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Kinetics and Mechanism of Electron Exchange between Chromium(II) and Some Chromium(III)–Oxalate Complexes[1]

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Chromium(II) catalyzes the aquation of one oxalate group from $Cr(C_2O_4)_3^{3-}$ and the *trans–cis* isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$. Both reactions obey the rate law $-d[Cr(III)]/dt = k[Cr(II)][Cr(III)]$ for the chromium(II)-catalyzed path. The values of k in M^{-1} sec^{-1} (enthalpies of activation follow in parentheses) at 25° and 1.2 M ionic strength are 0.129 (8.2) and 0.108 (11.9) for $Cr(C_2O_4)_3^{3-}$ and *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, respectively. The results are discussed in terms of a chromium(II)–chromium(III) electron exchange utilizing two oxalate ligands as bridging groups. Evidence for such a mechanism is adduced from isotope tracer studies on the above reactions and the electron exchange between chromium(II) and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$.

The electron-exchange reaction between the aquo ions of chromium(II) and chromium(III) in acidic perchlorate solutions is very slow.[2] Addition of various anions, either free in solution[3] or coordinated to the chromium(III), results in an increase in the rate of the electron-exchange process.[4] Spinner and Harris[5] have studied the rate of electron exchange between chromium(II) and $Cr(C_2O_4)(H_2O)_4^+$ using isotopically labeled chromium, the net reaction being

$$Cr(H_2O)_6^{2+} + {}^*Cr(C_2O_4)(H_2O)_4^+ \longrightarrow Cr(C_2O_4)(H_2O)_4^+ + {}^*Cr(H_2O)_6^{2+} \quad (1)$$

We report here the results of a study of the electron exchange between aquochromium(II) and the complexes $Cr(C_2O_4)_3^{3-}$ and *trans*- and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$. The feature of a net chemical reaction for the first two reactions

$$Cr(H_2O)_6^{2+} + Cr(C_2O_4)_3^{3-} \longrightarrow cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + Cr(H_2O)_6^{2+} + C_2O_4^{2-} \quad (2)$$

$$Cr(H_2O)_6^{2+} + trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- \longrightarrow cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- + Cr(H_2O)_6^{2+} \quad (3)$$

allows for the compilation of rate data without resort to isotopic labeling.

Experiments using isotopically labeled complexes are reported in an effort to adduce a mechanism for the above reactions. The results indicate that an electron-exchange process is taking place between chromium(II) and the various chromium(III) complexes with the transfer of two oxalate groups.

Experimental Section

Materials.—Sodium tris(oxalato)chromate(III) was prepared following the procedure given in ref 6. *Anal.* Calcd for $Na_3[Cr(C_2O_4)_3]\cdot 5H_2O$: Cr, 10.9; C, 15.17; H, 2.12. Found: Cr, 10.9; C, 14.94; H, 2.14.

Sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method of Werner.[7] The purity of the complex was ascertained by analysis for chromium, carbon, and hydrogen and by comparing the absorption spectrum of the *cis* isomerization product with the spectrum reported in the literature.[8] *Anal.* Calcd for $Na[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$: Cr, 16.1; C, 14.87; H, 2.50. Found: Cr, 16.3; C, 15.07; H, 2.47.

Solutions of chromium(II) perchlorate were prepared by zinc amalgam reduction of chromium(III) perchlorate. The concentration of chromium(II) was assumed to be equal to that of the chromium(III) solution from which it was made. The concentration of chromium(III) was determined by conversion to CrO_4^{2-} with alkaline peroxide and measuring the optical density at 373 mμ (ϵ_{373} 4815).[9] In a few cases this procedure was checked by oxidation of the chromium(II) solution with excess iron(III) followed by titration of the released iron(II) with standard dichromate.[10]

Kinetics Measurements.—The reaction vessels were 2-cm quartz absorption cells with narrow openings. For the tris(oxalato)chromate(III) reactions, all reagents except chromous ion were added to the cell which was then fitted with a serum cap. The cell and contents were aerated with argon for 15 min using a 23 gauge hypodermic syringe needle for an inlet and a 25 gauge needle for an outlet. Chromous ion was added to initiate the reaction. Spectrophotometric measurements indicated no aquation occurred prior to the addition of chromous ion.

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[1] Presented in part before the Division of Inorganic Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] M. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

[3] J. B. Hunt and J. E. Earley, *ibid.*, **82**, 5312 (1960).

