This dissymmetry would be expected for the *l*-propylenediamine in the *trans*-[Co(*l*-pn)(EDDA)]$^+$ isomers.

The N_1–H and N_2–H protons directly opposed to the H_a's in the $\Delta(C_2)$ isomer have a different relative orientation as a consequence of the dissymmetry, placing the H_a's in slightly different chemical environments. A doublet is observed for each component of the low-field portion of the AB spectrum (H_a region) reflecting this. The calculated chemical shifts in Table II show a difference of 0.03 ppm between the two protons. The spectrum of the Δ isomer was obtained at 100 Mc, and the separation between the doublets widened indicating a change in the chemical shifts of the protons ruling out H–N–C–H coupling previously observed in the H_a region of similar complexes.[23] The amine proton chemical shifts (for EDDA and en prior to N H–D exchange) are also slightly different in the two isomers, as would be expected. These observations are consistent with the assignment of absolute configuration made on the basis of CD spectra.

[23] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

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Substitution Reactions of Oxalato Complex Ions. VI. The Kinetics of the Anation Reaction of *cis*-Bis(oxalato)diaquochromium(III) Ion with Oxalate Ion in Aqueous Solution[1]

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The complex ion *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ undergoes reaction in aqueous solution with either $HC_2O_4^-$ or $C_2O_4^{2-}$ ion to give the tris(oxalato)chromium(III) complex ion. The rate-determining step appears to be ligand water dissociation from the diaquo complex ion, following an outer-sphere associative equilibration of the latter with bioxalate or oxalate ion. The observed pseudo-first-order rate constant is described by

$$k = k_w\{K_1(HC_2O_4^-)/[1 + K_1(HC_2O_4^-)] + K_2(C_2O_4^{2-})/[1 + K_2(C_2O_4^{2-})]\}$$

where K_1 and K_2 are the association constants for bioxalate and oxalate, respectively, and k_w is the rate constant of the water replacement. K_1 and K_2 have values of 0.85 and 1.9, respectively, at 50° and are independent of the ionic strength, I. At 50°, k_w varies between about 10^{-3} sec^{-1} at $I = 0$ and about 7×10^{-3} sec^{-1} at $I = 2.7$ M. The ionic strength effects are not altered by changes in the nature of the "inert" 1-1 electrolyte used. Temperature dependence studies indicate that the enthalpy of activation of the rate-determining process is close to 22 kcal/mole.

The only previous data on the rate of the addition of oxalate ion to the complex ion $Cr(C_2O_4)_2(H_2O)_2^-$ are those reported by Hamm and Davis[2a] as part of their study of the successive substitutions (n = 0, 1, or 2)

$$Cr(C_2O_4)_n(H_2O)_{6-2n}{}^{3-2n} + C_2O_4^{2-} \longrightarrow Cr(C_2O_4)_{n+1}(H_2O)_{4-2n} + 2H_2O \quad (1)$$

They proposed rate-determining chelate ring closure following rapid monodentate equilibration with the entering oxalate group. This conclusion was based on an apparent lack of dependence of the rate of reaction on oxalate concentration.[2b] In a succeeding study of reactions of several organic acid anions, including acetate and citrate, with $Cr(H_2O)_6^{3+}$ cation, Hamm and co-workers[3] adduced strong evidence for an alternative mechanism for this kind of process. This proposal involves outer-sphere ion-pair equilibration, followed by rate-determining ligand–water dissociation, very similar to the mechanism now widely accepted for many aquo cation–ligand anion substitution reactions.[4] There still remains at issue the question as to whether reaction 1, with n = 2, conforms to this latter pattern, since in this case, both reactants are anions. In fact, recent studies of chloride-for-water replacement in the hexaaquorhodium(III) cation[5] and the pentachloroaquorhodium(III) anion[6] suggest contrasting mechanisms in the two types of reaction. Furthermore, the usual inverse acidity dependence of these anation processes, often readily explainable in terms of the acid–base properties of the aquo ion,[5] is more complicated in systems involving basic ligand anions such as oxalate. In these cases, the acid–base equilibria of the entering anion itself are of significance to the acidity dependence characteristics.

An earlier investigation in our laboratory[7] clarified several aspects of the mechanism of acid-catalyzed aquation of the tris(oxalato)chromium(III) ion, *viz.*

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[1] Part V in this series: K. V. Krishnamurty, *Inorg. Chem.*, **1**, 422 (1962).

[2] (a) R. E. Hamm and R. E. Davis, *J. Am. Chem. Soc.*, **75**, 3085 (1953); (b) Hamm has since reported (private communication, 1963) that the extent of oxalate concentration variation was in fact not large enough to make the nondependence conclusion unequivocal.

[3] R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958).

