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Iron(III) Catalysis of the Aquation of *cis*-Bis(oxalato)diaquochromate(III) Ion[1a]

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Reactions of the form $Fe^{3+} + X^- = FeX^{2+}$ [2] have been the subject of many kinetic studies,[3] using a variety of anions as X^-. Before beginning the work reported here, we attempted to find evidence for the reaction shown above, with X^- being $Cr(C_2O_4)_2^-$. No rapid ultraviolet or visible spectral changes occurred upon mixing the two metal ions but slow changes were observed and were identified with reaction 1. A kinetic study of reaction 1 is the subject of this paper.

$$Fe^{3+} + Cr(C_2O_4)_2^- = FeC_2O_4^+ + CrC_2O_4^+ \qquad (1)$$

Metal ion catalysis of racemization[4] and hydrogen ion catalysis of aquation[4,5] of tris(oxalato)chromate(III) ion have been studied. Metal ion catalysis of the cis–trans isomerization reactions of bis(oxalato)chromate(III) has been studied,[6] and acid-catalyzed aquation of the *cis*-bis(oxalato) complex has been investigated.[7] No studies of the metal ion catalyzed aquations of the cis–trans isomers have been reported, however; the principal isomer in eq 1 is the cis isomer.[6,8]

Experimental Section

Reagents.—Potassium *trans*-bis(oxalato)diaquochromate(III) was prepared from potassium dichromate and oxalic acid as described by Palmer.[8] Successive small yields of the crystalline, less soluble trans salt were induced by overnight refrigeration of the equilibrium cis–trans solution;[9] the equilibrium solution is dominantly cis.[6,8] Iron(III) perchlorate and sodium perchlorate were prepared and analyzed as described previously.[3] Diluted reagent grade perchloric acid was used directly. The water used in all solutions was redistilled from laboratory distilled water.

Stoichiometry.—The stoichiometry indicated in eq 1 was observed in two ways. First, the measured absorbance increases at 310 nm, at 25°, agreed with the increase calculated for eq 1. The calculations were based on equilibrium data for mono(oxalato)iron(III) and for acid dissociation of oxalic acid and upon $\epsilon(FeC_2O_4^+)$ being $1.3 \times 10^3\ M^{-1}\ cm^{-1}$, all from the report of Moorhead and Sutin.[10] To confirm experimentally that only one oxalate is lost from the chromium reactant, a spent reaction mixture was passed through Dowex 50 W-X8 ion-exchange resin in the H^+ form. The column was rinsed with 2 *M* $HClO_4$ and then with 3 *M* $HClO_4$. The 3 *M* $HClO_4$ should have contained any $Cr(H_2O)_6^{3+}$ that was formed, but chromium could not be detected[11] in the 3 *M* acid.

Rate Measurements.—The rate of reaction 1 was measured spectrophotometrically by observing the increase in absorbance at 310 nm, where the absorbances of all species except $FeC_2O_4^+$ and hydrolyzed Fe(III) species are small. The absorbance of hydrolyzed Fe(III) species is appreciable at 310 nm and increases with temperature, owing to the increasing extent of hydrolysis.[12] The absorbance measurements were done with a Beckman ACTA V spectrophotometer. Rate measurements at 57.5 and 40.0° were carried out in stoppered silica cells placed in the thermostated cell compartment; the absorbance was monitored continuously, using the recorder chart drive to measure time. Solutions reacting at 25° were kept in an opaque, thermostated water bath, outside the spectrophotometer, except during periodic absorbance measurements.

Light was excluded to prevent possible photodecomposition of oxalatoiron species.[13] The bis(oxalato)chromate(III) solution used in rate measurements was prepared from the potassium salt at least 24 hr before mixing with iron(III) solution, to ensure that cis–trans equilibrium was achieved.[6] The ionic strength was adjusted to 1.00 *M* in all reaction mixtures.

Pseudo-first-order rate constants were evaluated by using either the conventional log $(A - A_\infty)$ *vs.* time plots or by using Guggenheim plots.[14] The reactions were followed for at least 4 half-times. The plots were linear for 3 or more half-times for most experiments but were only linear to 2 half-times for experiments at 0.04 *M* H^+ at 40 or 57.5°.

Results

Reaction 1 was found to conform to the rate law given in eq I. Since [Fe(III)] and $[H^+]$ were always

$$\frac{d[CrC_2O_4^+]}{dt} = (k_1[Fe^{3+}] + k_2[H^+])[Cr(C_2O_4)_2^-] \qquad (I)$$

at least tenfold greater than $[Cr(C_2O_4)_2^-]$, first-order behavior was observed, with $k_{obsd} = k_1[Fe^{3+}] + k_2[H^+]$. The measured rate constants for each experiment are listed in Table I.

