Kinetics of Oxidation of Benzene-1,2-diol Derivatives by Cobalt(III) in Aqueous Acidic Perchlorate Media

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The kinetics of reaction of benzene-1,2-diol, (−)-4-[1-hydroxy-2(methylamino)ethyl]benzene-1,2-diol, 3-methylbenzene-1,2-diol, 4-methylbenzene-1,2-diol, 2,3-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, and 3,4-dihydroxybenzonitrile with Co^{III} in aqueous acidic perchlorate media have been investigated with the stopped-flow method, at different temperatures (7.5—35 °C), acidities (0.20—2.00 mol dm^{-3} $HClO_4$), and I = 2.0 mol dm^{-3} (Na[ClO_4]). The reactions are first order in the concentrations of both reactants and the dependence of the second-order rate constants on acidity is given by the expression $k_0 = A + B[H^+]^{-1}$. This behaviour is explained by assuming the formation of two differently protonated activated complexes. The substituents largely effect the contribution of the path which is independent of acidity and involves Co^{3+}(aq), and a linear relation between $\Delta G^{\ddagger}$ and $\Delta G^{\ominus}$ suggests an outer-sphere mechanism. However, the path involving $[Co(OH)]^{2+}$(aq) is not affected by the nature of the organic substrate: because of its high rate with respect to water substitution, an outer-sphere limiting mechanism is advanced.

PURSUING the investigation concerning the kinetics and mechanism of the oxidation of reversible organic systems (such as dihydroxy-aromatic compounds) by means of metal ions (Fe^{III},[1a] V^{V},[1b] Tl^{III},[1c,d] and Mn^{III} [1e]), the reactions of a series of benzene-1,2-diol derivatives, namely benzene-1,2-diol (catechol, later referred to as I), (—)-4-[1-hydroxy-2-(methylamino)ethyl]benzene-1,2-diol (adrenalin, II), 3-methylbenzene-1,2-diol (III), 4-methylbenzene-1,2-diol (IV), 2,3-dihydroxybenzoic

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[1] (*a*) E. Mentasti, E. Pelizzetti, and G. Saini, *J.C.S. Dalton*, 1973, 2609; (*b*) E. Pelizzetti, E. Mentasti, and G. Saini, *Gazzetta*, 1974, **104**, 1015; (*c*) *J.C.S. Dalton*, 1974, 721; (*d*) E. Pelizzetti, E. Mentasti, M. E. Carlotti, and G. Giraudi, *ibid.*, 1975, 794; (*e*) E. Mentasti, E. Pelizzetti, E. Pramauro, and G. Giraudi, *Inorg. Chim. Acta*, 1975, **12**, 61.

acid (V), 3,4-dihydroxybenzoic acid (VI), and 3,4-dihydroxybenzonitrile (VII), with $\mathrm{Co^{III}}$ in aqueous acidic perchlorate solution have been investigated at different acidities and temperatures.

Cobalt(III) species present in aqueous acidic perchlorate media have been the subject of several investigations.[2] Both the value of the first hydrolysis constant and the existence of a dimer or polymer in solution have been controversial, although recently evidence was put forward which indicates that monomeric species predominate under the present experimental conditions.[2g]

EXPERIMENTAL

Reagents.—Cobalt(III) solutions were prepared by anodic oxidation of cobalt(II) perchlorate solutions (*ca.* 5×10^{-2} mol $\mathrm{dm^{-3}}$) as previously described (0 °C, $[\mathrm{HClO_4}] = 3$ mol $\mathrm{dm^{-3}}$).[2] The concentration of $\mathrm{Co^{III}}$ and $\mathrm{Co^{II}}$ were determined spectrophotometrically (ε_{605} 35.3 and ε_{509} 4.84 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, respectively).[3] Additional data for $\mathrm{Co^{III}}$ were obtained by adding an excess of $\mathrm{Fe^{II}}$ and titrating with standard $\mathrm{Cr^{VI}}$ (diphenylamine indicator), and by complexi-metric (ethylenediaminetetra-acetic acid) titration for $\mathrm{Co^{II}}$. Sodium perchlorate was used to adjust the ionic strength to 2.0 mol $\mathrm{dm^{-3}}$. Organic substrate solutions were prepared immediately before use from reagent grade compounds (K & K or Merck). Doubly distilled water was used.

