Electron-transfer Reactions of Benzene-1,2-diols with Hexachloroiridate(IV) in Acidic Perchlorate Media

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The kinetics of oxidation of a series of benzene-1,2-diols by hexachloroiridate(IV) have been investigated by the stopped-flow technique in aqueous acidic perchlorate media. The reactions are first order in the concentrations of both reactants and independent of acidity and added $[IrCl_6]^{3-}$. The experimental results are discussed in the light of Marcus theory with reference to previous findings on the kinetic behaviour of benzene-1,4-diols. The dependence of the free energies of activation on the free energies of reaction provides information on the mechanism of these non-complementary redox reactions.

IN previous work we have investigated in detail the mechanism of oxidation of substituted aromatic *ortho*-diols by inorganic oxidizing ions in acidic perchlorate media.[1] The observed behaviour was related to the possibility of prior inner-sphere substitution of co-ordinated water and of weak or strong metal–ligand interactions. In some cases, linear free-energy relations allowed us to point out only that the electron-transfer steps were rate limiting rather than to distinguish between outer- or inner-sphere mechanisms.

In connection with the above findings we have studied the kinetics of oxidation of a series of quinols by hexachloroiridate(IV),[2] and in the present paper we report an investigation of the reaction of a series of substituted benzene-1,2-diols with the same oxidant. Hexachloroiridate(IV) is stable towards substitution or hydrolysis over a wide range of acidity, so that the present reactions occur without formation and decomposition of organic substrate complexes; thus these redox reactions can be classified as outer sphere. Differences in the behaviour of the substrates are then strictly governed by their intrinsic tendency to oxidation, irrespective of their co-ordination abilities. The rather wide range of their standard redox potentials (from 0.739 V for 4-methylbenzene-1,2-diol to 0.955 V for 4,5-dihydroxybenzene-1,3-disulphonic acid) [3] allows us to correlate standard free-energy variations with reactivities, in order to obtain additional information on the detailed mechanistic and kinetic features of these reversible redox reactions.

EXPERIMENTAL

Reagents.—The investigated substrates, namely benzene-1,2-diol (catechol, later referred to as 1, supplied by C. Erba), 4-methylbenzene-1,2-diol (2, E. Merck), 3-(3,4-dihydroxyphenyl)alanine (L-Dopa, 3, E. Merck), adrenaline (4, E. Merck), 2,3-dihydroxybenzoic acid (5, Aldrich), 3,4-dihydroxybenzoic acid (6, Aldrich), 3,4-dihydroxybenzonitrile (7, K & K), 4,5-dihydroxybenzene-1,3-disulphonic acid (8, Erba), were reagent grade chemicals. Acid solutions of the diols were prepared immediately before use from weighed amounts and were protected from direct light. Sodium hexachloroiridate(IV) was used as supplied by E. Merck, and solutions were prepared daily and stored in the dark at 0 °C. Aqueous solutions of the complex gave a spectrum in good agreement with that in the literature ($\lambda_{max.}$ 487 nm, ε 4 075 $dm^3 mol^{-1} cm^{-1}$).[4] Ultraviolet- and visible-absorption measurements on acidic solutions of the complex, as such or after addition of aqueous chlorine-saturated perchloric acid, ensured that no hydrolysis [with formation of aquapentachloroiridate(IV), ε 2 345 $dm^3 mol^{-1} cm^{-1}$ at 487 nm] or reduction (yielding Ir^{III} which is eventually rapidly oxidized to Ir^{IV} by Cl_2) [4] occurred during 1 d after preparation. Standardization was then effected spectrophotometrically at 487 nm and the solutions were used within a few hours of preparation. Solutions of $[IrCl_6]^{3-}$ were obtained by cathodic reduction of $[IrCl_6]^{2-}$ at a platinum electrode or by dissolution of $K_3[IrCl_6]$ (Alfa); both solutions gave the same kinetic responses. Perchloric acid and sodium perchlorate (Erba) were used to adjust the solutions to the desired acidity ($0.030 \leqslant [HClO_4] \leqslant 1.00$ mol dm^{-3}) and ionic strength ($I = 1.0$ mol dm^{-3}). For some runs, as described below, the ionic strength was maintained by addition of $Li[ClO_4]$ (E. Merck).

