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Oxidation of benzenediols by hexabromoiridate(IV): kinetics at ambient and elevated pressures †

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The kinetics of oxidation of several benzenediols by the hexabromoiridate(IV) ion have been studied spectrophotometrically by the stopped-flow method. In 0.010 mol dm^{-3} $HClO_4$ and an ionic strength of 0.10 mol dm^{-3} ($NaClO_4$) at 25.0 °C the second-order rate constants (the reaction is first order in each reactant concentration), vary from 1.26×10^2 to 9.3×10^4 dm^3 mol^{-1} s^{-1}. The enthalpies of activation range from about 44 kJ mol^{-1} for the slowest reacting substrate to about 20 kJ mol^{-1} for the faster reactions. The $\Delta S^‡$ values do not vary over a wide range; the reaction rates are governed more by the enthalpy barrier. Application of pressure (up to 125 MPa) causes significant rate accelerations, giving rise to $\Delta V^‡$ values in the -17 to -26 cm^3 mol^{-1} range, consistent with the large, negative $\Delta S^‡$ values. This indicates that the rate limiting step is largely characterised by an increase in species ordering and electrostriction, and in the present case slightly less than for the corresponding reactions with the less bulky hexachloroiridate(IV) ion.

Introduction

The kinetics at high pressures of several inorganic self-exchange electron transfer reactions, frequently in aqueous solution, has been the subject of elegant and exacting experimental studies.[1] In addition, adaptation of the Marcus–Hush theory of electron transfer to kinetics at elevated pressures has led to calculation of the volume of activation, $\Delta V^‡$, for comparison with values determined experimentally.[1,2] The outcome is a fairly sophisticated understanding of many self-exchange electron transfer reactions, with explanations involving, for example, non-adiabaticity, influence of a change of spin state, closed or open form of chelate being advanced to account for cases in which there are marked differences between experimental and calculated values of $\Delta V^‡$.[1] While progress has been made, there is less success in understanding completely outer-sphere electron transfer and the parameters obtained from kinetics measurements at high pressures, for redox partners that are not a symmetrical pair. Clearly for the latter the volume of reaction, ΔV, is not zero.[2,3] There are several examples where the position of the transition state is characterised by a volume change that is close to half of that of the overall volume change of reaction.[3] In other reports $\Delta V^‡$ has been found to be more negative than might be expected, leading to the idea of overlap or interpenetration of redox partners following the formation of the encounter complex.[4,5] When charge change accompanies formation of the activated complex, electrostriction of solvent increases or decreases and contributes significantly to $\Delta V^‡$.This is usually the case in electron transfer reactions; however, these contributions are not quantitatively assigned.

In natural systems the importance of redox reactions involving quinones is well known.[6] We have chosen simple metal center oxidants to study the kinetics of oxidation of benzenediols to quinones,[5,7] since at present the results from more complex reactions will assuredly be not readily resolved, even if the systems were experimentally accessible. In earlier reports we have found that the volume reduction upon electron transfer varies little with variation in diol for a given oxidant,[5,7] from which it may be concluded that a common electrostriction change dominates within the measured value of $\Delta V^‡$. In an effort to define further those factors involved in partial molar volume changes in electron transfer reactions we have investigated the reaction kinetics at various pressures of the iridium(IV) hexabromide ion oxidation of some benzenediols in acidic aqueous solution. Results for the hexabromoiridate(IV) ion should provide an interesting comparison with those established[5] for the reaction of the hexachloroiridate(IV) ion with diols, and those for other systems.

