Chromium(II) and Vanadium(II) Reductions of Hexa-aquocobalt(III) in Aqueous Perchlorate Media

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A full kinetic study has been made of the reaction of Cr^{2+} with hexa-aquocobalt(III), $[H^+] = 0{\cdot}10$—$3{\cdot}0$M, $\mu = 3{\cdot}0$M ($LiClO_4$). The rate law is of the form $-d[Co^{III}]/dt = (k_1 + k_2[H^+]^{-1})[Cr^{2+}][Co^{III}]$ and at 25 °C: $k_1 = 1{\cdot}25 \times 10^4$ l mol^{-1} s^{-1}, $\Delta H_1^{\ddagger} = 9{\cdot}5 \pm 0{\cdot}4$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = -7{\cdot}8 \pm 1{\cdot}5$ e.u.; $k_2 = 6{\cdot}59 \times 10^3$ s^{-1}, $\Delta H_2^{\ddagger} = 12{\cdot}7 \pm 0{\cdot}6$ kcal mol^{-1}, $\Delta S_2^{\ddagger} = 1{\cdot}7 \pm 2{\cdot}0$ e.u. Chloride ions catalyse the reaction and the products $CrCl^{2+}$ and Cr^{3+} were determined quantitatively after ion-exchange separation. The formation of $CoCl^{2+}$ proceeds relatively slowly and it was possible to identify two chloride-dependent terms, $k_3[Cr^{2+}][CoCl^{2+}]$ and $k_4[Cr^{2+}][Co^{3+}][Cl^-]$.

The reaction of V^{2+} with hexa-aquocobalt(III) was too fast to study directly. Competition studies indicated a rate constant k_V *ca.* $8{\cdot}8 \times 10^5$ l mol^{-1} s^{-1} at 25 °C and $\mu = 3{\cdot}0$M ($HClO_4$).

VARIOUS aspects of the solution chemistry of hexa-aquocobalt(III) [hereafter cobalt(III)] have been considered in a recent review [1] and much information is available for redox processes in which cobalt(III) is the oxidant.[2,3] In a recent study,[4] the reactions with manganese(II) and iron(II) have been re-investigated with ionic strength $\mu = 3{\cdot}0$M ($LiClO_4$) and $\mu = 3{\cdot}0$M ($NaClO_4$). Despite the extensive information available no studies have yet been made of the chromium(II) and vanadium(II) reductions of cobalt(III). Both reactions have very favourable free-energy changes, and the differences in standard reduction potentials for the relevant couples are 2·25 V (Co^{2+}/Co^{3+} and Cr^{2+}/Cr^{3+}) [5] and 2·10 V (Co^{2+}/Co^{3+} and V^{2+}/V^{3+}).[5] Studies on both these reactions are now reported.

RESULTS

Stoicheiometry.—Preliminary experiments confirmed that both reactions are rapid and that the stopped-flow technique was required. The initial products of the oxidations are chromium(III) and vanadium(III) respectively. Subsequent oxidations of the chromium(III) to chromium(VI),[6] and vanadium(III) to vanadium(IV) [7] are slow. Since the concentration of reductant used was always in excess of that of the oxidant, the reactions were assumed to be as in equations (1) and (2) respectively. Kinetic data are consistent with 1 : 1 stoicheiometries.

$$Cr^{II} + Co^{III} \longrightarrow Cr^{III} + Co^{II} \tag{1}$$

$$V^{II} + Co^{III} \longrightarrow V^{III} + Co^{II} \tag{2}$$

The Reaction with Chromium(II).—Second-order reaction conditions were used and the decrease in absorbance with time monitored at the 605 nm peak position for cobalt(III). At this wavelength cobalt(III) has an absorption coefficient $\varepsilon = 35{\cdot}3$ l mol^{-1} cm^{-1} [1] and $\Delta\varepsilon$ for the reaction is 26·9 l mol^{-1} cm^{-1}. A Durrum–Gibson stopped-flow spectrophotometer (light path $l = 1{\cdot}92$ cm) was used. Plots of log $\{1 + ([Cr^{II}]_0 - [Co^{III}]_0)(\Delta\varepsilon l[\Delta OD]^{-1})\}$ against time, where $[Cr^{II}]_0$ and $[Co^{III}]_0$ are the initial concentrations of chromium(II) and cobalt(III) respectively, and ΔOD is the change in absorbance, were generally linear to at least 80% reaction. At constant $[H^+]$, k_{obs}, evaluated from the gradients, $k_{obs}([Cr^{II}]_0 - [Co^{III}]_0)/2{\cdot}303$, was shown to be independent of initial reactant concentrations. The rate law is therefore as in (3).

$$-d[Co^{III}]/dt = k_{obs}[Cr^{II}][Co^{III}] \tag{3}$$

When the hydrogen-ion concentration was varied over the range $[H^+] = 0{\cdot}105$—$3{\cdot}0$M, k_{obs} gave a good fit to (4).