Kinetics of Reaction.—Kinetic measurements were made with a Durrum–Gibson stopped-flow spectrophotometer at 10.0, 25.0, and 38.0 °C, by following the decrease in absorbance at 487 nm due to disappearance of $[IrCl_6]^{2-}$. Oscilloscope traces were photographed and the data were treated by a weighted least-squares method.[5]

RESULTS AND DISCUSSION

Stoicheiometry.—The addition of hexachloroiridate(IV) to an acidic solution of compound (1) showed that a fast reaction occurs with formation of *o*-benzoquinone, as confirmed by the spectrum of the reaction mixture, corrected to account for the $[IrCl_6]^{3-}$ formed. A spectrophotometric titration showed that Ir^{IV} and catechols (H_2cat) reacted in a 2 : 1 ratio, according to equation (1)

$$2[IrCl_6]^{2-} + H_2cat \longrightarrow 2[IrCl_6]^{3-} + qno + 2H^+ \quad (1)$$

where qno is the corresponding *o*-benzoquinone. For compounds (7) and (8), owing to the closeness of their standard potentials (qno–H_2cat couples) with that of Ir^{IV}–Ir^{III}, reaction (1) went to completion only in the presence of a large excess of organic substrate, as in the present investigation.

Orders of Reaction.—In order to assess the reaction

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[1] E. Pelizzetti, E. Mentasti, and E. Pramauro, *J.C.S. Dalton*, 1976, 23; E. Pelizzetti and E. Mentasti, *ibid.*, in the press; E. Pelizzetti, E. Mentasti, and G. Giraudi, *Inorg. Chim. Acta*, 1975, **15**, L1; E. Mentasti, E. Pelizzetti, and C. Baiocchi, *J. Inorg. Nuclear Chem.*, in the press; E. Pelizzetti, E. Mentasti, and G. Saini, *Gazzetta*, in the press.

[2] E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Phys. Chem.*, in the press.

[3] E. Mentasti, E. Pelizzetti, and G. Giraudi, *Z. phys. Chem. (Frankfurt)*, 1976, **100**, 17.

[4] I. A. Poulsen and C. S. Garner, *J. Amer. Chem. Soc.*, 1962, **84**, 2032.

[5] G. Giraudi, E. Mentasti, and E. Pelizzetti, *Atti Accad. Sci. Torino*, 1974, **108**, 825.

orders and the empirical rate law, solutions containing different catechol concentrations, in at least 10-fold equivalent excess, were mixed in the stopped-flow apparatus with a solution containing $[IrCl_6]^{2-}$. All these solutions were adjusted to the same acidity and ionic strength. Plots of ln A_t against time (A_t is the absorbance at time t, at 487 nm, where Ir^{IV} is the only absorbing species) were always linear to 80% completion of reaction, and the observed pseudo-first-order rate constants, $k_{obs.}$, exhibited a linear dependence on the excess catechol concentration. Some kinetic runs were performed {at 25.0 °C, $[HClO_4] = 1.00$ mol dm^{-3}, and with compounds (1), (4), and (7)} with the addition of $[IrCl_6]^{3-}$ (up to 12 times the initial concentration of $[IrCl_6]^{2-}$); no kinetic effect was displayed by this addition and thus reverse reactions are not operating. Hence the empirical rate law is as in (2) where k_0 is the overall second-order rate constant.

$$-d[Ir^{IV}]/dt = k_0[Ir^{IV}][H_2cat] \qquad (2)$$

TABLE 1

Pseudo-first-order, $k_{obs.}$ (s^{-1}) and overall second-order rate constants k_0 (dm^3 mol^{-1} s^{-1}) for the oxidation of catechol by $[IrCl_6]^{2-}$ under different experimental conditions (ionic strength 1.0 mol dm^{-3} was obtained by addition of Na[ClO$_4$], unless otherwise stated); $[IrCl_6]^{2-} = 1 \times 10^{-5}$—$2 \times 10^{-5}$ mol dm^{-3}