[4] M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

[5] K. Swaminathan and G. M. Harris, *J. Am. Chem. Soc.*, **88**, 4411 (1966).

[6] W. Robb and G. M. Harris, *ibid.*, **87**, 4472 (1965).

[7] K. V. Krishnamurty, and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960) (part II of present series).

$$Cr(C_2O_4)_3^{3-} + H_3O^+ + H_2O \longrightarrow Cr(C_2O_4)_2(H_2O)_2^- + HC_2O_4^- \quad (2)$$

The data were consistent with a rapidly attained preprotonation–dechelation equilibrium followed by rate-determining oxalate elimination, probably of a solvent-assisted dissociative nature. One would therefore expect that the anation process (the inverse of reaction 2) might also occur in two stages. The first of these should be rate determining and can be visualized in terms of either ligand–water dissociation or oxalate ion attack as the rate-determining process. The present detailed reinvestigation of the anation was therefore undertaken to provide evidence concerning this latter question. The stoichiometries of the reactions studied were

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + C_2O_4^{2-} \longrightarrow Cr(C_2O_4)_3^{3-} + 2H_2O \quad (3)$$

and

$$cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + HC_2O_4^- \longrightarrow Cr(C_2O_4)_3^{3-} + H_3O^+ + H_2O \quad (4)$$

The rates have been determined as functions of total free oxalate concentration, pH in the range 1.3–6.0, additions of "inert salt" sufficient to give total ionic strengths as high as 2.7 *M*, and variation of temperature between 40 and 70°. The mechanism appears to involve an outer-sphere ion-association preequilibration, followed by rate-determining oxalate-for-water substitution, probably limited by the rate of water dissociation. A discussion is given of the significance of the observed effects of added salts as they relate to the proposed anation mechanism.

Experimental Section

The *trans*-$KCr(C_2O_4)_2(H_2O)_2$ complex salt was prepared according to standard procedure[8] and recrystallized several times from water at room temperature. Its high purity was confirmed by duplicate analyses for chromium (by peroxide oxidation in basic solution and iodometric determination of the resultant chromate) and for oxalate (by permanganate titration).

Anal. Calcd for $KCr(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$: Cr, 14.6, C_2O_4, 49.3. Found: Cr, 14.4 ± 0.2; C_2O_4, 49.4 ± 0.2.

Analogous preparative procedures were employed for the corresponding lithium and sodium salts of the complex for use in the "inert salt" effect experiments, and a similar degree of purity was obtainable. Aqueous solutions of the salt were aged for at least 1 day prior to use in kinetic runs, to ensure completion of the *trans* to *cis* conversion.[9,10]

Measurements were made titrimetrically of the p*K*'s of the OH_2 ligands of the *cis*-diaquo complex, utilizing a Beckman Research Model pH meter. For this complex, $pK_1 = 7.1$ and $pK_2 = 9.3$ at room temperature.[11] The "inert salt" effect data were obtained in runs in which measured additions of reagent grade KNO_3, $LiNO_3$, $NaNO_3$, and $NaClO_4$ were made as required. Self-buffering of the solutions at the desired pH was effected by the addition of free oxalate to the system in the necessary proportions[12-14] of $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$. The acidity was established thereby to within ±0.1 pH unit at the commencement of each kinetic experiment.[12b] The course of the reaction was followed spectrophotometrically, employing a Beckman DU instrument, modified by a Gilford Model 220 absorbance readout attachment for most of the runs. For some of the faster runs at high oxalate concentration, a Cary 15 spectrophotometer with time-drive chart recording was used. Temperature control to ±0.2° in the optical cells was achieved by means of suitably thermostated metal-block cell holders. Samples were made up such that the free oxalate was always in some excess, preferably severalfold. This ensured that the final equilibrium strongly favored the trisoxalato product even under the most acidic conditions employed (pH 1.3). The total changes in the measured absorbance[15] at 417 mμ were thus maximized and the kinetic complications of an equilibration process avoided. All runs were carried out at 50° except in the temperature-dependence studies.

Each pseudo-first-order rate constant, *k*, reported is the average of two or more determinations from identical runs, and is precise to about ±5%. They have been evaluated by means of plots of the standard semilogarithmic integrated equation making use of the optical density data in the conventional manner. In most cases, linearity of the plot was obtained over a considerable fraction of the reaction (2 or 3 half-times), since the oxalate concentration generally greatly exceeded that of the complex ion, and self-buffering of the solution at a constant acidity was possible. Where earlier curvature of the plot took place, as in some of the runs at low oxalate concentration, the initial straight-line portion of the curve still provided an adequate rate-constant determination.

