}) \rightarrow 0$ and the increase in slope of the curves with increasing acidity, though much less than in direct proportion. The common intercept suggests a mechanism in which there is a limiting acidity-independent rate constant of reaction, k_0, reached only at very high oxalate concentrations, while the acid variation of k suggests a higher associative propensity for $HC_2O_4^-$ as compared to $H_2C_2O_4$, though not by a large factor.

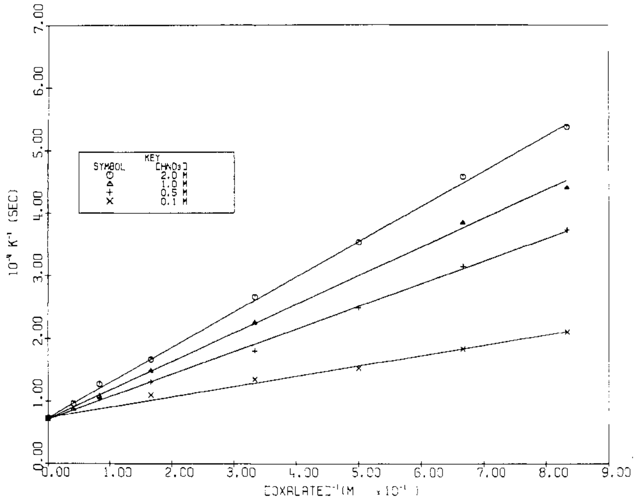

Figure 2.—Reciprocal plot of observed rate constant *vs.* oxalate concentration at 50°. Concentration of $Co(en)_2(H_2O)_2^{3+}$ was 5.81×10^{-3} *M*.

Two kinds of reaction mechanism lead to rate laws which are consistent with the recorded data. The first of these is the reactant association–water dissociation type already mentioned. As applied to the present system, the various equilibria existing and reactions possible may be symbolized as

$$cis\text{-}Co(en)_2(H_2O)_2^{3+} \left\{\begin{array}{ccc} +H_2C_2O_4 & \overset{K_3}{\rightleftharpoons} & Co(en)_2(H_2O)_2^{3+}\cdot H_2C_2O_4 \\ K_1\uparrow\downarrow & & \downarrow\uparrow K_2 \\ +HC_2O_4^- & \underset{K_4}{\leftrightharpoons} & Co(en)_2(H_2O)_2^{3+}\cdot HC_2O_4^- \end{array}\right\} \xrightarrow{k_0} Co(en)_2C_2O_4^+ \quad (3)$$

In this, k_0, the rate constant for the rate-determining ligand–water dissociation, is assumed to be the same for both associated species. K_1 and K_2 are the acid dissociation constants for free and associated oxalic acid, respectively, and K_3 and K_4 are the association constants for oxalic acid and bioxalate ion with diaquo complex, respectively.[15] Conventional stationary-state kinetic analysis of this reaction scheme leads to the following expression for the pseudo-first-order observable rate constant in terms of k_0, the various K's, a (the total H^+ ion concentration), and b (the total oxalate concentration)

$$k = \frac{k_0K_3(K_2 + a)b}{K_3(K_2 + a)b + K_1 + a} \quad (4)$$

In reciprocal form, this becomes

$$1/k = (1/k_0) + [(K_1 + a)/k_0K_3(K_2 + a)b] \quad (5)$$

It is seen from (5) that a plot of $1/k$ *vs.* $1/b$ should give a straight line of intercept $1/k_0$ and slope $(K_1 + a)/k_0K_3(K_2 + a)$. Then, since a is known[16a] and K_1 can be estimated from published data concerning the effect of temperature and ionic strength on oxalic acid dissociation,[16b] one can solve eq 5 for the values of k_0, K_2, and K_3. The results of this analysis are collected in Table III together with the conventionally derived temperature variation parameters.

