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Electrostriction and counter ion effects in an outer-sphere electron transfer reaction. Kinetics of the reduction of hexachloroiridate(IV) by iodide ion †

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The kinetics of the reaction between the hexachloroiridate(IV) ion and iodide ion in aqueous acidic media has been monitored spectrophotometrically in the temperature range 20 to 40 °C, at ambient and at elevated pressures (up to 125 MPa). With suitable selection of reactant concentrations the reaction can be studied as simple pseudo first-order (iodide ion in excess) yielding a second-order rate constant of 1.42×10^3 M^{-1} s^{-1} at 25 °C and atmospheric pressure. This compares favourably with a value of 1.38×10^3 M^{-1} s^{-1} for the same parameter, determined previously under the same conditions. The reaction rate varies to a limited degree with variation in the conjugate base of the acids employed, which may be the result of a secondary medium effect. Potassium ions exert a significant catalytic effect, a finding that parallels those reported for other anion–anion redox reactions. The reaction is moderately sensitive to temperature: $\Delta H^‡$ ranges from 18 to 34 kJ mol^{-1} depending on the reaction medium. All $\Delta S^‡$ values are distinctly negative, suggesting a degree of molecular ordering and/or increasing electrostriction in the rate limiting step. Under all conditions employed pressure accelerates the reaction rate, resulting in large negative volumes of activation, typically −20 to −25 cm^3 mol^{-1}. How the thermal and activation parameters relate to the mechanism is discussed.

Introduction

The complete understanding of the mechanisms of inner-sphere or outer-sphere electron transfer in a broad range of chemical or biochemical systems is a goal of fundamental importance. Much progress has been made in experimental investigations of metal complex redox reactions since earlier work, for example by Taube.[1a] In fact there are several general accounts that review the progess in this field.[1b] The development of theories[2] which in many cases[3] explain kinetic results in terms of equilibrium redox properties has brought cohesion to the subject of electron transfer. Self-exchange[4] and non-symmetrical redox reactions[5] have been monitored by, among other methods, NMR and UV-Vis spectroscopy, and other media beside aqueous solution have been used as necessary. Only in the past few years has the pressure variable become somewhat more widely used[6] despite early reports of the promise of this method.[7] Many investigators are restricted to application of the temperature variable, which yielding $\Delta H^‡$ and $\Delta S^‡$ can help to distinguish in unobvious cases between outer-sphere and inner-sphere mechanisms and can point to the influence, if any, of solvent. The volume of activation, $\Delta V^‡$, derived from kinetic parameters obtained as a function of pressure, under optimal circumstances[7] can be divided into contributions which are compatible with Marcus–Hush–Stranks theory.

One of our objectives[8] has been to ascertain the effect of charge, or lack thereof, upon the kinetic and activation parameters for reaction between various redox partners. Implicit in these studies is that analysis of volume changes can be based upon the observed second-order rate constant, k_2, being a composite product of the ion-pair, or ion–molecule encounter complex, formation constant, K_{os}, and the rate-determining electron-transfer rate constant k_{ET}, for formation of the successor complex from the precursor complex, *i.e.* as in eqn. (1).

$$k_2 = K_{os}k_{ET} \qquad (1)$$

Incipient **net changes** in charge will develop on the redox partners, during the electron transfer step. The extent of any charge development, of course, depends on the position of the transition state along the reaction coordinate. Unsymmetrical reactions normally would have unequal charge densities among reactants and products and have a non-zero reaction volume, ΔV, whereas self-exchange reactions can be predicted to have a zero ΔV, providing there is no bond shortening or lengthening during the transfer. In acetonitrile some reactions between redox partners in which there is no net charge change have negative $\Delta V^‡$ values which have been interpreted as due to overlapping of reactants in the encounter species.[6b] This feature would need to pertain to at least as far as the transition state along the reaction coordinate, otherwise total or partial molar volume expansion would counteract the compression and restore the value of $\Delta V^‡$ toward zero.

