ence alcohol is the stronger base.[5,28-30] Methanol was chosen as the reference acid for CH_3OSiH_3 and $CH_3OSiH_2CH_3$ since phenol has previously been found to undergo a rapid reaction with compounds of this type.[31] Data for the isomers and other systems of interest are listed in Table II.

TABLE II

METHANOL AND PHENOL FREQUENCY SHIFT DATA[a]

Ether	Ether concn, *M*	$\Delta\nu_{OH}$ Methanol	$\Delta\nu_{OH}$ Phenol
CH_3OCH_3[b]	0.25	128	251
$CH_3OCH_2CH_3$	0.12	142	268
$CH_3OCH_2SiH_3$	0.12	*d*	246
CH_3OSiH_3[c]	0.25	92	183[e]
$CH_3OSiH_2CH_3$	0.12	114	221[e]

[a] Solvent, CCl_4; concentrations: phenol, 0.005 *M;* methanol, 0.01 *M;* values reproducible to ±3 cm^{-1}. [b] Reference 5. [c] Reference 31. [d] No hydrogen-bonded OH absorption observed. [e] Values extrapolated from methanol data. Phenol frequency shifts (±4 cm^{-1}) for a number of ethers are related to methanol frequency shifts by the relationship $\Delta\nu(\text{phenol}) = 1.76\Delta\nu(\text{methanol}) + 21.0$ (G. A. Gibbon, J. T. Wang, and C. H. Van Dyke, unpublished results).

The results indicate that when phenol is employed as reference acid, $CH_3OCH_2SiH_3$ acts as a stronger base than the silicon-substituted isomer $CH_3OSiH_2CH_3$. Although this behavior is not that predicted from simple electronegativity considerations, the results are in accord with other experimental observations that the donor properties of various mono- and dimethoxysilanes are less than their carbon analogs.[30,32] This has been attributed to (p→d) π bonding in the Si–O linkage.[1,2,30,32] The fact that no hydrogen-bonding interaction was observed between $CH_3OCH_2SiH_3$ and methanol cannot be explained at the present time. Weak intermolecular association of the $CH_3OCH_2SiH_3$ (broken up when phenol is employed as reference acid) could be responsible for this, although in dilute solutions association should not be very important. In addition, no appreciable association of pure $CH_3OCH_2SiH_3$ has been reported.[4]

The observation that $CH_3OSiH_2CH_3$ is a stronger base than CH_3OSiH_3 can be attributed to the well-known electron-releasing characteristics ($+I$ effect) of the CH_3 group.[33] The relative basicities of $(CH_3)_2O$ and $CH_3OCH_2CH_3$ also reflect this $+I$ effect. It also appears that the CH_3 group is more electron releasing through the SiH_2 group than it is through the CH_2 group.

It is of particular interest to note that in the present hydrogen-bonding study $CH_3OCH_2SiH_3$ acts as a weaker base than $CH_3OCH_2CH_3$. This indicates that to a CH_2 group in these ether systems, the CH_3 group is more electron releasing than the SiH_3 group. This is also contrary to simple electronegativity considerations. It is unlikely that steric factors are responsible for this behavior, since the steric requirements for methanol and phenol in hydrogen-bond formation are low.[5,30] Recently, evidence has been gathered which points to a possible interaction between the unshared electrons of a potential donor atom, *e.g.*, Cl or N, and the d orbitals of silicon through an intervening CH_2 group.[12,34] The effect of this interaction in the case of ethers with $-OCH_2Si-$ linkages would be to reduce their Lewis basicity relative to ethers where such an interaction is not possible. The base strength data which we have obtained are in agreement with such a postulate. However, before definite conclusions can be drawn, further work on this general topic needs to be done.

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[28] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

[29] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965.

[30] R. West, L. S. Whatley, and K. J. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).

[31] C. H. Van Dyke and A. G. MacDiarmid, unpublished results.

[32] B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961).

[33] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 70.

[34] O. W. Steward and O. R. Pierce, *J. Am. Chem. Soc.*, **83**, 4932 (1961).

