Kinetics and Mechanisms of Oxidation of Reversible Organic Systems with Cobalt(III) in Acidic Perchlorate Media

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The oxidation kinetics of some quinols with cobalt(III) perchlorate have been investigated at different temperatures and acidities by means of a stopped-flow technique. The rate law is of the form $-\frac{1}{2}\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = (k_a + k_bK_h[\mathrm{H^+}]^{-1})$-$[\mathrm{Co^{III}}]$[Quinol]; the term k_a refers to $\mathrm{Co^{3+}}$(aq) and k_b to $[\mathrm{Co(OH)}]^{2+}$(aq) species. For $\mathrm{Co^{3+}}$(aq), comparison has been made with other systems in the light of the Marcus theory: a large number of reaction rates agree with an experimental correlation of the form $k = \alpha Z\exp(-\Delta G^*/RT)$, where $\alpha = 10^{-5}$—10^{-6} and $\Delta G^* = \lambda[1 + (\Delta G^\ominus/\lambda)^2]/4$, according to Marcus theory. However, the small range of values of the second-order rate constants for $[\mathrm{Co(OH)}]^{2+}$-(aq) suggests a limiting behaviour for this species.

RELATIONS between the rate constants and the corresponding free energies of redox reactions have provided insight into the mechanisms involved.[1] Only a limited set of data is available on the behaviour of redox-reversible organic systems reacting with metal-ion complexes.[2] In previous papers from this laboratory, such correlations between thermodynamic and kinetic properties have been discussed for the oxidation of catechols by $\mathrm{Mn^{III}}$,[3] $\mathrm{Co^{III}}$,[4] and hexachloroiridate(IV),[5] and of quinols by $\mathrm{Tl^{III}}$ [6] and $[\mathrm{IrCl_6}]^{2-}$.[7]

The present paper deals with the behaviour of $\mathrm{Co^{III}}$ in aqueous acidic perchlorate media and its significance in the general picture of relations between reactivities and free energies. Oxidation reactions of $\mathrm{Co^{III}}$ in this medium give experimental rates which are up to five orders of magnitude lower than those predicted by the Marcus theory, which is one of the more successful theoretical models.[1,8] The application of this model to cobalt(III) reactions must be viewed with some reservations since many of these reactions are either inner sphere or may be catalysed by $\mathrm{Co^{II}}$, in that $\mathrm{Co^{2+}}$ is always present.

EXPERIMENTAL

Reagents and Procedure.—The investigated quinols ($\mathrm{H_2L}$), 2,3,5-trimethylbenzene-1,4-diol, 2,5-dihydroxybenzoic acid (gentisic acid), 2,5-dihydroxybenzene-1,4-disulphonic acid, and 2,3-dicyanobenzene-1,4-diol, were supplied by K & K. The other reagents and procedure were as previously described.[4,9]

RESULTS

The reaction rates were first order with respect to the concentrations of reagents. The second-order rate constants, k_0, at different acidities are collected in Table 1. Increase of acidity caused the overall rate constants to decrease, as observed in the reactions of $\mathrm{Co^{III}}$ with the other organic substrates hitherto investigated.

The results agree with the following mechanism in equations (1)—(4) where $\mathrm{HL^{\bullet}}$ is the semiquinone radical and

$$\mathrm{Co^{3+}(aq)} \overset{K_h}{\rightleftharpoons} \mathrm{Co^{2+}(aq)} + \mathrm{H^+(aq)} \tag{1}$$

$$\mathrm{Co^{3+}(aq)} + \mathrm{H_2L} \xrightarrow{k_a} \mathrm{Co^{II}} + \mathrm{HL^{\bullet}} + \mathrm{H^+(aq)} \tag{2}$$

$$[\mathrm{Co(OH)}]^{2+}\mathrm{(aq)} + \mathrm{H_2L} \xrightarrow{k_b} \mathrm{Co^{II}} + \mathrm{HL^{\bullet}} \tag{3}$$

$$\mathrm{Co^{III}} + \mathrm{HL^{\bullet}} \xrightarrow{\text{fast}} \mathrm{Co^{II}} + \mathrm{L} + \mathrm{H^+(aq)} \tag{4}$$