When $[Fe(bpy)(CN)_4]^-$, $IrCl_6^{2-}$ or $IrBr_6^{2-}$ serve as oxidising agents on uncharged benzenediols large negative $\Delta V^‡$ values are obtained (−18,[6c] −27,[8a] and −23 cm^3 mol^{-1},[8b] respectively) at pH values where the reaction rates are essentially independent of pH. The $\Delta V^‡$ values show virtually no variance with each benzenediol used for either of the two iridium oxidants. These reactions are not associative in the normal sense where covalent or donor–acceptor bonds are formed by reactant partners, but yet demonstrate a significant volume compression. Solvation effects can be invoked qualitatively to account, partly at least, for the observations. The changing charged

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† Electronic supplementary information (ESI) available: observed rate constants as functions of [I⁻], temperature and pressure. See http://www.rsc.org/suppdata/dt/b0/b009363g/

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environments provide increasing electrostriction of solvent water, and considerably so if all the volume reduction is caused by this effect, since electrostricted water molecules have a volume of about 3 $\mathrm{cm^3\ mol^{-1}}$ less than bulk water molecules.[4a,9] The slightly less negative values for reaction of the hexabromoiridium(IV) ion relative to the hexachloro analogue may be due to the effect of charge density difference, albeit a minor one, for the more bulky bromo compound.

The kinetics of the reaction between $\mathrm{IrCl_6}^{2-}$ and I^- has been studied earlier and there was no consensus on the rate limiting step, although there was agreement on the reaction steps themselves.[3a,10,11] Further, several efforts to comprehend fully volume changes which accompany non-symmetrical redox reactions have not been completely successful. Having studied the effect of different oxidants, $[\mathrm{Fe(bpy)(CN)_4}]^-$, $\mathrm{IrCl_6}^{2-}$ and $\mathrm{IrBr_6}^{2-}$ with common uncharged reductants, and finding a significant electrostriction increase, it seemed necessary to try to identify the contribution of each charge change to the overall solvation effect. Consequently, with these thoughts in mind we have studied the kinetics over a range of pressures for the reaction of $\mathrm{IrCl_6}^{2-}$ with iodide ion, where the precursor complex, assumed to be formed by a diffusion controlled process, contains ions of $2-$ and $1-$ charges, while the successor complex should possess a $3-$ species ($\mathrm{IrCl_6}^{3-}$), and the iodine atom radical,[3a,10,11] as indicated in reactions (2)–(4). Reaction (3) is a rate determining step and the rate of reaction (4) has been the subject of discussion. Subsequent steps,[3a] shown in eqns. (5)–(7), lead to the final products of the reaction. Steps (5)–(7) are either rapid, post rate determining events or their involvement is negligible owing to the selection of reaction conditions.

$$\mathrm{IrCl_6}^{2-} + \mathrm{I}^- \longrightarrow [\mathrm{IrCl_6}^{2-}, \mathrm{I}^-] \qquad (2)$$

$$[\mathrm{IrCl_6}^{2-}, \mathrm{I}^-] \longrightarrow [\mathrm{IrCl_6}^{3-}, \mathrm{I}^{\bullet}] \qquad (3)$$

$$[\mathrm{IrCl_6}^{3-}, \mathrm{I}^{\bullet}] \longrightarrow \mathrm{IrCl_6}^{3-} + \mathrm{I}^{\bullet} \qquad (4)$$

$$[\mathrm{IrCl_6}^{3-}, \mathrm{I}^{\bullet}] + \mathrm{I}^- \longrightarrow \mathrm{IrCl_6}^{3-} + \mathrm{I_2}^{\bullet -} \qquad (5)$$

$$[\mathrm{IrCl_6}^{3-}, \mathrm{I}^{\bullet}] + \mathrm{I}^{\bullet} \longrightarrow \mathrm{IrCl_6}^{3-} + \mathrm{I_2} \qquad (6)$$

$$[\mathrm{IrCl_6}^{3-}, \mathrm{I}^{\bullet}] + \mathrm{I_2}^{\bullet -} \longrightarrow \mathrm{IrCl_6}^{3-} + \mathrm{I_3}^- \qquad (7)$$