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Substitution Reactions of Oxalato Complex Ions. VII. Inert Salt Effects on the Acid-Catalyzed Aquation of Tris(oxalato)chromium(III) Anion[1]

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In an earlier study[2] of the acid-catalyzed aquation of the tris(oxalato)chromium(III) anion, the kinetics were evaluated at constant ionic strength ($I = 1.0$). The rate studies, which included deuterium solvent isotope effect experiments, led to the conclusion that the reaction took place by the following dual-path mechanism: (a) Rapid protonation–dechelation equilibration

$$\mathrm{Cr(C_2O_4)_3^{3-} + H_3O^+ \rightleftarrows Cr(C_2O_4)_2\cdot OC_2O_3H\cdot OH_2^{2-}}, \quad K \tag{1}$$

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[1] Part VI in this series: H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 706 (1967).

[2] Part II in this series: K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

(b) Uncatalyzed and proton-catalyzed rate-determining water-for-oxalate substitutions

$$\mathrm{Cr(C_2O_4)_2\cdot OC_2O_3H\cdot OH_2{}^{2-} + H_2O \longrightarrow Cr(C_2O_4)_2(H_2O)_2{}^- + HC_2O_4{}^-,}\quad k_1 \quad (2)$$

$$\mathrm{Cr(C_2O_4)_2\cdot OC_2O_3H\cdot OH_2{}^{2-} + H_3O^+ \longrightarrow Cr(C_2O_4)_2(H_2O)_2{}^- + H_2C_2O_4,}\quad k_2 \quad (3)$$

The corresponding rate equation consists of two terms with the observed pseudo-first-order rate constant k at a given hydrogen ion concentration[3] having the value

$$k = k'(\mathrm{H^+}) + k''(\mathrm{H^+})^2 \quad (4)$$

where $k' = Kk_1$ and $k'' = Kk_2$.

The above conclusions are partially duplicated in studies reported by Bunton and co-workers,[4] who carried out rate measurements over a much wider range of acidities. While adopting in part the concept of reaction 1, they differ in proposing a five-coordinate dechelated intermediate, instead of allowing a solvent water molecule to fill out the sixth coordination position at this stage. They also exclude reaction 3, preferring to account for the positive deviation of the hydrogen ion dependence from first order in terms of a Hammett acidity function treatment. Since their data were obtained without control of the ionic strength of the aqueous medium, no direct comparison with our earlier study[2] is possible.

The dual-path mechanism has recently been offered strong support by the comprehensive temperature dependence studies under controlled ionic strength conditions of Banerjea and Mohan.[5] These authors show that at $I = 2.0$, $\Delta S_1^{\ddagger} = -8.4$ eu, $\Delta H_1^{\ddagger} = 21.6$ kcal/mole, $\Delta S_2^{\ddagger} = 14.7$ eu, and $\Delta H_2^{\ddagger} = 28.5$ kcal/mole. This contrast in the rate parameters is consistent with the types of transition state one can logically assume for reactions like (2) and (3). They also presented some limited data on the effect of ionic strength variation on the over-all rate constant, noting that k in 0.1 M $\mathrm{HClO_4}$ was decreased by a factor of more than 2 as I was increased from 0.1 to 1.0 M, though there was little additional change at higher values of I.

Recently, we have investigated the anation of the $\mathrm{Cr(C_2O_4)_2(H_2O)_2{}^-}$ ion by oxalate under a wide variety of concentration conditions.[1] Only $\mathrm{HC_2O_4{}^-}$ and $\mathrm{C_2O_4{}^-}$ appear to be effective in the process, since anation is negligibly slow in the presence of $\mathrm{H_2C_2O_4}$ alone. The rate is determined by ligand water dissociation from the diaquo ion, subsequent to associative equilibration of the latter with bioxalate or oxalate ion. Special attention has been given in the present study, therefore, to the aquation behavior of $\mathrm{Cr(C_2O_4)_3{}^{3-}}$ at the lower end of the acidity range, where the aquation–anation equilibration is observable. This has allowed for a correlation of the mechanistic interpretation of the opposite processes. In addition, the effect of "inert salt" concentration variations on the rate of aquation has been examined rather thoroughly, providing further confirmation of the dual-path mechanism[2,5] which we continue to favor over the acidity-function explanation of Bunton, *et al.*[4]

