Kinetics of the Reduction of Trisoxalatocobaltate(III) Ion by Iron(II)

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The reaction $Fe^{2+} + [Co(C_2O_4)_3]^{3-}$ proceeds by parallel paths with the rate law $-d[Fe^{2+}]/dt = k_2[Fe^{2+}][Co^{III}] + k_3[Fe^{2+}][Co^{III}]^2$. At 25 °C and ionic strength 3.0 mol dm^{-3} ($Na[ClO_4]$), $k_2 = 6.9$ dm^3 mol^{-1} s^{-1}, and $k_3 = 1.50 \times 10^3$ dm^3 mol^{-1} s^{-1}. Values of k_2 are tabulated for other ionic media.

THE reduction of trisoxalatocobaltate(III) ion by iron(II) was first studied by Barrett and Baxendale [1] who established the stoicheiometry and kinetics under conditions of high dilution; later Haim and Sutin [2] identified the primary iron(III) product and thus demonstrated the inner-sphere mechanism (1). Our initial interest in the

$$[Co(C_2O_4)_3]^{3-} + Fe^{2+} + 2H^+ \longrightarrow Co^{2+} + 2[HC_2O_4]^- + [Fe(C_2O_4)]^+ \qquad (1)$$

reaction was in the hope of detecting the ion pair $Fe^{2+}\cdot[Co(C_2O_4)_3]^{3-}$ which might be expected as an intermediate in the electron-transfer step [see equation (7) below]. This expectation has not been realised: instead we have found a two-term rate law with evidence of a hitherto unreported reaction path involving two cobalt complexes in the transition state.

EXPERIMENTAL

Materials.—Trisoxalatocobaltate(III) ion was prepared and used as the sodium salt $Na_3[Co(C_2O_4)_3]\cdot3.5H_2O$.[3] Solutions of $Fe[ClO_4]_2$ were prepared, stored, analysed, and dispensed as previously described.[4] Solutions of $Na[ClO_4]$ were made by neutralising AnalaR sodium hydroxide with AnalaR perchloric acid; solutions of $Mg[ClO_4]_2$ were prepared by dissolving magnesium turnings (' special for Grignard reactions ') in AnalaR perchloric acid.

Kinetic Measurements.—All reactions were monitored spectrophotometrically. A Beckman DB spectrophotometer with 10 in chart recorder was used for the slower runs, and an Aminco–Morrow stopped-flow apparatus with output to a storage oscilloscope was used for the faster runs. In intermediate cases, it was convenient to use the stopped-flow apparatus but to take the signal directly to the chart recorder, with a suitable potentiometer circuit to lower the applied voltage. Reactions with iron in excess over cobalt were followed by means of the decrease in absorption due to $[Co(C_2O_4)_3]^{3-}$ ion at 600 nm; reactions with cobalt in excess over iron were followed by the increase in absorbance, mainly due to Fe^{III}, at 380 nm. (This is not the absorption maximum, but it gave a convenient overall change in absorbance.)

TABLE 1

Rates * of the reaction $[Co(C_2O_4)_3]^{3-} + Fe^{2+}$ with Co^{III} in excess over Fe^{II}

$10^3[Co^{III}]_0$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}	$k_{obs.}/[Co^{III}]_0$ / dm^3 mol^{-1} s^{-1}
5.0	0.154	30.8
7.5	0.281	37.4
10.0	0.405	40.5
12.5	0.495	39.6
15.0	0.990	66.0
20.0	1.28	64.2
25.0	2.77	110.9
30.0	4.13	137.5
40.0	7.53	188.3
50.0	9.49	189.9

* $[Fe^{II}]_T = 1.80 \times 10^{-3}$ mol dm^{-3} initially, 25 °C, and ionic strength 3.0 mol dm^{-3} ($Na[ClO_4]$).