TABLE I

OBSERVED AND CALCULATED RATE CONSTANTS FOR REACTION 1 AT 1.00 *M* IONIC STRENGTH[a]

$[H^+]$, *M*	Total [Fe(III)] × 10^3, *M*	$[Fe^{3+}]$ × 10^3,[b] *M*	Temp, °C	10^6k, sec^{-1}	
				Obsd	Calcd
0.04	4.00	3.84	25	4.08	4.10
0.20	4.00	3.97	25	5.66	4.84
0.20	6.00	5.97	25	7.70	6.89
0.20	8.00	7.94	25	8.95	8.93
0.20	10.00	9.93	25	11.60	10.98
0.20	4.00	3.93	40	30.4	33.6
0.20	8.00	7.92	40	60.2	64.1
0.90	4.00	4.00	40	37.2	46.8
0.90	8.00	8.00	40	64.2	77.4
0.04	4.00	3.18	57.5	241	204
0.20	0.80	0.77	57.5	64.0	67.5
0.20	2.00	1.83	57.5	160	134
0.20	4.00	3.96	57.5	271[c]	269
0.20	8.00	7.66	57.5	523	502
0.57	4.00	3.94	57.5	274	302
0.57	8.00	7.88	57.5	550	550
0.90	2.00	1.99	57.5	190	209
0.90	4.00	3.98	57.5	314[c]	337
0.90	4.00	3.98	57.5	308[d]	337
0.90	8.00	7.96	57.5	562	587
1.0	0	0	45	25[e]	29.6

[a] The initial $[Cr(C_2O_4)_2^-]/[Fe(III)]$ ratio was always 0.10. [b] Total iron(III) concentration was corrected by subtracting the concentrations of hydrolyzed species, using the data of ref 12. [c] Average of two to three experiments. [d] 0.004 *M* hexaaquochromium(III) was added. [e] From the data of ref 7, we calculate 30×10^{-6}.

Our data require the k_2 term previously found by Banerjea and Mohan,[7] but owing to the dominance of the k_1 term, our evaluation of k_2 is uncertain. The concentration of Fe^{3+} was obtained by correcting the total iron(III) concentration for $FeOH^{2+}$ and Fe_2-

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[1] (a) Supported by the Robert A. Welch Foundation. (b) Robert A. Welch Predoctoral Fellow, 1971.

[2] In writing the formula for an aqueous ion, we will omit coordinated water molecules.

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TABLE II

RATE PARAMETERS FOR ISOMERIZATION OF *trans*-$Cr(C_2O_4)_2^-$ AND FOR AQUATION OF *cis*-$Cr(C_2O_4)_2^-$

Process	Form of rate term	Magnitude of *k*, 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
Aquation	$k[H^+][cis]$	2.6×10^{-6}	24	−5	6
Aquation	$k[Fe^{3+}][cis]$	1.0×10^{-3}	24	9	This work
Isomerization	$k[trans]$	5.9×10^{-4}	18	−13	6
Isomerization	$k[H^+][trans]$	2.5×10^{-3}	17	−15	6
Isomerization	$k[M^{3+}][trans]^a$	$(3.2\text{–}160) \times 10^{-3}$	14–23	−15 to +6	6

[a] M = Al, La, and Ce.

$(OH)_2^{4+}$, using numbers reported by Milburn.[12] These corrections are small and are indicated in Table I.

The data were fitted to eq I and to the absolute rate theory equation, using a nonlinear least-squares computer program,[15] with rate constants weighted as $1/(k_{obsd})^2$. The average deviation between k_{calcd} and k_{obsd} was 8%. The results of three experiments were deleted from the final calculation, because of an excessive difference between k_{calcd} and k_{obsd}. The experiments that were deleted were all done at 57.5° in 0.04 *M* H^+. In each of these experiments, k_{obsd} was larger than k_{calcd}, suggesting that eq I is not valid at low acidity and high temperature, possibly owing to reactivity of hydrolyzed iron species. Results obtained under these conditions were very imprecise, however. Owing to the extensive hydrolysis of iron(III), we could only observe a small absorbance increase, superimposed on a large (>2) absorbance background. We believe that eq I includes as many terms as are warranted by the precision of the data. The k_{calcd} values, based on eq I, are listed in Table I. The activation parameters obtained from the least-squares fitting procedure are $\Delta H_1^{\ddagger} = 24.2 \pm 0.5$ kcal/mol and $\Delta S_1^{\ddagger} = 8.9 \pm 1.6$ eu; the calculated value of k_1 at 25° is $1.03 \times 10^{-3}\ M^{-1}\ sec^{-1}$.