L the corresponding 1,4-benzoquinone. Hence, we can write the rate law below, and, from plots of $k_0(1 + K_h[\mathrm{H^+}]^{-1})$ against $[\mathrm{H^+}]^{-1}$, the values of k_a and k_bK_h can be evaluated.

$$-\frac{1}{2}\frac{\mathrm{d}[\mathrm{Co^{III}}]}{\mathrm{d}t} = \frac{(k_a + k_bK_h[\mathrm{H^+}]^{-1})[\mathrm{H_2L}][\mathrm{Co^{III}}]}{1 + K_h[\mathrm{H^+}]^{-1}} = k_0[\mathrm{H_2L}][\mathrm{Co^{III}}]$$

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[1] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155; N. Sutin, *ibid.*, 1966, **17**, 119 and *Chem. in Britain*, 1972, **8**, 148; J. E. Earley, *Progr. Inorg. Chem.*, 1970, **13**, 243; A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 153; W. L. Reynolds and R. W. Lumry, ' Mechanisms of Electron Transfer,' Ronald Press, New York, 1966.

[2] R. A. Marcus, *J. Chem. Phys.*, 1957, **26**, 872; S. A. Levison and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 358; K. Reinschmiedt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, 1973, **12**, 1639.

[3] E. Pelizzetti, E. Mentasti, and G. Giraudi, *Inorg. Chim. Acta*, 1975, **15**, L1.

[4] E. Pelizzetti, E. Mentasti, and E. Pramauro, *J.C.S. Dalton*, 1976, 26.

[5] E. Mentasti, E. Pelizzetti, and C. Baiocchi, *J.C.S. Dalton*, in the press.

[6] E. Pelizzetti and E. Mentasti, *J. Inorg. Nuclear Chem.*, in the press.

[7] E. Pelizzetti, E. Mentasti, and C. Baiocchi, submitted for publication.

[8] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891 and refs. therein.

[9] E. Mentasti, E. Pelizzetti, and G. Giraudi, *J. Inorg. Nuclear Chem.*, 1976, **38**, 795.

TABLE 1

Second-order rate constants, k_0 ($dm^3\ mol^{-1}\ s^{-1}$),* for reactions of Co^{III} at different acidities, 25.0 °C, and $I = 2.0$ mol dm^{-3}

	$[HClO_4]$/mol dm^{-3}			
Compound	0.30	0.50	1.00	2.00
2,3,5-Trimethylbenzene-1,4-diol	1.5×10^4	$1.1_5 \times 10^4$	8.0×10^3	7.0×10^3
2,5-Dihydroxybenzoic acid	1.4×10^3	9.0×10^2	5.0×10^2	3.6×10^2
2,5-Dihydroxybenzene-1,4-disulphonic acid	4.0×10^3	2.5×10^3	1.35×10^3	8.0×10^2
2,3-Dicyanobenzene-1,4-diol	1.1×10^3	6.5×10^2	4.0×10^2	1.5×10^2

* The error of the rate constants is within ±5%.

TABLE 2

Kinetic parameters for oxidation reactions of Co^{III} in aqueous acidic perchlorate media at 25 °C and $I = 2.0$ mol dm^{-3}