θ_c/°C	$10^3[H_2cat]$/mol dm^{-3}	HClO$_4$/mol dm^{-3}				
		0.030	0.070	0.100	0.500	1.00
10	0.40	2.1	1.82	1.79	1.36	1.14
	0.70	3.2	3.25	3.1	2.5	2.1
	1.0	4.8	4.6	4.3	3.7	3.0
	1.5	6.8	6.8	6.4	5.2	4.4
	2.0	9.4	9.3	8.3	7.5	6.4
	4.0	18.2	18.9	17.8	15.1	13.0
	8.0		34	34	26	23
	$10^{-3}k_0 =$	4.7	4.6	4.4	3.6	3.2
25	0.70	5.8	5.8	5.5	5.0	3.8
	1.0	8.7	8.6	8.0	6.9	5.1
	1.5	12.6	12.1	12.1	10.1	8.1
	2.0	17.2	16.5	15.1	13.5	10.9
	$10^{-3}k_0 =$	8.5	8.3	7.9	6.9	5.3
25 *	1.0	6.6	6.3	5.8	5.6	
	2.0	13.1	12.3	11.6	11.2	
	4.0	26	24	23	22	
	$10^{-3}k_0 =$	6.6	6.2	5.8	5.6	
38	0.50	5.7	5.3	5.2	4.6	3.9
	1.0	11.3	10.5	10.1	8.9	7.8
	1.5	16.5	16.0	15.5	13.3	11.5
	2.0	21.8	20.8	20.7	18.1	15.9
	$10^{-4}k_0 =$	1.12	1.05	1.03	0.9	0.78

* $I = 1.0$ mol dm^{-3} with Li[ClO$_4$].

TABLE 2

Values of k_1, $\Delta H^‡$, $\Delta S^‡$, and $E^\ominus$ for the oxidation of benzene-1,2-diols by $[IrCl_6]^{2-}$ at 25.0 °C and $I = 1.0$ mol dm^{-3} (NaClO$_4$)

Compound	$10^{-2}k_1$ [a]/dm^3 mol^{-1} s^{-1}			$\Delta H^‡$ [b]/kcal mol^{-1}	$\Delta S^‡$ [c]/cal K^{-1} mol^{-1}	$E^\ominus$ [d]/V
	10.0	25.0	38.0			
Benzene-1,2-diol (1)	15.6	27	39	5.2	−26	0.792
4-Methylbenzene-1,2-diol (2)	270	400	560	4.0	−24	0.739
3-(3,4-Dihydroxyphenyl)alanine (3)	69	97	140	3.8	−27	0.798
Adrenaline (4)	42	54	68	2.4	−33	0.812
2,3-Dihydroxybenzoic acid (5)	1.22	2.5	3.8	6.6	−26	0.870
3,4-Dihydroxybenzoic acid (6)	0.41	0.71	1.05	5.3	−32	0.885
3,4-Dihydroxybenzonitrile (7)	0.108	0.154	0.25	4.6	−38	0.924
4,5-Dihydroxybenzene-1,3-disulphonic acid (8)	0.015	0.024	0.037	5.1	−40	0.955

[a] Each value is the average of at least four separate measurements; the error is ±6 — 8%. [b] The uncertainty is ±0.8 kcal mol^{-1}. [c] The uncertainty is ±3 cal K^{-1} mol^{-1}. [d] Taken from ref. 3.

Acid Dependence.—Table 1 collects the pseudo-first-order rate constants and the values of k_0 obtained under various experimental conditions, for the parent compound (1). The data show that the effect of perchloric acid concentration is to decrease the reaction rate with increasing acidity. The acid dependence could be explained in terms of association of the reactants with H^+ to yield protonated forms of the organic substrates or of the oxidizing anion. The first case seems to be excluded, due to the absence of this effect for redox reactions of benzene-1,2-diols with other oxidizing agents in media of higher acidity.[1] Protonation of $[IrCl_6]^{2-}$ could account for the observed effect if $[H_nIrCl_6]^{(2-n)-}$ species are less reactive. However, the effect is small and may well be due to a salt effect; moreover such protonated species were not previously found in comparable conditions of acidity. Additional runs were carried out by substituting Na^+ by Li^+; the low inverse-acidity dependence of the rates was depressed (but however not cancelled), confirming that the observed behaviour is due mainly to a medium effect (see Table 1).