$$k_{obs} = k_1 + k_2[H^+]^{-1} \tag{4}$$

Rate constants, k_{obs}, at temperatures in the range 3·8—25 °C are listed in Table 1, and the hydrogen-ion dependence is illustrated in Figure 1. The lines which are drawn are as

TABLE 1

Kinetic data for the chromium(II) reduction of cobalt(III), $\mu = 3{\cdot}0$M ($LiClO_4$).[a] Figures in parentheses indicate number of runs averaged

Temp. (°C)	$[H^+]$ (M)	$10^3[Cr^{II}]$ (M)	$10^3[Co^{III}]$ (M)	$10^{-3}k_{obs}$ (l mol^{-1} s^{-1})
3·8 [b]	3·00	10·65	3·01	3·46(4)
	3·00	3·82	3·01	3·30(2)
	3·00	6·95	3·01	3·47(2)
	3·00	1·70	1·56	3·37(2)
	3·00	1·07	1·56	3·54(2)
	2·00	19·7	6·05	3·84(1)
	1·00	10·5	3·03	4·23(2)
	0·67	10·5	3·04	5·34(2)
	0·50	10·3	3·03	6·06(2)
	0·30	7·40	2·05	7·15(2)
	0·20	4·72	1·29	9·80(2)
	0·105	2·49	0·65	14·0(2)
10·0	3·00	22·7	9·65	5·8(2)
	1·54	15·9	9·65	6·46(2)
	0·90	6·65	3·70	7·40(2)
	0·61	6·65	3·70	8·25(2)
	0·41	4·67	2·33	9·84(2)
17·0	3·00	7·83	5·82	9·25(2)
	1·52	8·09	5·82	10·6(2)
	0·90	3·27	2·19	12·7(2)
	0·61	3·63	2·19	13·8(3)
	0·41	2·49	1·35	17·7(2)
25·0	3·00	7·78	4·92	14·5(2)
	1·54	8·40	4·92	16·9(2)
	0·90	3·63	2·22	19·5(2)
	0·61	3·63	2·22	22·7(2)

[a] $\mu = 3{\cdot}00 \pm 0{\cdot}04$M. [b] Temp. = 3·8° ± 0·1 °C.

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[1] G. Davies and B. Warnqvist, *Co-ordination Chem. Rev.*, 1970, **5**, 349.

[2] R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, 1964, **3**, 1091.

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

[4] G. Davies, *Inorg. Chem.*, 1971, **10**, 1155.

[5] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice-Hall Inc., New York, 1952.

[6] J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1964, **60**, 119.

[7] D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 1960, 31.

computed using a non-linear least-squares program,[8] with a weighting factor of unity. Values of k_1 and k_2 at the different temperatures are listed in Table 2 and activation parameters computed using the same procedure are in Table 5.

The Effect of Chloride.—The reaction between chromium(II) and cobalt(III) is catalysed by chloride ions. We found it difficult to obtain precise rate constants using the stopped-flow technique, because of the redox reaction between chloride ions and cobalt(III),[9,10] and it was decided to determine quantitatively the chromium(III) products after separation using an ion-exchange procedure. Reactant solutions were 2·9M in perchloric acid (μ = 3·0M), the temperature 3° ± 1 °C, and chloride concentrations in the range 0·005—0·042M. The reaction was investigated in two different ways, with chloride ions (i) solely in the chromium(II) solution, and (ii) in both the chromium(II) and cobalt(III) solutions (equal concentrations in both). The concentration of chromium(II) was varied from 6·0 × 10^{-3} to 11·4 × 10^{-3}M, and cobalt(III) from 9·1 × 10^{-3} to 20·5 × 10^{-3}M. Cobalt(III) solutions were always in excess (from 1·5 : 1 to 3 : 1), thus ensuring complete consumption of chromium(II). With an excess of chromium(II) aerial oxidation of the residual chromium(II) occurred, and although such a process gives predominantly the chromium(III) dimer, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$,[11] we found non-reproducible amounts of monomeric chromium(III) were also produced. Inner-sphere complexing of chloride to cobalt(III) [9,10] is very slow compared to the chromium(II) reduction and can be ignored in (i). The contact time of the chloride and cobalt(III) in (ii) was between 15 and 40 s (depending on the concentration of chloride used) before the chromium(II) solution was introduced. This time interval is sufficient for the formation of monochlorocobalt(III), whilst the subsequent reduction of the cobalt(III) by the inner-sphere chloride is negligible.