[4] N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

[5] T. Spinner and G. M. Harris, Paper INOR-36, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[6] J. C. Bailar and E. M. Jones, *Inorg. Syn.*, **1**, 37 (1939).

[7] A. Werner, *Ann. Chem.*, **406**, 216 (1914).

[8] K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

[9] G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 579.

For the *trans*-bis(oxalato)diaquochromate(III) ion the presence of isomerization paths other than the desired chromium(II) path required a special procedure prior to the addition of chromous ion. Three milliliters of distilled water was added to the cell and flushed with argon for a few minutes. Solid *trans*-sodium bis(oxalato)diaquochromate(III) was added and the cell was vigorously shaken until dissolution had occurred. This was followed by the addition of previously aerated sodium or lithium perchlorate and/or perchloric acid. The cell was purged with argon once more for a few minutes before chromous ion was added. All solutions were immersed in a constant-temperature bath for 30 min prior to the start of the reaction procedure.

The reactions were followed at either 568, 562, or 416 mμ. Since the reactions were always pseudo first order in chromium(II), first-order rate constants were obtained from slopes of plots of log $(D_\infty - D_t)$ *vs.* time where D_t and D_∞ are the absorbancies of time t and after the reaction is complete. All spectrophotometric studies were performed using a Cary Model 15 recording spectrophotometer.

Radiotracer Experiments.—Radiochemical experiments were carried out using chromium-51-labeled sodium tris(oxalato)chromate(III) and sodium *cis*- and *trans*-bis(oxalato)diaquochromate(III). The complexes were prepared in the usual manner with the addition of labeled chromium-51 in the form of a sodium chromate solution. The conditions for the tracer experiments were identical with those for kinetics experiments (*viz.*, [Cr(III)] ≈ 0.007 *M*, [Cr(II)] ≈ 0.042 *M*, $\mu = 1.2$ *M*). The reaction cells were 10-ml erlenmeyer flasks fitted with airtight serum caps At appropriate times the flasks were flushed with oxygen to quench the exchange The chromium(II) oxidation product was concentrated on Biorad AG 50X-8 cation-exchange resin contained in a transparent Tygon column. Slices of the column were taken and the chromium-51 activity in the resin counted directly using a well-type scintillation counter.

Results

Spectrophotometric Data.—Extinction coefficients at wavelengths of maximum absorption (and other wavelengths of interest) for hexaaquochromium(II), hexaaquochromium(III), and the various oxalatoaquochromium(III) complexes are presented in Table I. The value for the *trans*-bis(oxalato)diaquochromate(III) complex was obtained by rapidly mixing excess solid in cold water (10°), decanting the dissolved material into a spectrophotometric cell, and scanning the appropriate regions of the spectrum. The concentration of the complex was determined by analysis for chromium.[9] This was checked by allowing complete isomerization to occur and measuring the absorbance of the *cis* product with agreement to ±1–2%. The extinction coefficients reported represent the lowest values obtained after many attempts.

The spectrum of the *cis* product for the *trans* → *cis* isomerization does not vary with the acid concentration of the solution. The average extinction coefficient values for ten samples (three in pure water, one in 1.00 *M* $NaClO_4$, and six in $HClO_4$–$NaClO_4$ mixtures ranging from 0.1 to 1.0 *M* $HClO_4$) were 50.8 ± 0.8 and 68.0 ± 0.7 M^{-1} cm^{-1} at 562 and 416 mμ, respectively. These are within 1–2% of literature values as reported in Table I. No trends, either to lower or higher extinction coefficients, with increasing acidity were observed. Chang[11] has reported the isolation of a protonated monodentate oxalate complex $[Cr(C_2O_4)(HC_2O_4)(H_2O)_3]$ from acidic solutions of the *cis* complex using anion-exchange chromatography in perchlorate solutions. His spectrum of this neutral complex agrees to within 4% of the spectrum of the *cis* complex (Table I). We have reproduced Chang's experimental procedure and have confirmed his results. However, when a chloride column is used instead of a perchlorate column, the complex adheres tightly to the column at all acidities and cannot be eluted with water thus indicating a negatively charged species. At the higher acid concentrations, the complex band does move through the resin and might be interpreted as a neutral species. The cause of the error in interpretation of this so called neutral species lies in the ion-exchange procedure. Specifically, the use of perchlorate ion as the supporting electrolyte in the solution or as the exchangeable anion on the column decreases the ability of the bidentate *cis* complex to adhere to the resin.

