Electron Transfer between Benzenediols and Aquapentachloro-, Diaquatetrachloro-, and Hexabromo-iridate(IV)

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The agreement of the kinetic data concerning the oxidation of benzenediols by aquapentachloro-, diaquatetrachloro-, and hexabromo-iridate(IV) with a model proposed in the light of the Marcus theory, suggests that an outer-sphere electron transfer is the operative mechanism. The same reorganizational parameter λ (26 kcal mol^{-1}) satisfies the reactions involving the chloro-complexes, whereas a lower value is valid for hexabromoiridate(IV) (21 kcal mol^{-1}). An estimation of the intrinsic parameters for the self-exchange reactions involving these Ir^{IV}–Ir^{III} pairs has been attempted.

HEXACHLOROIRIDATE(IV) has been extensively investigated as oxidizing agent both with inorganic ions [1] as well as with organic [2] and organometallic compounds.[3] However, little attention has been devoted to the kinetics and mechanism of reaction involving related species, like aquapentachloro-,[2] diaquatetrachloro-,[2] and hexabromo-iridate(IV).[2,4] In previous papers the kinetics and mechanisms of oxidation of quinols [5] and catechols [6] by means of hexachloroiridate(IV) were investigated and an electron transfer mechanism was suggested. Also a phenomenological model, developed in the light of the Marcus theory,[7] was proposed in order to account for the dependence of the observed reaction rates on the free energies of reaction.

We now examine the reaction mechanism of related Ir^{IV} species and evaluate the characteristic intrinsic parameters for these compounds.

EXPERIMENTAL

Reagents.—Sodium hexachloroiridate(IV) was supplied by Merck and the spectrum of fresh solution agreed with literature data. Sodium hexachloroiridate(III) solutions were prepared by cathodic reduction of $IrCl_6^{2-}$ at a platinum electrode or by dissolution of K_3IrCl_6 (Alfa). Sodium aquapentachloroiridate(III) solutions were prepared by aquating a sample of $IrCl_6^{3-}$ in acid solution at 40—50° for *ca.* 2 h,[8] and these solutions were anodically oxidized in order to obtain the aquapentachloroiridate(IV). Sodium diaquatetrachloroiridate(III) was prepared by operating the aquation of $IrCl_6^{3-}$ solutions for 2 min; [9] the corresponding Ir^{IV} compound was obtained by anodic oxidation. The spectra of Ir^{IV} species agreed with literature data.[8,9] Perchloric acid (Merck) was used to bring the solution to the desired acidity. The following benzenediols (Merck, Aldrich, K & K) were investigated: 2-methylbenzene-1,4-diol (I), benzene-1,4-diol (II), 2,5-dihydroxybenzoic acid (III), 2,5-dihydroxybenzenesulphonic acid (IV), 2,3-dicyanobenzene-1,4-diol (V), 4-methylbenzene-1,2-diol (VI), benzene-1,2-diol (VII), (−)-4-[1-hydroxy-2-(methylamino)-ethyl]benzene-1,2-diol (adrenalin) (VIII), 3,4-dihydroxybenzoic acid (IX), 4-[1-oxo-2-(methylamino)ethyl]benzene-1,2-diol (adrenalone) (X), 4-cyanobenzene-1,2-diol (XI), and 4,5-dihydroxybenzene-1,3-disulphonic acid (XII).

Procedure.—The reactions were followed with a Durrum–Gibson stopped-flow spectrophotometer at $\lambda_{max.}$ for Ir^{IV} species, *i.e.* 445 (ε 2 920 l mol^{-1} cm^{-1}) for $Ir(H_2O)_2Cl_4$,[8] 450 (3 320) for $Ir(H_2O)Cl_5^-$,[7] and 585 nm (3 800) for $IrBr_6^{2-}$.[4] Kinetic runs were performed with $[Ir^{IV}]$ 1—2 × 10^{-5}M and an excess of organic substrate (up to 2 × 10^{-3}M for less reactive compounds). Measurements were carried out at $[HClO_4]$ 1.00M and μ 1.0M. Kinetic runs were performed at two different temperatures in order to estimate the activation parameters. A series of runs was carried out in the presence of the corresponding Ir^{III} species: no effect was observed. The rate constants were evaluated with a weighted least squares method (based on the deviation of the single points of each run) and the other kinetic parameters were derived by assigning the weights on the basis of standard deviations.