Results

The dependence of the anation rate constant on free oxalate concentration was first investigated in series of runs made at pH 2.7 (free oxalate nearly all in the form $HC_2O_4^-$) and pH 6.0 (free oxalate nearly all in the form $C_2O_4^{2-}$). In these experiments, no inert salt was added, so that the ionic strength was also variable. It is seen in Figure 1 that the first-order constants *k* so determined are clearly dependent on free oxalate concentration with a pronounced positive deviation from linearity, expecially at the higher ionic strengths which obtain at pH ~6.

The variation of the rate constant of anation by $C_2O_4^{2-}$ ion alone (at pH ~6) was determined *as a function both of oxalate concentration and ionic strength.* The results are illustrated in Figure 2. Each curve represents the "best fit" data from separate series of experiments of fixed free oxalate and variable KNO_3 concentration as detailed in Table I. Points obtained from the curves

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[8] A. Werner, *Ann.*, **406**, 299 (1914).

[9] The half-time of the *trans–cis* equilibration under these conditions is about 25 min.[10] At equilibrium, more than 90% of the complex is in the *cis* form (private communication from D. R. Stranks, University of Adelaide, S. Australia). The complex ion reactant in all our studies is thus assumed to be the *cis* species.

[10] K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).

[11] (a) It is therefore clear that the proportion of complex in the form $[Cr(C_2O_4)_2OH_2 \cdot OH]^{2-}$ does not exceed 10% in any of the present studies, since in none of these was the pH greater than 6. The assumption is made that the pH dependence of the reaction is not influenced by the acid–base properties of the complex ion itself, a conclusion in no way put in doubt by the kinetic data. (b) D. M. Grant and R. E. Hamm (*J. Am. Chem. Soc.*, **78**, 3006 (1956)) deduced values of 6.4 and 8.4 for these p*K*'s from optical data. However, our experience is that this method of p*K* determination is subject to more error and tends to give low values for this compound.

[12] (a) The p*K* values for oxalic acid at 50° are[13] $pK_1 = 1.3$ and[14] $pK_2 = 4.3$, respectively. The significant pH values of approximately 1.3, 2.7, 4.3, and 6.0 are thus easily established by use of 1:1 oxalic acid–bioxalate salt, pure bioxalate salt, 1:1 bioxalate–oxalate salt, and pure oxalate salt, respectively. (b) The p*K* values are of course subject to ionic strength effects, but these are not large enough to be important in these experiments. For example, pK_2 changes only from 4.24 to 4.27 as the ionic strength is reduced from 0.8 *M* to zero: G. D. Pinching and R. G. Bates, *J. Res. Natl. Bur. Std.*, **40**, 405 (1948).

[13] A. McAuley and G. H. Nancollas, *J. Chem. Soc.*, 2215 (1961).

[14] H. S. Arned and L. C. Fallon, *J. Am. Chem. Soc.*, **61**, 3111 (1939).

[15] The absorption maxima (and the conventional extinction coefficients employed) were 417 mμ (ε 67) and 420 mμ (ε 96) for the bis- and trisoxalato complexes, respectively, under our conditions. No ionic strength corrections were found to be necessary. A few preliminary runs carried out using the absorption band at 570 mμ produced rate constants identical with those obtained at 417 mμ under the same conditions.