In order that any contributions to $\Delta V^{\ddagger}$ from secondary or medium effects can be detected, the kinetics has been studied in different acids, at different pH values, at different ionic strengths and in different salt solutions of the same ionic strength. Besides addressing the question of the role and extent of electrostriction, the further objective of developing an overall volume profile is important. Since the ultimate products, in addition to the $\mathrm{IrCl_6}^{3-}$ ion, are $\mathrm{I_2}$ and $\mathrm{I_3}^-$, the partial molar volumes of the reactants and products may be estimated. However, the reaction is multi-step and the observed rate-determining step (if for the moment this is in accord with eqn. (1)), contains, in addition to the pathway represented kinetically in eqn. (1) and stoichiometrically in eqns. (2)–(4), a second, minor component, under the experimental conditions, which reduces quantitative certainty in analysis of volume changes. This second pathway alluded to, but considered to contribute negligibly in earlier work describing the atmospheric pressure kinetics,[3a] cannot be ignored in the rate law, under all experimental conditions. Yet the high pressure kinetics reported here yielded $\Delta V^{\ddagger}$ values which are largely independent of concentration of reactants for a given pH, temperature and ionic strength. The values do vary somewhat depending upon the particular acid used, and show some sensitivity to the cation partner of added salts. There is increasing evidence of specific effects of cations in outer-sphere electron transfer reactions between negatively charged species, and indeed these effects can be formulated in terms of a catalytic pathway in well studied cases.[4]

In addition to the objectives of this research as detailed above another motive is that another report appeared in which the rate determining step in the title reaction was judged to be the dissociation apart of the partners of the successor complex,[10] that is reaction (4), and it is conceivable that analysis of volumes of activation could lead to a distinction between this and a scheme in which reaction (3) is rate determining. In both cases the actual rate constant will be a composite term and this then adds further potential complication in interpretation. The arguments relating to this point are presented below.

Experimental

Materials

Batches of highest quality available $\mathrm{K_2IrCl_6}$ were purchased from Johnson Matthey and in solution yielded the characteristic absorbance maximum and absorbance values at 478 nm. Lithium, sodium and potassium salts were reagent grade materials. Reagent grade concentrated $\mathrm{HClO_4}$, $\mathrm{H_2SO_4}$, HCl and $\mathrm{HNO_3}$ solutions were used to prepare stock solutions of appropriate acid concentration. All solutions were diluted to a desired concentration using Milli-Q water.

Methods

Concentrations of stock solutions of acids were checked by suitable dilution and titration with standard NaOH solution. Solutions of $\mathrm{K_2IrCl_6}$ and NaI were freshly made before use and used in kinetics experiments as quickly as possible. When not in immediate use, solutions were stored at 4 °C in the dark.

UV-visible spectra were recorded on a Shimadzu UV 250 spectrophotometer with the cell compartment thermostatted at 25 °C. Ambient pressure kinetic measurements were made using a Dionex (2 cm path length) stopped-flow instrument, employing a moderately large excess of NaI solution to ensure pseudo first-order conditions. Reactions were monitored at 478 nm where the reduction of $\mathrm{IrCl_6}^{2-}$ to $\mathrm{IrCl_6}^{3-}$ is followed. Data were acquired on an IBM compatible PC with OLIS (Bogart, Georgia) software. The temperature was controlled to within ±0.1 °C by circulating fluid. Kinetics at elevated pressure (up to 130 MPa) was followed using a home-built, high pressure stopped-flow instrument[12] thermostatted to within ±0.1 °C, again using an excess of iodide ion. Data acquisition and processing were accomplished in identical ways as were used for the atmospheric pressure kinetics. All first-order plots were linear for at least three half-lives of the reaction. In some kinetic traces a minor perturbation to the smooth exponential decay curve occurred within the first few milliseconds after mixing, and represents only a small fraction of the overall absorbance change. This feature was noted in earlier studies of this reaction at atmospheric pressure, and it was concluded that while further investigation using a stopped-flow instrument of shorter dead time (but not yet available) might reveal something kinetically meaningful, the effect could not be distinguished from an experimental artifact. The reported rate constants are the average of four or five replicate kinetic runs, and tabulated rate constants are subject to an error range that is often between ±5 and 10%, but in some cases is less. Activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$, were calculated using standard least squares programs. Tabulated values are quoted with their standard deviation.