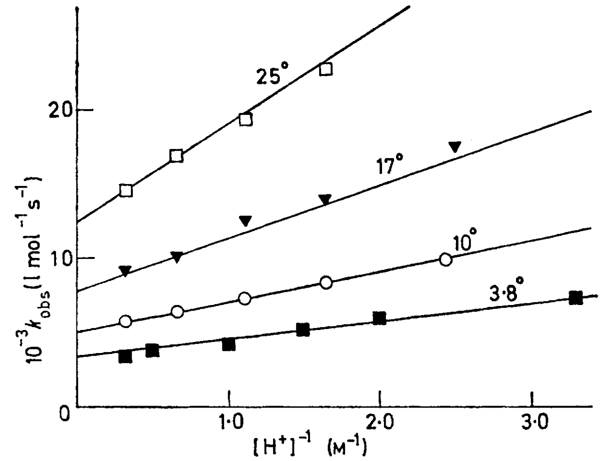

FIGURE 1 The inverse hydrogen-ion dependence of k_{obs} for the chromium(II) reduction of cobalt(III), μ = 3·0M ($LiClO_4$)

TABLE 2

The variation of k_1 and k_2 [(equation (4)] with temperature for the reaction of chromium(II) with cobalt(III), μ = 3·0M ($LiClO_4$)

Temp. (°C)	$10^{-3}k_1$ (l mol^{-1} s^{-1})	$10^{-3}k_2$ (s^{-1})
3·8	3·39 ± 0·12	1·18 ± 0·04
10·0	5·06 ± 0·06	2·00 ± 0·04
17·0	7·81 ± 0·36	3·54 ± 0·25
25·0	12·5 ± 0·18	6·59 ± 0·17

TABLE 3

The dependence of the ratio of products, $[CrCl^{2+}]/[Cr^{3+}]$, on the chloride-ion concentration, where in (i) the inner-sphere complex $CoCl^{2+}$ is not a reactant. Temp. 3° ± 1 °C, μ = 3·0M ($HClO_4$)

Run	$[Cl^-]$ (M)	$10^3[Cr^{II}]$ (M)	$10^3[Co^{III}]$ (M)	$[CrCl^{2+}]/[Cr^{3+}]$ [a]	Correspondence [b] (%)
(i) Chloride initially contained in chromium(II) reactant solution [c]					
A	0·0100	11·8	20·5	0·69	93·0
B	0·0120	6·0	18·7	0·72	100·0
C	0·0150	10·5	16·0	1·19	94·3
D	0·0215	10·5	20·0	1·94	96·3
E	0·0310	11·4	19·6	2·52	97·1
F	0·0420	6·5	9·06	2·51	99·0
G	0·0420 [d]	7·0	9·05	3·16	98·9
(ii) Chloride same concentration in both reactant solutions [c]					
H	0·0050	6·5	9·8	0·34	100·7
I	0·0107	6·9	13·0	0·95	94·0
J	0·0120	6·0	18·7	1·28	101·0
K	0·0215	6·8	12·8	2·03	97·5
L	0·0323	6·7	12·5	2·88	101·0
M	0·0420	6·5	9·1	3·77	100·2

[a] The $CrCl^{2+}$ and Cr^{3+} were determined separately after ion-exchange separation. [b] Ratio of total chromium(III) recovered to chromium(II) consumed. [c] *ca.* 2 ml Of chromium(II) solution syringed into 18 ml of cobalt(III). [d] 19·3 ml Of cobalt(III) solution syringed into 0·7 ml of chromium(II).

Details of the ion-exchange procedure are given in the Experimental section, and the results of the product analysis are given in Table 3. The following points should be noted. First, $CrCl^{2+}$ is produced in (i) even though no $CoCl^{2+}$ reactant is present. Second, for identical experiments (B and J, and F and M in Table 3), more $CrCl^{2+}$ is produced when $CoCl^{2+}$ is present. It is concluded that there are at least two chloride-dependent terms in the rate law (5),

$$\text{Rate} = k_1[Cr^{2+}][Co^{3+}] + k_2[Cr^{2+}][Co^{3+}][H^+]^{-1} + k_3[Cr^{2+}][CoCl^{2+}] + k_4[Cr^{2+}][Co^{3+}][Cl^-] \quad (5)$$

where k_1, k_2, and k_4 contribute in (i), and all four terms contribute in (ii). For k_4, it is not specified which reactant brings the chloride into the activated complex, only that it is not introduced in the form of the inner-sphere complex $CoCl^{2+}$. It is possible to evaluate k_4 from the ratio of chromium(III) products [equation (6)]. Figure 2 is a plot

$$[Cr^{3+}]/[CrCl^{2+}] = (k_1 + k_2[H^+]^{-1})/k_4[Cl^-] \quad (6)$$

of $[Cr^{3+}]/[CrCl^{2+}]$ against $[Cl^-]^{-1}$, the gradient of which was determined by an unweighted least-squares treatment, and since $k_1 + k_2[H^+]^{-1} = 3{\cdot}4 \times 10^3$ l mol^{-1} s^{-1} at 3 °C and $[H^+]$ = 2·9M, it is concluded that $k_4 = (2{\cdot}45 \pm 0{\cdot}35) \times 10^5$ l^2 mol^{-2} s^{-1} at 3° ± 1 °C and μ = 3·0M ($HClO_4$).