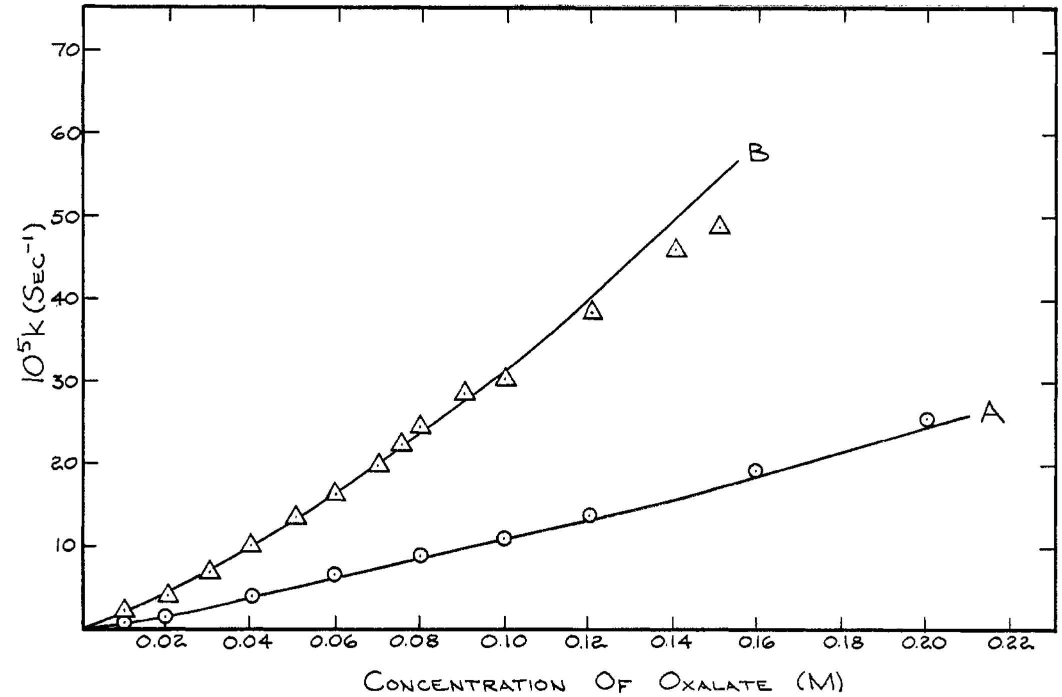

Figure 1.—Variation of anation rate constant with free oxalate concentration; (complex ion) = 7.5×10^{-3} *M*: ⊙, pH ~2.7, △, pH ~6.0.

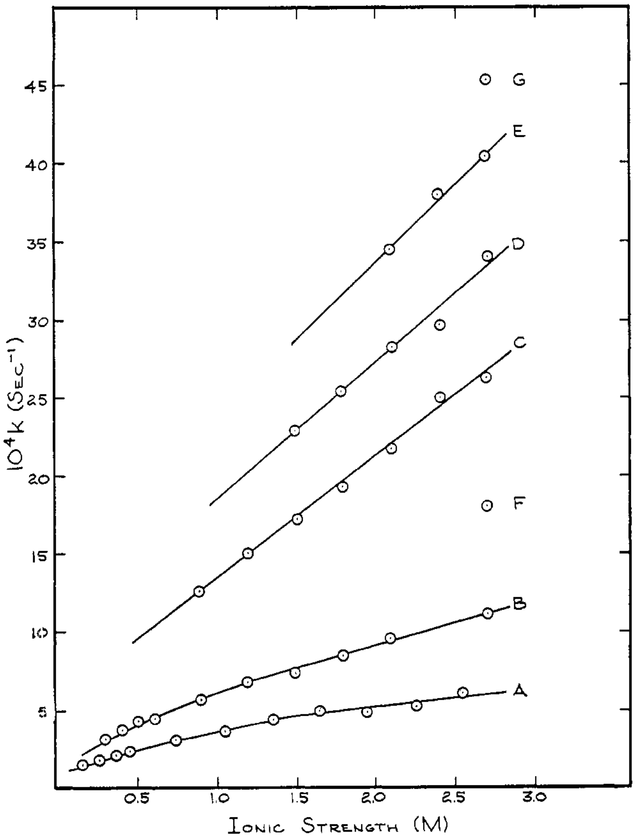

Figure 2.—Variation of anation rate constant with ionic strength at various oxalate concentrations; (complex ion) = 10^{-2} *M*; pH ~6.0; (oxalate): A, 0.05 *M*; B, 0.10 *M*; C, 0.30 *M*; D, 0.50 *M*; E, 0.70 *M*; F, 0.20 *M*; G, 0.90 *M*.

at the fixed ionic strength values of 0.5, 1.0, 1.5, 2.0, and 2.7 are replotted in the form of $1/k$ *vs.* $1/(C_2O_4^{2-})$ curves in Figure 3, good straight lines being obtained in each case, with nonzero intercepts. *The dependence of the rate constant on ionic strength at several other acidities* was also investigated, yielding the data presented in Figure 4 (which also includes the 0.1 *M* oxalate concentration points from Figure 2 for comparison purposes). A series of runs was then made at pH ~4.3 to *determine the effect of changing the nature of the inert salt.* These data appear in Figure 5 and include the results of anation runs made in the presence of KNO_3, $LiNO_3$, $NaNO_3$, and $NaClO_4$.[16] Finally, *the dependence of the rate on temperature* was studied at pH values of 2.7 and 6.0, with initial complex and oxalate ion concentrations fixed at 0.01 and 0.1 *M*, respectively. Values of k were obtained at 40, 59, and 69°, which, together with the earlier data obtained at 50°, were analyzed in terms of Eyring–Polyanyi rate theory to yield identical values of 21.7 ± 0.5 kcal/mole for the heats of activation, $\Delta H^{\ddagger}$.

