several other cations.[20] There is some evidence to suggest that, under some conditions, Mn^{2+} can reduce ClO_4^-.[21] We expect that the perchlorate complexes of Ti(III) and Ru(II) would also exhibit broadened ^{35}Cl resonance lines.

Acknowledgment.—We are grateful to the U. S. Air Force Office of Scientific Research for support under Grant AF-1225-67.

[20] F. Klanberg, J. P. Hunt, and H. W. Dodgen, *Inorg. Chem.*, **2**, 139 (1963).

[21] R. C. Dickinson and G. J. Long, *Chem. Eng. News*, **48** (28), 6 (1970).

CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORY,
UNIVERSITY OF KENT AT CANTERBURY, CANTERBURY, KENT, ENGLAND

Kinetics and Mechanism of the Cobalt(III) Oxidation of Manganese(II) and Iron(II) in Acid Perchlorate Solution[1]

BY GEOFFREY DAVIES

Received September 11, 1970

The stoichiometries and kinetics of the cobalt(III) oxidations of manganese(II) and iron(II) have been investigated in lithium perchlorate–perchloric acid and sodium perchlorate–perchloric acid mixtures at ionic strength 3.0 *M*. Stoichiometric measurements with excess reductant established that the products of oxidation are manganese(III) and iron(III), respectively, and kinetic measurements under the same conditions using the stopped-flow technique showed that the rate law for each reaction is given by $-d \ln (\mathrm{Co(III)})/dt = [a + b/(\mathrm{H^+})](\text{reductant})$, where a and b are interpreted in terms of rate constants for the reactions $\mathrm{Co_{aq}}^{3+} + \mathrm{M_{aq}}^{2+} \xrightarrow{k_0} \mathrm{Co(II)_{aq}} + \mathrm{M(III)_{aq}}$ $(a \equiv k_0)$ and $\mathrm{CoOH_{aq}}^{2+} + \mathrm{M_{aq}}^{2+} \xrightarrow{k_{-1}} \mathrm{Co(II)_{aq}} + \mathrm{M(III)_{aq}}$ $(b \equiv k_{-1}K_h)$, where K_h is the acid-dissociation constant of $\mathrm{Co_{aq}}^{3+}$. Activation parameters for a and b in the two media are reported and the mechanisms of the reactions are discussed.

Introduction

A comparison of rate constants for complexation reactions of the type

$$\mathrm{MOH_{aq}}^{2+} + \mathrm{B_{aq}} \overset{k_{-1}}{\rightleftharpoons} \mathrm{MOHB_{aq}}^{2+} \qquad K_1 \qquad (1)$$

suggests that when M is Cr, Fe, or Co the forward rate of complexation is largely determined by the rate of water exchange on the metal ion.[2-4] When M is Co, the complexation reaction (eq 1). is generally followed by oxidative decomposition of the complex, and studies with B = Cl^-,[4a] malic acid,[4b] thiomalic acid,[4c] and cysteine[4d] have allowed the kinetics of these two processes to be studied separately.

By contrast, there is no direct spectrophotometric or kinetic evidence for intermediate complex formation in the majority of oxidation reactions involving $\mathrm{CoOH_{aq}}^{2+}$.[5] However, in some of the faster reactions of this oxidant, notably those with B = H_2O_2,[6] HNO_2,[6] $H_2C_2O_4$,[7] HN_3,[8] Br^-,[6] SCN^-,[6] and $HC_2O_4^-$,[7] the rates of oxidation appear to be substitution controlled.[9] A comparison of activation parameters for these systems supports this view.[7]

The rate constants for reactions of aquocobalt(III) with manganese(II)[10] and iron(II)[11,12] are of the same order of magnitude as those reported for substitution-controlled complexation[4,5] and redox[5-8] reactions. However, the data[10] for the reaction with manganese(II) refer only to 3 *M* perchloric acid at 25.0° and the reaction with iron(II) has only been investigated at 1 *M* ionic strength[11] ($HClO_4$, $NaClO_4$) in the temperature range 0–14° and in 3 *M* perchloric acid[12] at 25.0°. We need to study the effect of changing acidity, medium, and temperature in these reactions under the same conditions as used in the majority of fast redox reactions[5-8] of cobalt(III) in order to make a valid comparison of the rates of the constituent redox steps.[5]

In this paper we report an investigation of the stoichiometry and kinetics of the cobalt(III) oxidation of manganese(II) and iron(II) in 3 *M* lithium perchlorate–perchloric acid and 3 *M* sodium perchlorate–perchloric acid media in the temperature range 0–50°. A comparison with previous kinetic data[4-8] enables an assignment of the probable mechanisms of the constituent reaction pathways to be made.