TABLE I

EXTINCTION COEFFICIENTS OF CHROMIUM(III) COMPLEXES

Complex	λ, mμ	ε, M^{-1} cm^{-1}	Ref
$Cr(C_2O_4)_3^{3-}$	(418)[e]	96.3	*a*
	(568)	76.9	
trans-$Cr(C_2O_4)_2(H_2O)_2^-$	(398)	17.0	This work
	416	16.1	
	(533)	16.7	
	562	14.7	
cis-$Cr(C_2O_4)_2(H_2O)_2^-$	(416)	67.3	*a*
	(562)	52.0	
	568	51.5	
$Cr(C_2O_4)(H_2O)_4^+$	(418)	40.1	*b*
	(556)	34.8	
$Cr(H_2O)_6^{3+}$	(408)	15.8	*c*
	(574)	13.3	
$Cr(H_2O)_6^{2+}$	416	0.07	*d*
	562	1.18	
	568	1.32	
	(710)	4.92	

[a] K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, **61,** 213 (1961). [b] H. J. Price and H. Taube, *Inorg. Chem.*, **7,** 1 (1968). [c] E. Deutsch and H. Taube, *ibid.*, **7,** 1532 (1968). [d] E. Deutsch, Ph.D. Thesis, Stanford University, 1967. [e] Maxima in parentheses.

Stoichiometry.—The stoichiometry of reactions 2 and 3 was checked by ion-exchange chromatography of reaction mixtures. The reactions were quenched after several half-lives by air oxidation of Cr(II). At low H^+ (*ca.* 0.02 *M*) the *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ complex was formed in >95% yield for both reactions. At higher hydrogen ion concentrations (0.2–1.0 *M*) the amount of *cis* complex produced decreased. Whether this was due to a further reaction of the *cis* complex or the direct formation of the mono complex was investigated further. A solution of the *cis* complex (obtained by allowing the *trans* complex to isomerize overnight at room temperature) was treated with chromous ion. At an acid concentration of 0.016 *M*, no spectral changes were observed over several hours. At higher acid concentrations (0.2–1.0 *M*) and/or when more acid is added to the above solution an absorbance decrease is noted. The extent of this decrease depended on the acid concentration employed, being highest at

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(11) J. C. Chang, *Inorg. Nucl. Chem. Letters*, **5**, 587 (1969).

the highest acid concentration used.[12] The rate of this reaction (aquation of one oxalate group catalyzed by chromous ion) taken with the results reported below indicates that the *cis* complex could be the primary product of the reactions at high acid concentrations. Furthermore, analyses of the kinetic runs for the reactions show that the absorbance changes cannot be accounted for solely by a direct product of the mono complex. It should be emphasized that these results do not rule out the possibility of another complex with absorbance behavior intermediate between the mono and *cis* complexes.

Rate Data. Tris(oxalato)chromate(III).—Kinetics results for the reaction of chromous ion with tris(oxalato)chromate(III) ion are reported in Table II.

Table II

Rate Data for the Reaction between Cr^{2+} and $Cr(C_2O_4)_3{}^{3-}$

Temp, °C	$10^3[Cr(C_2O_4)_3{}^{3-}]$, M	$10^2[Cr(H_2O)_6{}^{2+}]$, M	$[H^+]$,[a] M	k, M^{-1} sec^{-1}
15.0	6.13–7.00	3.80	0.99	0.0731 ± 0.0023 (av of 4 runs)
25.0	6.88	4.12	0.02	0.127
	6.88	4.12	0.33	0.132
	6.88	4.12	0.51	0.133
	6.88	4.12	0.78	0.136
	6.88	4.12	0.79	0.136
	6.88	4.12	0.96	0.129
	2.76	4.12	0.99	0.128
	4.82	4.12	0.99	0.130
	8.95	4.12	0.99	0.132
	11.7	4.12	0.99	0.128
	7.00	3.80	0.99	0.125 (av of 3 runs)
			Av of all runs	0.129 ± 0.003
	6.88	4.12	1.91[b]	0.150
35.0	6.70	3.80	0.99	0.200 (av of 4 runs)
	6.70	7.60	0.99	0.203
	7.00	3.80	0.99	0.195 (av of 2 runs)
			Av of all runs	0.199 ± 0.005
44.0	6.13	3.80	0.99	0.285

[a] Ionic strength is *ca.* 1.2 M using $NaClO_4$ as supporting electrolyte. [b] Ionic strength is 2.1 M.