Procedure.—The kinetic runs were made with $\mathrm{Co^{III}}$ not in excess (2×10^{-4}—4×10^{-4} mol $\mathrm{dm^{-3}}$); some runs were carried out with $[\mathrm{Co^{III}}] = 2 \times 10^{-4}$ mol $\mathrm{dm^{-3}}$ obtained by oxidation of an equimolar solution of $\mathrm{Co^{II}}$; the different preparations did not affect the kinetic data. The concentrations of organic substrates were varied from 2.0×10^{-3} to 20×10^{-3} mol $\mathrm{dm^{-3}}$ and the acidity range investigated was 0.20—2.00 mol $\mathrm{dm^{-3}}$. For (I), some runs were also made with excess of $\mathrm{Co^{III}}$ ($[\mathrm{I}] = 2 \times 10^{-4}$, $[\mathrm{Co^{III}}] = 2 \times 10^{-3}$—$5 \times 10^{-3}$ mol $\mathrm{dm^{-3}}$). A Durrum–Gibson stopped-flow spectrophotometer was used at the wavelength of maximum absorbance of the corresponding *o*-benzoquinone.[1] Some kinetic runs were carried out in the range 380—500 nm and showed good agreement between evaluated rate constants. The standard deviation computed for the pseudo-first-order rate constants ranged from 1 to 3%, as evaluated by a weighted least-squares method.[4]

RESULTS

Stoicheiometry.—The stoicheiometry of the reactions is given by (1) (where $\mathrm{H_2cat}$ is benzene-1,2-diol or a derivative

$$2\mathrm{Co^{III}} + \mathrm{H_2cat} \longrightarrow 2\mathrm{Co^{II}} + \mathrm{qno} + 2\mathrm{H^+} \qquad (1)$$

and qno is the corresponding *o*-quinone), as shown by spectrophotometric titration [1] of given amounts of $\mathrm{Co^{III}}$ with the substrates ($[\mathrm{Co^{III}}] = 2 \times 10^{-4}$—$5 \times 10^{-4}$, $[\mathrm{H_2cat}] = 5 \times 10^{-4}$—$50 \times 10^{-4}$, and $[\mathrm{H^+}] = 0.20$—2.00 mol $\mathrm{dm^{-3}}$).

Kinetics.—The reaction rates were first-order with respect to the concentrations of both reactants. Second-order rate constants were calculated by means of a weighted least-squares method, where weights were assigned by taking into account the standard deviation of the pseudo-first-order rate constants.* The second-order rate constants, k_0, obeyed expression (2). Some plots of equation (2) are given

$$k_0 = A + B[\mathrm{H^+}]^{-1} \qquad (2)$$

in Figure 1, which shows that, in some cases, the term A cannot be estimated with good accuracy. Compound (V) and, to a lesser degree (VII), showed a small deviation from equation (2) at high temperature and $[\mathrm{HClO_4}] \leqslant 0.70$ mol $\mathrm{dm^{-3}}$, indicating a probable higher-order dependence on acidity.

The presence of $\mathrm{Co^{II}}$ (5×10^{-3}—50×10^{-3} mol $\mathrm{dm^{-3}}$) in these reactions did not cause an appreciable effect, within experimental errors, on the rate parameters, so that no reverse reactions or equilibria involving $\mathrm{Co^{II}}$ seem to be significant. An increase of *ca.* 30% in reaction rate was found in the ionic strength range 0.50—4.0 mol $\mathrm{dm^{-3}}$ ($\mathrm{Na[ClO_4]}$) when working with compounds (I) and (II). Kinetic measurements made on the reaction with (I) ($\mathrm{Co^{III}}$ in excess) gave kinetic data in agreement with those obtained with the substrate in excess.