Experimental Section

Reagents and Analytical Methods.—All chemicals, except for the Li_2CO_3 used in the preparation of lithium perchlorate solutions, were of reagent grade and triply distilled water was used throughout. The perchlorates of cobalt(III), cobalt(II), and sodium were prepared and standardized as described previously.[6] Lithium perchlorate was recrystallized three times from water and was made up into stock solutions which were standardized gravimetrically. Manganese(III) solutions in perchloric acid were prepared by oxidation of excess manganese(II) with manganese(VII) or at a Pt anode[10,13] and were standardized

---

[1] The award of an I.C.I. fellowship in support of this work is gratefully acknowledged.

[2] J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969).

[3] D. Seewald and N. Sutin, *ibid.*, **2**, 643 (1963).

[4] (a) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *ibid.*, **5**, 1 (1966); (b) J. Hill and A. McAuley, *J. Chem Soc. A*, 1169 (1968); (c) J. Hill and A. McAuley, *ibid.*, *A*, 2405 (1968); (d) A. McAuley, *Coord. Chem. Rev.*, **5**, 245 (1970).

[5] For review see G. Davies and B. Warnqvist, *ibid.*, **5**, 349 (1970).

[6] G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).

[7] G. Davies and K. O. Watkins, *Inorg. Chem.*, **9**, 2735 (1970).

[8] R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *ibid.*, **7**, 1876 (1968); R. C. Thompson and J. C. Sullivan, *ibid.*, **9**, 1590 (1970).

[9] For other examples of substitution-controlled redox reactions see: (a) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968); (b) G. Davies, *Coord. Chem. Rev.*, **4**, 199 (1969).

[10] H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).

[11] L. E. Bennett and J. C. Sheppard, *ibid.*, **66**, 1275 (1962).

[12] T. J. Conocchioli, G. H., Nancollas, and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 1453 (1964).

[13] C. F. Wells and G. Davies, *J. Chem. Soc. A*, 1858 (1967).

as before.[13] Iron(II) perchlorate solutions were obtained by mixing a 2% excess of neutral barium perchlorate solution with iron(II) sulfate in perchloric acid, the barium sulfate precipitate being removed by filtration. The iron(III) concentration of these solutions was reduced to less than 0.05% of the total iron by electroreduction at a Pt electrode, and the solutions were standardized using cerium(IV) (ferroin indicator). Iron(III) solutions were prepared by oxidation of acidic iron(II) perchlorate solutions with the stoichiometric amount of hydrogen peroxide and were standardized spectrophotometrically ($\epsilon_{260}^{\mathrm{Fe(III)}}$ 2.88 × 10^3) at ($HClO_4$) > 1 M).[13,14]

Stoichiometric Measurements.—The stoichiometries of the two reactions were investigated by mixing acidic cobalt(III) solutions with solutions containing an excess of reductant. The final acidity of the mixtures was within the range used for kinetic measurements. The visible and uv spectra of the product of oxidation of manganese(II) were compared with the spectra of manganese(III) and manganese(VII) under the same conditions using a Unicam SP800 spectrophotometer with a temperature-controlled cell block. At low acidities the absorbance in the visible region due to the product decreased with time, as observed previously for oxidized solutions of manganese(II) under these conditions.[10,13] Extrapolation of absorbance readings to zero time gave the spectrum of the immediate products. These solutions subsequently precipitated solid material on standing.

Iron(III) formed in the oxidation of iron(II) was determined as described above. Small corrections were applied for the absorption due to cobalt(II), iron(II), and manganese(II) at the wavelengths used for measurement assuming a stoichiometry $\Delta(\mathrm{Co(III)})/\Delta(\mathrm{reductant}) = 1$ for both reactions.

Kinetic Measurements.—A glass–quartz stopped-flow spectrophotometer was used for kinetic measurements. The two main features of this otherwise conventional apparatus are the provision of a vertical helical coil in a thermostat bath between each drive syringe and the mixing chamber[15] and the use of quartz cones to pass the detecting light beam through the observation tube.[16] The helical coils, mixer, and observation tube are all immersed in the thermostat bath. Temperature control to within 0.05° is easily achieved with this arrangement. The quartz cones, which are fused to opposite sides of the square-section observation cell, pass through the walls of the thermostat bath (Dow-Corning silicone rubber sealant). The path length of the observation cell is 3.3 mm (measured by calibration with manganese(VII)) and the dead time is ~10 msec under normal operating conditions.