		k_a	$\Delta H_a^{\ddagger}$ [a]	$\Delta S_a^{\ddagger}$ [a]	$E^{\ominus}$ [b]	$-\Delta G_a^{\ominus}$ [a]	$10^{-5}k_b$	$\Delta H_b^{\ddagger}$ [a]	$\Delta S_b^{\ddagger}$ [a]	
	Compound	$dm^3\ mol^{-1}\ s^{-1}$	kcal mol^{-1}	cal $K^{-1}\ mol^{-1}$	V	kcal mol^{-1}	$dm^3\ mol^{-1}\ s^{-1}$	kcal mol^{-1}	cal $K^{-1}\ mol^{-1}$	Ref.
(1)	Benzene-1,4-diol	9.3×10^2	16	4	1.08	18.2	2.8	11	2	9
(2)	2-Methylbenzene-1,4-diol	1.45×10^3	16	6	1.02_5	19.5	5.6	9	−3	9
(3)	2-Chlorobenzene-1,4-diol	3.6×10^2	15	−1	1.09	17.95_5	4.0	6	−15	9
(4)	2,5-Dihydroxybenzenesulphonic acid	3.2×10^2	14	−9	1.16_5	16.2	3.5	5	−18	9
(5)	2,5-Dihydroxybenzene-1,4-disulphonic acid	2.5×10^2	12.2 [c]	−7.7 [c]	1.23	14.7_5	5.0	3 [c]	−22 [c]	*d*
(6)	2,3-Dicyanobenzene-1,4-diol	*ca.* 30			1.29	13.4	1.7	4 [c]	−22 [c]	*d*
(7)	2,5-Dihydroxybenzoic acid	1.6×10^2	14.4 [c]	−0.5 [c]	1.15	16.6	1.9	4 [c]	−22 [c]	*d*
(8)	2,3,5-Trimethylbenzene-1,4-diol	5.7×10^3	10.7 [c]	−5.3 [c]	0.90	22.4	13	2 [c]	−25 [c]	*d*
(9)	Benzene-1,2-diol	3.3×10^2	14.7	2.2	1.17	16.1	2.0	8	−10	4
(10)	Adrenalin	1.6×10^2	15.0	2.0	1.19	15.7	2.0	8	−10	4
(11)	3-Methylbenzene-1,2-diol	7.2×10^2	12.1	−5.0	1.13	17.1	3.4	8	−8	4
(12)	4-Methylbenzene-1,2-diol	8.8×10^2	14.8	4.7	1.12	17.3	3.9	8	−7	4
(13)	2,3-Dihydroxybenzoic acid	*ca.* 40			1.25	14.3	0.8	7	−13	4
(14)	3,4-Dihydroxybenzoic acid	*ca.* 30			1.26_5	13.9_5	1.5	8	−7	4
(15)	4-Cyanobenzene-1,2-diol	*ca.* 15			1.30_5	13.0_5	1.2	2	−30	4
(16)	$[Fe(5Me\text{-}phen)_3]^{2+}$ [e,f]	1.5×10^4			1.02	19.6				14
(17)	$[Fe(phen)_3]^{2+}$ [e,f]	1.4×10^4			1.06	18.7				14
(18)	$[Fe(5Cl\text{-}phen)_3]^{2+}$ [e,f]	5.0×10^3			1.12	17.3				14
(19)	$[Fe(5NO_2\text{-}phen)_3]^{2+}$ [e,f]	1.5×10^3			1.25	14.3				14
(20)	$[Co(terpy)_2]^{2+}$ [e,g]	7.4×10^4	3.4	−23	0.31	36.0				*h*
(21)	Mn^{2+} [e,f]	1.1×10^2	11.3	−9.5	1.51	8.3	0.29	6	−16	22
(22)	Fe^{2+} [e,f]	$2.2_5 \times 10^2$	15.2	4.7	0.74	26.0	1.9	6	−14	22
(23)	V^{2+} [e,f]	8.8×10^5			-0.25_5	49.1				16
(24)	Cr^{2+} [e,i]	$1.2_5 \times 10^4$	9.5	−7.8	−0.41	52.6	33	3	−20	16
(25)	Tl^{2+} [e,j]	9.5×10^6			0.33	35.5				17
(26)	Tl^{+} [e,k]	3.2×10^{-3}	26	20	2.22	−8.1				*l*