Results and discussion

Kinetics

In a previous study the atmospheric pressure kinetics, followed at 25.0 °C and in 0.50 M $\mathrm{H_2SO_4}$, over a $[\mathrm{I}^-]$ range of (1.0–

Table 1 Observed rate constants, k_{obs}, for the reaction of $IrCl_6^{2-}$ with I^- in various acidic media at 25.0 °C[a]

Acid	[Acid]/M	ave. k_{obs}/s^{-1}
H_2SO_4	0.50	2.81
	0.50	2.48
	0.33	1.75
	0.050	0.979
	0.033	0.892
$HClO_4$	1.0	3.82
	0.10	1.10
	0.10	1.20
HNO_3	1.0	5.61
	1.0	4.02
	1.0	4.20
	0.75	3.35
	0.50	2.48
	0.25	1.63
	0.10	1.14
	0.10	1.18
HCl	1.0	7.0
	1.0	6.91
	1.0	6.57
	1.0	6.52
	0.50	3.30
	0.10	1.29

[a] Concentrations for all experiments were: $[I^-] = 2.0 \times 10^{-3}$ M and $[IrCl_6^{2-}] = 6.25 \times 10^{-5}$ M. Duplicate experiments were carried out with newly prepared solutions.

80) × 10^{-3} M for a constant $[IrCl_6^{2-}]$ of 4.1×10^{-5} M, yielded a pseudo-first-order rate constant which when divided by $[I^-]$ produced values that were said to be independent of $[I^-]$.[3a] However, only values of $[I^-]$ up to about 16.0×10^{-3} M were shown in the figure, which formed part of the basis for this conclusion (that the k_{obs} is independent of $[I^-]$). It prevails that the remaining discussion[3a] was not adversely affected by this situation. ESI Supplementary Table S1 lists the kinetic results at atmospheric pressure in this study. There is an unmistakable trend of increasing magnitude of $k_{obs}/[I^-]$ with increasing $[I^-]$. A range of $[I^-]$ of (0.7–24) × 10^{-3} M is sufficient to illustrate the deviation from simple second-order kinetics. Therefore, if the rate law for the reaction is assumed to be (8) then from the data

$$-d[IrCl_6^{2-}]/dt = (k_1 + k_2[I^-])[IrCl_6^{2-}][I^-] \qquad (8)$$

of ESI Supplementary Table S1, by linear regression, plotting $k_{obs}/[I^-]$ (correlation coefficient 0.93) gives $k_1 = 1.42 \times 10^3$ M^{-1} s^{-1} and $k_2 = 24.0 \times 10^4$ M^{-2} s^{-1}, at 25.0 °C. Previous authors[3a] reported a value for the second order rate constant of 1.38×10^3 M^{-1} s^{-1}, at 25.0 °C, in 0.50 M H_2SO_4, which is very close to our value for k_1.