Experimental

Materials

The iridium compounds, K_2IrCl_6 and K_2IrBr_6, were obtained from Johnson Matthey/Alfa. They exhibited the characteristic absorbance maxima of 487 and 585 nm, respectively. The benzenediols employed, 2,3-, 3,4- and 2,5-dihydroxybenzoic acids, catechol (1,2-dihydroxybenzene), 4-*tert*-butylcatechol, 4-methylcatechol, L-DOPA [β-(3,4-dihydroxyphenyl)-L-alanine] and adrenaline [1-(3,4-dihydroxyphenyl)-2-(methylamino)-ethanol] and 1,4-hydroquinone were high grade commercial products obtained from Aldrich, Sigma or Merck, and used as received. Reagent grade $HClO_4$ (70%) or HCl (32%) when diluted was used to adjust the acid concentration of solutions, and reagent grade $NaClO_4$ to adjust the ionic strength of most solutions. Other salts used were also reagent grade. High purity water was used throughout.

Methods

All solutions were made up immediately prior to use. Iridium containing solutions were stored in the dark during a series of experiments; no change in the visible absorption spectrum could be detected whether or not this precaution was taken. The acidic medium avoids any potential base hydrolysis of the iridium species in solution. The UV-vis spectra were recorded on either a Shimadzu UV-2101PC spectrophotometer or a Hewlett-Packard 8452 spectrophotometer; the sample com-

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† Dedicated to Professor R. G. Wilkins, on the occasion of his 70th birthday. *Supplementary data available*: k_{obs} values. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/1503/, otherwise available from BLDSC (No. SUP 57517, 11 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

partments were thermostatted at 25.0 °C. The pH of solutions was measured with a Metrohm 20 pH meter.

Mixing solutions of the concentrations used in the kinetics experiments produced an absorbance spectrum characteristic of solutions of iridium(III), indicating that under the conditions employed the reduction of the Ir^{IV} is complete. Ambient pressure kinetic measurements were made on a Biologic stopped-flow spectrophotometer, which was equipped with an MPS-51 microprocessor unit, and has a 1 cm path length observation cuvette, or on an Applied Photophysics instrument, SK 18 MV model, also with a 1 cm cuvette. In each instrument the temperature was controlled to ±0.1 °C by circulating thermostatted water. High pressure (up to 125 MPa) kinetic measurements were made on a home-built stopped-flow spectrophotometer[8] in which the temperature was controlled to ±0.1 °C. Data from stopped-flow instruments were acquired and processed (Olis, Bogart, Georgia) using an on-line computer system, or using software supplied by Applied Photophysics for instrument control, data acquisition and processing. A large excess of benzenediol over the iridium(IV) species was used to convert the expected second-order reaction into a pseudo first-order process. The observed traces obtained by following the loss of absorbance at 487 (chloro compound) or 585 nm (bromo compound) were fitted very well by a single exponential function indicating first-order kinetics. A minimum of four, and frequently many more, replicate measurements was made at each set of conditions. All reported rate constants are averages of these replicate determinations.

Results and discussion

Kinetics and mechanism

The reactions under discussion follow second-order kinetics, first order in each reactant concentration, under the conditions of the experiments. Plots of k_{obs}, the pseudo first-order rate constant, *versus* excess diol concentration (usually 2.5 to 10 mmol dm^{-3}, and $[Ir^{IV}]$ typically 0.080 mmol dm^{-3}) were linear and with a few exceptions, noted below, pass through the origin, indicating reactions go to completion, and there are no complicating kinetic features. There is no evidence, based on the spectrum of the product solution, that there is any reoxidation to Ir^{IV}. The excess of diol present clearly suppresses this tendency; however, such reoxidation can occur in other circumstances, when for example tin(II) halides are present.[9,10] The kinetic results are consistent with expectation based upon reactions described earlier.[5] Thus the overall reaction is as in eqn. (1).

$$2IrBr_6^{2-} + H_2Q \longrightarrow 2IrBr_6^{3-} + Q + 2H^+ \qquad (1)$$

The rate determining step in oxidation of diols is considered to be the formation of a semiquinone intermediate, *i.e.* one of the two electrons has been transferred,[11] with the final quinone being formed rapidly. The extent to which the first proton is released in the rate determining step is not known. The empirical second-order rate constant, k, can be shown from a steady state treatment relating to the semiquinone intermediate to be equal to $2k_1$,[11] where k_1 is the second-order rate constant for formation of the intermediate. In terms of an outer sphere mechanism, $k_1 = K_{OS}k_{ET}$, where K_{OS} is the equilibrium constant for the formation of the encounter complex and k_{ET} is the rate constant for the actual electron transfer.