RESULTS

Experiments with Co^{III} in excess over Fe^{II} are listed in Table 1. In each case the data conformed to equation (2)

$$(A - A_\infty) = (A_0 - A_\infty)\exp(-k_{obs.}t) \qquad (2)$$

where A_0, A, and A_∞ denote absorbance readings at times 0, t, and infinity, thus giving the pseudo-first-order rate law (3). Values of $k_{obs.}$ were obtained in the usual way by

$$-d[Fe^{II}]/dt = k_{obs.}[Fe^{II}] \qquad (3)$$

plotting $\log(A - A_\infty)$ against t. In the concentration range 5×10^{-3}—5×10^{-2} mol dm^{-3}, $k_{obs.}$ increased approximately as the square of the cobalt concentration. A plot of $k_{obs.}/[Co^{III}]$ against $[Co^{III}]$ was effectively linear (Figure). On the other hand, experiments at the same temperature and ionic strength with a low cobalt concentration and with Fe^{II} in excess (Table 2) also conformed to equation (2),

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[1] J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, 1956, **52**, 210.

[2] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 1966, **88**, 5343.

[3] R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2207.

[4] R. D. Cannon and J. Gardiner, *J.C.S. Dalton*, 1972, 887.

implying a first-order dependence on cobalt, and the variation with iron(II) concentration was linear [equation (5)].

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k_{\mathrm{obs.}}'[\mathrm{Co^{III}}] \qquad (4)$$

$$k_{\mathrm{obs.}}' = k_2'[\mathrm{Fe^{II}}] \qquad (5)$$

Hence we require a two-term rate law [equation (6)] in which k_2 predominates at the lower end of the cobalt concentration range and k_3 predominates at the upper end.

$$-\mathrm{d}[\mathrm{Fe^{II}}]/\mathrm{d}t = -\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k_2[\mathrm{Fe^{II}}][\mathrm{Co^{III}}] + k_3[\mathrm{Fe^{II}}][\mathrm{Co^{III}}]^2 \qquad (6)$$

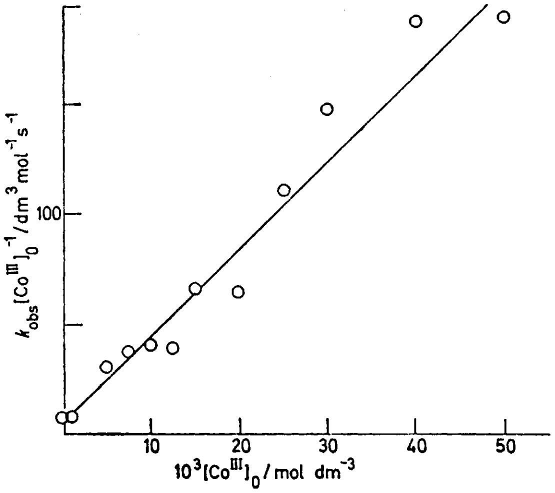
Thus $k_{\mathrm{obs.}} = k_2[\mathrm{Co^{III}}] + k_3[\mathrm{Co^{III}}]^2$ and k_2' is the average value of $(k_2 + k_3[\mathrm{Co^{III}}])$ for experiments in which $[\mathrm{Co^{III}}]$ varies with time from 1.0×10^{-3} mol dm^{-3} to zero. At 25 °C and ionic strength 3.0 mol dm^{-3} (Na[ClO$_4$]), the experiments with cobalt in excess yielded $k_3 = 1.50 \times 10^3$ dm^6 mol^{-2} s^{-1} and those with iron in excess gave $k_2' = 7.65$ dm^3 mol^{-1} s^{-1}. Taking an average value $[\mathrm{Co^{III}}] = 5 \times 10^{-4}$ mol dm^{-3} for the latter experiments, we obtain $k_2 = 6.9$ dm^3 mol^{-1} s^{-1}. The uncertainty involved in taking the average cobalt concentration is probably not greater than the experimental error.