The combined aquation–anation equilibration mechanism near pH ~2.6 now appears to consist of modifications of reactions 1–3 above, including the additional ion–ion associative equilibrium suggested by the anation study.[1] The four reactions are

$$\mathrm{Cr(C_2O_4)_3{}^{3-} + H_3O^+ \rightleftharpoons Cr(C_2O_4)_2(OC_2O_3H)^{2-} + H_2O,}\quad K\ (1\mathrm{A})$$

$$\mathrm{Cr(C_2O_4)_2(OC_2O_3H)^{2-} + 2H_2O \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2{}^-\cdot HC_2O_4{}^-,}\quad k_1,\ k_\mathrm{w}\ (2\mathrm{A})$$

$$\mathrm{Cr(C_2O_4)_2(H_2O)_2{}^-\cdot HC_2O_4{}^- \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2{}^- + HC_2O_4{}^-,}\quad 1/K_\mathrm{I}\ (2\mathrm{B})$$

$$\mathrm{Cr(C_2O_4)_2(OC_2O_3H)^{2-} + H_3O^+ + H_2O \longrightarrow Cr(C_2O_4)_2(H_2O)_2{}^- + H_2C_2O_4,}\quad k_2\ (3\mathrm{A})$$

In these, k_w is the rate constant of water dissociation and K_I the ion–ion association equilibrium constant described in the preceding paper in this series.[6] The equilibrium constant for the over-all reaction[7]

$$\mathrm{Cr(C_2O_4)_3{}^{3-} + H_3O^+ + H_2O \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2{}^- + HC_2O_4{}^-} \quad (5)$$

is given by

$$K_\mathrm{t} = k_1K/k_\mathrm{w}K_\mathrm{I} \quad (6)$$

Values for K_t at various ionic strengths have been determined at 50°.

Experimental Section

Potassium tris(oxalato)chromium(III) was prepared according to standard procedures and its purity was checked both chemically and spectrophotometrically.[2] As the "inert salts," reagent grade lithium and sodium perchlorates were employed. The desired acidities were obtained by addition of the requisite amounts of reagent grade perchloric acid. The rate of aquation was determined spectrophotometrically[8] as previously described.[2] In general, pseudo-first-order conditions were maintained, since the complex ion concentration (set at 0.001 M) was much lower than that of the acid. The first-order plots deviated from linearity only in runs at the lowest acid concentration (0.0025 M) where an appreciable fraction of the acid is consumed. In these cases, only the initial linear portion of the log $(1 - F)$ *vs.* time plot[9,10] was utilized in rate constant evaluation. All rate constants[11] were determined at 50°, except those obtained in the temperature dependence study. The temperature in the reaction cell was maintained within ±0.2° by use of a specially constructed copper-block thermostated cell-holder placed in the spectrophotometer.

Results and Discussion

The *dependence of the aquation rate on the acidity* within the limits 0.0025 and 1.0 M $\mathrm{HClO_4}$ was studied both under controlled ionic strength conditions and in the absence of such control. In one set of experi-

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(3) The assumption is inherent that reaction 1 takes place only to a slight extent over the acidity range in question.

(4) C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964).

(5) D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965).

(6) See eq 5 and 3, respectively, in ref 1.

(7) Direct involvement of a second proton in the anation process to correspond to the reverse of reaction 3A does not occur, as already noted.

(8) A Beckman DU spectrophotometer with a Gilford digital readout attachment was used. The absorbance measurements were made at 420 mμ, where both the tris- and bisoxalato species show spectral maxima.

(9) The fraction of complex aquated at time t is given by $F = (D_0 - D_t)/(D_t - D_\infty)$, where the D's are the conventionally defined optical densities.

(10) The set of data at 0.0025 M acid concentration is therefore subject to more uncertainty than the other results reported.

(11) Each plotted k is the mean of at least two determinations of the rate constant in separate runs.

ments the ionic strength was kept constant at 1.0 *M* by additions of $NaClO_4$ or $LiClO_4$. The rate-constant data so obtained are recorded in an appendix.[12] No differences appear in the effects of the two inert salts. A plot of the data $(k/(H^+)$ *vs.* (H^+) (curve A of Figure 1) yields values for k' and k'' which are compared with previous findings under the same conditions.