RESULTS

Stoicheiometry.—By means of spectrophotometric measurements with Ir^{IV} species in excess, the overall equation (1) was derived where H_2Q represents the benzenediols and Q the corresponding quinones.

$$2\ Ir^{IV} + H_2Q \longrightarrow 2\ Ir^{III} + Q + 2\ H^+ \qquad (1)$$

The values of the potentials for the pairs Ir^{IV}–Ir^{III} and Q–H_2Q show that all the investigated reactions go to completion. Experiments with parent quinol as reductant were carried out in order to detect the inorganic products. When $Ir(H_2O)Cl_5^-$ was the oxidant, $Ir(H_2O)Cl_5^{2-}$ was formed quantitatively,[8] and the same behaviour was observed for $Ir(H_2O)_2Cl_4$ and for $IrBr_6^{2-}$ [which form $Ir(H_2O)_2Cl_4^-$ and $IrBr_6^{3-}$ respectively].[9]

Kinetics.—When operating with a large excess of organic substrates, plots of $\ln(A_t - A_\infty)$, where A_t and A_∞ are the absorbance at time t and at equilibrium respectively, against time, were linear for at least two half-lives; the observed rate constants were also linearly dependent on the concentration of the organic substrates. Hence equation (2)

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obtains. For the more reactive compounds, second-order conditions were adopted and the corresponding second-order plots were also linear to at least 75% completion.

$$-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = k_0[\mathrm{Ir^{IV}}][\mathrm{H_2Q}] \qquad (2)$$

DISCUSSION

The reaction scheme can be represented by equations (3) and (4) where SQ represents the semiquinone radical.

TABLE 1

Kinetic and thermodynamic parameters for the oxidation of benzenediols by $\mathrm{IrCl_5(H_2O)^-}$

Substrate	k (7.0 °C) [b]	k (25.0 °C) [b]	$\Delta H^\ddagger$ [c,d]	$\Delta S^\ddagger$ [e]	$\Delta G^*_{\mathrm{exp}}$ [c,f]	E° [g]	$E^{\circ\prime}$ [h]	ΔG° [c,i]	$\Delta G^*_{\mathrm{calc.}}$ [c,l]
(II)	5.0×10^5	8.8×10^5	4.6	−16	6.9	0.699	1.14	1.2	7.1
(III)	2.9×10^4	5.4×10^4	5.2	−20	8.5_5	0.769	1.23	3.3	8.2_5
(IV)	2.6×10^4	4.6×10^4	4.7	−22	8.6_5	0.787	1.25	3.7	8.5
(V)	4.3×10^2	7.0×10^2	3.9	−32	11.1	0.910	1.41	7.4	10.7
(VII)	3.8×10^4	6.2×10^4	3.9	−23	8.4_5	0.792	1.25	3.7	8.5
(VIII)	6.8×10^4	8.9×10^4	1.9	−30	8.2_5	0.812	1.28	4.4	8.9
(IX)	1.25×10^3	2.7×10^3	6.5	−21	10.3	0.885	1.38	6.7	10.3
(X)	1.15×10^3	2.3×10^3	5.8	−24	10.4	0.910	1.41	7.4	10.7
(XI)	3.2×10^2	7.2×10^2	6.9	−22	11.1	0.924	1.43	7.9	11.0_5
(XII)	6.2×10^1	1.4×10^2	7.0	−25	12.1	0.955	1.47	8.8	11.7

[a] $[\mathrm{HClO_4}] = 1.00\mathrm{M}$, $\mu = 1.0\mathrm{M}$. [b] l mol^{-1} s^{-1} (error is ±3—5%). [c] kcal mol^{-1}. [d] Error ±0.7—1.2 kcal mol^{-1}. [e] cal mol^{-1} K^{-1} (error ±2.4—4.0 cal mol^{-1} K^{-1}). [f] At 25.0 °C, calculated from $k = Z \exp(-\Delta G^*/RT)$. [g] Reduction potential (V) for $\mathrm{Q + 2H^+ + 2e \rightleftharpoons H_2Q}$ couples. [h] Reduction potential (V) for $\mathrm{H_2Q^{\cdot +} + e \rightleftharpoons H_2Q}$ pairs calculated as reported in refs. 5 and 6. [i] Calculated by assuming E° 1.088 V for the $\mathrm{IrCl_5(H_2O)^{-/2-}}$ pair (ref. 2). [l] Calculated from equation (6) with λ 26 kcal mol^{-1}.