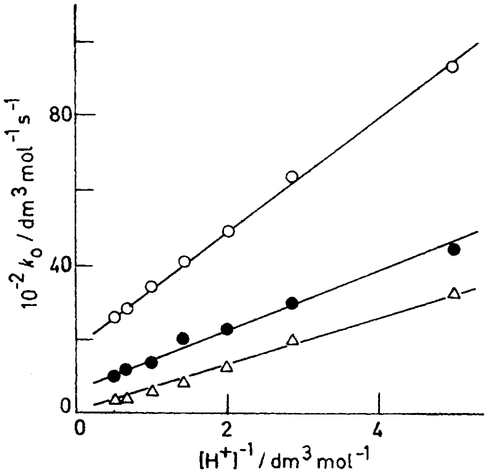

FIGURE 1 Plots of the experimental data, according to equation (2), for the oxidation by $\mathrm{Co^{III}}$ of catechols (I) (●), (IV) (○), and (VI) (I = 2.0 mol $\mathrm{dm^{-3}}$, 25.0 °C)

DISCUSSION

The kinetic data, together with previous findings with other oxidizing metal ions, suggest the reaction sequence (3)—(6). Assuming that reactions (3) and (6) are fast compared to (4) and (5), equation (7) can be obtained and hence (8). Expression (8) agrees with the experi-

$$\mathrm{Co^{3+}(aq)} \xrightleftharpoons{K_h} [\mathrm{Co(OH)}]^{2+}\mathrm{(aq)} + \mathrm{H^+} \qquad (3)$$

$$\mathrm{Co^{3+}(aq)} + \mathrm{H_2cat} \xrightarrow{k_a} \mathrm{Co^{II}} + \mathrm{Hcat{\cdot}} + \mathrm{H^+} \qquad (4)$$

$$[\mathrm{Co(OH)}]^{2+}\mathrm{(aq)} + \mathrm{H_2cat} \xrightarrow{k_b} \mathrm{Co^{II}} + \mathrm{Hcat{\cdot}} \qquad (5)$$

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* Values of the individual constants are in Supplementary Publication No. SUP 21595 (5 pp.). For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[2] (*a*) G. Davies and B. Warnqvist, *Co-ordination Chem. Rev.*, 1970, **5**, 349; (*b*) A. McAuley, *ibid.*, p. 245; (*c*) C. F. Wells, *Discuss. Faraday Soc.*, 1968, **46**, 197; (*d*) B. Warnqvist, *Inorg. Chem.*, 1970, **9**, 682; (*e*) R. K. Murmann, *ibid.*, 1971, **10**, 2070; (*f*) C. F. Wells and D. Mays, *J. Chem. Soc.* (*A*), 1969, 2176; (*g*) G. Davies and B. Warnqvist, *J.C.S. Dalton*, 1973, 900.

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

[4] G. Giraudi, E. Mentasti, and E. Pelizzetti, *Atti R. Accad. Sci. Torino*, 1975, **108**, 825.

Values of the specific rate constants, k_a and k_b ($dm^3 mol^{-1}s^{-1}$), and activation parameters, $\Delta H^\ddagger$ (kcal mol^{-1}) and $\Delta S^\ddagger$ (cal K^{-1} mol^{-1}), for the oxidation of catechols by Co^{III} (I = 2.0 mol dm^{-3}, 25.0 °C)

Compound	k_a	$10^{-5}k_b$	$\Delta H_a^\ddagger$	$\Delta S_a^\ddagger$	$\Delta H_b^{\ddagger\,a}$	$\Delta S_b^{\ddagger\,a}$
I	330 ± 30	$2.0 \pm 0.1_5$	14.7 ± 1.5	+2.2 ± 5.1	17.6 ± 1.5	+12.4 ± 5.1
II	160 ± 20	$2.0 \pm 0.1_5$	15.0 ± 1.7	+2.0 ± 5.8	17.6 ± 1.5	+12.4 ± 5.1
III	720 ± 60	$3.4 \pm 0.2_5$	12.1 ± 1.9	−5.0 ± 6.5	17.9 ± 1.8	+14.4 ± 6.1
IV	880 ± 70	3.9 ± 0.3	14.8 ± 1.8	+4.7 ± 6.1	18.0 ± 2.0	+15.0 ± 6.8
V [b]	*ca.* 40	0.75 ± 0.10			16.9 ± 3.3	+9.4 ± 11.2
VI	*ca.* 30	$1.5 \pm 0.1_5$			18.4 ± 2.4	+14.6 ± 8.2
VII	*ca.* 15	1.15 ± 0.10			11.9 ± 2.3	−8.0 ± 7.7