In a few cases at higher temperatures, *ca.* 40 °C, or at higher diol concentrations the reaction rates approach the time limit of the Biologic instrument (k_{obs} of the order of 200 s^{-1}). Since totally satisfactory data cannot be acquired under these circumstances there is some uncertainty regarding the linearity of the plots of k_{obs} *versus* diol concentration, and therefore whether they pass exactly through the origin. Hence the second-order rate constants derived from measurements at lower temperatures were used in these cases for determining thermal activation parameters. The reaction of 4-methylcatechol was too rapid for even a reliable estimate to be made of the second-order rate constant, and consequently no parameters are reported. A compilation of the average k_{obs} values for a given set of conditions, *viz.* concentration of reactants, temperature, acid and electrolyte concentrations is provided in SUP 57517. Except as described separately or noted in SUP, all reactions were carried out in a 0.010 mol dm^{-3} $HClO_4$ and 0.090 mol dm^{-3} $NaClO_4$ medium. Examples of plots of k_{obs} *versus* benzenediol concentration are presented in Fig. 1.

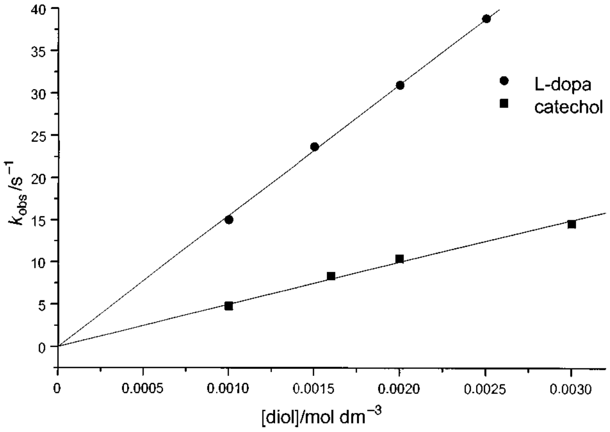

Fig. 1 Plots of k_{obs} *versus* [diol] for the reaction of $IrBr_6^{2-}$ with two different diols at 25.0 °C.

Table 1 Rate constants at 25.0 °C and thermal activation parameters for the reaction of $IrBr_6^{2-}$ with benzenediols[a]

Benzenediol	10^{-3} k/ dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
3,4-DHBA[b]	0.126 ± 0.002	44 ± 2	−57 ± 6
2,3-DHBA	5.55 ± 0.45	32.8 ± 0.3	−63 ± 1
2,5-DHBA	17.6 ± 0.4	32.6 ± 0.5	−55 ± 1
Adrenaline	12.1 ± 0.6	26 ± 1	−81 ± 4
L-DOPA	15.6 ± 0.2	25 ± 1	−80 ± 3
Catechol	4.8 ± 0.3	20 ± 2	−106 ± 6
4-*tert*-Butylcatechol	28.3 ± 0.7	27.7 ± 0.5	−66 ± 2
1,4-Hydroquinone	93 ± 3	26.1 ± 0.5	−61 ± 2

[a] All measurements were made at an ionic strength = 0.10 mol dm^{-3} (0.090 mol dm^{-3} $NaClO_4$ and 0.010 mol dm^{-3} $HClO_4$) except as noted in footnote *b*. [b] DHBA = Dihydroxybenzoic acid. In the presence of 0.090 mol dm^{-3} $LiClO_4$ and 0.010 mol dm^{-3} $HClO_4$, $\Delta H^‡ = 44 + 3$ kJ mol^{-1} and $\Delta S^‡ = -59 \pm 6$ J K^{-1} mol^{-1}.