Since the hydrogen-ion concentration was not varied we

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[8] Los Alamos Report LA 2367 (1959) and addenda by R. H. Moore and R. K. Zeigler. We are grateful to Dr. T. W. Newton for sending us details of this program.

[9] T. J. Connocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1.

[10] A. McAuley, M. N. Malik, and J. Hill, *J. Chem. Soc.* (*A*), 1970, 2461.

[11] M. G. Thompson, Ph.D. Thesis, University of California, Berkeley, 1964, UCRC 11410.

are not able to comment as to whether other chloride-dependent paths exhibiting an $[H^+]^{-1}$ dependence are effective.[12]

The Reaction with Vanadium(II).—With reactant concentrations $[V^{II}] = 4{\cdot}5 \times 10^{-3}$M, $[Co^{III}] = 2 \times 10^{-3}$M, $[H^+] = 3{\cdot}0$M, and the temperature 4 °C, absorbance changes at 605 nm were too fast to follow. We conclude that $k_V > 1{\cdot}2 \times 10^5$ l mol^{-1} s^{-1}. It was therefore decided to carry out experiments in which chromium(II) and vanadium(II) were allowed to compete for the cobalt(III), the chromium(II) being in *ca.* 30-fold excess of the vanadium(II). Since so many different ions were present it was difficult to determine accurately the relative amounts of chromium(III) and vanadium(III) produced. Instead we decided to monitor the subsequent absorbance change at 575 nm which corresponds to the much slower chromium(II) reduction of vanadium(III).[13] From the theoretical absorbance change, $\Delta\varepsilon$, of 10·3 l mol^{-1} cm^{-1}, we were able to estimate the amount of vanadium(III) produced. A typical run solution at 25° contained $[V^{II}] = 3{\cdot}22 \times 10^{-3}$M, $[Cr^{II}] = 9{\cdot}5 \times 10^{-2}$M, $[Co^{III}] = 9{\cdot}0 \times 10^{-4}$M, and $[H^+] = 2{\cdot}96$M ($\mu = 3{\cdot}0$M). A 1·5% transmittance change was observed over 75 s at 575 nm. This corresponds to a change in absorbance of 0·012 and it is estimated therefore that 66% of the cobalt(III) is reduced by vanadium(II). Since under these conditions k_{obs} for chromium(II) is $1{\cdot}48 \times 10^4$ l mol^{-1} s^{-1}, it follows that at 25° k_V is *ca.* $8{\cdot}8 \times 10^5$ l mol^{-1} s^{-1}.

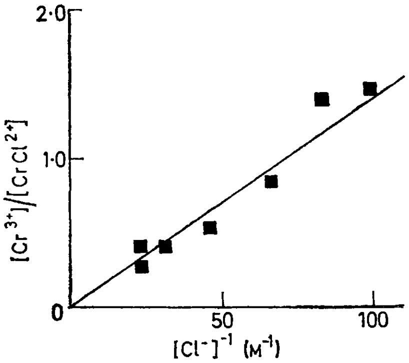

FIGURE 2 The chloride catalysis of the reaction of chromium(II) with cobalt(III) at 3° ± 1 °C, $\mu = 3{\cdot}0$M ($HClO_4$). The ratio of $[Cr^{3+}]/[CrCl^{2+}]$ was determined after ion-exchange separation of the two components

DISCUSSION

Rate constants for substitution reactions of vanadium(II) and cobalt(III) hexa-aquo ions in which a water ligand is replaced are typically 10—100 s^{-1} [14] and *ca.* 10 s^{-1} [3,15] respectively at 25°. It can therefore be concluded that electron transfer between V^{2+} and Co^{3+} ($k_V = ca.\ 8{\cdot}8 \times 10^5$ l mol^{-1} s^{-1} at 25°) is occurring by an outer-sphere mechanism. The rate constant, k_1, for the reaction of Cr^{2+} with Co^{3+} is $1{\cdot}25 \times 10^4$ l mol^{-1} s^{-1} at 25°, and the ratio of rate constants for the Cr^{2+} and V^{2+} reactions is *ca.* 0·017. This is in agreement with values of *ca.* 0·02 which Toppen and Linck [16] have noted for Cr^{2+} and V^{2+} outer-sphere reductions of other oxidants. We therefore assign an outer-sphere mechanism to k_1. The term k_2 probably corresponds to an inner-sphere reaction. We leave open the question as to whether the activated complex is formed by the reaction of Cr^{2+} and $CoOH^{2+}$, or by loss of a proton concomitant with, or immediately following, formation of the binuclear species $[(H_2O)_5CrH_2OCo(H_2O)_5]^{5+}$. If the former, assuming an acid dissociation constant of $(2 \pm 1) \times 10^{-3}$ mol l^{-1} for Co^{3+}, the rate constant for the reaction of Cr^{2+} with $CoOH^{2+}$ at 25° is $3{\cdot}3 \times 10^6$ l mol^{-1} s^{-1}.