A sample spectrophotometric kinetic run is shown in Figure 1. In the upper curve, followed at 568 mμ, a slow decrease in absorbance is observed. This is followed by a slower absorbance increase. Our initial thoughts were that this represented the formation and disappearance of the *trans* isomer of $Cr(C_2O_4)_2(H_2O)_2{}^-$. We can reject this on the basis of the following evidence. First, the absorbance values never go below that expected for complete conversion to *cis*-bis(oxalato)diaquochromate(III). Second, if the reaction is run at 346 mμ where ϵ_{tris} is 11.0 and ϵ_{bis} is 4.0 (isosbestic point for *trans* and *cis* isomers) the same absorbance changes are seen but that for the slower step is more pronounced. The slow changes at 568 and 346 mμ can be attributed to the reaction of chromous ion with free oxalate ion released from the tris(oxalato)chromate(III) complex. Using the expected absorbance, of *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$ (based on 100% conversion of the tris complex) as our infinity absorbance, plots of log $(A_t - A_\infty)$ *vs.* time are linear for up to 2–3 half-lives. The concentration of Cr^{2+} remained constant during this time as demonstrated by analysis for Cr^{2+} during the reaction in some control experiments. Table II reports the summary of data collected in this manner. The rate of reaction is independent of acid over the range 0.02–0.96 M $HClO_4$.

Rate Data. *trans*-Bis(oxalato)diaquochromate(III)—The *trans–cis* isomerization of bis(oxalato)diaquochromate(III) has been studied by many workers. In addition to the expected first-order isomerization,[13,14] other paths dependent upon hydrogen ion[15,16] and other cations[15] have been observed. In the presence of chromous ion the complete rate law for the loss of the *trans* complex is

$$\frac{-d[trans]/dt}{[trans]} = k_{obsd} = k_0 + k_1[H^+] + k_2[M^{n+}] + k_3[Cr^{2+}] \quad (4)$$

Experiments in the absence of chromous ion verified the rate constants for the first two paths in eq 4. The results are $k_0 = 5.78 \times 10^{-4}$ sec^{-1} (1.0 M $NaClO_4$ as supporting electrolyte), 6.24×10^{-4} sec^{-1} (1.0 M $LiClO_4$), and 2.55×10^{-3} M^{-1} sec^{-1} (1.0 M $HClO_4$) compared with literature values of 5.86×10^{-4} sec^{-1} and 2.47×10^{-3} M^{-1} sec^{-1} for 1.0 M $NaClO_4$ and 1.0 M $HClO_4$, respectively. The value of the rate constant for the Zn^{2+}-catalyzed isomerization is reported in ref 16.

Values of the rate constants for the k_3 path are reported in Table III. The value of the rate constant for the chromium(II)-catalyzed isomerization was calculated by subtraction from the observed first-order rate constant of the uncatalyzed rate constant and the appropriate rate constants for the acid- and cation-catalyzed paths multiplied by the respective acid and cation concentrations Division of the resulting first-order rate constants by the concentration of chromium(II) gave the second-order rate constants reported in Table III. Data reported are those in which the hydrogen ion concentration was low. At higher hydrogen ion concentrations the value of k_3 becomes greater than that reported in Table IV. Attempts to fit these results to another term in the rate law were unsuccessful. Analyses of the spectra for these runs indicated this was due to the fact that the *cis* product was undergoing further reaction.[12]

Rate Data. Temperature Dependencies of the Rate Constants.—A least-squares computer program was used to calculate the best values of ΔH^* and ΔS^* for the rate constants reported in Tables II and III. The results are: $\Delta H^* = 8.2 \pm 0.3$ kcal/mol, $\Delta S^* = -35.1 \pm 0.5$ eu for $Cr(C_2O_4)_3{}^{3-}$–Cr^{2+} and $\Delta H^* = 11.9 \pm 0.6$ kcal/mol, $\Delta S^* = -23.2 \pm 1.1$ eu for *trans*-$Cr(C_2O_4)_2(H_2O)_2{}^-$–Cr^{2+}.

Tracer Experiments.—Experiments using labeled

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(12) A more detailed study of this reaction has been made by T. Spinner and G. M. Harris, private communication.

(13) G. E. Cunningham, *Nature*, **169**, 1103 (1952).

(14) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 609 (1953).

(15) H. L. Schlafer, H. Gausmann, and W. Tauche, *Z. Physik. Chem.*, **34**, 113 (1962).