	This work	K and H[2]	B and M[5]
$10^5k'$ M^{-1} sec^{-1}	22	17	33
$10^5k''$, M^{-2} sec^{-1}	55	50	69

Reasonable agreement prevails among the three independently obtained sets of data, all, of course, interpreted in like manner.

A second set of experiments was performed in which the $HClO_4$ concentration was again varied between 0.0025 and 1.0 *M*, but no salt was added to maintain constant ionic strength. These results also appear in the appendix and are compared therein with data calculated from the results reported by Bunton, *et al.*,[4] for 44.4°, using their activation energy figure of 24.4 kcal/mole. There is again good agreement, especially at the low acidity values, notwithstanding the use of HCl in the runs by Bunton, *et al.*, in place of $HClO_4$.

A complete set of data relative to the *variation of the rate constant of aquation with ionic strength at several fixed acidities* is also recorded in the appendix. It shows, as previously noted,[13] that k is sensitive to changes in I only at the lower values of the latter. Precise extrapolations of the k data to zero ionic strength are impossible, but a method for analyzing the ionic strength effect at its higher values is presented in Figure 1. In the latter, graphically interpolated $k/(H^+)$ values at several fixed values of I (less than unity) are plotted against (H^+), as has already been done at $I = 1.0$ *M* (curve A). The straight-line plots are used to evaluate k' and k'', which are plotted in Figure 2 as a semilogarithmic function of I, together with the ratio k''/k' (which equals k_2/k_1 in our interpretation).

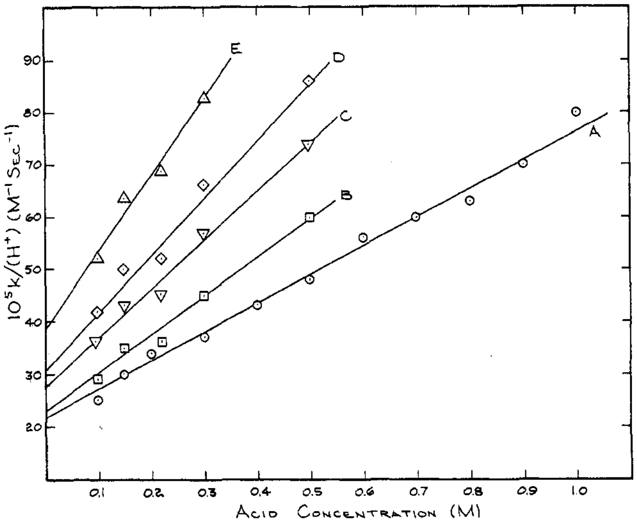

Figure 1.—Reciprocal acidity plot of the observed pseudo-first-order rate constant: A, $I = 1.0$ *M;* B, $I = 0.6$ *M;* C, $I = 0.4$ *M;* D, $I = 0.3$ *M;* E, $I = 0.2$ *M.*

It is now possible to interpret the low ionic strength data (acidities less than 0.1 *M*) in a manner reasonably acceptable on theoretical grounds. Each of the experimental k values at these lower acidities can be converted into a k' value by use of the fact (apparent from Figure 2) that $k''/k' \sim 4$ and the known acidities.[14] These k' values are plotted in Figure 3 as log k' *vs.* $\sqrt{I}/(1 + \sqrt{I})$.[15,16] The curve which fits these data seems to approach linearity quite satisfactorily at the low ionic strength end of the scale, with a slope close to −3. This is in keeping with the mechanism applicable at low acidity (reactions 1A, 2A, and 2B). The Debye–Hückel activity correction applies, of course, only to the magnitude of K, since the ion–molecule reaction described by k_1 should show little sensitivity to ionic strength at low values of the latter.

A temperature dependence study of the aquation reaction was carried out under fixed concentration conditions such that [complex] = 0.001 *M*, $[HClO_4]$ = 0.0025 *M*, and $I = 0.11$ *M* (adjusted with $NaClO_4$). The rate constant data so obtained are given below.