This interpretation appears to make good sense for a number of reasons other than the fact that the data are quite accurately fitted. First, the figure for K_4 is of the order of magnitude expected for a (3+)–(1−) outer-sphere ionic association. A simple calculation based on coulombic force concepts[17] yields a value of $K_4 \cong 15\ M^{-1}$ at 50°. This same type of calculation suggests a value of $K_3 \cong 0.5\ M^{-1}$. However, both of these theoretical figures can set only a minimum value, as is obvious from data on other ion-pairing systems.[18]

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[13] M. Mori, R. Tsuchiya, and E. Matsuda, *Bull. Chem. Soc. Japan*, **34**, 1761 (1961).

[14] A computer-assisted curve-fitting procedure was used. The cooperation of Dr. George Chappell in this analysis is gratefully acknowledged.

[15] Note that, because of the cyclic nature of the equilibria, $K_1K_4 = K_2K_3$. Thus, only three of the equilibrium quotients are independently variable quantities.

[16] (a) At the lowest nitric acid concentration (0.10 *M*) and highest oxalate (0.06 *M*), oxalic acid dissociation contributes about 20% to the total hydrogen ion concentration. However, this correction is down to 6.5% at 0.03 *M* and 3% at 0.02 *M* oxalate. It has been ignored in the evaluation of the slopes of the reciprocal plots (such as given in Figure 2), since only the first few points at 0.10 *M* nitric acid concentration are affected. Furthermore, these errors are slight, since at the higher oxalate concentrations, k is only slightly dependent on acidity. At acidities of 0.50 *M* and higher, the corrections are <1% at all oxalate concentrations used. (b) Values for K_1 at various temperatures and ionic strengths are given in several recent references: N. K. Dutt and B. Sur, *Z. Anorg. Allgem. Chem.*, **293**, 195 (1957); A. McAuley and G. H. Nancollas, *Trans. Faraday Soc.*, **56**, 1165 (1960); *J. Chem. Soc.*, 2215 (1961); R. F. Bauer and W. M. Smith, *Can. J. Chem.*, **43**, 2755 (1965); E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966). A reasonable judgment of the data suggests $K_1 = 0.06\ M^{-1}$ at an ionic strength of 2 *M* and at 50°, with negligible temperature variation in the range of our work.

[17] See, for example, G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962), for the method of calculation. In our computations, a figure of 6 Å is assumed for the distance of closest approach of the associating species.

[18] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 37, Table 1.11.

TABLE III

CONSTANTS DESCRIBING THE RATE OF REACTION of $Co(en)_2(H_2O)_2^{3+}$ ION WITH OXALATE

Temp, °C	10^5k_0, sec^{-1}	K_1,[a] M	K_2, M	K_3, M^{-1}	K_4,[b] M^{-1}
40	4.1	0.060	0.55	13	119
50	14	0.060	0.55	11	100
60	48	0.060	0.55	7	64

$\Delta H^{\ddagger} = 24.8 \pm 0.5$ kcal/mol

$\Delta S^{\ddagger} = 1.5 \pm 1.5$ eu

$\Delta H^{c} = 6 \pm 3$ kcal/mol

[a] Temperature variation appears to be within experimental error of the determinations in this range.[16] [b] Calculated from $K_4 = K_2K_3/K_1$.[15] [c] Value which governs the variation of K_3 and K_4.

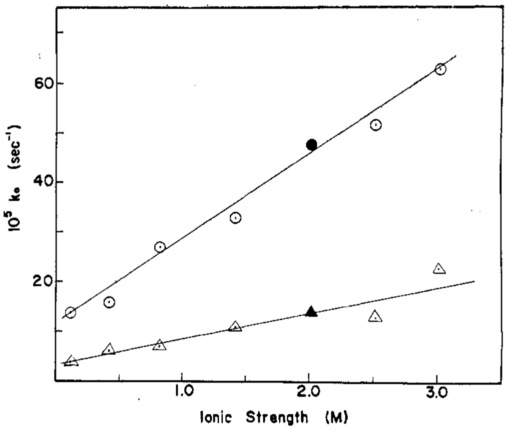

Figure 3.—Effect of ionic strength on value of k_0: circles, at 60°; triangles, at 50°. Solid points are from data of Table III; others are from Table II.