Discussion

The inversely linear plot of Figure 3 suggests a mechanism in which the rate approaches a limiting value at high oxalate concentration. The most logical possibility, based on the associative–dissociative concept frequently observed for anation of aquo cations, as mentioned earlier, is

$$Cr(C_2O_4)_2(H_2O)_2^- + HC_2O_4^- \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2^- \cdot HC_2O_4^- \qquad K_1 \quad (5)$$

$$Cr(C_2O_4)_2(H_2O)_2^- + C_2O_4^{2-} \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2^- \cdot C_2O_4^{2-} \qquad K_2 \quad (6)$$

$$Cr(C_2O_4)_2(H_2O)_2^- \cdot HC_2O_4^- \longrightarrow Cr(C_2O_4)^{3-} + H_3O^+ + H_2O \qquad k_w \quad (7)$$

$$Cr(C_2O_4)_2(H_2O)_2^- \cdot C_2O_4^{2-} \longrightarrow Cr(C_2O_4)_3^{3-} + 2H_2O \qquad k_w \quad (8)$$

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[16] Data could not be obtained at high $NaClO_4$ concentrations owing to the limited solubility of sodium oxalate.

TABLE I

VARIATION OF RATE CONSTANT OF ANATION WITH IONIC STRENGTH AND OXALATE CONCENTRATION AT pH ~6 AND 50°; (COMPLEX ION) = 0.01 *M*

Ionic strength, *M*	0.05 *M* $C_2O_4^{2-}$		0.10 *M* $C_2O_4^{2-}$		0.30 *M* $C_2O_4^{2-}$		0.50 *M* $C_2O_4^{2-}$		0.70 *M* $C_2O_4^{2-}$	
	10^5k, sec^{-1}	10^4k_w,[a] sec^{-1}	10^5k, sec^{-1}	10^4k_w,[a] sec^{-1}	10^5k, sec^{-1}	10^4k_w,[a] sec^{-1}	10^5k, sec^{-1}	10^4k_w,[a] sec^{-1}	10^5k, sec^{-1}	10^4k_w,[a] sec^{-1}
0.16	1.5	17								
0.26	1.8	21								
0.31			3.2	20						
0.36	2.1	24								
0.41			3.8	24						
0.46	2.4	28								
0.51			4.3	27						
0.61			4.5	28						
0.76	2.9	33								
0.91			5.8	36	12.6	35				
1.06	3.6	41								
1.21			6.9	43	15.0	41				
1.36	4.3	49								
1.51			7.4	46	17.1	47	22.9	47		
1.66	4.9	56								
1.81			8.4	53	19.2	53	25.4	52		
1.96	4.8	55								
2.11			9.7	61	21.7	60	28.3	58	34.5	60
2.26	5.2	60								
2.41					25.0	69	29.5	61	38.0	67
2.56	6.0	69								
2.71			11.0	69	26.1	72	34.0	70	40.3	71
2.71			18.0[b]	66					45.3[c]	72

[a] Calculated from the expression $k_w = k(1 + Kb)/Kb$ where $K = 1.9$ and $b = (C_2O_4^{2-})$. [b] $(C_2O_4^{2-}) = 0.2$ *M*. [c] $(C_2O_4^{2-}) = 0.9$ *M*.

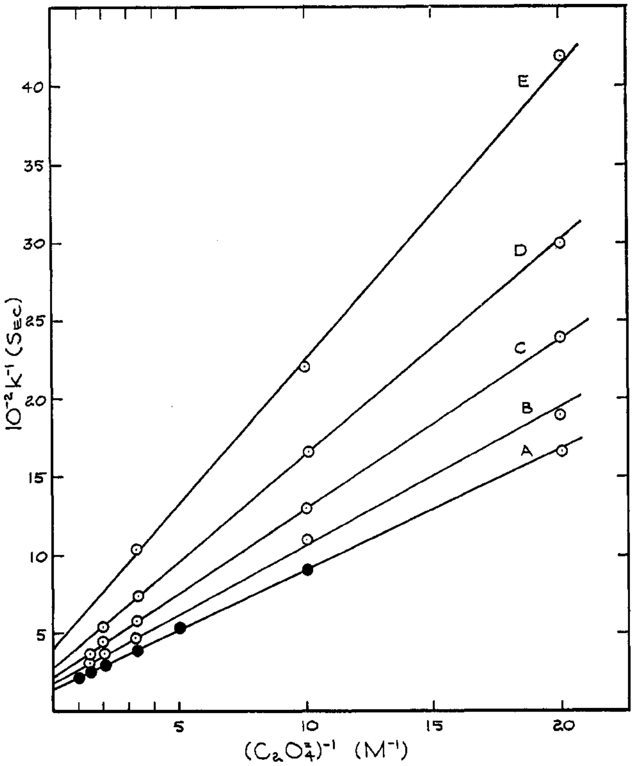

Figure 3.—Inverse relationship between observed anation rate constant and oxalate concentration; (complex ion) = 10^{-2} *M*; pH ~6.0; ●, observed points; ⊙, points interpolated from Figure 2. Ionic strengths (*M*): A, 2.7; B, 2.0; C, 1.5; D, 1.0; E, 0.5.