Table 2 Rate constant comparison: reactions of $IrBr_6^{2-}$ and $IrCl_6^{2-}$ with benzenediols at 25.0 °C

Benzenediol	10^{-3} k/dm^3 mol^{-1} s^{-1}	
	$IrBr_6^{2-}$ [a]	$IrCl_6^{2-}$ [b]
3,4-DHBA	0.126 ± 0.002	0.14
2,3-DHBA	5.55 ± 0.45	0.50
2,5-DHBA	17.6 ± 0.4	4.6
Adrenaline	12.1 ± 0.6	10.8
L-DOPA	15.6 ± 0.2	19.4
Catechol	4.8 ± 0.3	0.49
4-*tert*-Butylcatechol	28.3 ± 0.7	26.0
1,4-Hydroquinone	93 ± 3	[c]

[a] Ionic strength = 0.10 mol dm^{-3} (0.090 mol dm^{-3} $NaClO_4$ and 0.010 mol dm^{-3} $HClO_4$). [b] All values except where indicated are taken from ref. 11(*a*). The value for 2,5-DHBA was taken from ref. 12, and values for reaction of catechol and 4-*tert*-butylcatechol from ref. 5. [c] Reaction too rapid for determining a reliable value.

In Table 1 the second-order rate constants at 25.0 °C and the thermal activation parameters are assembled. Where direct comparison between reactions of the $IrCl_6^{2-}$ ion and the $IrBr_6^{2-}$ ion is possible (see Table 2) it is clear that the rates of oxidation by the two ions are not very different. The rate constants in Table 2 were obtained at different ionic strengths and different acid concentrations; however, the rate limiting step in both cases is thought to be between an ion and a neutral species, and the rate constants are essentially independent of acid concentration, so the comparison is valid. The order of reactivity is the same for the isomeric dihydroxybenzoic acids, and also for the rapidly reacting L-DOPA and adrenaline, but a totally smooth trend is not evident. A free energy correlation approach is precluded since the substituents do not have any systematic electronic effect at the reaction site. Earlier work[12] has shown that there is a correlation between the logarithm of the forward rate constant and the standard redox potential for the reaction quinone to diol and related quinols. As expected for outer-sphere electron transfer reactions the enthalpies of activation are not large, being in the range of 20–44 kJ mol^{-1} and generally decrease with increasing rapidity of reaction. Based upon the kinetic scheme described above $\Delta H^\ddagger$ values are equal to the sum of the enthalpy change for formation of the encounter complex, ΔH° and the enthalpy of activation for the actual electron transfer step itself, $\Delta H^\ddagger_{ET}$. The former term is the difference between the enthalpy changes for diffusion together and diffusion apart of the redox partners, and therefore this is not expected to be very large or very different for variation in diol. Consequently the difference in measured $\Delta H^\ddagger$ values should reside mainly in the electron transfer step itself, yet it is difficult to pinpoint which property of the diols is principally responsible for the differences. The entropies of activation will be discussed in concert with the volumes of activation.

Several examples of catalysis of electron transfer reactions between anionic reaction partners by alkali metal ions have been noted.[13–19] Rate constants are virtually identical when the supporting electrolyte is formed from a lithium salt or a sodium salt, but significant rate acceleration has been observed for reaction in the presence of high (0.1 to 1.0 mol dm^{-3}) concentrations of K^+, Rb^+ and also NH_4^+ ions. The acceleration could arise from a more strongly bound encounter complex or from a more rapid electron transfer step, or both could be contributing factors. The results suggest that there is an uncatalysed path and a catalysed path, the latter involving the K^+ ion or other ion in reducing the repulsion between the two reactants and possibly forming a bridge which facilitates electron transfer. Reducing repulsion would result in an increase in the value of K_{OS} and a three species complex could enhance k_{ET}. It remains a puzzling aspect that K^+, having a lower charge density than Li^+ and Na^+ or H^+, is able to impart a catalytic effect on an anion–anion reaction, and the others (Li^+, Na^+ and H^+) do not, or the effect is marginal. The diameter of the hydrated monopositive ion appears to be more important than the charge density. The size or the steric organization of the anions seems to be of little significance, although correlations between the magnitude of the catalytic effect and the nature of the anions have not been attempted. This will be possible when more kinetic data on such catalytic systems become available.