The values $\Delta H_2^{\ddagger} = 18.8$ kcal/mol and $\Delta S_2^{\ddagger} = -20.3$ eu were selected graphically as being in best accord with our data. These values compare with 23.9 kcal/mol and −4.5 eu, respectively, reported by Banerjea and Mohan.[7] The contributions to our k_{obsd} values, from the k_2 pathway, were small, and our activation parameters for k_2 are not precise. Our activation parameters lead to $k_2 = 29.6 \times 10^{-6} \cdot M^{-1}\ sec^{-1}$, at 45°, in agreement with Banerjea and Mohan's 30×10^{-6} at 45° (see Table I).

In order to learn whether the k_2 term in eq I represents a general or a specific cation effect, the substitutionally inert species Cr^{3+} was added to one reaction mixture. The rate constant obtained from this mixture, containing 0.004 *M* Fe^{3+} and 0.004 *M* Cr^{3+}, was the same as for a mixture that was identical, except that it did not contain Cr^{3+} ions.

Discussion

Possible mechanisms for reaction 1 include eq 2 and eq 3. Since we consider it unlikely that *trans*-$Cr(C_2O_4)_2^-$ is far more reactive than the dominant *cis*-$Cr(C_2O_4)_2^-$, we have not proposed metal-catalyzed isomerization, followed by fast aquation. The failure of the inert hexaaquochromium(III) ion to catalyze the aquation is in accord with our suggestion that the catalytic metal ion must coordinate to the leaving oxalate. The form of the rate law is not consistent

$$Cr(C_2O_4)_2^- + Fe^{3+} \rightleftharpoons Cr(C_2O_4)OC_2O_3Fe^{2+} \qquad (2a)$$

$$Cr(C_2O_4)OC_2O_3Fe^{2+} \longrightarrow CrC_2O_4^+ + FeC_2O_4^+ \qquad (2b)$$

$$Cr(C_2O_4)_2^- \rightleftharpoons Cr(C_2O_4)OC_2O_3^- \qquad (3a)$$

$$Cr(C_2O_4)OC_2O_3^- + Fe^{3+} \longrightarrow CrC_2O_4^+ + FeC_2O_4^+ \qquad (3b)$$

with disproportionation[16] to $CrC_2O_4^+$ and $Cr(C_2O_4)_3^{3-}$, followed by fast aquation of $Cr(C_2O_4)_3^{3-}$.

In each of mechanisms 2 and 3, the bonds to leaving oxalate are broken singly, so that a monodentate intermediate is formed. The effect of Fe^{3+} in mechanism 2 is to help break the first chromium–oxygen bond and then to help break the second. The effect in mechanism 3 is to help break only the second bond. A reliable basis for distinguishing the mechanisms has not been established, but using the assumption that bond-breaking processes are similar in cis and trans isomers, we think mechanism 2 is slightly more probable. We prefer mechanism 2 because only the first chromium–oxygen bond is broken[6] in the isomerization of *trans*-$Cr(C_2O_4)_2^-$, yet that reaction is also catalyzed by metal ions, as shown in Table II. For metal ion catalysis of isomerization, the proposal has been made[6] that the first step is analogous to eq 2a. We suggest also that if reaction 2a occurs, *both* aquation and isomerization are logical consequences. An alternate isomerization proposal can be made, however, in which the first bond-breaking step is fast, but the subsequent bond forming nearly always occurs without isomerization. The role of the metal would then be to interact with the complex, after chromium–oxygen bond breaking, and to change the position of bond forming. This mechanism could be equivalent to making reactions analogous to (2a) occur in two steps, but if applicable, it is of the form of our mechanism 3. Even though we think mechanism 2 is more likely, the data in Tables I and II indicate that it is possible for the spontaneous and acid-catalyzed breaking of the first bond to occur rapidly enough to allow mechanism 3. From Table II, the spontaneous and acid-catalyzed isomerizations would occur with a half-time of the order of 700 sec in 0.2 *M* H^+ at 25°. Under these conditions then, and assuming isomerization does not occur without bond breaking, 700 sec is the lower limit for the half-time for aquation by mechanism 3. From Table I, the observed half-time was 6000 sec, not inconsistent with mechanism 3.

The activation parameters for acid-catalyzed and iron-catalyzed aquation, shown in Table II, are similar. The more positive entropy of activation for the Fe^{3+}-catalyzed pathway is consistent with either of the proposed mechanisms and reflects the greater charge of Fe^{3+}.

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