TABLE 2

Rates of the reaction $[\mathrm{Co(C_2O_4)_3}]^{3-} + \mathrm{Fe^{2+}}$ with Fe$^{\mathrm{II}}$ in excess over Co$^{\mathrm{III}}$

$10^3[\mathrm{Fe^{II}}]_0$ / mol dm^{-3}	k_{obs}' / s^{-1}	$k_{\mathrm{obs.}}'/[\mathrm{Fe^{II}}]_0$ / dm^3 mol^{-1} s^{-1}
(*a*) 25 °C, I = 1.0 mol dm^{-3} (Na[ClO$_4$]) [a]		
8.75	0.222	25.4
17.5	0.40	22.8
26.25	0.559	21.3
35.0	0.815	23.3
52.5	1.17	22.3
70.0	1.54	22.0
87.5	2.1	24.0
	Mean:	23.0 ± 1.0
(*b*) 25 °C, I = 1.0 mol dm^{-3} (HClO$_4$) [a]		
17.5	0.654	37.4
35.0	1.019	29.1
52.5	1.582	30.1
70.0	2.635	37.6
87.5	3.013	34.4
	Mean:	33.7 ± 3.6
(*c*) 25 °C, I = 3.0 mol dm^{-3} (Na[ClO$_4$]) [a]		
22.9	0.227	9.93
34.3	0.304	8.86
45.7	0.380	8.33
57.1	0.415	7.26
80.0	0.568	7.08
91.4	0.619	6.77
114.3	0.779	6.82
171.5	1.260	7.35
228.6	1.475	6.45
	Mean:	7.65 ± 1.1
(*d*) 5.2 °C, I = 3.0 mol dm^{-3}(Na[ClO$_4$]) [b]		
5.95	0.0346	5.82
5.95	0.0343	5.77
11.9	0.0576	4.84
11.9	0.0587	4.94
14.9	0.0556	3.74
14.9	0.055	3.70
17.8	0.065	3.64
17.8	0.0664	3.72
20.8	0.076	3.67
23.8	0.134	5.63
23.8	0.139	5.84
35.7	0.150	4.20
35.7	0.176	4.94
47.6	0.216	4.55
47.6	0.278	5.86
59.5	0.213	3.58
59.5	0.223	3.75
119	0.365	3.07
178	0.649	3.64
178	0.604	3.39
238	0.921	3.88
238	1.048	4.41
238	1.118	4.70
238	1.197	4.03
	Mean:	4.39 ± 0.85
(*e*) 5.5 °C, [H$^+$] = 0.10 mol dm^{-3}, I = 3.0 mol dm^{-3} (Mg[ClO$_4$]$_2$) [b]		
4.87	0.0262	5.37
4.87	0.0258	5.30
9.74	0.0658	6.76
9.74	0.0532	5.46
14.6	0.0947	6.48
14.6	0.0914	6.26
19.5	0.152	7.79
19.5	0.129	6.64
24.3	0.124	5.11
24.3	0.124	5.10
29.2	0.155	5.29
34.1	0.215	6.30
43.8	0.207	4.73
43.8	0.204	4.65
48.7	0.238	4.89
48.7	0.227	4.67
73.1	0.455	6.23
97.4	0.585	6.01
121.7	0.767	6.30
146.1	0.991	6.78
	Mean:	5.81 ± 0.85

[a] $[\mathrm{Co^{III}}] = 1.00 \times 10^{-3}$ mol dm^{-3} initially. [b] $[\mathrm{Co^{III}}] = 5 \times 10^{-4}$ mol dm^{-3} initially.



Cobalt(III) dependence of the specific rate $k_{\mathrm{obs.}}$ [equation (3)] for the reaction $\mathrm{Fe^{2+}} + [\mathrm{Co(C_2O_4)_3}]^{3-}$ at 25 °C and ionic strength 3.0 mol dm^{-3} (Na[ClO$_4$]) (see Table 1). The quantity plotted for the range $[\mathrm{Co^{III}}] = 0$—1.0×10^{-3} mol dm^{-3} is the value of $k_{\mathrm{obs.}}'/[\mathrm{Fe^{II}}]$ for reactions with iron(II) in excess [equation(5)].

Further experiments with Fe$^{\mathrm{II}}$ in large excess over Co$^{\mathrm{III}}$ are listed in Table 2. At 25 °C and ionic strength 1.0 mol dm^{-3} the iron(II) dependences showed no deviation from linearity and rate constants k_2' agree satisfactorily with those previously reported both for zero acid concentration and for 1.0 mol dm^{-3} perchloric acid (Table 3).