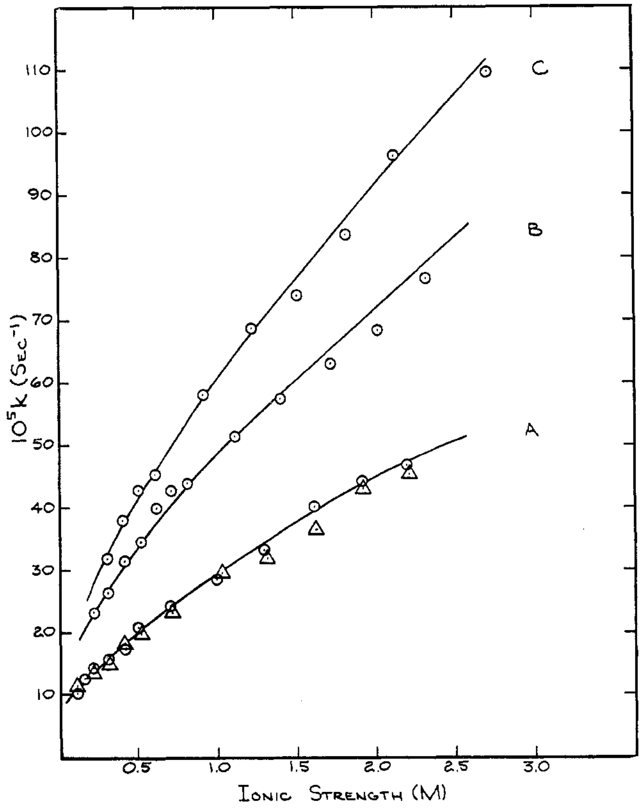

Figure 4.—Variation of anation rate constant with ionic strength and acidity; (complex ion) = 10^{-2} *M*. A: ⊙, $(H_2C_2O_4)$ = $(HC_2O_4^-)$ = 0.1 *M*; pH ~1.3. A: ⚠, $(HC_2O_4^-)$ = 0.1 *M*; pH ~2.7. B: $(HC_2O_4^-)$ = $(C_2O_4^{2-})$ = 0.05 *M*; pH ~4.3. C: $(C_2O_4^{2-})$ = 0.1 *M*; pH ~6.0.

A rate law may now be derived by assuming that the ion-association equilibria are rapidly established and maintained (with constants K_1 and K_2) and that the oxalate substitutions symbolized by reactions 7 and 8 are governed by the same rate-determining process (with rate constant k_w). The resultant expression for the observed pseudo-first-order rate constant is