	Temp, °C			
	50.2	61.3	70.8	80.0
$10^6k'$, sec^{-1}	1.60	5.25	13.27	33.7

The enthalpy of activation, $\Delta H^{\ddagger}$, derived from these figures is 22.5 ± 0.5 kcal/mole, equal within experimental error to that for the anation reaction under similar conditions (21.7 ± 0.5 kcal/mole). Since $k' = k_1K$ and since K is an acid association constant with a relatively small temperature dependence, it is fair to assume that most of the temperature dependence of k' may be assigned to k_1. For the anation reaction,[1] the corresponding temperature-dependent rate constant was k_w, identified with a water dissociation rate. Since k_1 and k_w have such similar enthalpies of activation, it seems likely that the forward rate-determining process in reaction 2A is also a metal–oxygen bond breakage—in this case involving oxalate oxygen instead of water oxygen. Thus k_1 can be assumed to be of the same order of magnitude as k_w. At 50° and $I = 1.0$, the known value[1] of k_w is 36×10^{-4} sec^{-1}. Since $k_1K = 22 \times 10^{-5}$ M^{-1} sec^{-1} under the specified conditions, $K \sim 5 \times 10^{-2}$ M^{-1}. This latter value is very much less than one would expect for simple proton equilibration with a monodentate oxalate ligand.[17,18] One explana-

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[12] An appendix containing material supplementary to this article has been deposited as Document No. 9524 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[13] The Banerjea and Mohan data[5] agree tolerably well with our results, though their k values are consistently about 30% higher.

[14] This follows from eq 4, which yields the expression $k' = k/[(H^+) + 4(H^+)^2]$ when $k'' = 4k'$. The "correction factor," $4(H^+)^2$, is very small at low acidities in any case, so the degree of accuracy of the k''/k' ratio is not of great significance.

[15] The "extended" form of the theoretical equation[16] (found to be useful for $I \leq 0.2$ *M*) defining the ionic strength effect on rate constants relating to ionic reactions in aqueous solution is: $\log k = \log k_0 + Z_AZ_B\sqrt{I}/(1 + \sqrt{I})$ (for large ions of equal size and temperatures not far from 300°K).

[16] G. M. Harris, "Chemical Kinetics," D. C. Heath and Co., Boston, Mass., 1966, p 102.

[17] A value of 10^2 is to be expected on the basis of studies[18] of the complex ion $Co(NH_3)_5C_2O_4^+$.

[18] S.-F. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966).

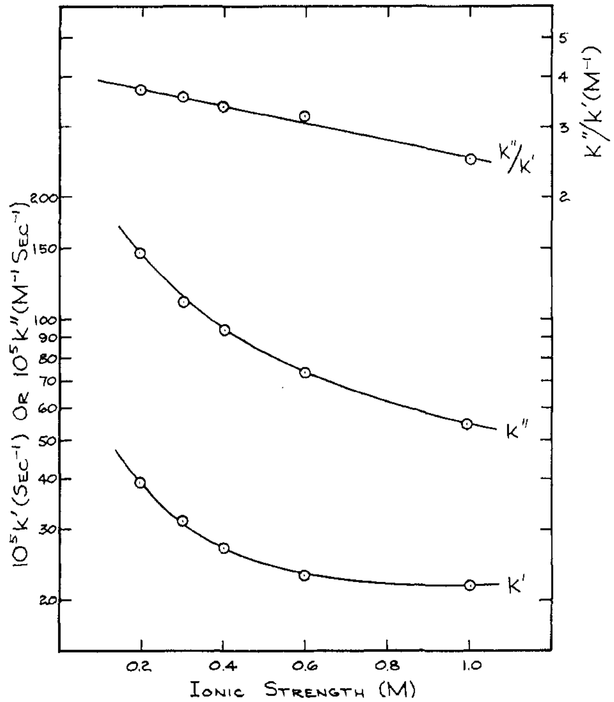

Figure 2.—Variation of k', k'', and k''/k' with ionic strength.