DISCUSSION

The simplest interpretation of equation (6) is that there are two reaction paths, involving respectively an ion pair and an ion triplet, both of which remain at low concentrations compared with the reactants.* Thus $k_2 =$

$$\mathrm{Fe^{2+} + [Co(C_2O_4)_3]^{3-} \overset{K_{11}}{\rightleftharpoons} Fe^{2+}{\cdot}[Co(C_2O_4)_3]^{3-} \xrightarrow{k_{11}} Products} \quad (7)$$

$$\mathrm{Fe^{2+}{\cdot}[Co(C_2O_4)_3]^{3-} + [Co(C_2O_4)_3]^{3-} \overset{K_{21}}{\rightleftharpoons} Fe^{2+}{\cdot}2[Co(C_2O_4)_3]^{3-} \xrightarrow{k_{21}} Products} \quad (8)$$

$k_{11}K_{11}$ and $k_3 = k_{21}K_{11}K_{21}$. It might have been expected that the ion pair would be appreciably formed at the higher reagent concentrations, in which case, for the experiments with iron in excess over cobalt, the iron(II) dependence would have shown deviations from first-order as shown in equation (9), and similarly the cobalt(III) dependence would be less than second-order as

$$k_{\mathrm{obs.}}' = \frac{k_{11}K_{11}[\mathrm{Fe^{II}}]_{\mathrm{T}}}{1 + K_{11}[\mathrm{Fe^{II}}]_{\mathrm{T}}} \quad (9)$$

shown in equation (10). {In these equations $[\mathrm{Fe^{II}}]_{\mathrm{T}}$ and

$$k_{\mathrm{obs.}} = \frac{k_{11}K_{11}[\mathrm{Co^{III}}]_{\mathrm{T}} + k_{21}K_{11}K_{21}[\mathrm{Co^{III}}]_{\mathrm{T}}^2}{1 + K_{11}[\mathrm{Co^{III}}]_{\mathrm{T}}} \quad (10)$$

$[\mathrm{Co^{III}}]_{\mathrm{T}}$ denote total concentrations ($[\mathrm{Fe^{2+}}] + [\mathrm{Fe^{2+}{\cdot}Co(C_2O_4)_3{}^{3-}}]$) and ($[\mathrm{Co(C_2O_4)_3{}^{3-}}] + [\mathrm{Fe^{2+}{\cdot}Co(C_2O_4)_3{}^{3-}}]$) respectively.} Approximate upper limits for the value of K_{11} can be obtained by plotting $(k_{\mathrm{obs.}}')^{-1}$ against $[\mathrm{Fe^{II}}]^{-1}$ for the experiments with iron in excess, and $(k_{\mathrm{obs.}}[\mathrm{Co^{III}}]^{-1} - k_2)^{-1}$ against $[\mathrm{Co^{III}}]^{-1}$ for the experiments with cobalt in excess. In no case did we obtain a statistically significant value, and the estimated upper limits range from 0 to 10 dm^3 mol^{-1} depending on the precision of the data (Table 3).

TABLE 3

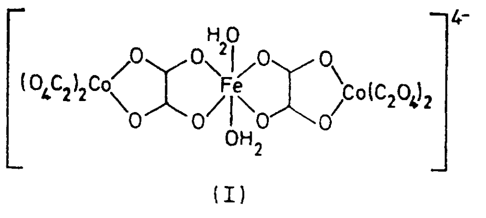
Summary of rates of the reaction $[\mathrm{Co(C_2O_4)_3}]^{3-} + \mathrm{Fe^{2+}}$

Medium	Ionic strength / mol dm^{-3}	$[\mathrm{H^+}]$ / mol dm^{-3}	θ_c / °C	K_{11} [a] / dm^3 mol^{-1}	k_2' [b] / dm^3 mol^{-1} s^{-1}	k_2 / dm^3 mol^{-1} s^{-1}
	0	0	25			1.50×10^3 [c]
Na[ClO$_4$]	1.0	0	25	5 ± 5	23.0	19 [d]
HClO$_4$	1.0	1.0	25	2 ± 5	33.7	33 [e]
Na[ClO$_4$]	3.0	0	25	4 ± 4 -2 ± 10 [f]	7.65	
			5.2	1.6 ± 0.6	4.39	
Mg[ClO$_4$]$_2$	3.0	0.1	5.5	-0.4 ± 0.4	5.8	