TABLE 2 [a]

Kinetic and thermodynamic parameters for the oxidation of benzenediols by $\mathrm{IrCl_4(H_2O)_2}$

Substrate	k (8.0 °C)	k (25.0 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^*_{\mathrm{exp}}$	ΔG°	$\Delta G^*_{\mathrm{calc}}$
(III)	3.1×10^5	6.6×10^5	6.8	−9	7.0_5	0.6	6.8
(IV)	2.7×10^5	5.4×10^5	6.2	−11	7.6	1.1	7.0_5
(V)	5.2×10^3	9.0×10^3	4.8	−24	9.6	4.8	9.1
(VII)	3.6×10^5	6.4×10^5	5.1	−15	7.1	1.1	7.0_5
(VIII)	5.5×10^5	7.8×10^5	2.8	−22	6.9_5	1.8	7.4
(IX)	1.6×10^4	3.2×10^4	6.2	−17	8.8_5	4.1	8.7
(X)	1.15×10^4	2.2×10^4	5.8	−19	9.1	4.8	9.1
(XI)	3.8×10^3	8.6×10^3	7.0	−17	9.6_5	5.2	9.4
(XII)	1.85×10^3	3.6×10^3	6.0	−22	10.1_5	6.2	9.9_5

[a] Footnotes as for Table 1; E° for $\mathrm{IrCl_4(H_2O)_2}$–$\mathrm{IrCl_4(H_2O)_2^-}$ is taken as 1.023 V (ref. 2).

TABLE 3 [a]

Kinetic and thermodynamic parameters for the oxidant of benzenediols by $\mathrm{IrBr_6^{2-}}$

Substrate	k (7.0 °C)	k (25.0 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^*_{\mathrm{exp}}$	ΔG°	$\Delta G^*_{\mathrm{calc}}$ [b]
(I) [c]	2.5×10^5	4.1×10^5	4.0	−20	7.3_5	4.2	7.5_5
(II)	4.2×10^4	7.4×10^4	4.7	−21	8.3_5	5.9_5	8.6_5
(III)	1.0×10^3	1.75×10^3	4.6	−28	10.6	8.0	10.0
(IV)	8.0×10^2	1.45×10^3	4.9	−28	10.7	8.5	10.4
(VI)	2.0×10^4	3.8×10^4	5.4	−20	8.7_5	7.1	9.4
(VII) [d]	1.25×10^3	2.7×10^3	6.5	−21	10.3	8.5	10.4
(VIII)	1.8×10^3	3.6×10^3	5.8	−22	10.1_5	9.2	10.8

[a] Footnotes as for Tables 1 and 2; E° for the $\mathrm{IrBr_6^{2-/3-}}$ pair is taken as 0.882 V (ref. 2). [b] Calculated from equation (6) with λ 21 kcal mol^{-1}. [c] E° 0.644, $E^{\circ\prime}$ 1.065 V. [d] E° 0.739, $E^{\circ\prime}$ 1.19 V.

The application of the steady-state treatment to SQ leads to the rate equation (5). The observed rate law

$$\mathrm{Ir^{IV} + H_2Q \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ir^{III} + SQ} \qquad (3)$$

$$\mathrm{Ir^{IV} + SQ \xrightarrow{k_4} Ir^{III} + Q} \qquad (4)$$

$$-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = 2k_3k_4\,[\mathrm{Ir^{IV}}]^2[\mathrm{H_2Q}]/(k_{-3}[\mathrm{Ir^{III}}] + k_4[\mathrm{Ir^{IV}}]) \qquad (5)$$

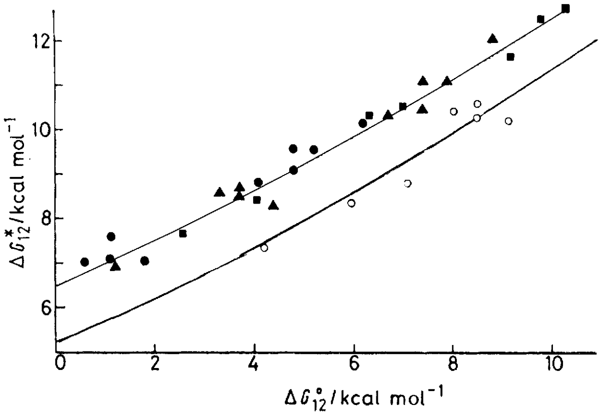
and the absence of $\mathrm{Ir^{III}}$ species effect suggest that $k_4[\mathrm{Ir^{IV}}] \gg k_{-3}[\mathrm{Ir^{III}}]$, hence $k_0 = 2k_3$. The values of k_3 at different temperatures were collected in Tables 1—3.