All the kinetic measurements were carried out with a sufficient excess of reductant to ensure pseudo-first-order conditions. Reactant solutions were thermostated for at least 30 min before mixing. The appearance of manganese(III) was followed at 470 nm in the reaction with manganese(II), and the disappearance of cobalt(III) was monitored at 400 or 605 nm as a function of time in the reaction with iron(II). Photographs of stopped-flow traces were analyzed using the analog method of Crooks, *et al.*,[17] which is applicable to exponential curves with total transmittance changes of $\leqslant 5\%$, as was the case in most kinetic runs. Random samples from this class and for reactions involving larger per cent transmittance changes were analyzed using conventional techniques. Satisfactory internal consistency between the two methods of data analysis was observed. Each kinetic experiment was repeated at least twice, the maximum average error being 5%.

Results

Stoichiometry.—The stoichiometric measurements showed that the oxidation of 1 mol of reductant requires 1 mol of cobalt(III); *i.e.*, under the conditions used for kinetic measurements the reactions taking place are[18]

$$\mathrm{Co(III)} + \mathrm{Mn(II)} \longrightarrow \mathrm{Co(II)} + \mathrm{Mn(III)} \qquad (2)$$

$$\mathrm{Co(III)} + \mathrm{Fe(II)} \longrightarrow \mathrm{Co(II)} + \mathrm{Fe(III)} \qquad (3)$$

TABLE I

KINETIC DATA FOR COBALT(III) OXIDATIONS OF MANGANESE(II) AND IRON(II) IN 3 *M* ACID PERCHLORATE MEDIA[a]

(a) Manganese(II)

$LiClO_4$–$HClO_4$[a]			$NaClO_4$–$HClO_4$[b]		
(H^+), M	Temp, °C	$10^{-2}k_{\mathrm{obsd}}$, M^{-1} sec^{-1}	(H^+), M	Temp, °C	$10^{-2}k_{\mathrm{obsd}}$, M^{-1} sec^{-1}
0.25	2.9	0.58	0.25	7.0	0.625
	13.0	1.15		15.0	1.39
	23.1	2.65		22.8	2.68
	33.0	5.86		32.2	5.72
0.33	2.4	0.476	0.50	0.1	0.278
	12.5	1.10		14.1	0.885
	16.1	1.27		21.9	1.86
	23.3	2.33		33.5	4.69
0.50	2.6	0.434		41.5	8.45
	15.4	1.04	0.75	−0.1	0.217
	30.4	2.40		10.5	0.555
1.50	2.5	0.290		11.8	0.610
	16.3	0.910		21.2	1.30
	30.4	2.42		30.6	3.25
	45.9	6.06		40.6	5.75
3.00	7.6	0.375	1.00	−0.2	0.202
	24.9	1.21		12.0	0.601
	35.0	2.60		24.9	1.59
	50.0	6.30		40.3	4.43
			1.50	7.6	0.335
				25.0	1.19
				35.0	2.59
				50.0	8.01

(b) Iron(II)

$LiClO_4$–$HClO_4$[c]			$NaClO_4$–$HClO_4$[d]		
(H^+), M	Temp, °C	$10^{-2}k_{\mathrm{obsd}}$, M^{-1} sec^{-1}	(H^+), M	Temp, °C	$10^{-2}k_{\mathrm{obsd}}$, M^{-1} sec^{-1}
0.25	1.0	1.28	0.25	0.2	1.22
	11.2	3.86		15.0	6.58
	20.4	9.24		23.2	13.0
	34.6	30.5		29.8	29.4
0.33	0.05	0.945		42.1	75.1
	11.6	3.44	0.33	0.4	1.09
	20.7	7.15		12.4	4.68
	36.6	25.1		22.6	11.5
0.50	4.4	1.40		31.8	27.5
	16.9	3.88	0.50	1.8	0.851
	25.7	7.95		3.1	0.958
	34.7	18.8		10.8	1.97
1.50	2.4	0.484		21.1	4.73
	17.6	2.54		26.8	11.4
	28.5	5.70		37.3	23.6
	34.6	10.8		40.7	31.1
3.00	3.9	0.433	1.50	3.2	0.475
	15.5	1.24		15.9	1.90
	32.0	5.34		30.1	6.22
	49.9	29.4			

[a] Concentration ranges: (Co(III)) = (2.88–15.0) × 10^{-4} M, (Co(II)) = (2.17–150) × 10^{-4} M, (Mn(II)) = (1.23–12.3) × 10^{-2} M. [b] Concentration ranges: (Co(III)) = (1.55–13.8) × 10^{-4} M, (Co(II)) = (3.45–150) × 10^{-4} M, (Mn(II)) = (1.18–11.8) × 10^{-2} M. [c] Concentration ranges: (Co(III)) = (1.54–14.3) × 10^{-4} M, (Co(II)) = (3.46–150) × 10^{-4} M, (Fe(II)) = (4.82–48.2) × 10^{-2} M. [d] Concentration ranges: (Co(III)) = (1.55–13.8) × 10^{-4} M, (Co(II)) = (3.45–150) × 10^{-4} M, (Fe(II)) = (5.15–51.5) × 10^{-2} M.