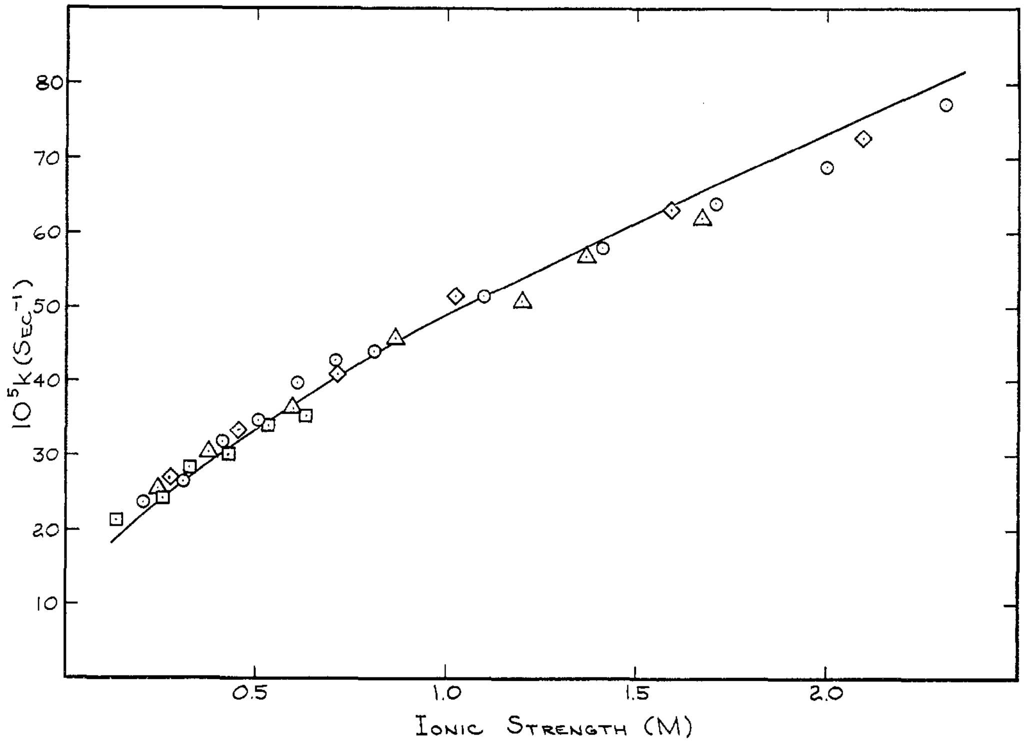

Figure 5.—Variation of anation rate constant with ionic strength using different salts; (complex ion) = 10^{-2} *M;* (oxalate) = 0.1 *M;* ⊙, KNO_3; ◬, $LiNO_3$; ◈, $NaNO_3$; ⊡, $NaClO_4$.

$$k = k_w\left[\frac{K_1(HC_2O_4^-)}{1 + K_1(HC_2O_4^-)} + \frac{K_2(C_2O_4^{2-})}{1 + K_2(C_2O_4^{2-})}\right] \qquad (9)$$

At pH ~6, the concentration of $HC_2O_4^-$ is negligible, so one may write

$$1/k = 1/k_w + (1/k_w)K_2(C_2O_4^{2-}) \qquad (10)$$

From the intercepts[17] and slopes of the curves of Figure 3, one derives the data

	Ionic strength, *M*				
	0.5	1.0	1.5	2.0	2.7
10^4k_w sec^{-1}	25	36	45	56	72
K_2, M^{-1}	2.0	1.8	2.0	2.0	1.8

It is clear that K_2 is essentially independent of ionic strength and has a mean value of about 1.9. Using this number for K_2, figures for k_w were obtained for all of the experiments recorded in Table I, as shown in the parallel columns. All of these data, together with the k_w figures tabulated above, have been plotted in Figure 6 and the "best-fit" curve shown is now used to evaluate k_w at any desired ionic strength. Such k_w values, together with the known figure for K_2 (1.9) and the oxalate concentrations, enable calculation of k for other sets of data at pH ~6. Curve B of Figure 1 and curve C of Figure 4 were derived in this manner and are seen to provide an excellent fit to the experimental points. At the lowest pH's (1.3 and 2.7) for which experimental points appear in Figures 1 and 4, the calculation was done by setting K_1 = 0.85 M^{-1}, using however the same best-fit k_w data provided by the curve in Figure 6 as before, together with the known values for $HC_2O_4^-$ concentration. Curves A of Figures 1 and 4 were calculated in this manner, again providing an excellent fit to the observed data. Finally, the experimental points at pH ~4.3, where $(HC_2O_4^-) = (C_2O_4^{2-})$, were fitted by use of the complete eq 7 and the k_w, K_1, and K_2 values already derived, once more with very satisfactory results as shown in curve B of Figure 4 and the single curve of Figure 5.

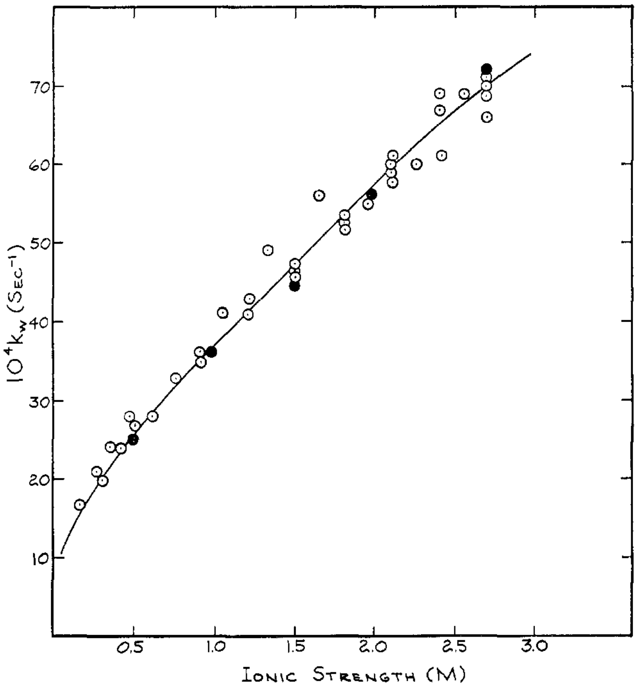

Figure 6.—Variation of k_w with ionic strength; (complex ion) = 10^{-2} *M;* pH ~6.0: ●, values from intercepts in Figure 3; ⊙, values calculated as shown in Table I.