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

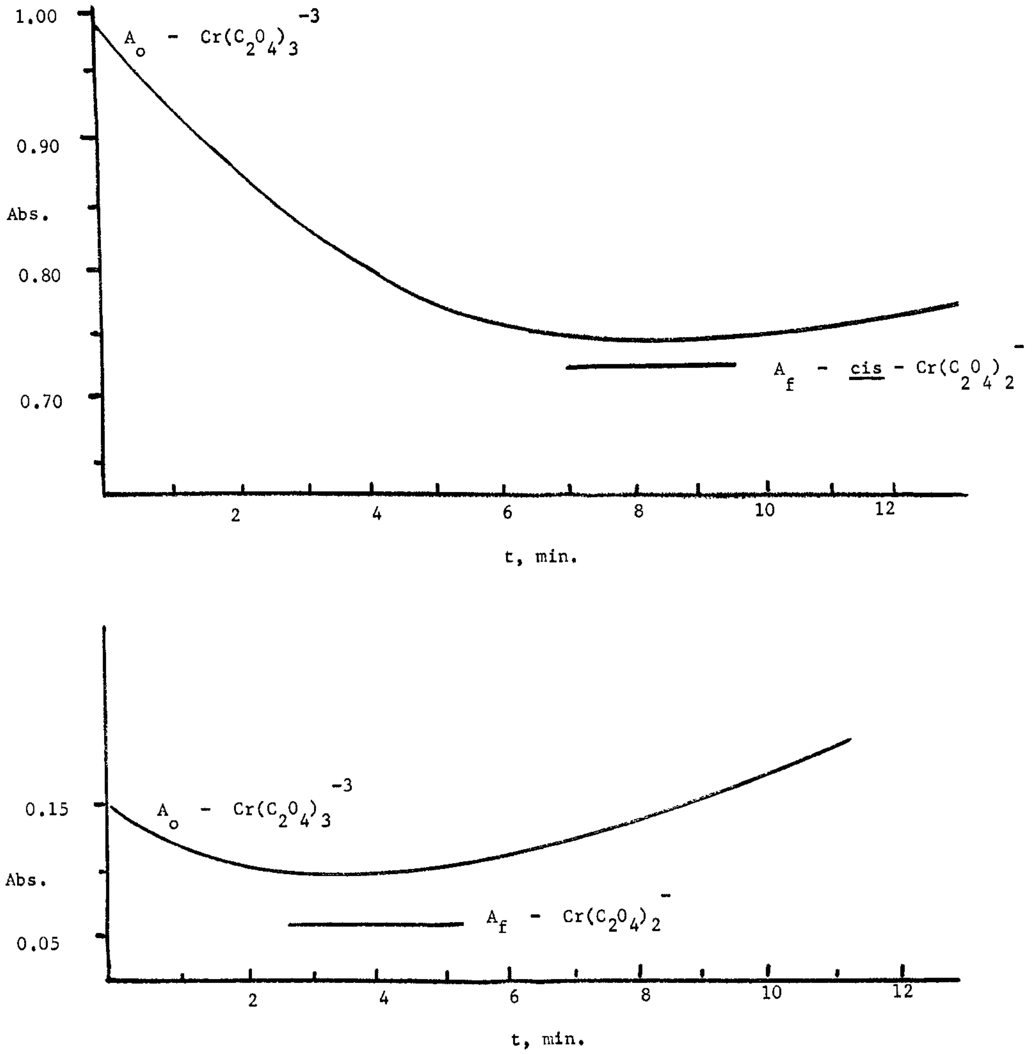


Figure 1. Trace of absorbance *vs.* time for the reaction between Cr^{2+} and $Cr(C_2O_4)_3^{3-}$. $[Cr^{2+}] = 0.0412\ M$; $[Cr(C_2O_4)_3^{3-}] = 0.00688\ M$; $H^+ = 0.02\ M$; temperature 25°: upper curve, λ 568 mμ; lower curve, λ 346 mμ; 2-cm path length.