The comparison of the activation parameters of the reactions investigated with those for displacement of ligands from the co-ordination sphere of $\mathrm{Ir^{IV}}$ complexes, and the detection of the $\mathrm{Ir^{III}}$ end species, suggest that an electron transfer mechanism is operative, as previously established for oxidation of benzenediol with $\mathrm{IrCl_6^{2-}}$ (with $\mathrm{H_2Q^{\cdot +}}$ radical species formation).[5,6] The Marcus theory[7] predicts, for this class of reaction, a relationship between the free energy of activation and the free energy change of the form (6) where $k = Z$

$$\Delta G^*_{12} = w_{12} + \lambda(1 + \Delta G^\circ_{12}{}'(\lambda)^2/4 \qquad (6)$$

$\exp(-\Delta G^*_{12}/RT)$, Z being the collision frequency in solution (10^{11} l mol^{-1} s^{-1}), is defined as $2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22})$, where ΔG^*_{11} and ΔG^*_{22} refer to the self-exchange reactions of the reagents and w_{11} and w_{22} represent the work terms involved in the self-exchange reactions; $\Delta G^\circ_{12}{}' = \Delta G^\circ_{12} + w_{21} - w_{12}$, where w_{21} and w_{12} are the work terms required to bring the products or reactants together at the separation distance in the activated complex, and ΔG°_{12} is the free energy of reaction for the prevailing medium and temperature. At our high ionic strength and with one of the reactants uncharged, the work terms can be neglected.

For the reaction of benzenediols with hexachloroiridate(IV), equation (6) was found to be satisfied by adopting λ 26 kcal mol^{-1} and by calculating ΔG°_{12} on the assumption of the dependence of deprotonation constants of $H_2Q^{\cdot +}$ species on the redox potentials of Q–H_2Q pairs.[5,6] For the Ir^{IV} species investigated, the experimental points concerning aquapentachloro- and diaquatetrachloro-iridate(IV) lie on the same curve for hexachloroiridate(IV), drawn with λ 26 kcal mol^{-1} (see Figure); the values of ΔG°_{12} were calculated as for the $IrCl_6^{2-}$ reaction, that is assuming $H_2Q^{\cdot +}$ as the product of the rate-determining step.[5,6] The observed agreement implies that the substitution of chloride with water into the co-ordination sphere of Ir^{IV} does not change the reaction mechanism. Also the oxidation of cyclohexanone by the same oxidizing species suggested that the same intrinsic parameter ΔG^{**} holds for this family of chloro-complexes of Ir^{IV}.[2]



Plot of ΔG^*_{12} as a function of ΔG°_{12} for the oxidation of benzenediols by Ir^{IV} species: ▲, $Ir(H_2O)Cl_5^-$; ●, $Ir(H_2O)_2Cl_4$; ■, $IrCl_6^{2-}$ (taken from refs. 5 and 6); ○, $IrBr_6^{2-}$; upper curve calculated from equation (6) with λ 26 and lower curve with λ 21 kcal mol^{-1}

However, the oxidation rates of benzenediols by $IrBr_6^{2-}$ were higher than those for chloro-derivatives, when the same free energy of reaction is involved (similarly, the cyclohexanone oxidation rate was higher for $IrBr_6^{2-}$ than for $IrCl_6^{2+}$, although the free energy of reaction is more favourable for this last complex).[2] Satisfactory agreement with the experimental data is obtained for λ 21 kcal mol^{-1} (see Figure).

These two λ values imply that $\Delta G^{**}_{IrCl^{2-/3-}} - \Delta G^{**}_{IrBr_6{}^{2-/3-}} = 2.5$ kcal mol^{-1} (where $\Delta G^{**} = \Delta G^* - w$). Consequently, taking into account, by means of equation (6), the contribution of ΔG°_{12} (due to the different reduction potentials of $IrCl_6^{2-/3-}$ and $IrBr_6^{2-/3-}$ pairs), it can be expected that the reaction rates of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ toward the same reducing agent should be of the same order of magnitude (namely the reaction rate of $IrBr_6^{2-}$ toward a substrate should be twice that of the same substrate with $IrCl_6^{2-}$). It is worth mentioning that the the reaction rates for cyclohexanone (2.57×10^{-2} and 9.4×10^{-2} l mol^{-1} s^{-1} at 25.0° for $IrCl_6^{2-}$ and $IrBr_6^{2+}$, respectively)[2] are in moderate agreement with these estimates and there are similar results for the reactions with tris(5,6-dimethyl-1,10-phenanthroline)iron(II) (2.2×10^8 and 1.8×10^8 l mol^{-1} s^{-1}) and with tris(4,4′-dimethyl-2,2′-bipyridine)-iron(II) (9.6×10^8 and 6.8×10^8 l mol^{-1} s^{-1}).[4]