In order to examine whether the catalytic effect occurs only when the redox partners are both anionic, we have determined the rates of some of the reactions studied here in the presence of different alkali metal ions that are part of the electrolyte medium. The rate constants for the reaction of 3,4-dihydroxybenzoic acid and $IrBr_6^{2-}$ in 0.090 mol dm^{-3} $LiClO_4$ and 0.090 mol dm^{-3} $NaClO_4$ solutions both containing 0.010 mol dm^{-3} $HClO_4$ have been obtained at several diol concentrations, and in the presence of $LiClO_4$ at different temperatures. These results and activation parameters are given in Table 3, as are the k_{obs} values for the same reaction in nitrate and chloride salts of Li^+, Na^+ and K^+ (parallel concentrations) at 25.0 °C.

Table 3 First-order rate constants for reaction of $IrBr_6^{2-}$ with 2,3- and 3,4-dihydroxybenzoic acids and catechol in different media at 25.0 °C

Benzenediol	Salt	[Salt]/ mol dm^{-3}	k_{obs}/ s^{-1} (average)
3,4-DHBA[a]	$LiNO_3$	0.090	0.309
	$NaNO_3$	0.090	0.297
	KNO_3	0.090	0.386
	LiCl	0.090	0.284
	NaCl	0.090	0.305
	KCl	0.090	0.367
	$LiClO_4$[b]	0.090	0.263
2,3-DHBA[c]	NaCl	0.90	8.17
	KCl	0.90	14.5
Catechol[d]	$NaNO_3$	0.49	9.23
	KNO_3	0.49	9.39
	$NaClO_4$	0.010	4.17

[a] [DHBA] = 2.5×10^{-3} mol dm^{-3} and [$IrBr_6^{2-}$] = 8.0×10^{-5} mol dm^{-3} in all experiments, except as indicated in footnote *d*. Ionic strength of 0.10 mol dm^{-3} (0.090 mol dm^{-3} and 0.010 mol dm^{-3} of the corresponding acid). [b] Rate constants obtained at other [DHBA] values and at three different temperatures, yielding $\Delta H^\ddagger = 45 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -59 \pm 9$ J K^{-1} mol^{-1}. [c] 0.10 mol dm^{-3} HCl. [d] [catechol] = 8.0×10^{-4} mol dm^{-3}, [$HClO_4$] = 0.010 mol dm^{-3}.

The reaction may be slightly accelerated in the presence of potassium ions, but the rate constant differences are barely outside of the experimental error range and indeed could arise from a secondary medium effect. In other studies the concentration levels of K^+ have been much higher; accordingly the kinetics of reaction of the 2,3-DHBA isomer with $IrBr_6^{2-}$ at an ionic strength of 1.0 mol dm^{-3}, comprising 0.10 mol dm^{-3} HCl and either 0.90 mol dm^{-3} NaCl or KCl, have been followed. The reaction is about 80% faster in the presence of this concentration of K^+ ions (Table 3). Yet in the presence of 0.49 mol dm^{-3} $NaNO_3$ or KNO_3 rate constants for the oxidation of catechol are identical (Table 3). For anion–anion reactions, depending on the system and the anion of the added salt, accelerations of a factor of three to seven have been noted.[18,19] These facts and that a substantially more marked acceleration occurs in the presence of Cs^+ ions[18a] suggest that a thorough examination of this form of catalysis be conducted. Some aspects will be addressed in a forthcoming article[19] on the reaction of the $IrCl_6^{2-}$ ion with I^-. It may be concluded that for the present reactions any catalytic effect is relatively minor or non-existent and rate constant differences may relate to a secondary medium effect or arise as a consequence of a minor influence on the encounter complex formation constant.