The reaction rate constant does vary, in a modest way with source of H^+, but only at higher acid concentrations (see Table 1). The variation with respect to $[H^+]$ was found to be not particularly significant.[3a] In addition, the approximately three- to four-fold change in rate constant for a ten-fold change in $[H^+]$ (0.1 to 1.0 M) could be mostly due to an ionic strength effect. Part of the rate constant difference for the reaction in 0.50 M H_2SO_4 from that in other sources of 1 M H^+ may arise from the incomplete dissociation of HSO_4^-. For example, the observed first-order rate constants for reactants of common concentrations, $[K_2IrCl_6] = 6.5 \times 10^{-5}$ M and $[I^-] = 2 \times 10^{-3}$ M, have average values of 2.7, 3.82, 4.7 and 6.8 s^{-1}, for reactions in 0.50 M H_2SO_4, 1.0 M $HClO_4$, 1.0 M HNO_3 and 1.0 M HCl, respectively. It is perhaps surprising that for a reaction in which an electron is transferred between two negatively charged species the anion (conjugate base) has an influence of this magnitude. This point will be addressed shortly. The effect of ionic strength on reactivity, which would be relevant in comparing these rate constants in different acids, *vis-à-vis* H_2SO_4 *versus* the other acids, will be considered later. Specific effects of the conjugate bases upon reaction rates are only manifest at higher concentrations of acid since a comparison of rate constants for the same reactant concentrations with a nominal 0.1 M H^+ medium shows only a relatively small range: k_{obs} (s^{-1}) is 0.98 in 0.050 M H_2SO_4, 1.15 in 0.10 M $HClO_4$, 1.16 in 0.10 M HNO_3 and 1.29 in 0.10 M HCl. These variations are hardly outside of experimental error, which realistically is ±5 to 10%, and this indicates that the differences at higher concentrations are probably due to secondary specific medium effects upon either or both the electron transfer itself and the encounter complex formation, within the presumed mechanism. Of course in energy terms a factor of two variation in rate constant (2.7 s^{-1} in 0.50 M H_2SO_4 and 6.8 s^{-1} in 1.0 M HCl) is very small. The reaction is fastest in the acidic medium in which the conjugate base does not have the ability to hydrogen bond to the solvent. Thus the medium effect may be related to the enthalpies of hydration of the congugate bases. It should be noted also that the reaction in progressively higher concentrations of nitrate ion leads to instability of the iodide ion and less certainty can be attached to kinetic parameters in higher $[NO_3^-]$ concentrations.

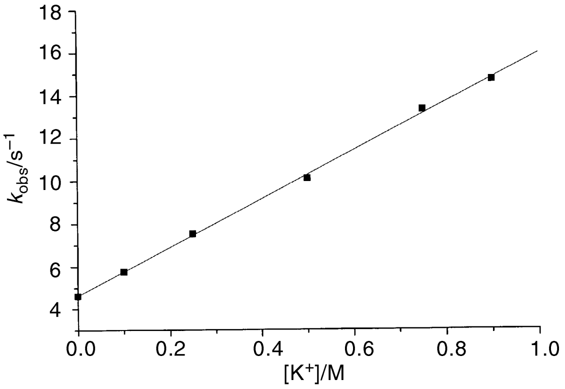

Fig. 1 Plot of k_{obs} (s^{-1}) for the reaction of $IrCl_6^{2-}$ with I^- *versus* $[K^+]$ (KNO_3) at 25.0 °C and a constant ionic strength (1.0 M). The ionic strength was maintained with HNO_3: details in Table 2.

In Table 2 the rate constants for the reaction using common reactant concentrations in different salt media are compiled. As expected the reaction rate does depend upon ionic strength, but the electrolyte concentrations are higher than those which allow a quantitative test of standard equations relating rate constant to ionic strength. Clearly the reaction is sensitive to the cation of added salt, although a modest dependence of the reaction rate upon acid concentration could be disguised within these data. Lithium ions have virtually no effect. In fact if there is one it is a slight rate retardation. In the case of added sodium ions the rate is indifferent to them when $NaNO_3$ is used, but a modest rate acceleration occurs for the other sodium salts. The most dramatic effect is seen with added potassium salts (see Fig. 1 and Table 2); there is a threefold increase in the observed rate constant when the ionic strength is 1.0 M, and the potassium salt contributes 90% to this value. Preliminary results over a relatively small concentration range of added electrolyte indicate that Ba^{2+} ions also catalyse the reaction.