chromium(III) complexes are summarized herein. The results at short (10–15 sec) quench times indicate that rapid electron exchange does not occur. The extent of exchange was 10 ± 3% for the chromium(II)–tris(oxalato)chromate(III) exchange (three runs) and 10% for the chromium(II)-*trans*-bis(oxalato)diaquochromate(III) exchange (one run). Longer (30–45 min) quench times for all samples show the same result—virtually complete exchange (>85%) between chromium(II) and the chromium(III) complex during the reaction. These results, however, are not conclusive because the product of the chemical processes (*cis*-$Cr(C_2O_4)_2(H_2O)_2^-$) was found to undergo electron exchange (in the absence of chemical change) with chromium(II). An experiment on the exchange between labeled *cis*-bis(oxalato)diaquochromate(III) ion (obtained from the isomerization of the labeled *trans* complex) and chromium(II) was performed at $[H^+] = 0.016\ M$. A plot of log (1 − *F*) *vs.* time, where *F* is the fraction exchanged, was linear and gave a rate constant for exchange of 0.17 M^{-1} sec^{-1} for the reaction

$$cis\text{-}{}^{51}Cr(C_2O_4)_2(H_2O)_2^- + Cr^{2+} \longrightarrow {}^{51}Cr^{2+} + cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- \quad (5)$$

where [Cr(II)] = 0.042 *M*, [Cr(III)] = 0.0070 *M*, ionic strength is 1.1 *M* ($LiClO_4$), and temperature is 25°. Control experiments adding chromous ion already oxidized by air to labeled complexes showed no exchange of chromium-51 activity.

TABLE III

RATE DATA ON *trans–cis* ISOMERIZATION OF $Cr(C_2O_4)_2(H_2O)_2^-$–Cr^{2+} CATALYSIS[a]

Temp, °C	10^3k_{obsd}, sec^{-1}	$10^2[Cr^{2+}]$,[b] *M*	k_3, M^{-1} sec^{-1}
15.0	2.56	4.20	0.0516 ± 0.0017 (av of 3 runs)
17.5	3.11	4.20	0.0620
25.0	5.03	3.82	0.104 (av of 4 runs)
	5.66	4.14	0.111
	5.34	4.23	0.101
	6.35	4.41	0.119
	9.49	6.65[c]	0.121
		Av of all runs	0.108 ± 0.008
29.0	7.30	4.20	0.136 (av of 2 runs)
32.0	9.63	4.20	0.177

[a] $[Cr(C_2O_4)_2(H_2O)_2^-]$ for all runs is (7.0 ± 0.4) × 10^{-3} *M*; $[H^+] = 0.016 \pm 0.002\ M$. [b] $[Zn^{2+}] = {}^1/_2[Cr^{2+}]$. [c] $[H^+] = 0.024\ M$.

TABLE IV
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REACTIONS OF CHROMIUM(II) WITH SOME CHROMIUM(III)–OXALATE COMPLEXES

Complex	k, M^{-1} sec^{-1} [a]	ΔH^*, kcal/mol	ΔS^*, eu	Ref
$Cr(C_2O_4)(H_2O)_4^+$	0.13[b]	10.8	−26.4	c
trans-$Cr(C_2O_4)_2(H_2O)_2^-$	0.108	11.9 ± 0.6	−23.2 ± 1.1	This work
cis-$Cr(C_2O_4)_2(H_2O)_2^-$	0.17[d]	...	...	This work
$Cr(C_2O_4)_3^{3-}$	0.129	8.2 ± 0.3	−35.1 ± 0.5	This work

[a] At 25°. [b] Ionic strength 2.0. [c] Reference 5. [d] Electron-exchange rate constant.

Discussion

A summary of rate constants and the corresponding activation parameters for the electron-exchange reaction between chromium(II) and some chromium(III)–oxalate complexes is presented in Table IV.

The principal feature of the chromium(II) catalysis of the aquation of one oxalate group from $Cr(C_2O_4)_3^{3-}$ and the *trans–cis* isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ which distinguishes it from the acid-catalyzed and/or cation-catalyzed reactions is the possibility of electron exchange between chromium(II) and chromium(III) accompanied by atom transfer. The results of this study indicate that such a path is operative and that two oxalate groups are transferred during the electron-exchange process.

The value of k_3, the rate constant for the chromium(II)-catalyzed isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, is larger than any k_2 value (see eq 4) for a series of +2 metal ions (*e.g.*, Co^{2+}, 0.011 M^{-1} sec^{-1}; Cu^{2+}, 0.047 M^{-1} sec^{-1}). This may be due, in part, to a strong affinity of Cr^{2+} for oxalate. Ashley and Hamm[16] have demonstrated a relationship between the first formation constant of +2 metal ion–oxalate complexes and the catalytic rate constant for isomerization (k_2). For chromous ion, however, the formation constant cannot be obtained due to reduction of oxalate ion.[17] Thus, on the basis of kinetic data alone one cannot distinguish between chromium(II) catalysis of the *trans–cis* isomerization utilizing the "one-ended" dissociation mechanism proposed by Ashley and Hamm for the other +2 cations and a mechanism involving electron exchange accompanied by transfer of both oxalate groups. Trace experiments were designed to learn whether the latter path is important to the isomerization.