Furthermore, other chemical forces such as hydrogen-bond-type interactions, which are bound to exist between the diaquo species and oxalate, are also ignored in the theory.

The magnitude of K_2 ($\sim$0.55 M over the experimental temperature range) is quite reasonable also. It is known[19] that the protonated "inner-sphere" oxalate in the complex ion $Co(NH_3)_5C_2O_4H^{2+}$ has an acid dissociation constant about 100 times greater than that of the corresponding free ion, $HC_2O_4^-$. The factor of approximately 10 between K_2 and K_1 is thus about what one might predict for the increased acidity of loosely coordinated oxalic acid as compared to the free acid, and it should exhibit the same negligible temperature dependence. The magnitude of ΔH governing the variation of K_3 and K_4 is also within expectation for relatively weak associations of this type, though theory would suggest a somewhat larger value for ΔH_3. The value of k_0 under our conditions is what one would deduce on the basis of the data of Kruse and Taube[20] for water exchange of *cis*-$Co(en)_2(H_2O)_2^{3+}$. Their value for the water-exchange rate at $I \cong 1$ and at $\sim$40° is $k_{ex} = 7.7 \times 10^{-5}$ sec^{-1}, about twice our k_0 value. The temperature-dependence parameters also parallel ours.[21] It is therefore reasonable to conclude that water exchange and oxalate addition are both governed by the same rate-determining water dissociation process. Our value of $k_0 = 4.1 \times 10^{-5}$ sec^{-1} at 40° was obtained at an ionic strength of 2.0 M. It is seen from Figure 3 that increasing the ionic strength from 1.0 to 2.9 approximately doubles k_0 at both 50 and 60°. One can reasonably assume a similar effect at 40°, so that the true factor relating k_0 to k_{ex} is close to 4. This is in good agreement with the factor observed in several other anation processes,[2] which averages out at about 5. This is in keeping with the concept of the statistical advantage "outer-sphere" water has in substituting for the leaving "inner-sphere" water.

An alternative explanation for all the quoted data may be based on the standard five-coordinate "reactive intermediate" mechanism,[2] involving several competitive paths

$$\underset{}{Co(en)_2(H_2O)_2^{3+}} \xrightarrow{k_0} \underset{I}{Co(en)_2(H_2O)^{3+}} + H_2O \tag{6}$$

$$I + H_2O \xrightarrow{k_1} Co(en)_2(H_2O)_2^{3+} \tag{7}$$

$$I + H_2C_2O_4 \xrightarrow{k_2} Co(en)_2C_2O_4^+ + 2H^+ \tag{8}$$

$$I + HC_2O_4^- \xrightarrow{k_3} Co(en)_2C_2O_4^+ + H^+ \tag{9}$$

This leads to a rate law of mathematical form identical with that already given (eq 5), *viz.*

$$1/k_{obsd} = (1/k_0) + [(K_1 + a)/k_0(k_2/k_1)((k_3/k_2)K_1 + a)b] \tag{10}$$

It readily follows[15] that $k_2/k_1 = K_3$ and $k_3/k_1 = K_4$. Since the concentration of water is about 50 M, this interpretation requires that $H_2C_2O_4$ be (at 50°) about 500 times more reactive than H_2O in "picking up" the intermediate, quite contrary to reasonable expectation.

The type of argument just presented is even more useful in reconsideration of the $Cr(C_2O_4)_2^-$–oxalate reaction data.[6] Equations 5 and 10 are also applicable to that system. To support the "reactive intermediate" mechanism, one must assume that the neutral H_2O molecule (on a mole-for-mole basis) is only about $^1/_{50}$ as effective[22] as the $HC_2O_4^-$ ion in the competition for reaction with an assumed intermediate, $Cr(C_2O_4)_2(H_2O)^-$. This is unbelievable, especially if one is going to place emphasis on the repulsive forces between charged ionic species, as must be done if one is to rule out the ion-pair associative mechanism.[23] On

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(19) (a) S.-E. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966); (b) C. Andrade and H. Taube, *ibid.*, **5**, 1087 (1966).