Catalytic effects of this type have been observed before in outer sphere electron transfer reactions between negatively charged reactants.[3c,e,13] For example the rate of reaction between $IrCl_6^{2-}$ and $Fe(CN)_6^{4-}$ was found to be strongly influenced by the cations of added salts;[3c] the reaction was followed at pH 5 where protonated forms of $Fe(CN)_6^{4-}$ would be absent. The magnitudes of rate enhancement by alkali metal cations were independent of concentration of cation in the range from 10^{-3} to 10^{-1} M, and the increases followed the pattern $K^+ > Na^+ > Li^+$. The results were interpreted by invoking a catalytic effect of the cation in addition to a more facile encounter being created by shielding of the electrostatic

Table 2 Rate constants, k_{obs}, for reaction of $IrCl_6^{2-}$ with I^- in acidic and salt media at 25.0 °C[a]

Acid	[Acid]/M	Salt	[Salt]/M	I/M	ave. k_{obs}/s^{-1}
H_2SO_4	0.50	—		1.5	2.81
	0.50	—	—	1.5	2.48
	0.25	Na_2SO_4	0.25	1.5	3.40
	0.050	Na_2SO_4	0.45	1.5	3.46
	0.33	—	—	1.0	1.75
	0.033	Na_2SO_4	0.30	1.0	2.45
	0.25	—	—	0.75	1.70
$HClO_4$	1.0	—	—	1.0	3.82
	0.10	$LiClO_4$	0.90	1.0	3.63
	0.50	$NaClO_4$	0.50	1.0	4.65
	0.10	$NaClO_4$	0.90	1.0	4.89
	0.20	—	—	0.20	1.42
	0.10	—	—	0.10	1.20
	0.10	—	—	0.10	1.10
	0.010	$NaClO_4$	0.090	0.10	1.22
	0.10	$KClO_4$	0.10	0.20	2.06
HNO_3	1.0	—	—	1.0	5.61
	1.0	—	—	1.0	4.02
	1.0	—	—	1.0	4.20
	0.50	$LiNO_3$	0.50	1.0	3.46
	0.10	$LiNO_3$	0.90	1.0	3.11
	0.75	$NaNO_3$	0.25	1.0	4.30
	0.50	$NaNO_3$	0.50	1.0	4.25
	0.25	$NaNO_3$	0.75	1.0	4.26
	0.10	$NaNO_3$	0.90	1.0	4.52
	0.90	KNO_3	0.10	1.0	5.76
	0.75	KNO_3	0.25	1.0	7.53
	0.50	KNO_3	0.50	1.0	10.1
	0.25	KNO_3	0.75	1.0	13.3
	0.10	KNO_3	0.90	1.0	14.7
HCl	1.0	—	—	1.0	7.00
	1.0	—	—	1.0	6.91
	1.0	—	—	1.0	6.57
	1.0	—	—	1.0	6.52
	0.10	NaCl	0.90	1.0	8.87
	0.10	NaCl	0.90	1.0	8.46
	0.50	KCl	0.50	1.0	18.9
	0.10	KCl	0.90	1.0	26.8
	0.50	—	—	0.50	3.30
	0.10	—	—	0.10	1.29

[a] Concentrations for all experiments were: $[I^-] = 2.0 \times 10^{-3}$ M and $[IrCl_6^{2-}] = 6.25 \times 10^{-5}$ M. Duplicate experiments were carried out using newly prepared solutions.

repulsion between the negatively charged reactants. In the present study the iodide ion of −1 charge forms an encounter complex with the $IrCl_6^{2-}$ ion, and subsequently an activated complex which on electrostatic grounds attracts cations less strongly than does the corresponding activated complex containing $Fe(CN)_6^{4-}$. This is the probable reason that only the K^+ ion manifests any significant rate enhancement in the reaction of I^- with $IrCl_6^{2-}$.