[a] These values also include ΔH_h and ΔS_h. [b] 18.0 °C.

$$Co^{III} + Hcat\cdot \xrightarrow{\text{fast}} Co^{II} + qno + H^+ \quad (6)$$

$$-\frac{d[Co^{III}]}{dt} = \frac{2(k_a + k_bK_h[H^+]^{-1})[H_2cat][Co^{III}]}{1 + K_h[H^+]^{-1}} = k_o[H_2cat][Co^{III}] \quad (7)$$

$$k_o(1 + K_h[H^+]^{-1}) = 2k_a + 2k_bK_h[H^+]^{-1} \quad (8)$$

mental dependence (2) if $K_h[H^+]^{-1} \ll 1$, as can be assumed in the present acidity range.[2] The calculated values of k_a and k_b (k_b was calculated on the assumption that K_h = 2 × 10^{-3} mol dm^{-3}, ΔH_h = 10 kcal mol^{-1}, and ΔS_h = 22 cal K^{-1} mol^{-1})[2a,3] are in the Table, with the corresponding activation parameters.*

The chemistry of Co^{III} has been the subject of many investigations reviewed by Davies [2a,5] and a comparison with previous kinetic data enables us to assign probable mechanisms to the present reaction paths. In fact, by comparing the present data with previous reactions of this oxidant (*i.e.* with malic acid, thiomalic acid, and chloride),[2a,b] where complex formation occurs, it seems reasonable to suggest that water exchange in the co-ordination sphere of Co^{III} is not rate determining in the reactions under investigation. Moreover, for path (4) the rate increases as the estimated overall free-energy change becomes more negative. This suggests an outer-sphere mechanism and the rate-determining step is the electron transfer. The Marcus relation (9) [6] has been

$$\Delta G_{12}^\ddagger = \tfrac{1}{2}(\Delta G_{11}^\ddagger + \Delta G_{22}^\ddagger) + \tfrac{1}{2}\Delta G_{12}^\ominus + \frac{(\Delta G_{12}^\ominus)^2}{8(\Delta G_{11}^\ddagger + \Delta G_{22}^\ddagger)} \quad (9)$$

successfully applied in reactions involving variations of overall free energy where the last term of the equation is negligible; this relation has been tentatively applied to reversible organic redox systems involving oxidizing metal ions.[7] In the present case, the evaluation of $\Delta G_{12}^\ominus$ for reaction (4) requires a knowledge of the standard redox potential of the couples H_2cat–$Hcat\cdot$ and unfortunately no data are available for these systems. For the hydroquinone–semiquinone system (and for the substituted derivatives) this potential[8] differs from that of the corresponding hydroquinone–*p*-benzoquinone couple by a nearly constant $\Delta E^\ominus$; if the same behaviour is accepted for catechol systems, expression (10) can be obtained, where $\Delta G^\ominus$ is the overall free energy for equation (1) and a includes both $\tfrac{1}{2}(\Delta G_{11}^\ddagger +$

$$\Delta G^\ddagger = a + 0.25\Delta G^\ominus \quad (10)$$

$\Delta G_{22}^\ddagger)$ and the term $11.5\Delta E^\ominus$. The present data give a straight line (see Figure 2) with a gradient of *ca.* 0.30. Taking into account the recent work of Rillema and Endicott,[9] concerning an analogous linear free-energy relation in redox reactions involving complexes of Co^{III} and Co^{II}, this result is satisfactory.