(20) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

(21) They report[20] $\Delta H^{\ddagger} = 28.8$ kcal/mol and $\Delta S^{\ddagger} = 15$ eu for water exchange with *cis*-$Co(en)_2(H_2O)_2^{3+}$ ion over the temperature range 14–40°. The discrepancies between these data and ours are not remarkable, considering the wide differences in the styles of the experiments performed and the procedures for evaluating the rate constants.

(22) The magnitudes of the various constants K for the chromioxalate system, using the terminology of eq 3 above (with $Cr(C_2O_4)_2(H_2O)_2^-$ substituted for $Co(en)_2(H_2O)_2^{3+}$, $HC_2O_4^-$ for $H_2C_2O_4$, and $C_2O_4^{2-}$ for $HC_2O_4^-$, etc.), are at 50°: $K_1 = 5 \times 10^{-5}$ M, $K_2 = 1.1 \times 10^{-4}$ M, $K_3 = 0.85$ M^{-1}, and $K_4 = 1.9$ M^{-1}. Since K_3 is close to unity, k_2/k_1 must thus be approximately 50, making allowance for the water concentration.

(23) There has recently beeen much interest in the mode of reaction of $Co(CN)_5H_2O^{2-}$ ions with anions such as I_3^-, 1^-, Br^-, and Cl^-: R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967), and references cited therein. A competitive SN1 mechanism has been favored, with $Co(CN)_5^{2-}$ as the reactive intermediate. However, this is a very special type of internally stabilized intermediate, not paralleled in any sense by $Cr(C_2O_4)_2H_2O^-$. Recent work relating to the Co(II) analog of $Co(CN)_5^{2-}$ confirms the existence of the former, and thereby supports the Co(III) assumption: J. H. Espenson, 154th National Meeting of American Chemical Society, Chicago, Ill., Sept 1967, Abstract O-107.

the other hand, the magnitude of K_3 for this system (0.85 at 50°) is only greater by a factor of about 6 than the theoretical value.[24] This is the same order of magnitude as exists between the comparable observed and calculated association constant values for the $Co(en)_2(H_2O)_2{}^{3+}$–$HC_2O_4{}^-$ system, as was indicated above.

The experiments listed in Table II show that k_0 is only moderately sensitive to ionic strength, as was found for the corresponding rate constant for water dissociation from the $Cr(C_2O_4)_2(H_2O)_2{}^-$ ion.[6] In fact, a plot of the variation of k_0 with ionic strength (Figure 3) resembles very closely the similar plot (Figure 6) in ref 6. It is observed that an essentially linear relationship occurs in both instances. The change in k_0 is approximately a factor of 4 in going from $I = 0$ to $I = 3$ in both sets of data in this work and in the chromioxalate study. There is no clear-cut evidence, either in this or in the previous study,[6] that the inert-salt influence is other than a nonspecific ionic strength effect, for which there is no suitable theoretical interpretation under the conditions of the studies. However, it is also reasonable to conceive of the nonsubstituting nitrate ion as facilitating metal ion–water ligand bond fission through specific attack on the coordinated water molecule which is not associated with oxalate. Consequent labilization of this water would catalyze the entry of the free end of the oxalate, as conceived for the oxalate substitution mechanism above. Such a concept would require a linear relationship between rate constant and nitrate concentration which is also evident from Figure 3.[25]

The preliminary study of the reaction in solutions of low acidity gave results which are within expectation. The pK for the first acid dissociation of $Co(en)_2(H_2O)_2{}^{3+}$ is about 5.8.[12] Thus, at pH 5.5, a large fraction of the complex is in the form $Co(en)_2(H_2O)(OH)^{2+}$. Water exchange with this ion is some 60 times more rapid than with the diaquo species,[20] undoubtedly owing to the well-known labilizing influence of hydroxide adjacent to the water ligand. The tendency in this case will therefore be for a reaction scheme of the form[26]

$$Co(en)_2(H_2O)(OH)^{2+}\cdot C_2O_4{}^{2-} \xrightarrow{k_0} Co(en)_2(OH)(C_2O_4) + H_2O \qquad (11)$$

$$Co(en)_2(OH)(C_2O_4) \xrightarrow{k_1} Co(en)_2C_2O_4{}^{2+} + OH^- \qquad (12)$$