Experiments in the presence of chloride indicate at least two chloride-dependent paths for electron transfer, both of which give $CrCl^{2+}$ as the primary product. The first path (k_3) is undoubtedly inner-sphere with Cr^{2+} and $CoCl^{2+}$ the reactants and chloride acting as a bridging ligand. The second (k_4) is probably outer-sphere since the chloride cannot in this case form a bridge by an inner-sphere mechanism, and H_2O is an unlikely bridging ligand. The chloride may be brought into the activated complex by the chromium(II) as $CrCl^+$, or alternatively by the cobalt(III) in the form of an outer-sphere complex $Co(H_2O)_6{}^{3+},Cl^-$. The activated complex probably closely resembles that for k_1, where the additional presence of chloride in the chromium(II) co-ordination sphere is beneficial to reaction. The occurrence of k_3 and k_4 terms has been observed previously for the reactions of chromium(II) with iron(III),[17] and europium(II) with iron(III).[18] A comparison of reactivity patterns is made in Table 4. The k_4 path is seen to make a more effective contribution in the present study.

TABLE 4

Comparison of kinetic data with other systems in which k_1, k_2, k_3, and k_4 terms [as defined in equation (5)] are observed. Temp. 25 °C, except where stated

Rate constant	$Cr^{2+} + Fe^{3+}$ [a]	$Cr^{2+} + Co^{3+}$ [b]	$Eu^{2+} + Fe^{3+}$ [c]
k_1(l mol^{-1} s^{-1})	$2{\cdot}3 \times 10^3$	$12{\cdot}5 \times 10^3$	$4{\cdot}77 \times 10^3$
k_2(s^{-1})	$5{\cdot}3 \times 10^3$	$6{\cdot}59 \times 10^3$	$13{\cdot}4 \times 10^3$
k_3(l mol^{-1} s^{-1})	2×10^7		$3{\cdot}4 \times 10^6$
k_4(l^2 mol^{-2} s^{-1})	2×10^4	$2{\cdot}45 \times 10^5$ [d]	$1{\cdot}22 \times 10^4$

[a] Ref. 17; $\mu = 1{\cdot}0$M ($NaClO_4$). [b] This work; $\mu = 3{\cdot}0$M ($LiClO_4$). [c] Ref. 18; $\mu = 1{\cdot}0$M ($LiClO_4$). [d] Temp. = 3°.

Rate constants and activation parameters for the reduction of cobalt(III) by 2+ ions in the first transition series are listed in Table 5. The most striking feature is that values of k_1 and k_2 respectively fall within comparatively small ranges. The reactions of Cr^{2+} and V^{2+} reported here have not been studied previously, presumably because higher rates were expected. The very favourable free-energy changes for both reactions have been noted above. It is possible that spin-multiplicity restrictions apply to reactions of cobalt(III) since not only does the t_{2g}^6 cobalt(III) ion have to accept an electron

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[12] For examples see: A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1967, 1504; E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 1967, **6**, 428.

[13] J. H. Espenson, *Inorg. Chem.*, 1965, **4**, 1025; A. Adin and A. G. Sykes, *J. Chem. Soc.* (*A*), 1968, 351.

[14] M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, 1969, **51**, 289.

[15] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 1169.

[16] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

[17] G. Dulz and N. Sutin, *J. Amer. Chem. Soc.*, 1964, **86**, 829.

[18] D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, 1968, **90**, 2272.

from the reductant, but the rearrangement of other d electrons is required to give high-spin $t_{2g}^5e_g^2$ cobalt(II). It has been suggested[19] that the reaction proceeds with the initial excitation (7). If this is indeed the case then

$$\mathrm{Co^{III}}(t_{2g}^6) \rightleftharpoons \mathrm{Co^{III}}(t_{2g}^5e_g^1) \qquad (7)$$

the equilibration must be more rapid than the Cr^{2+} reduction since a first-order dependence on the reductant is apparent. Current estimates[20] of the energy required for the excitation of cobalt(III) in (7) are in the range 15—20 kcal mol^{-1}, which seems high if this process is to occur prior to electron transfer. The application of the

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad (8)$$

Marcus equation (8)[21] has been considered, where k_{12} and K_{12} are rate and equilibrium constants respectively for the redox reaction, k_{11} and k_{22} are rate constants for the related exchange reactions, and f is as defined in (9) (Z is the collision frequency for uncharged particles).