Rates and Mechanism of Oxidation.—In order to compare the behaviour of the investigated substrates, kinetic measurements were made at $[HClO_4] = 1.00$ mol dm^{-3}, and in all cases the reaction was first order in the concentrations of both reagents. It is well established [1,6] that one-electron oxidants react with benzene-1,2-diols through a two-step mechanism with intermediate formation of a semiquinone radical as in equations (3) and (4) (protons are omitted); from this sequence, by assuming steady-state conditions for the semiquinone, the kinetic

$$Ir^{IV} + H_2cat \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ir^{III} + \text{semiquinone} \qquad (3)$$

$$Ir^{IV} + \text{semiquinone} \xrightarrow{k_2} Ir^{III} + \text{qno} \qquad (4)$$

law (5) may be derived. The previously mentioned first-order dependence on the concentration of the oxidant suggests that $k_{-1}[Ir^{III}] \ll k_2[Ir^{IV}]$ (as shown also in

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[6] E. Mentasti, E. Pelizzetti, and G. Saini, *J.C.S. Dalton*, 1973, 2609.

the measurements made with excess of Ir^{III}), so that

$$\frac{d[Ir^{IV}]}{dt} = \frac{2k_1k_2[Ir^{IV}]^2[H_2cat]}{k_{-1}[Ir^{III}] + k_2[Ir^{IV}]} \qquad (5)$$

equation (5) reduces to the empirical rate law (2) with $k_0 = 2k_1$.

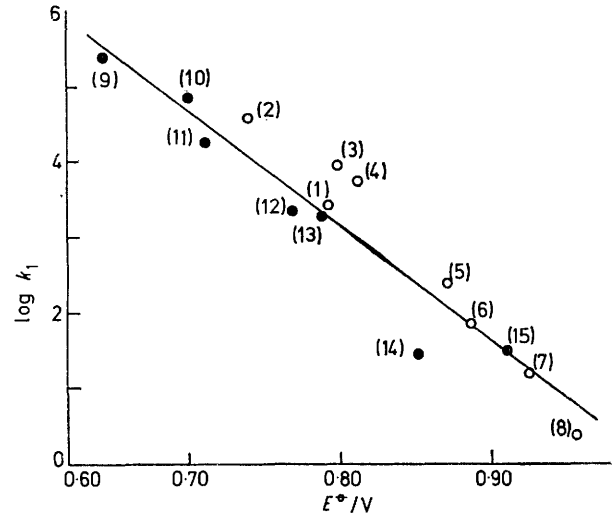


FIGURE 1 Plot of log k_1 as a function of $E^{\ominus}$, the standard redox potential of the couple quinone + $2e^- + 2H^+ \rightleftharpoons$ diol, for catechols (○) and quinols (●) at 25.0 °C and I = 1.0 mol dm^{-3}. For catechols [compounds (1)—(8)] see the Experimental section. Quinols: 2-methylbenzene-1,4-diol (9); benzene-1,4-diol (10); 2-chlorobenzene-1,4-diol (11); 2,5-dihydroxybenzoic acid (12); 2,5-dihydroxybenzenesulphonic acid (13); 2,5-dihydroxybenzene-1,4-disulphonic acid (14); 3,6-dihydroxybenzene-1,2-dicarbonitrile (15)