Since in general hydroxide is a difficult ligand to dislodge as compared to water, k_1 should share the rate determination with k_0, and $Co(en)_2(OH)(C_2O_4)$ must appear as an intermediate.[27] The spectrum observed for the intermediate supports this view in that it differs little from the spectrum of the related monodentate oxalato complex, $Co(NH_3)_5C_2O_4$, as shown in Figure 1.[28]

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[24] Using the equations of ref 17, one calculates $K_3 = 0.15$ at 50°, assuming $a = 6$ Å.

[25] The contribution to the ionic strength made by compounds other than nitrates is only 0.02 M, so $I \simeq$ (nitrate).

[26] Since the pK of $HC_2O_4{}^-$ is 4.3,[16] nearly all of the oxalate will be in the form of $C_2O_4{}^{2-}$ at pH 5.5. This should associate strongly with $Co(en)_2(H_2O)(OH)^{2+}$, to produce the reactive ion pair of reaction 11, with an equilibrium constant perhaps in excess of 100.

[27] This intermediate has been invoked[5] in explaining the kinetics of the base hydrolysis of $Co(en)_2C_2O_4{}^+$. Unfortunately, no conclusions concerning its rate of further hydrolysis under the conditions of the present study can be derived from the data of the earlier work. It is perhaps of interest, however, that the pseudo-first-order rate constant at 71° for base hydrolysis of $Co(en)_2C_2O_4{}^+$ at unit (OH^-) is 3×10^{-2} sec^{-1}, not drastically divergent from that for $HC_2O_4{}^-$ attack on $Co(en)_2(H_2O)_2{}^{3+}$ at unit concentration of the oxalate ion, $\sim 2 \times 10^{-3}$ sec^{-1}. (This is predicted by assuming pH $\sim$3, where $HC_2O_4{}^-$ is the predominant oxalate species. Then, as seen from eq 4, $k = k_0$, and k_0 is easily extrapolated to 71° from the data of Table III.) Similarity between these rate constants should occur if cobalt–oxygen bond fission is the rate-limiting process in both instances (to bioxalate in one case and to water in the other).

[28] The spectrum is as given in ref 13. Data obtained by these authors on the reaction of $Co(NH_3)_4(H_2O)_2{}^{3+}$ ion with oxalic acid at 25° and pH $\sim$3 suggest the formation of an intermediate of the type $Co(NH_3)_4(OH_2)(C_2O_4)^+$, with ring closure becoming observable at higher temperatures.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

A Kinetic Study of the Reduction of Cobalt(III) by Hydrazoic Acid in Aqueous Perchlorate Media[1]

BY R. KENT MURMANN,[2] JAMES C. SULLIVAN, AND R. C. THOMPSON[2]

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The reaction of Co(III) with HN_3 in acid perchlorate media yields primarily, if not solely, Co(II) and N_2. The empirical form of the rate law is: $-d[Co(III)]/dt = k'[HN_3][Co(III)]$, where $\log k' = n \log [H^+] +$ constant. At 25°, $\mu = 2.0$ ($LiClO_4$), $n = -0.973 \pm 0.026$, and $k' = 17.5 \pm 2\ M^{-1}$ sec^{-1} at 2.00 M $HClO_4$. The apparent activation energy of k' is 25.4 kcal/mol. The results of ^{15}N tracer studies are: $Co(III) + HN^*\text{–}N\text{–}N^* \rightarrow N^*\text{–}N + 0.5N^*\text{–}N^* + Co(II) + H^+$. Plausible mechanisms for this reaction are discussed.

The variety of products that result when HN_3 is oxidized by metal ions in aqueous solutions reaffirms the statement by Audrieth:[3] "From whatever point of view hydrazoic acid be considered, it is bound to excite and stimulate curiosity, if not wonderment and amazement."

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[2] Department of Chemistry, University of Missouri, Columbia, Mo. 65201.

[3] L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).