Kinetics.—First-order plots for the appearance of manganese(III) in reaction 2 or the disappearance of cobalt(III) in reaction 3 were linear for at least 4 half-lives. Additions of cobalt(II) (1.1 × 10^{-2} M) in either reaction or manganese(III) (8.3 × 10^{-4} M in 3.00 M acid) or iron(III) (1.4 × 10^{-3} M in 1.50 M acid), in the reactions with manganese(II) and iron(II), respectively, had no observable effect on the rate. Both reactions were also found to be first-order in (reductant) at each acidity and temperature employed.

---

[14] R. Bastian, R. Weberling, and F. Palilla, *Anal. Chem.*, **28**, 459 (1956).

[15] H. P. Bennetto and E. F. Caldin, submitted for publication.

[16] G. Czerlinski, *Rev. Sci. Instrum.*, **33**, 1184 (1962).

[17] J. E. Crooks, M. S. Zetter, and P. A. Tregloan, *J. Sci. Instrum.*, **3**, 73 (1970).

[18] The limits of uncertainty are ±2 and ±5% in the reactions with iron(II) and manganese(II), respectively.

TABLE II

KINETIC DATA FOR SOME COBALT(III) REACTIONS AT 3 *M* IONIC STRENGTH IN ACID PERCHLORATE SOLUTION

Reductant	k_0[a]	$k_{-1}K_h$[b]	$\Delta H_0^{\ddagger}$[c]	$\Delta S_0^{\ddagger}$[d]	$\Delta H_{-1}^{\ddagger}$[c]	$\Delta S_{-1}^{\ddagger}$[d]	Ref
Co^{2+}[e]	3.3	1.0	10.3	−21	21.8	+16	*f*
Mn^{2+}[e]	107	58.0	11.3 ± 0.5	−9.5 ± 1	16.1 ± 0.5	+6 ± 1	*h*
Mn^{2+}[g]	127	46.5	11.7 ± 0.5	−12.5 ± 1.0	12.3 + 0.5	−7.7 ± 1.0	*h*
Fe^{2+}[e]	225	385	15.2 ± 0.8	+4.7 ± 2	15.8 ± 0.5	+8.2 ± 1.0	*h*
Fe^{2+}[g]	248	275	15.7 ± 0.5	+7.1 ± 1.5	13.8 ± 0.6	+1 ± 1	*h*
H_2O[e]	2200	1280	18.2	+18	18.6	+17	*i*
I^-[e]	8000	2860	19.4	+25	21.5	+30	*i*

[a] Units are M^{-1} sec^{-1} at 25°. [b] Units are sec^{-1} at 25°. [c] Units are kcal mol^{-1} (see ref 5 and 27 for discussion of components of $\Delta H_{-1}^{\ddagger}$). [d] Units are cal deg^{-1} mol^{-1} (see ref 5 and 27 for discussion of components of $\Delta S_{-1}^{\ddagger}$). [e] Sodium perchlorate–perchloric acid media. [f] H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, **88,** 1668 (1966). [g] Lithium perchlorate–perchloric acid media. [h] This work. [i] Reference 6.

The rate law for each reaction is thus

$$\frac{-\mathrm{d}(\mathrm{Co(III)})}{\mathrm{d}t} = \frac{\mathrm{d(product)}}{\mathrm{d}t} = k_{\mathrm{obsd}}(\mathrm{Co(III)})(\mathrm{reductant}) \qquad (4)$$

where k_{obsd} is the observed second-order rate constant. These findings are in agreement with the results of the previous investigations.[10–12] As a check of the reliability of the apparatus and analytical procedures we repeated the experiments of Bennett and Sheppard[11] for the reaction with iron(II) in 1.00 *M* perchloric acid at ionic strength 1 *M*. The temperature was varied between 1.1 and 49.9°. Good agreement was observed between the two studies, bearing in mind that the previous measurements[11] were made by a quenching technique over a narrower temperature range (0–14°). Derived enthalpies and entropies of activation in 1.0 *M* perchloric acid at ionic strength 1 *M* are as follows: Bennett and Sheppard,[11] $\Delta H^{\ddagger} = 15 \pm 3$ kcal mol^{-1}, $\Delta S^{\ddagger} = 5 \pm 7$ cal deg^{-1} mol^{-1}; this work, $\Delta H^{\ddagger} = 15.9 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = 10.0 \pm 0.7$ cal deg^{-1} mol^{-1}. The kinetic data obtained in this study at ionic strength 3 *M* are presented in Table I. Plots of k_{obsd} *vs.* $1/(H^+)$ at constant temperature are linear within experimental error: an example is shown in Figure 1.[19] The observed rate constant for each reaction obeys the empirical form

$$k_{\mathrm{obsd}} = a + b/(H^+) \qquad (5)$$

where *a* and *b* are constants.