The difference in the effect of the presence of anions on outer sphere electron transfer reactions between positively charged ions from the effect of cations upon electron transfer between two negatively charged species has been pointed out.[14] In addition, a detailed analysis of the catalytic effect of alkali metal ions on the reaction of MnO_4^- with MnO_4^{2-} has been presented.[3e] In this latter study the kinetic effect at atmospheric pressure manifests itself as a reaction acceleration effect, with the order being $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, which is consistent with the more limited findings in the present study. The observed rate constant in this self-exchange reaction, studied by NMR spectroscopy, may be divided into two components: one which is independent of the added cation and a second in which the observed rate constant is a linear function of the alkali metal ion concentration. Sufficient data were collected enabling $\Delta H^\ddagger$ and $\Delta S^\ddagger$ to be calculated for each metal ion as well as for the cation independent path. These values are 46 kJ mol^{-1} and −35 J K^{-1} mol^{-1}, respectively, for the cation independent path, and virtually constant at 33 kJ mol^{-1} for $\Delta H^\ddagger$, and modest changes in $\Delta S^\ddagger$ over the range from −68 to −59 J K^{-1} mol^{-1} were found, in proceeding from Li^+ to Rb^+ for the cation dependent pathway. Thus the trend in the catalytic effect is governed by an entropic effect.

A model to account for the catalysis of anion–anion electron transfer reactions by monopositive cations, has been presented recently. The reactions investigated exhibited large positive volumes of activation that were accounted for in terms of desolvation of the cation prior to catalysis of the electron transfer process by the cation.[15] Another recent report describes the calculation of an ion–triplet association constant, K_{IT}, and specifically for an anion–cation–anion triplet.[16] This work has implications for kinetics studies where a bridging cation may facilitate electron transfer by minimising repulsion. However, as the authors[16] point out it is far from definite that only one cation would be involved per anion–anion partner pair. The concentrations of alkali metal ions at which catalysis is readily manifest in this study are very much higher than both reactant species. This suggests that more than one cation may participate. This was also proposed in an early comprehensive examination[5d] of cation effects on the kinetics of an anion–anion electron transfer reaction.

Activation parameters

The thermal activation parameters for the reaction of I^- with $IrCl_6^{2-}$ in different acidic media are assembled in Table 3, and are derived from the primary data compiled in ESI Supplementary Table S2. Values of $\Delta H^\ddagger$ vary over a range from 18 to 34 kJ

Table 3 Thermal activation parameters for the reaction between $IrCl_6^{2-}$ and I^- [a]

Medium		$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
Acid	Salt		
0.50 M H_2SO_4	—	22.3 ± 0.8	−113 ± 5
0.50 M H_2SO_4	—	21.4 ± 1.6	−110 ± 3
0.050 M H_2SO_4	—	24.2 ± 0.8	−112 ± 3
0.050 M H_2SO_4	0.45 M Na_2SO_4	34 ± 2	−68 ± 8
1.0 M $HClO_4$	—	25.1 ± 1.0	−95 ± 3
1.0 M $HClO_4$	—	28.9 ± 0.8	−84 ± 3
1.0 M $HClO_4$	—	25.5 ± 1.2	−95 ± 4
0.10 M $HClO_4$	—	24.6 ± 0.6	−109 ± 2
0.10 M $HClO_4$	0.90 M $LiClO_4$	33.2 ± 1.1	−71 ± 4
1.0 M HNO_3	—	27.4 ± 1.2	−88 ± 4
0.10 M HNO_3	—	25.1 ± 0.5	−108 ± 2
0.10 M HNO_3	0.90 M $NaNO_3$	34 ± 3	−65 ± 9
0.10 M HNO_3	0.90 M $NaNO_3$	32 ± 2	−71 ± 7
1.0 M HCl	—	29 ± 2	−81 ± 5
1.0 M HCl	—	30.9 ± 1.2	−73 ± 4
1.0 M HCl	—	26.5 ± 2.1	−88 ± 7
0.50 M HCl	—	17.8 ± 1.2	−124 ± 4
0.10 M HCl	—	18.9 ± 0.7	−128 ± 2.0
0.10 M HCl	0.90 M NaCl	27.1 ± 1.4	−84 ± 5
0.10 M HNO_3	0.90 M $NaClO_4$	31.2 ± 1.8	−74 ± 6

[a] The reactant concentrations and temperature ranges employed in determining these parameters are given in ESI Supplementary Table S2.