Justification for the mechanism proposed, beyond the fact of the very acceptable curve fitting to the data

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[17] A blown-up version of Figure 3 was used in the intercept determinations.

it enables, can be provided by other arguments. The ion–ion association equilibria seem at first sight to be unusual, inasmuch as the ions are of like charge and the more highly charged pairs associate more strongly. However, the associating ions are quite large and certainly far from the "point-charge" concept of Coulomb's law. There is, moreover, an excellent possibility of weak but specific outer-sphere associative forces through hydrogen bonding involving the protons of the aquo ligands of the chromioxalate complex ion and the ionic oxygens of the oxalate species. This concept allows for stronger bonding by the $C_2O_4^{2-}$ than by $HC_2O_4^-$, since the latter has one of the two ionic oxygens blocked by the undissociated proton. The factor of approximately 2 favoring K_2 over K_1 is consistent with this picture.

One might question how any real distinction can take place between the two forms of oxalate ion in the type of process visualized, since they are continuously subject to acid–base equilibration. However, there are data[18] which show that the deprotonation half-lives for acidic oxalate species are greater than 10^{-8} sec. This is several orders of magnitude larger than the time one might assume necessary for formation and breakdown of the activated complex associated with k_w (10^{-12} sec). Since the equilibrations governed by K_1 and K_2 are dynamic and thus statistical in nature, one can understand how discrimination between protonated and deprotonated carboxylate may become possible.

The exact nature of the rate-determining step is more difficult to elucidate. The only reasonable conclusion is to identify k_w with the rate of water dissociation from the $Cr(C_2O_4)_2(H_2O)_2^-$ species within the outer-sphere-associated ion pairs. Formation of the trisoxalato complex then results, with the substitution consisting of an oxalate successfully competing with water in the first solvation shell for the inner-sphere position vacated by the dissociating aquo ligand. k_w should then bear some relation to the rate of solvent water exchange with the dioxalatodiaquochromium(III) ion, no experimental measurement of which has as yet been made. However, it is of considerable significance that recent studies[19] of the exchange of DMSO for water in a DMSO solution of $Cr(C_2O_4)_2(H_2O)_2^-$ and of water for DMSO in aqueous $Cr(C_2O_4)_2(DMSO)_2^-$ lead to identical first-step values of the rate constant of about 8×10^{-3} sec^{-1} at 50° in low ionic strength solutions. This is to be compared with our k_w value of about 10^{-3} sec^{-1} under similar circumstances. It is tempting to ascribe the 1:8 factor to the relative availability of oxalate as compared to water in the outer-sphere-solvated complexes formed in reactions 5 and 6 in the fashion suggested by Langford for other anation processes.[20]

The inert-salt effects observed in this study appear to be of the nonspecific type usually associated with the ionic strength concept. There is no theory applicable at the high ionic strengths of this work, though the increase of the rate with increasing I is what one expects for a reaction in which the activated complex derives from the interaction of ions of like charge.[21,22] It is, however, worth noting that the water-exchange rates for systems involving cation–anion association[23,24] are similarly increased by ionic strength increase, and by quite appreciable factors. It certainly appears wiser to ascribe the environmental effects observed in our study to facilitation of the metal ion–water ligand bond fission, not to changes of activity coefficients of the ions involved.

The temperature variation data show that the enthalpy of activation is essentially independent of whether the reactant is $HC_2O_4^-$ or $C_2O_4^{2-}$. This is perfectly reasonable, since K_1 and K_2 are equilibrium constants for weak associative processes and will vary but little over a limited temperature range, and to a similar extent. Since the observed $\Delta H^{\ddagger}$ values are thus largely determined by the temperature dependence of k_w, they must necessarily be almost identical, whichever oxalate species is involved in the preassociation.

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(18) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1964); M. Eigen and W. Kruse, *Z. Naturforsch.*, **18B**, 857 (1963). (The lifetime is estimated from $K_D = k_D/k_R$, where the recombination process, described by k_R, is diffusion controlled with a half-time of the order 10^{-10} sec.)

(19) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).

(20) C. Langford, "Dissociative Interchange in Octahedral Substitution," paper presented at Symposium on Inorganic Reaction Mechanisms, University of Toronto, Toronto, Ontario, Canada, June 1966.

(21) The theoretical expression[22] is approximately $\log k = \log k_0 + Z_A Z_B \sqrt{I}/(1 + \sqrt{I})$ for large ions of equal size at temperatures not far from 300°K. When the present k_w data are plotted in this fashion, a good straight line is obtained with $Z_A Z_B = 2$ and $k_0 = 5 \times 10^{-4}$ sec^{-1}. This is helpful for interpolation purposes.

(22) G. M. Harris, "Chemical Kinetics," D. C. Heath and Co., Boston, Mass., 1966, p 102.

(23) W. Plumb and G. M. Harris, *Inorg. Chem.*, **3**, 542 (1964).

(24) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).