Table 2 collects the derived k_1 values and the activation parameters. The data show that the reactivity of the investigated substrates parallels their tendency to oxidation, as previously ascertained for the oxidation of quinols by Ir^{IV}.[2] In fact the experimental points (log k_1) lie reasonably well on a straight line when plotted as a function of the standard redox potentials $E^{\ominus}$ (for the couples qno + $2e^- + 2H^+ \rightleftharpoons H_2cat$) [3,7] (see Figure 1). This comparable behaviour suggests an analogous mechanism for both groups of compounds (benzene-1,2- and benzene-1,4-diols) and that the same step is rate determining [forward reaction (3)]. Reaction (3) can give rise to a radical Hcat• or $H_2cat^{+\bullet}$, depending on whether the first one-electron step takes place with proton release or abstraction of the first electron occurs before the reacting OH group dissociates as found for phenol,[8] according to (6) or (7). Information on the mechanism involved can be obtained by examining the dependence of free energies of activation on the free energies of reaction for the proposed rate-determining step (6) or (7). It is worth mentioning that the activation parameters show that there is a small barrier to the reaction: the activation enthalpies are low and much smaller than those expected for any reaction involving breakage of a chloride–metal bond in the oxidizing complex ($\Delta H^‡$ for solvolysis of $[IrCl_6]^{3-}$ is 30.4 kcal mol^{-1},* and a comparable value is expected for $[IrCl_6]^{2-}$),[4,8] again confirming that the mechanism is of the outer-sphere type with small interactions between the reactants. Under these conditions, Marcus theory[9] predicts the relations (8) and (9). In these equation, $\Delta G_r^{\ominus} = \Delta G^{\ominus} + w_p - w_r$, where $\Delta G^{\ominus}$ is the standard free-energy change

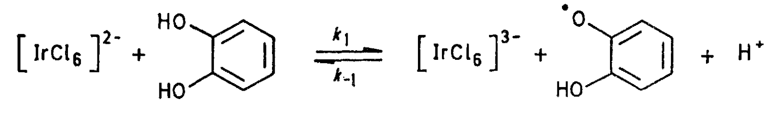
$$\Delta G_{12}^‡ = w_r + \lambda_{12}[1 + (\Delta G_r^{\ominus}/\lambda_{12})]^2/4 \qquad \text{for } |\Delta G_r^{\ominus}| \leqslant \lambda_{12} \qquad (8a)$$

$$\Delta G_{12}^‡ = w_r \qquad \text{for } \Delta G_r^{\ominus} \leqslant -\lambda_{12} \qquad (8b)$$

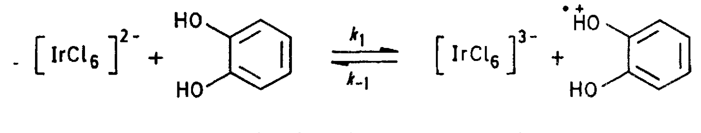
$$\Delta G_{12}^‡ = \Delta G^{\ominus} + w_p \qquad \text{for } \Delta G_r^{\ominus} \geqslant \lambda_{12} \qquad (8c)$$

$$\Delta G_{12}^‡ = -RT \ln(k_{rate}/Z) \qquad (9)$$

of the rate-determining step, w_r and w_p are the work terms required to bring the reactants and products to their mean separation distance, Z is the frequency of bimolecular collision in solution (10^{11} dm^3 mol^{-1} s^{-1}), and λ_{12} is an additive function of the two redox reagents 1 and 2, defined as $\lambda_{12} = 2(\Delta G_{11}^‡ + \Delta G_{22}^‡)$, where $\Delta G_{11}^‡$ and $\Delta G_{22}^‡$ refer through equation (9) to the rates of self-redox exchange for the individual reagent redox couples.



(6)



(7)

In order to examine the applicability of Marcus theory, $\Delta G^{\ominus}$ for reactions (6) and (7) must be computed through a knowledge of the redox potentials of the couples (10) and (11). Unfortunately no data are available for

$$H_2cat^{+\bullet} + e^- \xrightleftharpoons{E^{\ominus\prime}} H_2cat \qquad (10)$$

$$Hcat\bullet + e^- + H^+ \xrightleftharpoons{E^{\ominus\prime\prime}} H_2cat \qquad (11)$$

deriving $E^{\ominus\prime}$ and $E^{\ominus\prime\prime}$. (The disproportionation constants of semiquinone radicals and their dissociation constants have not been reported.) If, however, one

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* 1 cal = 4.184 J.