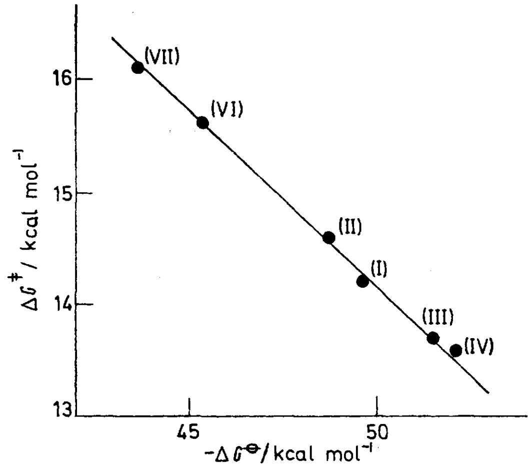

FIGURE 2 Plot of $\Delta G^\ddagger$ against $\Delta G^\ominus$ for the reactions of catechols with $Co^{3+}(aq)$ (I = 2.0 mol dm^{-3} and 25.0 °C). Values of $\Delta G^\ddagger$ were calculated from $k = (\boldsymbol{k}T/\boldsymbol{h})\exp - \Delta G^\ddagger/RT$ and $\Delta G^\ominus$ from the standard potentials. For Co^{III}–Co^{II} the potential was taken to be 1.87 V [2d] and for H_2cat–qno couples the following data were used: (I), 0.792; (II), 0.812; (III), 0.749; (IV), 0.739; (VI), 0.885; and (VII), 0.924 V (see ref. 10 and W. M. Clarke, ' Oxidation-Reduction Potentials of Organic Systems,' Williams and Wilkins Co., Baltimore, 1960.)

However, the acid-dependent path [equation (5)] shows a narrow range of kinetic parameters and a plot of $\Delta G^\ddagger$ against $\Delta G^\ominus$, according to equation (10), was also approximately linear with a gradient of *ca.* 0.07. The values of k_b are of the same order of magnitude of those found in the reactions with Fe^{2+}, hydroquinone, and I^-.[2a,5] The observed differences in rate constant for these last three reagents were attributed to a compromise

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* 1 cal = 4.184 J.

[5] I. Bodek and G. Davies, *Co-ordination Chem. Rev.*, 1974, **14**, 269; G. Davies, *ibid.*, p. 287.

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

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[8] C. A. Bishop and L. K. J. Tong, *J. Amer. Chem. Soc.*, 1965, **87**, 501; P. S. Rao and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 2274.

[9] D. P. Rillema and J. F. Endicott, *J. Amer. Chem. Soc.*, 1972, **94**, 8711.

between the ion-association constant and the distribution coefficient for the optimum configuration of the OH^- ligand in bridging the reactants in the activated complex for the electron transfer.[5] The present compounds give values of k_b which lie between those for Fe^{2+} and hydroquinone. This corresponds to the establishment of a limiting behaviour which requires activation of the oxidizing ion, which Davies attributed to the thermal spin cross-over of the metal centre.[5] The very high ratio of $k_b : k_a$ can be attributed to the distributive character of the OH^- ligand as suggested by Davies in explaining the catalytic properties of the hydroxy-group in reactions of metal ions.[5]

In the oxidation of organic systems by Co^{III} and other metal ions (*i.e.* Mn^{III}),[10a] as well as by other oxidizing agents such as I^{VII},[10b] it must be noted that the relative contribution of the two paths of reaction can be related to the effect of the substituents: in fact a linear relation is obtained on plotting log (k_b/k_a) against the pK_a of the reagents (or the Hammett σ values). A final remark concerns the absence of higher-order rate terms with respect to [Co^{III}] when the metal ion is in excess: this is to be expected because these are outer-sphere reactions and the presence of 1 : 2 activated complexes has been pointed out only when detectable 1 : 1 complexes are present (*i.e.* in the reaction of catechol with Fe^{III} and V^V [11] and of hydroquinone with V^V).[11]

[5/480 *Received, 11th March,* 1975]

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[10] (*a*) E. Pelizzetti, E. Mentasti, and G. Giraudi, *Inorg. Chim. Acta*, 1975, **15**, L1; (*b*) E. Mentasti, E. Pelizzetti, and G. Giraudi, *Z. phys. Chem.* (*Frankfurt*), in the press.

[11] E. Pelizzetti, E. Mentasti, E. Pramauro, and G. Saini, *J.C.S. Dalton*, 1974, 1940; K. Kustin, C. Nicolini, and D. Toppen, *J. Amer. Chem. Soc.*, 1974, **96**, 7416.