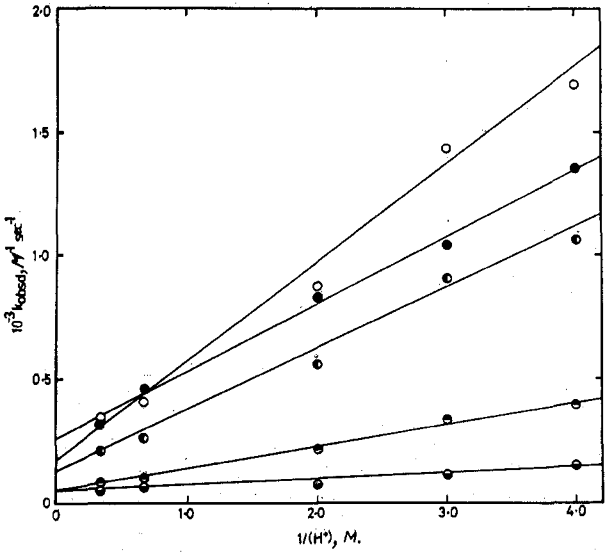

Figure 1.—Plots of $10^{-3}k_{\mathrm{obsd}}$ *vs.* $1/(H^+)$ for the reaction with iron(II) at various temperatures in sodium perchlorate–perchloric acid mixtures at ionic strength 3 *M*. Data points are interpolated[19] as follows: ○, 25.0°; ◐, 20.0°; ◓, 10.0°; ◒, 0.0°. A plot at 25.0° for the same reaction in lithium perchlorate–perchloric acid media at ionic strength 3 *M* is shown for comparison (●).

Mechanism.—The following mechanism is consistent with the observed kinetic dependencies

$$Co_{aq}^{3+} \rightleftharpoons CoOH_{aq}^{2+} + H_{aq}^{+} \qquad K_h \qquad (6)$$

$$Co_{aq}^{3+} + M_{aq}^{2+} \xrightarrow{k_0} Co(II)_{aq} + M(III)_{aq} \qquad (7)$$

$$CoOH_{aq}^{2+} + M_{aq}^{2+} \xrightarrow{k_{-1}} Co(II)_{aq} + M(III)_{aq} \qquad (8)$$

Here M is Mn or Fe and K_h is the acid-dissociation constant of Co_{aq}^{3+}. In terms of this mechanism we have $a \equiv k_0$ and $b \equiv k_{-1}K_h$.[5] Values for k_0, $k_{-1}K_h$, and their activation parameters in the two media are collected together with data for other cobalt(III) reactions in Table II.

Discussion

The results of this investigation are in satisfactory agreement with previous data for the reactions with manganese(II)[10] and iron(II)[12] in 3.0 *M* perchloric acid at 25°. The rate law observed for both reactions (eq 5) is of the same form as that found in the reaction with iron(II) at ionic strength 1 *M* ($NaClO_4$, $HClO_4$).[11]

The rate constants k_0 and $k_{-1}K_h$ and the corresponding activation parameters (Table II) are noticeably sensitive to the detailed reaction medium, the changes being much more marked for reactions of $CoOH_{aq}^{2+}$ than for those of Co_{aq}^{3+}.

Two factors govern the observed medium effect for the $CoOH_{aq}^{2+}$ reactions. The first is the temperature dependence of K_h, *i.e.*, the values of ΔH_h and ΔS_h in the two media. Since $\Delta H_{-1}^{\ddagger}$ and $\Delta S_{-1}^{\ddagger}$ both decrease on replacing Na_{aq}^{+} with Li_{aq}^{+} at ionic strength 3 *M* it seems reasonable to suppose that, other things being equal, the parameters ΔH_h and ΔS_h are both less positive in the medium with Li_{aq}^{+} as the counterion. It is unfortunate that the temperature dependencies of K_h in the two media are not amenable to direct study[20] since they undoubtedly affect the apparent activation parameters of $k_{-1}K_h$ in the different media, especially at high ionic strength.[21] It is interesting to note, however, that a change from $LiClO_4$–$HClO_4$ to $NaClO_4$–$HClO_4$ media has a very much smaller effect at ionic strengths of 0.5 and 1.0 *M* in the cobalt(III)–cobalt(II) exchange reaction.[22]

The second factor which influences the observed medium effect is the detailed mechanism of the re-

---

(19) Arrhenius plots are sufficiently linear to allow accurate interpolation of data so that plots of k_{obsd} *vs.* $1/(H^+)$ can be made at constant temperature as in Figure 1.