[7] W. M. Clark, 'Oxidation-Reduction Potentials of Organic Systems,' Williams and Wilkins, Baltimore, 1960.

[8] R. Cecil and J. S. Littler, *J. Chem. Soc.* (*B*), 1968, 1420.

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

TABLE 3

Relevant experimental and calculated thermodynamic quantities for the oxidation of benzene-1,2-diols by hexachloroiridate(IV) at 25.0 °C and I = 1.0 mol dm^{-3}

Compd.	$E^{\ominus\prime\prime}$ / V	$\Delta G_6^{\ominus}$ / kcal mol^{-1}	$K_{1(sq)}$ / mol dm^{-3}	$\Delta G_7^{\ominus}$ / kcal mol^{-1}	$\Delta G_7^{\ddagger}$/kcal mol^{-1} expt.	$\Delta G_7^{\ddagger}$/kcal mol^{-1} calc.*	$10^{-8}k_{-1}$ / dm^3 mol^{-1} s^{-1}	$\Delta G_{-7}^{\ddagger}$/kcal mol^{-1} expt.	$\Delta G_{-7}^{\ddagger}$/kcal mol^{-1} calc.*
(1)	1.17	4.95	32	7.0	10.3	10.5	3.7	3.3	3.5
(2)	1.12	3.7	17	5.4	8.7	9.5	3.7	3.3	4.1
(3)	1.18	5.1	36	7.2	9.6	10.6	19	2.4	3.4
(4)	1.19	5.4	41	7.6	9.9	10.9	21	2.3	3.3
(5)	1.25	6.8	83	9.4	11.7	12.0	19	2.4	2.7
(6)	1.26$_5$	7.1	100	9.8	12.5	12.3	11	2.7	2.5
(7)	1.30	8.0	166	11.0	13.4	13.2	19	2.3	2.2
(8)	1.33$_5$	8.7	240	12.0	14.5	13.9	14	2.5	1.9

* Computed from equation (8a) with λ_{12} = 26 kcal mol^{-1}; the term w_r can be neglected owing to the high ionic strength, and one of the reagents being uncharged.

considers the common dependence of log k_1 on $E^{\ominus}$ (see Figure 1) for the catechol–radical half-reaction involved in the rate-determining step, it seems reasonable to assume that, as in the case of quinol (H_2quin) and a series of substituted quinols,[2] $E^{\ominus\prime\prime} - E^{\ominus} = 0.38$ V, irrespective of the substituent present on the ring. Moreover, on the basis of a comparison, an estimate of the first dissociation constants of *p*-semiquinone radicals can be made [$K_{1(sq)}$ for $H_2quin^{+\cdot} \rightleftharpoons Hquin^{\cdot} + H^+$ (ref. 2)] and the logarithm of such values has been assumed to be a linear function of $E^{\ominus}$. Such a dependence has been observed for the first and second dissociation-equilibrium constants of quinols and for the second dissociation constants of *p*-semiquinones.[2] The values of K_1 for a series of catechols [10] and of $K_{2(sq)}$ for adrenaline and adrenalone [11] can be inserted in the above linear dependences which show similar gradients. On the basis of these observations, the same dependence of $K_{1(sq)}$ for *o*-semiquinones has been assumed to hold, and the values of $K_{1(sq)}$ (Table 3) have been estimated. It should be pointed out that, in the case of benzene-1,2-diols, hydrogen bonding stabilizes $Hcat^-$ species with respect to cat^{2-}, increasing the pK_2 value by 3—4 units in comparison with 1,4 isomers. However, this effect does not involve H_2cat and $Hcat^{\cdot}$. This is supported by the common linear dependence of pK_1 and p$K_{2(sq)}$ on $E^{\ominus}$ for the available data on catechols and quinols.