[a] See footnote on p. 2224. [b] For compounds (1)—(15) this potential refers to the couples $HL^{\bullet}$–H_2L, calculated as in the text; for the Co^{III}–Co^{II} couple a value of 1.87 V has been adopted.[11] [c] The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated from other kinetic runs at 7.0 °C. Errors in $\Delta H^{\ddagger}$ are ±1.5—2.0 kcal mol^{-1} and in $\Delta S^{\ddagger}$ are ±5—7 cal $K^{-1}\ mol^{-1}$. [d] This work. [e] The following self-exchange rate constants ($dm^3\ mol^{-1}\ s^{-1}$) were used: $[Fe(phen)_3]^{3+}$–$[Fe(phen)_3]^{2+}$, *ca.* 5×10^8;[19,21] $[Co(terpy)_2]^{3+}$–$[Co(terpy)_2]^{2+}$ (terpy = 2,2′ : 6′ : 2″-terpyridyl), 48 (see footnote *h*); Fe^{3+}–Fe^{2+}, 4.2 (J. Silverman and R. W. Dodson, *J. Phys. Chem.*, 1952, **56**, 846); V^{3+}–V^{2+}, 1.0×10^{-2} (K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921); Cr^{3+}–Cr^{2+}, *ca.* 2×10^{-5} (A. Anderson and N. A. Bonner, *J. Amer. Chem. Soc.*, 1954, **76**, 3826); Tl^{3+}–Tl^{2+}, *ca.* 10^5 (D. R. Stranks and J. K. Yandell, *J. Phys. Chem.*, 1969, **73**, 840); Tl^{2+}–Tl^{+}, *ca.* 5×10^4 (see previous ref.). [f] $I = 3.0$ mol dm^{-3}. [g] $I = 1.0$ mol dm^{-3}. [h] R. Farina and R. G. Wilkins, *Inorg. Chem.*, 1968, **7**, 514. [i] $I = 3.0$ mol dm^{-3} ($Li[ClO_4]$). [j] $I = 0.55$ mol dm^{-3}. [k] $I = 2.7$ mol dm^{-3}. [l] K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 1956, 343.

The data are collected in Table 2, together with the activation parameters. The values of $K_h = 2 \times 10^{-3}$ mol dm^{-3}, with the associated $\Delta H_h = 10$ kcal mol^{-1} and $\Delta S_h = 22$ cal $K^{-1}\ mol^{-1}$,* have been adopted.[10,11]

DISCUSSION

Data concerning the investigated quinols, together with related reactions of Co^{III} in aqueous perchlorate media, are collected in Table 2. The values of k_a exceed the rate of water substitution in the co-ordination sphere of Co^{3+}(aq),[11,12] thus suggesting an outer-sphere mechanism. When this reaction mechanism is operating, it can be expected that the reaction rates will be affected by the magnitude of $\Delta G^{\ominus}$, the free energy of reaction. In the present systems, the substituents have no direct effect on the reaction sites but their action is related to the ability of the reactants to donate electrons.

The evaluation of $\Delta G_{12}^{\ominus}$, the free energy of reactions of the rate-determining steps (2) and (3), requires the knowledge of the potentials $E_2^{\ominus}$ of the half-reactions $HL^{\bullet} + H^+ + e^- \rightleftharpoons H_2L$. It has been shown in previous papers, concerning the oxidation of quinols [7] and catechols [5] with $[IrCl_6]^{2-}$, that in both cases a reasonable estimate of $E_2^{\ominus}$ can be made by adding a constant

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* 1 cal = 4.184 J.

[10] I. Bodek and G. Davies, *Co-ordination Chem. Rev.*, 1974, **14**, 269.

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

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

quantity (0.38 V) to the corresponding potential of the two-electron reactions $L + 2H^+ + 2e^- \rightleftharpoons H_2L$. Values of $\Delta G_{12}^{\ominus}$ calculated in this way (that is by assuming $HL^{\bullet}$ as the product of the first step of reaction) for the compounds investigated, together with those for other systems, are also in Table 2.

For quinols, a plot of ΔG_{12}^{*} [obtained from the values of k_a, see equation (6)] as a function of $\Delta G_{12}^{\ominus}$ is satisfactorily linear, according to an empirical equation of the form (5). In equation (6) Z is the collision frequency for bimolecular reactions in solution, assumed to be 10^{11} dm^3 mol^{-1} s^{-1}.* From the plot of equation (6), $a = 17.5 \pm 2.8$ kcal mol^{-1} and $b = 0.35 \pm 0.06$ were obtained. A similar expression was adopted by Rillema and Endicott,[13] for oxidation-reduction reactions involving complexes of Co^{III} and Co^{II} with macrocyclic ligands. Their formulation accounts for the observed asymmetry of the coefficients b in the oxidation of cobalt(II) or in the reduction of cobalt(III) complexes. Moreover the term a was not very sensitive to the activation free energies of the self-exchange reactions of either oxidant or reductant. These workers suggested some rational explanations for accounting for such behaviour.