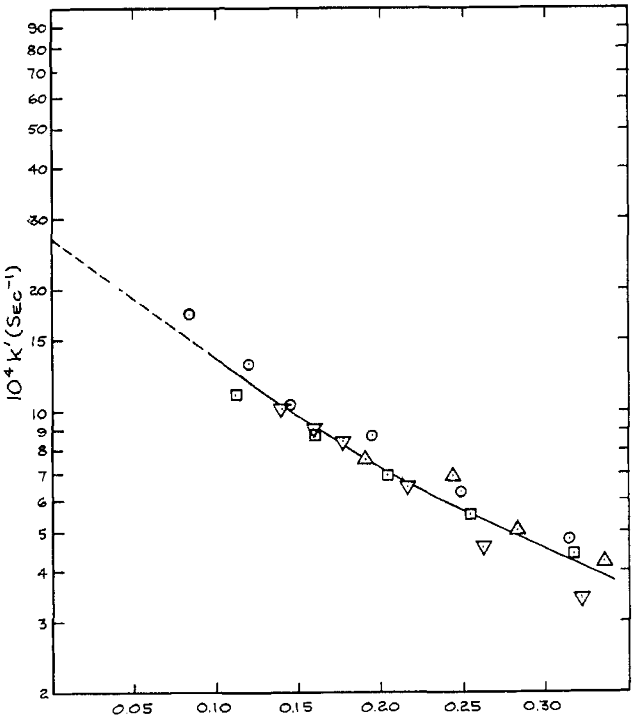

Figure 3.—Variation of k' at low ionic strength with $\sqrt{I}/(1 + \sqrt{I})$. Acidities are as follows: ⊙, 0.0025 M; ⊡, 0.01 M; ▽, 0.02 M; △, 0.05 M. The dotted portion of the curve has a slope of -3.

tion is that the dechelation process is far from complete, so that K in reality describes a double equilibrium

$$Cr(C_2O_4)_3^{3-} \rightleftarrows Cr(C_2O_4)_2OC_2O_3^{3-}, \qquad K' \quad (1A')$$

$$Cr(C_2O_4)_2OC_2O_3^{3-} + H_3O^+ \rightleftarrows Cr(C_2O_4)_2OC_2O_3H^{2-} + H_2O, \quad K'' \quad (1B)$$

Then, since $K = K'K'' \sim 5 \times 10^{-2}$ and $K'' \sim 10^2$, K' must be no greater than 5×10^{-4}. With this low a value for the dechelation equilibrium, it seems unlikely that water is entering the sixth coordination position, as in our earlier suggestion (eq 1), since this would have a large stabilizing influence favoring the monodentate oxalato species. This revised view of the dechelation–protonation process is similar to the one supported by Bunton, *et al.*, differing only in the order of the events, a kind of question it is impossible to answer from kinetic data.

We can now consider in some detail the total equilibrium system defined by reactions 1A, 2A, and 2B. Utilizing the known k' values in the present paper and the previously determined[1] $k_\mathrm{w}K_1$ values, one can tabulate the magnitude of K_t at 50° and various ionic strengths,[19] as shown in Table I. At low ionic strength, where theory is applicable, it has already been noted (Figure 3) that the plot of log k_1 *vs.* $\sqrt{I}/(1 + \sqrt{I})$ has the expected limiting slope of -3. The dependence on I becomes negligible at the higher ionic strengths where, apparently, the cancellation of competitive activity effects is complete. Unfortunately, theory does not allow us quantitative interpretation of such phenomena.

Table I

Equilibrium Data for the Aquation–Anation System

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

Ionic strength, M	10^5k_1K, M^{-1} sec^{-1}	$10^4k_\mathrm{w}K_1$, M^{-1} sec^{-1}	K_t
0.00	270	5	5.4
0.10	60	11	0.55
0.20	39	15	0.26
0.50	25	21	0.12
1.00	22	31	0.07

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(19) K_t is essentially independent of temperature since the enthalpies of activation of k' and $k_\mathrm{w}K$ are identical within experimental error.

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Optical Rotatory Dispersion Study on the Iron Complex with L-Cysteine and Its Reaction with Carbon Monoxide and Nitric Oxide

By Akira Tomita, Hidefumi Hirai, and Shoji Makishima

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The reversible reaction between bis(cysteinato)iron(II) and carbon monoxide was discovered by Cremer.[1] Bis(cysteinato)dicarbonyliron(II), isolated later by

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(1) W. Cremer, *Biochem. Z.*, **206**, 228 (1929).