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \qquad (9)$$

Reactions of cobalt(III) invariably give theoretical rate constants, k_{12}, which are up to five orders of magnitude greater than those determined experimentally.[21-24] The reaction of high-spin $\mathrm{Co(bipyridyl)_3}^{2+}$ with low-spin $\mathrm{Co(terpyridyl)_2}^{3+}$ has been found to conform to (8), but in this case the $\mathrm{Co(terpyridyl)_2}^{2+}$ product is low-spin.[23] The rate constant for the V^{2+} reduction of $\mathrm{Co(bipyridyl)_3}^{3+}$ is also in satisfactory agreement with that obtained from (8).[25] In all these estimates of k_{12} the work terms have been considered negligible.

TABLE 5

Summary of rate constants and activation parameters for cobalt(III) oxidations. k_1 And k_2 are as defined in equation (4) and are at 25 °C, μ = 3·0M ($LiClO_4$), except where stated

Reductant	k_1 (l mol^{-1} s^{-1})	k_2 (s^{-1})	$\Delta H_1^‡$ (kcal mol^{-1})	$\Delta S_1^‡$ (e.u.)	$\Delta H_2^‡$ (kcal mol^{-1})	$\Delta S_2^‡$ (e.u.)	Reference
Co^{2+} [a]	3·3	1·0	10·3	−21	18·0	−1	*b*
Mn^{2+}	1·27 × 10^2	46·5	11·7	−12·5	12·3	−7·7	4
$\mathrm{Fe(5\text{-}NO_2\text{-}phen)_3}^{2+}$	1·49 × 10^3						2
$\mathrm{Fe(5\text{-}Cl\text{-}phen)_3}^{2+}$ [c]	5·02 × 10^3						2
Hydroquinone	2·2 × 10^3	1·28 × 10^3	18·2	+18	18·6	+17	3
$\mathrm{Fe(phen)_3}^{2+}$ [c]	1·4 × 10^4						2
$\mathrm{Fe(5\text{-}Me\text{-}phen)_3}^{2+}$ [c]	1·5 × 10^4						2
Fe^{2+}	2·48 × 10^2	2·75 × 10^2	15·7	+7·1	13·8	+1	4
V^{2+} [d]	*ca.* 8·8 × 10^5						This work
Cr^{2+}	1·25 × 10^4	6·59 × 10^3	9·5	−7·8	12·7	+1·7	This work

[a] μ = 0·5M ($LiClO_4$). Activation parameters with μ = 1·0M ($NaClO_4$) are $\Delta H_1^‡$ = 11·8 kcal mol^{-1} and $\Delta S_1^‡$ = −17 e.u. [b] H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 1668. [c] μ = 3·0M ($HClO_4$). Activation parameters not determined; k_2 not observed. [d] The rate constant was determined at μ = 3·0M ($HClO_4$) and is assumed to correspond to k_1. No information is available as to whether k_2 makes any contribution.

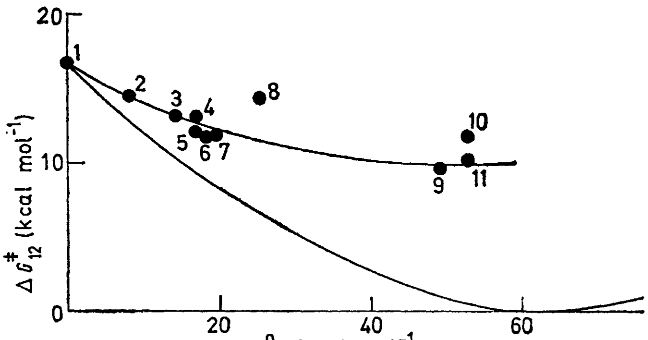

FIGURE 3 Plot of $\Delta G_{12}^‡$ against ΔG^0_{12} at 25 °C and μ 3·0M, for reactions of Co^{3+} listed in Table 5. The reductants are: 1, Co^{2+}; 2, Mn^{2+}; 3, tris(5-nitro-1,10-phenanthroline)iron(II); 4, hydroquinone; 5, tris(5-chloro-1,10-phenanthroline)iron(II); 6, tris(1,10-phenanthroline)iron(II); 7, tris(5-methyl-1,10-phenanthroline)iron(II); 8, Fe^{2+}; 9, V^{2+}; 10, Cr^{2+}; 11, Eu^{2+} (the latter is an estimated value, see text). The lower curve is that predicted by the Marcus equation (10) but neglecting all work terms

Figure 3 is a plot of $\Delta G^‡_{12}$ (corresponding to rate constants k_1 in Table 5) against ΔG^0_{12} (calculated from standard reduction potentials[5,26]) for a number of Co^{3+} redox reactions. The relevant expression from Marcus theory[21,24] is that of (10), where $\Delta G^* = \Delta G^‡ - w$ and

$$\Delta G^*_{12} = \tfrac{1}{2}(\Delta G^*_{11} + \Delta G^*_{22}) + \tfrac{1}{2}(\Delta G^0_{12} + w_{21} - w_{12}) + (\Delta G^0_{12} + w_{21} - w_{12})^2/8(\Delta G^*_{11} + \Delta G^*_{22}) \qquad (10)$$