$$\Delta G_{12}^{*} = a + b\Delta G_{12}^{\ominus} \qquad (5)$$

$$k = Z\exp\left(-\Delta G_{12}^{*}/RT\right) \qquad (6)$$

Another approach to the free-energy correlation is the Marcus cross-relation [1,8] (7), where λ_{12} is the intrinsic reorganization barrier required to achieve the nuclear configuration of the activated complex, and is related to the free energies of activation observed in the self-exchange reactions of the interacting species, *i.e.* $\lambda_{12} = 2(\Delta G_{11}^{*} - w_{11} + \Delta G_{22}^{*} - w_{22})$, where w_{11} and w_{22} represent the work terms involved in the self-exchange reactions; $\Delta G_{12}^{\ominus\prime} = \Delta G_{12}^{\ominus} + w^{p} - w^{r}$, where w^{p} and w^{r} are the work terms required to bring the products or reactants together at the separation distance in the activated complex.

$$\Delta G_{12}^{*} = w^{r} + \frac{\lambda_{12}}{4} + \frac{\Delta G_{12}^{\ominus\prime}}{2} + \frac{(\Delta G_{12}^{\ominus\prime})^2}{4\lambda_{12}} \qquad (7)$$

Equation (7), which has found wide applicability to redox reactions between metal-ion complexes,[1] failed in the interpretation of some cobalt(III) reactions, as reported above. In particular, by oxidizing members of an homogeneous series with Co^{III},[14] it was found that, on plotting ΔG_{12}^{*} against $\Delta G_{12}^{\ominus}$, the gradient obtained was in agreement with expectation but the intercept was different from that predicted (*i.e.* observed rate constants were lower by a factor of 10^5—10^6 compared with the calculated values). Several arguments have been suggested to account for this discrepancy, *e.g.* multiplicity change and non-adiabaticity, and the formation of radical intermediate species.[1,15]

Recently, reactions of Co^{3+}(aq) with Cr^{II},[16] V^{II},[16] and Tl^{II},[17] involving large variations in $\Delta G_{12}^{\ominus}$, were investigated. With these ions the observed rate constants were not as large as would be expected and the limiting condition predicted by equation (7) was invoked. The data collected in plots by Hyde *et al.*[16] and by Falcinella *et al.*[17] showed that the intrinsic parameters play an important role compared with the thermodynamic parameters (*i.e.* comparison of systems with large differences in $\Delta G^{\ominus}$ shows similar kinetic parameters).

The difficulty in the application of the Marcus theory arises mainly from the lack of knowledge of the intrinsic parameters (ΔG_{11}^{*}, ΔG_{22}^{*}; the work terms, owing to the high ionic strength at which the reported investigations were made, probably play a minor role), so that a comparison between different reacting pairs can often give only qualitative conclusions. In the present systems the reactants (quinols and catechols) are chemically similar so that the reacting part of the molecule remains effectively the same throughout the series and thus the term ΔG_{22}^{*} can be assumed constant. A recent determination by Meisel and Fessenden [18] of the rates of exchange between semiquinone radical ions and their parent quinones showed that the rate constants fall in the range $0.5 \times 10^8 - 2 \times 10^8$ dm^3 mol^{-1} s^{-1}, on going from the parent benzoquinone to duroquinone. Thus, by extending the similarity to $HL^{\bullet}$–H_2L systems, the assumption of the constancy of ΔG_{22}^{*} seems to be confirmed within *ca.* 1 kcal mol^{-1} [which corresponds to a maximum variation of *ca.* 0.3 kcal mol^{-1} in the term on the right-hand side of equation (7)]. The intrinsic parameter for the $HL^{\bullet}$–H_2L couple was calculated from the previously investigated reactions of Mn^{III} with catechols,[3] for which a Marcus trend was observed. [Owing to the similarity in the intrinsic parameters observed for quinols [7] and catechols [5] in their oxidation by Ir^{IV} and with tris(1,10-phenanthroline)iron(III),[19] the same value was adopted for all the organic substrates.] From the estimated ΔG^{*} for Mn^{III}–Mn^{II} exchange (*ca.* 20 kcal mol^{-1}) [20] a value of $\Delta G_{22}^{*} = 6.5$ kcal mol^{-1} can be adopted for $HL^{\bullet}$–H_2L exchange (corresponding to a rate constant of *ca.* 2×10^6 dm^3 mol^{-1} s^{-1} for the reaction between the radical and the parent molecule). This