Experiments using labeled *trans*- and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ clearly demonstrate a transfer of activity from chromium(III) to chromium(II) for the *cis* complex. Results for the *trans* isomer are inclusive due to the observed exchange of the *cis* isomer. However, it is reasonable to assume that exchange of activity accompanies rather than follows the isomerization reaction. Exchange of activity for the *cis* complex occurs in the same time scale as isomerization.

The results of the tracer work can be taken as evidence of electron exchange between chromium(II) and the chromium(III) complexes utilizing both (or two in the tris case) oxalate ligands as bridging groups. One can envision this process taking place in several ways. One possibility for all three complexes studied is a prior one-ended dissociation of the chromium(III) oxalate complex[18] catalyzed by the presence of chromous ion followed by the electron-exchange reaction to give the observed *cis* product. This seems an unlikely mechanism on the basis of the accumulated rate data. If such a path were operative in the tris(oxalato)chromate(III)–chromium(II) reaction, one would expect, on the basis of studies on the acid-catalyzed aquation of the tris(oxalato)chromate(III) anion,[19] a path directly dependent on the concentration of H^+ in the region 0.01–1.0 M. No such dependence was noted. Furthermore, the values of the kinetic parameters for the chromium(II)-catalyzed isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ are quite different from those observed for nine other +2 ions[16] (ΔH^*'s range from 14.4 to 17.0 kcal/mol; ΔS^*'s from −10 to −21 eu).

A second possibility involving the transfer of only one oxalate group followed by chromous-catalyzed anation of the mono(oxalato)chromium(III) complex to the observed product can also be ruled out. No spectral changes, either rapid[20] or on the time scale of the isomerization, were noted when chromous ion was added to a solution of 0.007 M $Cr(C_2O_4)(H_2O)_4^+$ and 0.007 M $Na_2C_2O_4$ at either low or high acidity. A slow increase in absorbance is observed which can be attributed to the reaction of chromous ion with free oxalate ion.[17]

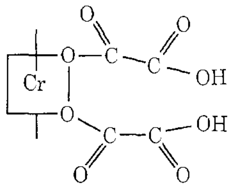
If the isomerization proceeds by an inner-sphere mechanism with a double oxalate bridge, a brief examination of a model of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ leads us to postulate that the reaction occurs in two steps, *viz.*

$$trans\text{-}Cr(C_2O_4)_2(H_2O)_2^- + Cr^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Cr^{2+} + I \qquad (6)$$

$$I + Cr^{2+} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Cr^{2+} + cis\text{-}Cr(C_2O_4)_2(H_2O)_2^- \qquad (7)$$

A similar mechanism may be operative for the chromium(II)-catalyzed aquation of $Cr(C_2O_4)_3^{3-}$. The reverse of reaction 7 can be considered the mechanism for the electron exchange between Cr^{2+} and *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$.

From an examination of models it is apparent that Cr^{2+} cannot bond to more than one oxygen atom on each oxalate group in the *trans* complex and still effect the transfer of two oxalate groups. Therefore we postulate the intermediate (I) in eq 6 as



I

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(17) R. M. Milburn and H. Taube, *J. Phys. Chem.*, **64**, 1776 (1960).

(18) This one-ended dissociation mechanism has been proposed as the mechanism for the *trans–cis* isomerization[14] and as a rapid preequilibrium step in the acid-catalyzed aquation of $Cr(C_2O_4)_3^{3-}$: C. A. Bunton, *et al.*, *J. Chem. Soc.*, 4615 (1964).

(19) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).

(20) Chromium(II)-catalyzed anation of hexaaquochromium(III) with oxalate ion is expected[3] and was found to be very rapid. The second oxalate, however, adds too slowly to be observed.