$k = Ze^{-\Delta G^‡/RT}$. This takes into account the work, w, required to bring the reactants from an infinite separation to the positions they occupy in the activated complex (w_{12}, w_{21} referring to the reactants and products of the redox reaction). The quantities ΔG^*_{12}, ΔG^*_{11}, and ΔG^*_{22} are the free energies required to reorganize the inner- and outer-co-ordination shells of the reactants in the redox and exchange reactions respectively, and $\Delta G^‡_{11}$, $\Delta G^‡_{22}$ are the experimentally observed free energies of activation for the latter. As ΔG^0_{12}, the overall free-energy change, becomes more favourable the third term on the right-hand side of (10) becomes more

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[26] Standard reduction potentials for substituted $\mathrm{Fe(phen)_3}^{3+}$ complexes are taken from G. F. Smith and W. M. Banick, *Talanta*, 1959, **2**, 348.

effective and experimental points are therefore expected to move away from a line of gradient 0·5. The lower curve in Figure 3 indicates the sort of behaviour to be expected for $\Delta G^{\ddagger}_{12}$ when no allowance for the work terms is made, *i.e.*, w_{21} and w_{12} are both zero and $\Delta G^{*}_{11} = \Delta G^{\ddagger}_{11}$, *etc.* A numerical value of 16·7 kcal mol^{-1} has been assumed to apply * to both $\Delta G^{\ddagger}_{11}$ and $\Delta G^{\ddagger}_{22}$.

A further derivation by Marcus[29] is equation (11),

$$\alpha \simeq (1 + \Delta G^{0}_{12}/4\Delta G^{\ddagger}_{0})/2 \qquad (11)$$

where $\alpha = d(\Delta G^{\ddagger}_{12})/d(\Delta G^{0}_{12})$ and $\Delta G^{\ddagger}_{0}$ is the activation free energy (for the Co^{2+}/Co^{3+} exchange, 16·7 kcal mol^{-1}). From this it can be deduced that a minimum ($\alpha = 0$) should occur in Figure 3 with ΔG^{0}_{12} *ca.* −67 kcal mol^{-1}, and an inversion in redox behaviour is therefore to be expected in this region. We feel the upper curve in Figure 3 is significant because it illustrates for the first time the approach of $\Delta G^{\ddagger}_{12}$ to a minimum. This behaviour is possible, as Sutin has pointed out,[30] because the intersection of two potential-energy surfaces for the reactants and products respectively can occur at the minimum of the curve for the reactants (see A and C in Figure 4). The potential-energy surfaces represent the intrinsic barriers to electron transfer, and other work terms, *e.g.* coulombic repulsion, solvent effects, *etc.*, will also contribute to the overall barrier, thus ensuring a non-zero value of $\Delta G^{\ddagger}_{12}$ even at the minimum. Decreasing ΔG^{0}_{12} still further can cause the intersection (curve D) to start rising on the left-hand side of the curve for the reactants with a corresponding increase in $\Delta G^{\ddagger}_{12}$.

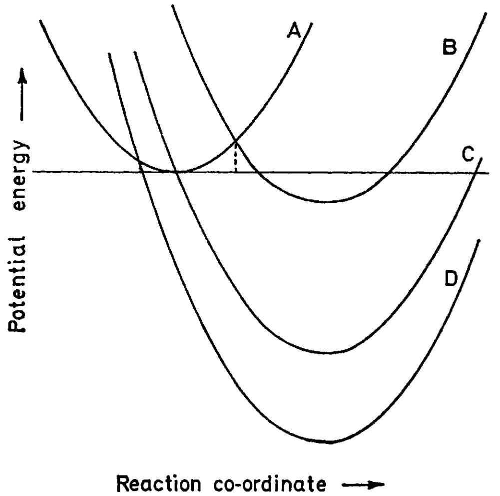

FIGURE 4 The intersection of parabolas representing potential-energy surfaces. Curve A is for the sum of the potential energies of the reactants including the common oxidant cobalt(III) and B, C, and D are for the sum of the potential energies of the products and correspond to reactions in which ΔG^{0}_{12} becomes more favourable. More negative ΔG^{0}_{12} values correspond to reactions of Co^{3+} with reductants of increasing strength. The activation-energy requirements are seen to decrease and then increase again in going from B to C to D