[a] From data of Table 2, plotting $(k_{\mathrm{obs.}}')^{-1}$ aginst $[\mathrm{Fe^{II}}]^{-1}$ [*cf.* equation (9)]. [b] This work. [c] Ref. 1. [d] M. Thottyill, Ph.D. Thesis, Manchester University, 1965, cited by P. B. Wood and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1966, 1645. [e] Ref. 2. [f] From data of Table 1, plotting $(k_{\mathrm{obs.}}[\mathrm{Co^{III}}]^{-1} - k_2)^{-1}$ against $[\mathrm{Co^{III}}]^{-1}$ [*cf.* equation (10)].

Tanaka and Koseki [5] reported formation constants of a number of ion pairs involving the $[\mathrm{Co(C_2O_4)_3}]^{3-}$ ion. For $\mathrm{Al^{3+}{\cdot}[Co(C_2O_4)_3]^{3-}}$ they obtained $K_{11} = 5.0 \times 10^3$ dm^3 mol^{-1} at 25 °C and zero ionic strength, decreasing to 1.2×10^2 dm^3 mol^{-1} at ionic strength 0.1 mol dm^{-3}. From studies of the metal-ion catalysed aquation of $[\mathrm{Co(C_2O_4)_3}]^{3-}$ Schneider [6] estimated $K_{11} = 2$ dm^3 mol^{-1} for the same ion pair at 32.5 °C and ionic strength 1.5 mol dm^{-3}. There are no data for ion pairs of bivalent transition metals with this anion, but for the alkaline-earth cations $\mathrm{Mg^{2+}}$ to $\mathrm{Ba^{2+}}$ Tanaka and Koseki found closely similar values, *ca.* 800 dm^3 mol^{-1} at zero ionic strength, and 55 dm^3 mol^{-1} at ionic strength 0.1 mol dm^{-3}. It is difficult to extrapolate from these data to the complex $\mathrm{Fe^{2+}{\cdot}[Co(C_2O_4)_3]^{3-}}$ under our experimental conditions, but a value $K_{11} = 1$—5 dm^3 mol^{-1} would seem reasonable, and is not excluded by our data. On the other hand, for the apparently similar complex $\mathrm{Cu^{2+}{\cdot}[Cr(C_2O_4)_3]^{3-}}$, Aggett [7] found K_{11} as high as 340 dm^3 mol^{-1} at 25 °C and ionic strength 0.5 mol dm^{-3}.

The importance of the second term in equation (6) suggests that both trisoxalatocobaltate ions play a definite structural role. It seems likely that they enter the co-ordination sphere of the $\mathrm{Fe^{II}}$ to give the symmetrical intermediate (I). Comparing the reaction



(I)

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* Other mechanisms are consistent with the experimental rate law, and these can include appreciable formation of the ion pair, provided that special relations between the rate and equilibrium constants are satisfied. For example, if (when iron is in excess over cobalt) there is an additional path (12), this gives (13)

$$\mathrm{2Fe^{2+} + [Co(C_2O_4)_3]^{3-} \overset{\beta_{12}}{\rightleftharpoons} [2Fe^{2+}]{\cdot}[Co(C_2O_4)_3]^{3-} \xrightarrow{k_{12}} Products} \quad (12)$$

$$k_{\mathrm{obs.}}' = \frac{k_{11}K_{11}[\mathrm{Fe^{2+}}] + k_{12}K_{11}K_{12}[\mathrm{Fe^{2+}}]^2}{1 + K_{11}[\mathrm{Fe^{2+}}]} \quad (13)$$

where $K_{12} = \beta_{12}/K_{11}$; if in addition we have $k_{12}K_{12} = k_{11}K_{11}$, equation (13) reduces to (14) irrespective of the position of the

$$k_{\mathrm{obs.}}' = k_{11}K_{11}[\mathrm{Fe^{2+}}] \quad (14)$$

equilibrium (7). However, this still entails a cobalt(III) dependence less than second-order [equation (10)] unless there is still another path such as (15).

$$\mathrm{Fe^{2+} + 3[Co(C_2O_4)_3]^{3-} \overset{\beta_{31}}{\rightleftharpoons} Fe^{2+}{\cdot}3[Co(C_2O_4)_3]^{3-} \xrightarrow{k_{31}} Products} \quad (15)$$

[5] N. Tanaka and K. Koseki, *Bull. Chem. Soc. Japan*, 1968, **41**, 2067.