(20) Although the acid-dissociation constant K_h is believed[6] to be *ca.* 2×10^{-3} *M* at 25° and ionic strength 1 *M*, the rapid oxidation of water at low acidity precludes direct confirmation of this estimate.

(21) A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66,** 1065 (1962).

(22) H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, **88,** 1668 (1966).

action, characterized by the activation enthalpies and entropies of steps 7 and 8. The transition states for different mechanisms would be expected to show differing sensitivity to the detailed reaction environment, thereby influencing the observed medium effects. However, at present there is insufficient evidence available to allow the use of this argument in the diagnosis of mechanism at high ionic strength.[5,21]

Since most recent kinetic data for the more rapid reactions of cobalt(III) have been obtained in sodium perchlorate–perchloric acid mixtures, we shall restrict the remainder of our discussion to results obtained in this medium.

The reactions in Table II are all too fast for substitution into the inner-sphere of Co_{aq}^{3+} or $CoOH_{aq}^{2+}$ to be rate determining.[5–7] Another indication that these reactions are not substitution controlled is that the rates of reaction increase as the estimated overall free energy change, $\Delta G^\circ{}_{estd}$, becomes more negative. An exception to this trend is found in the reactions with iron(II), as discussed below. A plot of $\Delta G_0^{\ddagger}$ *vs.* $\Delta G^\circ{}_{estd}$ for the reactions of Co_{aq}^{3+} is approximately linear at 25° (Figure 2).[23] This observation alone does not, of course, distinguish between inner- and outer-sphere mechanisms for these reactions. It is interesting to note, however, that data for the reactions with inert iron(II)–phenanthroline complexes[24,25] (points 6–9 in Figure 2) fall on the line drawn through the other points; this suggests that all the reactions in this group proceed *via* an outer-sphere mechanism.

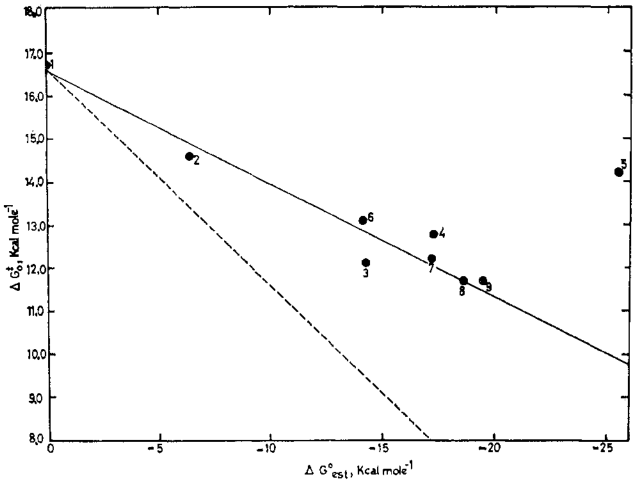

Figure 2.—Plot of $\Delta G_0^{\ddagger}$ *vs.* $\Delta G^\circ{}_{estd}$ at 25.0° and 3 *M* ionic strength for reactions of Co_{aq}^{3+}.[23] The reductants are shown as follows: 1, Co_{aq}^{2+};[22] 2, Mn_{aq}^{2+} (this work); 3, I^-;[6] 4, *p*-hydroquinone;[6] 5, Fe_{aq}^{2+} (this work); 6, tris-(5-nitro-1,10-phenanthroline)iron(II); 7, tris(5-chloro-1,10-phenanthroline)iron(II); 8, tris(1,10-phenanthroline)iron(II); 9, tris(5-methyl-1,10-phenanthroline)iron(II).[24,25] A line of the theoretical[26] slope 0.5 is shown for comparison.

Linear relationships between $\Delta G_i^{\ddagger}$ and $\Delta G^\circ{}_{estd,i}$ have been observed previously for series of related reactions with outer-sphere mechanisms.[25,26] The Marcus theory[26] for such reactions predicts a relationship of the form[9a]

$$\Delta G_{12}^* = \frac{\Delta G_1^* + \Delta G_2^*}{2} + \frac{\Delta G_r^\circ}{2} + \frac{(\Delta G_r^\circ)^2}{8(\Delta G_1^* + \Delta G_2^*)} \tag{9}$$

where

$$\Delta G^* = \Delta G^{\ddagger} - w \tag{10}$$

and

$$\Delta G_r^\circ = \Delta G^\circ{}_{estd} + w^p - w \tag{11}$$

Here w and w^p represent the work required to bring the reactants and products together, respectively. The fit of data for reductants carrying charges of 1− (I^-, point 3) to 2+ (points 6–9) in roughly the same region of Figure 2 suggests that, to a first approximation, we may neglect these work terms in explaining gross features of these reactions of Co_{aq}^{3+}.