Not only is a scatter of points to be expected in Figure 3 because equation (10) possesses variables which change with the nature of the reductant, *viz.* ΔG^{*}_{22}, w_{21}, and w_{12}, but the position of the minimum is also likely to be ill-defined. We have chosen only to indicate the downward trend in Figure 3 and not accept the Cr^{2+} point as being indicative of an upward trend. Our reasons for this are that $\Delta G^{\ddagger}_{22}$ for the exchange of Cr^{2+} with Cr^{3+} is particularly unfavourable, and that, as pointed out previously, outer-sphere reactions of V^{2+} are invariably about 50 times faster than those of Cr^{2+} even with much weaker oxidants such as $Co(NH_3)_6^{3+}$.[16] Also Eu^{2+} is as strong an oxidant as Cr^{2+} and we predict a rate constant of *ca.* 3×10^{5} l mol^{-1} s^{-1} at 25° for the reaction of Eu^{2+} with Co^{3+} based on reactivity patterns observed for outer sphere V^{2+}, Cr^{2+}, and Eu^{2+} reactions.[31] The question which remains to be answered is whether the work terms, *w*, can in this instance account for the difference between the theoretical and experimental curves in Figure 3.

EXPERIMENTAL

Solutions of cobalt(III) perchlorate in 3M perchloric acid were prepared electrolytically by the following procedure. Cobalt(II) perchlorate, $Co(ClO_4)_2,6H_2O$ (G. F. Smith, Chemical Co.), was dissolved in 3·0M-$HClO_4$ to give a *ca.* 2×10^{-2}M solution, and was oxidized at a platinum gauze electrode, current $\not>$ 20 mA/cm^{2}.[1] The cathode compartment contained 3·0M-$HClO_4$ and a mercury-pool electrode was used. The temperature was maintained at 0 °C throughout the electrolysis (15—17 h) and conversion to cobalt(III) was normally *ca.* 70%, sometimes 85%. The stock solution was pipetted into a pre-cooled flask and deoxygenated for 1 h using a stream of pre-cooled argon *via* a Teflon needle. The cobalt(III) solution was stored at 0° at all times and argon gas was bubbled through it periodically (*ca.* every 30 min). Fresh solutions were prepared each day. Solutions of chromium(II) and vanadium(II) were prepared as described in previous papers from these laboratories.

The ionic strength of solutions for kinetic runs was adjusted to $\mu = 3·0$M using $LiClO_4$. A Durrum–Gibson stopped-flow spectrophotometer was used. Stock solutions of cobalt(III) were diluted at 0° after deoxygenation, and were thermostatted at the required temperature for 10—20 min in the drive syringes. At 25°, the highest temperature used, cobalt(III) solutions in 3·0M-$HClO_4$ were stable (<3% decomposition) for at least 8 h. The cobalt(III) solution was standardized spectrophotometrically immediately after each run, $\varepsilon = 35·3$ l mol^{-1} cm^{-1} at 605 nm.

The ion-exchange procedure for the separation of the products Co^{2+}, $CrCl^{2+}$, and Cr^{3+} was as follows. The reaction mixture was first exchanged onto a column of Dowex

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* Values of $\Delta G^{\ddagger}_{22}$ for the exchange reactions of $Fe(phen)_3^{2+}$ with $Fe(phen)_3^{3+}$ (<7·6 kcal mol^{-1} [27]) and Cr^{2+} with Cr^{3+} (>23·7 kcal mol^{-1} [28]) differ considerably from the assumed value and these reactions should perhaps be omitted from consideration in Figure 3. The other reactions considered have $(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22})/2$ values in the range 16·7—19·5 kcal mol^{-1}. There is a tendency for differences in $\Delta G^{\ddagger}_{22}$ to cancel out since the latter contributes to both the first and third terms on the right-hand side of equation (10). Some scatter of points is to be expected in Figure 3 and it is only the general trend that we consider here.

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[30] Ref. 24, p. 164.

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50 W-X 12 cation exchange resin at 0°. The eluant was $0{\cdot}5\text{M-NaClO}_4$–$0{\cdot}1\text{M-HClO}_4$, using half-strength solutions to elute 2+ ions, and full-strength solutions to elute 3+ ions. Three distinct bands of $CrCl^{2+}$ (green), Co^{2+} (pink), and Cr^{3+} (blue) were observed. Solutions of these ions were collected and the two chromium fractions determined by oxidation to chromium(VI) using H_2O_2 in $1{\cdot}0\text{M-NaOH}$. The solutions of chromium(VI) were then determined spectrophotometrically ($\varepsilon = 4{\cdot}82 \times 10^3$ l mol^{-1} cm^{-1} for CrO_4^{2-} at 372 nm). After elution in the above manner, no dark green band of chromium(III) dimer was observed to remain at the top of the column. The total recovery of chromium(III) was within the range 93—101% after making an allowance for small amounts of monomeric chromium(III) initially present in the chromium(II) reactant. Chromium(III) concentrations were in one case checked using a Perkin-Elmer atomic absorption spectrometer. The agreement was to within 2%.

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