In order to estimate the values of ΔG^{**} for self-exchange reactions of Ir^{IV}–Ir^{III} systems, the data reported by Hurwitz and Kustin can be taken into account.[10] The main problem arises from the estimation of the work terms involved in reactions between charged ions. Formula (7), where z_1 and z_2 are the

$$w = \frac{z_1 z_2 e^2}{Dr} e^{-\chi r} \qquad (7)$$

charge on the reactants, e the electron charge, D the static dielectric constant, r the radius of the activated complex, and the exponential coefficient is the Debye–Hückel term, where χ is the reciprocal Debye radius, can be adopted for estimating the work terms. The importance of the correct evaluation of the work terms was recently pointed out by Haim and Sutin,[11] and without any doubt our ΔG^{**} values are affected by some uncertainties.

If the value of 2.3×10^5 l mol^{-1} s^{-1} is assumed for the rate of exchange for $IrCl_6^{2-/3-}$,[10] a value of w_{11} 1.20 (the radius is assumed to be 4.3 Å) leads to ΔG^{**} 6.5 kcal mol^{-1}. Consequently a value of ΔG^{**} of 4.0 kcal mol^{-1} should pertain to the $IrBr_6^{2-/3-}$ self-exchange reaction.

It is noteworthy that these data assign a value of *ca.* 6.5 kcal mol^{-1} to ΔG^{**} for the $H_2Q^{\cdot +}$–H_2Q exchange reaction (corresponding to a rate of *ca.* $2 \times 10_6$ l mol^{-1} s^{-1}, a value which seems slightly low in respect to other radical-parent molecule exchange rates).[12] Anyway, it must be also taken into account that the λ values estimated for the benzenediol oxidations are the upper values since the deprotonation constant of $H_2Q^{\cdot +}$ (for parent quinol) was chosen as the lower probable value (10M).[5] It follows that ΔG^{**} ($H_2Q^{\cdot +}$–H_2Q) $\leqslant 6.5$ kcal mol^{-1} (that is $\geqslant 2 \times 10^6$ l mol^{-1} s^{-1} for the self-exchange rate).

Analogous comparison with benzenediol oxidations by $Fe^{III}L_3$,[13] leads to ΔG^{**} ($IrCl_6^{2+/3+}$) $-\Delta G^{**}$($FeL_3^{3+/2+}$) = 5 kcal mol^{-1}, hence ΔG^{**}($FeL_3^{3+/2+} = 1.5$ kcal mol^{-1}). A value of 3×10^8 l mol^{-1} s^{-1} was reported for self-

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exchange reaction rate for $FeL_3^{3+/2+}$ in 1.84M-sodium sulphate;[14] this means $\Delta G^* = 3.4$ kcal mol^{-1}, but the evaluation of the work terms is rather uncertain at this ionic strength.

A test for these values of ΔG^{**} can be performed by calculating the cross-reaction rates with the aid of equation (6) and by comparing the results with the experimental data. For $IrCl_6^{2-}$ — $IrBr_6^{3-}$ a value of 6.4×10^6 l mol^{-1} s^{-1} is obtained from equations (6) and (7) (ΔE° 0.075 V)[2] to be compared with 1.2×10^7 l mol^{-1} s^{-1}, experimentally determined;[10] for $IrCl_6^{2+}$ — tris(4,4'-dimethyl-2,2'-bipyridineiron)$^{2+}$, calculated 6.5×10^8, experimental 9.6×10^8;[15] for $IrBr_6^{2-}$ — tris(4,4'-dimethyl-2,2'-bipyridine)iron $^{2+}$, calculated 1.6×10^9, experimental 6.8×10^8.[15] Unfortunately, no experimental data on electron-transfer reactions are available on mixed aquachloro-complexes of Ir^{IV}. Taking into account the difficulties in the estimation of the parameters involved, the agreement can be considered satisfactory.

It can be concluded that the proposed phenomenological model describes the presently investigated systems and that an outer-sphere mechanism operates in the oxidation of benzenediols by these related Ir^{IV} species; moreover the same intrinsic parameter can be adopted for the $IrCl_6^{2-/3-}$, $Ir(H_2O)Cl_5^{-/2-}$, $Ir(H_2O)_2Cl_4^{0/-}$ pairs (ΔG^{**} 6.5 kcal mol^{-1}), while a lower value pertains to the $IrBr_6^{2-/3-}$ pair (ΔG^{**} 4 kcal mol^{-1}

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