Evidence for such an intermediate has been presented by Wood and Higginson,[21] who proposed a similar complex as the product of the electron-transfer reaction between chromium(II) and tris(oxalato)cobaltate(III). Wood and Higginson reported that this intermediate slowly changes to the *cis*-bis(oxalato)diaquochromate(III) ion and that this change is accelerated by chromium(II). Cursory experiments in this laboratory[22] have produced results in agreement with the data of Wood and Higginson. Preliminary experiments have produced a rate constant for the chromium(II)-accelerated formation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ of *ca.* 5.0 M^{-1} sec^{-1}. Taking this value for k_4 in eq 6 and 7 with k_3 (0.11 M^{-1} sec^{-1}) $\approx$ k_{-4} (0.17 M^{-1} sec^{-1}) readily explains our inability to detect the intermediate (I).[23] Further work on the structure and reactions of the proposed intermediate is being carried out.

[21] P. B. Wood and W. C. E. Higginson, *J. Chem. Soc., A.*, 1645 (1966).

[22] M. Frank, C. Pasquale, and D. H. Huchital, work in progress.

[23] Since K_{eq} (= [*cis*]/[*trans*]) $\gg$ 1, as indicated by spectral measurements, k_{-3} must be $\ll$1. Thus, any intermediate formed reacts rapidly with Cr^{2+} to give the *cis* product.

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Ligand Field Information from Charge-Transfer Spectra of Substituted Tris(1,3-diketonato)iron(III) Chelates. Spectrochemical Series for 1,3-Diketones

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A series of tris(1,3-diketonato)iron(III) chelates has been prepared in which the 1,3-substituents are CH_3, CF_3, and C_6H_5. The spectra of this series in the 20–38-kK region were studied in order to make assignments based on the expected electronic effect of the substituents. Three electronic transitions can be successfully treated using a simple one-electron molecular orbital scheme. The data presented support the assignment of the most intense band between 30 and 37 kK to the intraligand π–π^* transition. The other two bands in this region are assigned to a metal-to-ligand ($t_{2g} \rightarrow \pi^*$) charge transfer between 24 and 29 kK, and a ligand-to-metal ($\pi \rightarrow e_g$) charge transfer between 20 and 23 kK. These assignments are justified on the basis of the relative energy separations in the simplified molecular orbital diagram. In connection with these energy separations, a spectrochemical series for the substituted 1,3-diketones was developed from the visible spectra of the corresponding Cr(III) chelates. The octahedral splitting parameter, Δ, for the Fe(III) chelates was then calculated using the relationship $\Delta = g(\text{metal ion})f(\text{ligand})$. The energy separations ($\pi - t_{2g}$) and ($e_g - \pi^*$) were determined from the charge-transfer spectra. The sum $(\pi - t_{2g}) + \Delta + (e_g - \pi^*)$ agrees very well with the observed $\pi \rightarrow \pi^*$ transition energy. In terms of ligand field effects, the CF_3 substituent on the chelate ring destabilizes all the metal levels relative to CH_3. The phenyl substituent stabilizes the metal levels relative to CH_3.

Introduction

A number of studies dealing with the electronic absorption spectra of the first-row transition metal acetylacetonates have been reported. Most of the results have been reviewed by Fackler.[1] The electronic structure of these chelates is of sufficient interest to prompt several workers to undertake orbital calculations using various degrees of sophistication.[2-4] As a result of experimental and theoretical work, many spectral assignments appear certain. On the other hand, several assignments are still the subject of controversy. The spectrum of $Fe(acac)_3$ is not yet clearly understood. There is general agreement that the intense absorption at 36,600 cm^{-1} is due to a $\pi \rightarrow \pi^*$ transition on the ligand. It is also reasonably well established that the absorption at 28,300 cm^{-1} is a $t_{2g} \rightarrow \pi^*$ charge transfer. The other intense band at 22,800 cm^{-1} has been variously assigned to an anomalous peak,[3] $\pi \rightarrow t_{2g}$,[4] and $O_n \rightarrow e_g$ charge transfer.[5] Clearly, one problem in assigning charge-transfer transitions is the limited knowledge about the energy differences between electrons located mainly on the ligand and those mainly on the metal. This study was undertaken to make definitve assignments in the charge-transfer region for tris(1,3-diketonate)iron(III) chelates, based on the effect of systematic substitution on the 1,3-diketonate ring. Making assignments on the basis of spectral shifts would be facilitated if the ligand field splitting parameters, Δ, were known for the series. Since the spin-forbidden "d–d" transitions are not easily observed, it is difficult to determine Δ directly in these iron(III) chelates. Therefore, an initial phase of this study involved developing a spectrochemical series for substituted 1,3-diketones from which the values of Δ could be calculated.

Experimental Section

The Fe(III) and Cr(III) chelates were synthesized using

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