Volumes of activation

The values of $\Delta V^\ddagger$ are presented in Table 4, together with some values previously obtained for oxidation by the $IrCl_6^{2-}$ ion (Examples of plots used to derive $\Delta V^\ddagger$ values are shown in Fig. 2).[5] These values were determined in a standard manner from primary data in SUP 57517. In addition a newly obtained value, that for the oxidation of 2,5-dihydroxybenzoic acid by $IrCl_6^{2-}$, is included. A detailed interpretation of the volume of activation requires a consideration of the possible intrinsic and solvational contributions within both the volume change in forming the encounter complex and in reaching the transition state of the electron transfer step (encounter complex to successor complex). Other properties which can be useful in delineating the contributions to the volume of activation are the crystal structures of reactants and products. These could provide indirect information on the intrinsic volume changes, while partial molar volumes of reactants and products would allow assessment of the solvational contribution. Furthermore, a method for determining reaction volumes for iron-(III)–(II) complexes and other systems in which intrinsic changes can be estimated has been developed[20,21] The reaction volume may be correlated with the change in the square of the charge of the

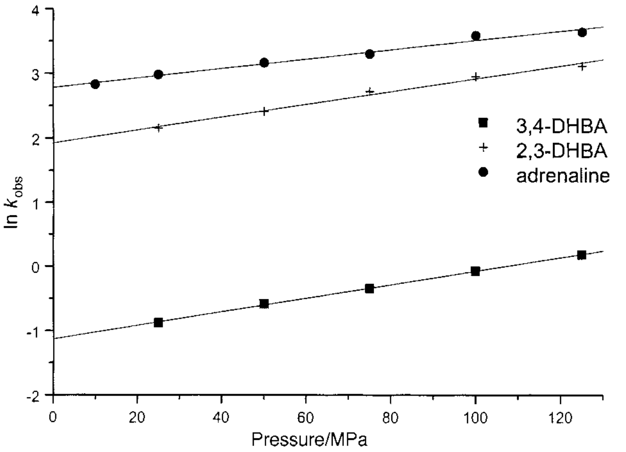

Fig. 2 Plots of ln k_{obs} *versus* pressure for the reaction of $IrBr_6^{2-}$ with three different diols at 25.0 °C (3,4-DHBA), 10.0 °C (2,3-DHBA) and 11.5 °C (adrenaline).

Table 4 Volumes of activation ($\Delta V^\ddagger$ in $cm^3\ mol^{-1}$) for reactions of $IrBr_6^{2-}$ and $IrCl_6^{2-}$ with benzenediols

Benzenediol	$IrBr_6^{2-\ a}$	$IrCl_6^{2-\ b}$
3,4-DHBA[c]	−25.9 ± 0.5	−30.3 ± 1.3
2,3-DHBA	−23.2 ± 1.4[d]	−26.0 ± 1.3
2,5-DHBA	−19.0 ± 1.0[e]	−26.7 ± 0.7
Adrenaline	−17.1 ± 1.2[d]	−25.9 ± 1.3[d]
L-DOPA	−18.9 ± 0.9[d]	−25.1 ± 1.4[f]
Catechol	−18 ± 2	−24.5 ± 0.9[d]
4-*tert*-Butylcatechol	−23.1 ± 1.0[g]	−24.6 ± 1.9[d]
1,4-Hydroquinone	−24.6 ± 1.9[g]	[h]