[6] W. Schneider, *Helv. Chim. Acta*, 1963, **46**, 1863.

[7] J. Aggett, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3319.

paths (7) and (8), the second $[Co(C_2O_4)_3]^{3-}$ ion in equation (8) may be regarded as a non-bridging ligand, facilitating the electron-transfer process. Such effects are well documented and have been rationalised in terms of the Marcus theory by considering the stabilisation of the electron-transfer products.[8] As adapted to the present case (see Appendix) the Marcus theory predicts expression (11), where K_{II} and K_{III} are the formation constants

$$k_3/k_2 = (K_{II}K_{III})^{\frac{1}{2}} \qquad (11)$$

of the ion pairs $Fe^{2+}\cdot[Co(C_2O_4)_3]^{3-}$ and $Fe^{3+}\cdot[Co(C_2O_4)_3]^{3-}$. From the work of Tanaka and Koseki, and from this work, both constants are evidently less than 5 dm^3 mol^{-1} under our conditions, yet $k_3/k_2 = 300$ dm^3 mol^{-1}. Clearly the rate enhancement by the second $[Co(C_2O_4)_3]^{3-}$ ion is greater than can be accounted for by ion pairing with the iron(III) product. It seems possible that in the transition state which follows on from the ion triplet (I), the transferring electron is delocalised on to both cobalt atoms. The additional stabilisation could be ascribed to resonance energy, or it may be that the binding of both cobalt atoms to oxygen is weakened, and the binding of the iron to oxygen correspondingly enhanced.

APPENDIX

Consider two reactions involving oxidant A^{III} and reductant B^{II} (where the valencies II and III are chosen merely for illustration), and a non-bridging ligand L. The rate constants k_0 and k_L are second- and -third order respectively. An equivalent form of (A.2) is (A.3) where $k_L' = k_L K_{II}^{-1}$ and

$$A^{III} + B^{II} \xrightarrow{k_0} A^{II} + B^{III} \qquad (A.1)$$

$$A^{III} + B^{II} + L \xrightarrow{k_L} A^{II} + [B^{III}L] \qquad (A.2)$$

$$A^{III} + [B^{II}L] \xrightarrow{k_L'} A^{II} + [B^{III}L] \qquad (A.3)$$

K_{II} is the stability constant of the complex $[B^{II}L]$. Then,

$$B^{II} + L \overset{K_{II}}{\rightleftharpoons} [B^{II}L] \qquad (A.4)$$

provided that the overall free-energy changes associated with electron transfer are small, the Marcus theory gives (A.5), where K_0 and K_L' are equilibrium constants for

$$k_L'/k_0 = (K_L'/K_0)^{\frac{1}{2}} = (K_{III}/K_{II})^{\frac{1}{2}} \qquad (A.5)$$

reactions (A.1) and (A.3) and K^{III} is the stability constant of the complex $[B^{III}L]$. Hence we obtain (A.7). In the

$$B^{III} + L \overset{K_{III}}{\rightleftharpoons} [B^{III}L] \qquad (A.6)$$

$$k_L/k_0 = (K_{II}K_{III})^{\frac{1}{2}} \qquad (A.7)$$

above discussion, $A^{III} = L = [Co(C_2O_4)_3]^{3-}$, $A^{II} = [Co(C_2O_4)_2]^{2-}$, $B^{II} = Fe^{2+}$, and $B^{III} = [Fe(C_2O_4)]^{+}$.

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[8] J. E. Earley, *Progr. Inorg. Chem.*, 1970, **13**, 243.