The first term in eq 9 may be calculated from the rates of the exchange reactions of the reactant couples. In reaction 7 the appropriate couples are

$$\begin{aligned} &Co^{3+} + e^- \rightleftharpoons Co^{2+} \qquad \Delta G_1^* \approx \Delta G_1^{\ddagger} = 16.7 \text{ kcal mol}^{-1} \\ &M^{2+} \rightleftharpoons M^{3+} + e^- \qquad \Delta G_2^* \approx \Delta G_2^{\ddagger} \end{aligned} \tag{12}$$

The average value for the first term in eq 9, derived from kinetic data for the exchange reactions corresponding to points 1, 5, and 6–9 in Figure 2, is 16.1 ± 0.5 kcal mol^{-1} at 25°. An exception to this average value is in the reaction with manganese(II) (point 2), for which the first term, calculated from an indirect average estimate[10] of 2×10^{-4} M^{-1} sec^{-1} for the Mn_{aq}^{3+}–Mn_{aq}^{2+} exchange reaction, amounts to 19.3 kcal mol^{-1} at 25°. Compensation for this different intercept for the manganese(II) reaction would put point 2 closer to the theoretical[26] line of slope 0.5 (also shown in Figure 2). If this correction is appropriate, then a curve with a slope which decreases as $\Delta G^\circ{}_{estd}$ becomes more negative would accommodate the data for these reactions of Co_{aq}^{3+} except that with iron(II). In agreement with this observation, eq 9 predicts that a plot of $\Delta G_0^{\ddagger}$ *vs.* $\Delta G^\circ{}_{estd}$ will have a slope given by $0.5\,(1 + \Delta G^\circ{}_{estd}/4(\Delta G_1^{\ddagger} + \Delta G_2^{\ddagger}))$, which decreases as $\Delta G^\circ{}_{estd}$ becomes more negative. We conclude that the general features of the data for Co_{aq}^{3+} reactions in Table II are in accord with the predictions of Marcus' theory,[26] which supports an outer-sphere mechanism for these reactions.

The reactions of cobalt(III) generally exhibit a significant acid-dependent term in the rate law.[5] Indeed, the extent to which the OH^- ligand apparently facilitates electron transfer in the reactions of Table II sugests[5,6] that these oxidations involving $CoOH_{aq}^{2+}$ proceed *via* predominantly inner-sphere mechanisms. The observation[12] that $FeCl_{aq}^{2+}$ is formed as a primary product in the oxidation of iron(II) by $CoCl_{aq}^{2+}$ offers mild support for this conclusion. However, a comparison of activation entropies[27] for the $CoOH_{aq}^{2+}$

---

[23] See ref 5 for details of the calculation of $\Delta G^\circ{}_{estd}$ for these reactions.

[24] These data were obtained in 3.0 *M* perchloric acid at 25.0° and ionic strength 3.0 *M*. We have assumed that the rate constants reported[25] are identical with the rate constant for Co_{aq}^{3+} + reductant → products, since the rates of these and other similar reactions are not greatly affected by changes of acidity.[25]

[25] R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964), and references therein.

[26] (a) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964); (b) N. Sutin, *ibid.*, **17**, 119 (1966).

[27] The activation enthalpies and entropies of reaction 8 may be roughly estimated by subtraction of the enthalpy and entropy of acid dissociation, eq 7, from the composite measured values. These are ΔH = 10 ± 2 kcal mol^{-1} and ΔS_h = 22 ± 8 cal deg^{-1} mol^{-1} at 25° and ionic strength 1 *M*.[5]

reactions shows that, except in the reaction with Co_{aq}^{2+}, the apparent activation entropies are more negative for $CoOH_{aq}^{2+}$ than for Co_{aq}^{3+}; this is counter to the effect anticipated from increased entropy in the transition state due to the dissociation of a water molecule on formation of the bridge[26,28] and it may be that the mechanisms of these reactions of $CoOH_{aq}^{2+}$ have substantial SN2 character.[29] It is unfortunate that the relatively large uncertainty in the estimated[5,27] entropy of acid dissociation (eq 6) somewhat reduces the usefulness of this criterion[28] in cases involving aquocobalt(III) as a reactant, especially at high ionic strengths.