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* The form utilized for evaluating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, reported in Table 2, was $k = (\boldsymbol{k}T/h)e^{-\Delta H^{\ddagger}/RT}\, e^{\Delta S^{\ddagger}/R}$. The relations between ΔG^{*}, ΔH^{*}, and ΔS^{*}, and the quantities $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are $\Delta G^{\ddagger} = \Delta G^{*} - RT\ln(\boldsymbol{h}Z/\boldsymbol{k}T)$, $\Delta S^{\ddagger} = \Delta S^{*} + R\ln(\boldsymbol{h}Z/\boldsymbol{k}T) - \frac{1}{2}R$, and $\Delta H^{\ddagger} = \Delta H^{*} - \frac{1}{2}RT$. Here $\boldsymbol{k}$, $\boldsymbol{h}$, R, and T are the Boltzmann constant, Plank constant, the universal gas constant, and the absolute temperature, respectively.

[13] D. P. Rillema and J. F. Endicott, *J. Amer. Chem. Soc.*, 1972, **94**, 8711 and their related papers.

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

[15] T. J. Pryzystas and N. Sutin, *J. Amer. Chem. Soc.*, 1973, **95**, 5545.

[16] M. R. Hyde, R. Davies, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1838.

[17] B. Falcinella, P. D. Felgate, and G. S. Laurence, *J.C.S. Dalton*, 1975, 1.

[18] D. Meisel and R. W. Fessenden, personal communication.

[19] E. Pelizzetti and E. Mentasti, *Int. J. Chem. Kinetics*, in the press.

[20] P. J. Proll, in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 7, ch. 2.

value of ΔG_{22}^* may be an overestimate (1—2 kcal mol^{-1}), since the data for Mn^{III}–Mn^{II} exchange were derived by assuming a low value for the $[Fe(phen)_3]^{3+}$–$[Fe(phen)_3]^{2+}$ exchange rate and neglecting the work terms. This fact could slightly affect the intercepts rather than the gradient of Figures 1 and 2. (For a decrease of 2 kcal mol^{-1} in ΔG_{22}^*, an increase of 0.8 kcal mol^{-1} in the ordinates should be observed.)

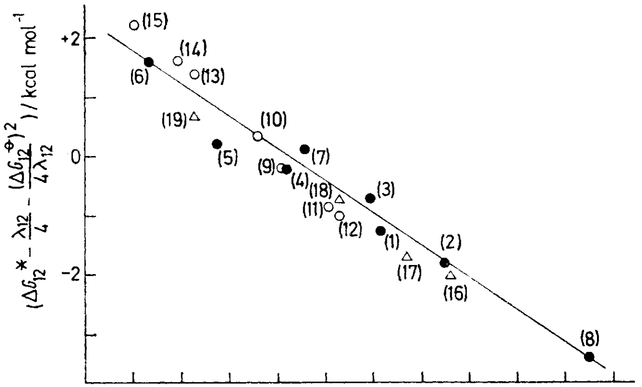

FIGURE 1 Plot of $\left(\Delta G_{12}^* - \frac{\lambda_{12}}{4} - \frac{(\Delta G_{12}^{\ominus})^2}{4\lambda_{12}}\right)$ as a function of $\Delta G_{12}^{\ominus}$, at 25 °C, for the Co^{3+}(aq) oxidation of reductants (1)—(19) of Table 2: (●) quinols; (○) catechols; and (△) tris(1,10-phenanthroline)iron(II) complexes