By assuming a reaction path involving step (6), a linear dependence of $\Delta G^{\ddagger}$ on $\Delta G_6^{\ominus}$ is found with a gradient of *ca.* 0.90. This gradient is not in accordance with equation (8a) and also the condition required for (8c) is not fulfilled, even if $\Delta G^{\ddagger}$ is very small, *i.e.* there is fast electron self-exchange for sq–H_2cat reactions; in fact $k_{ex} \simeq 10^5$ dm^3 mol^{-1} s^{-1} for $[IrCl_6]^{2-}$–$[IrCl_6]^{3-}$,[12] that is $\Delta G^{\ddagger} \simeq 8.5$ kcal mol^{-1}, so that λ_{12} should be greater than 17 kcal mol^{-1} = $2\Delta G^{\ddagger}$. By taking into consideration step (7) and computing $\Delta G_7^{\ominus}$ from the values of $E^{\ominus}$ = 0.957 V for the Ir^{IV}–Ir^{III} couple,[13] $E^{\ominus\prime\prime}$ and $K_{1(sq)}$, it has been found that the dependence of $\Delta G^{\ddagger}$ as a function of $\Delta G_7^{\ominus}$ fits equation (8a), with λ = 26 kcal mol^{-1} (see Figure 2). The data collected in Figure 2 include the findings of the present paper as well as those for quinols, both for the forward and reverse reaction, with the couple Ir^{IV}–Ir^{III}, showing that the same mechanism is operating in both cases, with the same intrinsic λ_{12} parameter, and suggesting that path (7) is the rate-determining step. This indicates that the self-exchange reaction rates for $H_2cat^{+\cdot}$–H_2cat as well as for $H_2quin^{+\cdot}$–H_2quin do not differ appreciably and can be estimated to be *ca.* 6 × 10^7 dm^3 mol^{-1} s^{-1} (corresponding to $\Delta G^{\ddagger} \simeq$ 4.5 kcal mol^{-1}), which agrees with literature data on the redox self-exchange reactivities between organic radicals and their parent molecules.[14]

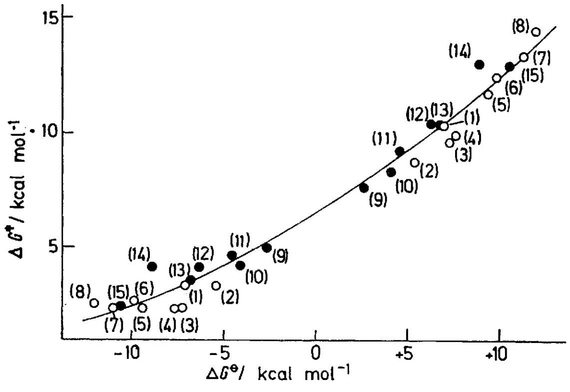

FIGURE 2 Plot of $\Delta G^{\ddagger}$ against $\Delta G^{\ominus}$ for reaction (7): (○), catechols; (●), quinols. The points at negative $\Delta G^{\ominus}$ values refer to the reverse reaction (the data for quinols are taken from ref. 2); the full line shows the behaviour predicted by equation (8a) with λ_{12} = 26 kcal mol^{-1}. For compounds see Figure 1

Further experimental work on redox reactions involving homogeneous series of organic substrates should give a deeper insight into the applicability of Marcus theory to these reversible organic systems.

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[6/668 *Received, 6th April,* 1976]

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[10] 'Stability Constants of Metal-Ion Complexes,' eds. L. G. Sillén and A. E. Martell, *Special Publ.*, no. 17 (1964) and no. 25 (1970), The Chemical Society, London.

[11] P. S. Rao and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 2274.

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

[13] R. Cecil, J. S. Littler, and G. Easton, *J. Chem. Soc.* (*B*), 1970, 626.

[14] I. B. Afanas'ev, S. V. Prigoda, T. Ya. Mal'tseva, and G. I. Samokhvalov, *Internat. J. Chem. Kinetics*, 1974, **6**, 643; D. Meisel, *Chem. Phys. Letters*, 1975, **34**, 263; D. Meisel and R. W. Fessenden, personal communication.