[a] Ionic strength = 0.10 mol dm^{-3} (0.090 mol dm^{-3} $NaClO_4$ and 0.010 mol dm^{-3} $HClO_4$), $T = 25.0$ °C except as noted. All values from this work. [b] Ionic strength = 1.0 mol dm^{-3}, $T = 25.0$ °C except as noted. Data from ref. 5, except the value for 2,5-DHBA which is from this work: k_{obs} values are, 5.80, 6.77, 9.23, 11.8 and 15.2 s^{-1} at 10, 25, 50, 75 and 100 MPa respectively. $[IrCl_6^{2-}] = 1.1 \times 10^{-4}$ mol dm^{-3}, [2,5-DHBA] $= 1.5 \times 10^{-3}$ mol dm^{-3}, $T = 25.0$ °C, pH 0 (1.0 mol dm^{-3} $HClO_4$). [c] $\Delta V^\ddagger = -27.0 \pm 0.4$ $cm^3\ mol^{-1}$ at 25.0 °C using 0.090 mol dm^{-3} $LiClO_4$ instead of 0.090 mol dm^{-3} $NaClO_4$. [d] $T = 10.0$ °C. [e] $T = 8.0$ °C. [f] $T = 9.9$ °C. [g] $T = 5.5$ °C. [h] The reaction is too rapid to be able to obtain its volume.

complex ion. Some aspects of this treatment are applicable to this work and will be discussed later. If the crystal structure results are relevant to the solution medium of this study then they indicate that the reduced form of the iridium species has only marginally shorter iridium–bromine bonds than those in the iridium(IV) species.[9,22] Consequently it would appear there is an insignificant intrinsic contribution to the volume of activation from this potential source. However, of course it is not clear whether any volume compression or expansion of the iridium species occurs on forming the transition state as electron transfer takes place. The intermediate product of the oxidation of the diol reactants is a diol radical cation species for which it is not known to what extent proton departure has begun in the transition state. In any event no crystallographic data are available. Therefore no assessment can be made of any intrinsic volume change arising from the conversion of the diol into its activated complex form.

Partial molar volumes were not available for any of the reactants or products, and indeed only for the iridium species the information would be of direct value since the final product quinone is not a product of the rate determining step. We have endeavoured to obtain the partial molar volumes of the $IrBr_6^{2-}$ and $IrBr_6^{3-}$ ions from density measurements at 25.0 °C using a Paar density meter (DMA 60), a Paar density measuring cell (DMA 602) and a Paar Precision Thermometer (CKT 100). The temperature could be controlled to 0.001 °C. In each case determination of highly reliable values was thwarted. Salts of the former ion are insufficiently soluble to obtain density measurements at concentration levels where the density differs sufficiently from the solvent to yield densities of requisite precision. Iridium(III) salts that are available are sufficiently soluble but in the absence of a strong reducing medium can be subject to spontaneous oxidation.[9,10] This possible interference adds an element of uncertainty to the measurements even though solutions were made up immediately before use and the density recorded within a few minutes. The approximate values of the partial molar volumes are 187 and 193 $cm^3\ mol^{-1}$ respectively for the $IrBr_6^{2-}$ and $IrBr_6^{3-}$ ions; the error margin is such that these results do not necessarily denote that the two species have the same volume, and indeed it would be surprising if they did given that the 3− ion will exert a greater electrostriction effect than the 2− ion. Consequently, the partial molar volume measurements are unfortunately not informative regarding the solvational contribution to the measured volumes of activation.