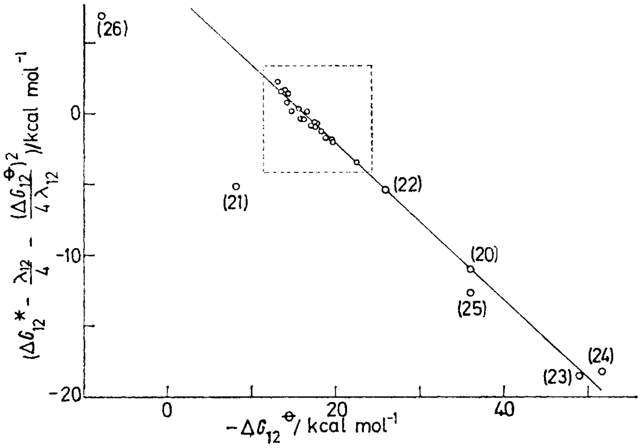

FIGURE 2 Plot of $\left(\Delta G_{12}^* - \frac{\lambda_{12}}{4} - \frac{(\Delta G_{12}^{\ominus})^2}{4\lambda_{12}}\right)$ as a function of $\Delta G_{12}^{\ominus}$, at 25 °C, for the Co^{3+}(aq) oxidation of the reductants of Table 2. In the broken square are reported the points in Figure 1. The straight line was calculated excluding points (21), (25), and (26)

In Figure 1, a plot of $\Delta G_{12}^* - (\lambda_{12}/4) - (\Delta G_{12}^{\ominus})^2/4\lambda_{12}$ is given as a function of $\Delta G_{12}^{\ominus}$ (ΔG^* for Co^{III}–Co^{II} was assumed to be 13.8 kcal mol^{-1}).[11] This plot also collects data for reactions of Co^{III} with $[Fe(phen)_3]^{2+}$.[14] (A value of $\Delta G^* = 3$ kcal mol^{-1}, *i.e.* $k_{ex.}$, *ca.* 5×10^8 dm^3 mol^{-1} s^{-1}, was adopted for the last complexes.)[19,21] The data lie rather well on a straight line of gradient 0.52 ± 0.05 and intercept 8.2 ± 1.1 kcal mol^{-1}. This suggested an extension of the treatment to data concerning cobalt(III) perchlorate oxidation of other substrates, particularly some aquametal ions (see Figure 2). The points with a large scatter concerned Mn^{2+}(aq)[22] and, to a lesser degree, Tl. (In the latter case the disagreement should be due, in part, to the uncertainty about the values of Tl^{III}–Tl^{II} and Tl^{II}–Tl^{I} self-exchange rates.) The gradient and intercept of the straight line are within the uncertainty reported above for the plot in Figure 1.

According to equation (7), the intercept should be zero (that is, the point corresponding to Co^{III}–Co^{II} self-exchange) which is not the case in the above plots. The difference found can be empirically taken into account by the inclusion of an additional factor in equation (6), as in (8). The factor α should probably reflect

$$k = \alpha Z \exp(-\Delta G_{12}^*/RT) \qquad (8)$$

the breakdown of one or more of the assumptions made in deriving equation (7), namely no differences in the precursor or successor complexes, adiabaticity of all the reactions involved, and absence of any rapid pre-equilibrium change (spin change).[23] Other factors such as the tunnelling effect or solvent effects could be responsible for these features. The value of α can be calculated to be 10^{-5}—10^{-6}, suggesting a maximum rate constant for reactions of Co^{3+}(aq) of *ca.* 10^5—10^6 dm^3 mol^{-1} s^{-1}. The present plots show that the oxidation of redox-reversible organic systems by Co^{3+}(aq) can be pictured according to a modified Marcus relation.[24]

Furthermore, the experimental data of the present investigation give additional evidence of a large acid-dependent term, attributed to the higher reactivity of $[Co(OH)]^{2+}$(aq) compared to Co^{3+}(aq) and showing for the former a limiting behaviour, as suggested by Davies.[10,25] Further work with complexes of Co^{III} in which the co-ordinated water molecules are completely, or only in part, substituted by other ligands, and with other organic systems should give additional information on the oxidation behaviour of Co^{III}.*

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* The data of a recent study on the kinetics of the Co^{III}–U^{III} reaction, which involves a large variation in $\Delta G^{\ominus}$ (−55.7 kcal mol^{-1}), can be included in the present treatment; in fact the related point (calculated using $\Delta G^* =$ *ca.* 20 kcal mol^{-1} for U^{IV}–U^{III} exchange, as estimated by comparison with other reactions of U^{III}) lies on the straight line of Figure 2 (A. Ekstrom, A. B. McLaren, and L. E. Smythe, *Inorg. Chem.*, 1975, **14**, 2899).

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