A plot of $\Delta G_{-1}^{\ddagger}$ *vs.* ΔG°_{estd} for the reactions of $CoOH_{aq}^{2+}$ with $0 \lesssim -\Delta G^\circ_{estd} \lesssim 20$ kcal mol^{-1} is also approximately linear with a slope of $\sim$0.23. This average slope may be accounted for in the same general terms as were used above to interpret the corresponding deviations in the Co_{aq}^{3+} reactions. We note, however, that the reaction between $CoOH_{aq}^{2+}$ and Fe_{aq}^{2+} is slower (by about two orders of magnitude) than would be predicted on the basis of the free energy changes for the other reactions. This behavior is similar to that noted above in the corresponding reaction with Co_{aq}^{3+}. The observation of anomalously slow reactions with iron(II) points to the appearance of a new rate-determining step in the activation process as the overall free energy change increases through the series.[9a,28,30] It seems likely that precursor complex formation[9a,31] coupled with conversion of the $Co_{aq}^{3+}(t_{2g}^{6})$[5,25] to some high-spin form accounts for this insensitivity of rate to an increasing driving force for electron transfer. It would be of considerable interest to test this hypothesis in other cobalt(III) reactions involving comparatively large overall free energy changes.

The arguments presented above for reactions in general do not, of course, give any detailed information concerning the electronic and other changes accompanying the transfer of Co_{aq}^{3+} from the ground state to a configuration appropriate for electron transfer. However, any high-spin form of cobalt(III) involved in the reactions must be more strongly oxidizing than the ground-state $Co_{aq}^{3+}(t_{2g}^{6})$.[5,32,33] Available evidence[5,34] suggests that spin-multiplicity restrictions are only of minor importance in the energetics of outer-sphere reactions between cobalt complexes in which *small* overall free energy changes are involved, but the extent to which such restrictions contribute to the energetics of these reactions as a whole cannot be evaluated at the present time.

Acknowledgments.—We wish to thank Drs. R. D. Gillard, N. Sutin, and A. G. Sykes for valuable discussion.

---

[28] N. Sutin, *Electrochim. Acta*, **13**, 1175 (1968).

[29] B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967); J. H. Espenspn, *ibid.*, **9**, 1380 (1970).

[30] R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *ibid.*, **9**, 23 (1970), and references therein.

[31] (a) For recent discussions of the estimation of free energy changes in redox reactions see G. Davies, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, **92**, 1892 (1970), and ref 9a. (b) For an estimate of the equilibrium constant for precursor complex formation between $Ru(NH_3)_5H_2O_{aq}^{2+}$ and $CrCl^{2+}$ see W. G. Movius and R. G. Linck, *ibid.*, **92**, 2677 (1970).

[32] B. Warnqvist, *Inorg. Chem.*, **9**, 682 (1970).

[33] D. A. Johnson and A. G. Sharpe, *J. Chem. Soc. A*, 798 (1966).

[34] R. Farina and R. G. Wilkins, *Inorg. Chem.*, **7**, 514 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Silicon–Transition Metal Chemistry. III. An Investigation of the Reaction between Trichlorosilane and Cyclopentadienyldicarbonyliron Dimer[1]

BY W. JETZ AND W. A. G. GRAHAM*

Received July 13, 1970

The reaction of $[C_5H_5Fe(CO)_2]_2$ with Cl_3SiH in the temperature range 110–180° yields four products: $Cl_3SiFe(CO)_2C_5H_5$ (**1**), $(Cl_3Si)_2FeH(CO)C_5H_5$ (**2**), $[C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)C_5H_5]^-$ (**3**), and $[C_5H_5Fe(CO)_3]^+[FeCl_4]^-$ (**4**). The critical dependence of relative yields on temperature has been investigated. Compound **2** is an acid in acetonitrile ($pK_a \simeq 2.6$) and is therefore a stronger acid in that solvent than the common mineral acids except perchloric. Compound **3** contains the anion of **2**, which has also been isolated as its tetraphenylarsonium salt. Methylcyclopentadienyl derivatives of **1**–**4** have also been prepared.

Introduction

There are innumerable cases in chemistry where the same reactants yield different products at different reaction conditions. Thus, the reaction between iron pentacarbonyl and trichlorosilane under ultraviolet irradiation below room temperature yields $Cl_3SiFeH(CO)_4$,[2] while heating these reagents in a sealed tube affords $(Cl_3Si)_2Fe(CO)_4$ at about 140° and $[Cl_2SiFe(CO)_4]_2$ above 160°.[3]

The reaction described in this paper yields four isolable products in amounts which are critically dependent upon reaction times and temperatures. Since these products were novel and inaccessable at the time by any other route, an extensive study of the reaction and the products was carried out.

---

[1] Part II: W. Jetz and W. A. G. Graham, *Inorg. Chem.*, in press.

[2] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969); *Inorg. Chem.*, **10**, 4 (1971).

[3] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967); a full paper will shortly be submitted.