No charges are changed and covalent bonds are not broken or formed in forming the encounter complex; therefore, little volume change is expected upon its formation. However, if the species assume direct contact, the solvent displaced from the periphery of the $IrBr_6^{2-}$ ion to the bulk solvent could give rise to a small positive volume change. In forming the activated complex in an outer-sphere electron transfer reaction no substantial intrinsic volume change should occur. The successor complex contains an iridium(III) species, $IrBr_6^{3-}$, and a semiquinone species, which may still have attached to it the proton which will have departed when the reaction is complete. The observation of large negative $\Delta V^\ddagger$ values (in the range of −17 to −26 $cm^3\ mol^{-1}$) indicates that incipient higher charge development in the activated complex is responsible for a considerable increase in electrostriction which clearly predominates over any minor positive volume changes. There is not much variation in this partial molar volume change with change in the diol oxidised. Although the variation of $\Delta V^\ddagger$ with temperature should be minimal [$\Delta V^\ddagger = -RT \times$ slope (of ln k_{obs} *versus* p plot)] it has been observed previously[5] for the $IrCl_6^{2-}$/benzenediol reactions that $\Delta V^\ddagger$ can be as much as 3 to 4 $cm^3\ mol^{-1}$ less negative upon reducing the temperature from 25 to 10 °C. The reactions of 3,4-DHBA and catechol were measured at 25 °C and the pressure dependence of the rate constant for the other compounds was measured at considerably lower temperatures. With this in mind the relative insensitivity of $\Delta V^\ddagger$ to variation of diol is placed in a better perspective. Hence the electronic effect of aromatic ring substitution only operates on the lability of the electron transfer and does not markedly affect the volume of activation. This is not surprising if the principal contribution to $\Delta V^\ddagger$ is a common electrostriction change, and the different substituents are not involved in a volume sense. The values of $\Delta V^\ddagger$ are all slightly less negative than those for oxidation by $IrCl_6^{2-}$, results which are compatible with the fact that the larger $IrBr_6^{2-}$ species has a slightly lower charge density.

As indicated earlier, an approach developed by Tregloan and co-workers[20,21] allows an estimation of the solvational change based on the charge change. From the correlation between the reaction volume and the difference between the square of the charge on the oxidised and reduced form for the electrochemical reduction of a series of $Fe^{III,II}$ couples (see Fig. 5 in ref. 20) a reaction volume of *ca.* −32 $cm^3\ mol^{-1}$ can be extrapolated for the reduction of $IrBr_6^{2-}$ to $IrBr_6^{3-}$. After correction for the contribution of the reference electrode (Ag–Ag^+) for which the reaction volume is −11.9 $cm^3\ mol^{-1}$,[20] it follows that the reduction of $IrBr_6^{2-}$ to $IrBr_6^{3-}$ can be accompanied by a volume collapse of *ca.* −20 $cm^3\ mol^{-1}$ based on this correlation. On the basis of the structural arguments presented above, this volume collapse will mainly be due to an increase in electrostriction. The predicted reaction volume is rather close to the observed volumes of activation in this study, which could indicate that the reaction has a "late" (*i.e.* product-like) transition state. An earlier transition state will only then be possible if the oxidation of the diol also involves a significant volume collapse due to charge creation (prior to the release of a proton), such that an even more negative reaction volume will be obtained than that predicted on the basis of the electrochemical correlation.[20]

In the reactions studied here the entropy of activation should be a combination of contributions from species reduction (formation of the encounter complex) and solvent restriction from increasing electrostriction; both will give rise to a decrease in entropy. The fact that the observed $\Delta S^{\ddagger}$ values are in the -55 to -106 J K^{-1} mol^{-1} range is consistent with expectation. Furthermore, $\Delta S^{\ddagger}$ values for the $IrCl_6^{2-}$/benzenediol reactions are more negative, in the -100 to -150 J K^{-1} mol^{-1} range, which can be linked to the influence of charge density differences on the halogenoiridium(IV) and -(III) ions. Interestingly, in the reaction between $IrCl_6^{2-}$ and I^- there is no net change in charge if the rate determining step in the redox process is the oxidation of I^- to $I^{\cdot}$;[23–25] but this reaction is also characterised in a variety of media by $\Delta V^{\ddagger}$ values between -20 and -30 cm^3 mol^{-1}.[17]

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