mol^{-1}. These are lower than would characterise bond breakage or bond formation and therefore are consistent with a reaction that proceeds by an outer-sphere electron transfer mechanism. A limited temperature range, usually 20–40 °C, precludes the acquisition of precise data, with the error in $\Delta H^‡$ typically approaching ±10%. However, some general trends are discernible and noteworthy. In experiments with no added salt, the enthalpy of activation barrier is slightly lower in 0.50 M H_2SO_4 than in 1.0 M H^+ supplied by $HClO_4$, HNO_3 or HCl. When there is a tenfold decrease in acid strength the enthalpy of activation barrier is essentially unchanged except for the reaction in 0.1 M HCl, where a decrease of about 8 kJ mol^{-1} is found. Since the reaction is between two negatively charged species it is difficult to explain why the bi-negative sulfate ion could lower the barrier, unless it is a consequence of a different indirect ion-pairing effect from that exerted by ion pairs involving uni-negative ions upon the redox rate, and upon $\Delta S^‡$. Envisaging what molecular ordering contribution this might be, of the magnitude of 20 J K^{-1} mol^{-1}, is not readily realisable. It is equally unclear why the chloride ion acts differently from the other conjugate bases, although this might be connected to the fact that this is the only non-oxo-anion, as noted earlier. A second trend is one in which an ionic strength of 1.0 M (about 1.5 M in the case of sulfate species), that results from preparing solutions of 0.10 M acid (0.050 M in the case of H_2SO_4) and 0.90 M of an alkali metal salt (0.45 M in the case of Na_2SO_4), produces a moderate increase (5 to 10 kJ mol^{-1}) in the enthalpy barrier of the reaction, with associated decreases in the entropy of activation, except in the case of chloride as the conjugate base. On the face of it, this would suggest that the alkali metal ions, of lower charge density than protons, create a less favourable electrostatic locale for the reacting species as the transition state for electron transfer is attained. However, there is no apparent reason why NaCl would not participate in a similar way to other salts. The argument also tends to contradict the observed catalytic influence of the larger K^+ ion. There is a good correlation between the two thermal activation parameters indicative of the isokinetic relationship.[17] This is not surprising since the parameters are for the same reaction but obtained under different conditions.

From the kinetic results at elevated pressures the volumes of activation have been calculated. These results are presented in Table 4 based on the data in ESI Supplementary Table S3.

Table 4 Volumes of activation for the reaction of $IrCl_6^{2-}$ with I^- in acidic media or acidic/salt media [a]

Run number	Medium	$\Delta V^‡$/cm^3 mol^{-1}
1	0.50 M H_2SO_4	−27.4 ± 0.9
2	0.50 M H_2SO_4	−27.4 ± 1.8
3	0.50 M H_2SO_4	−27.2 ± 1.5
4	0.050 M H_2SO_4	−26.1 ± 0.9
5	0.050 M H_2SO_4–0.45 M Na_2SO_4	−22.2 ± 1.2
6	1.0 M $HClO_4$	−23.2 ± 1.2
7	1.0 M $HClO_4$	−22.7 ± 0.5
8	0.10 M $HClO_4$	−18.8 ± 1.5
9	0.10 M $HClO_4$–0.90 M $NaClO_4$	−19.7 ± 1.5
10	1.0 M HNO_3	−23.6 ± 0.8
11	0.10 M HNO_3	−23.2 ± 0.6
12	1.0 M HCl	−29.2 ± 1.0
13	0.10 M HCl–0.90 M NaCl	−24.3 ± 1.0
14	0.10 M HCl–0.90 M NaCl	−19.8 ± 0.3
15	0.10 M HCl–0.90 M NaCl	−20.2 ± 0.1
16	0.10 M HCl–0.90 M KCl	−16.5 ± 0.7
17	0.10 M HCl–0.90 M KCl	−14.8 ± 1.1
18	0.10 M HCl–0.90 M KCl	−14.8 ± 1.9
19	0.10 M HCl–0.90 M NaCl	−18.1 ± 1.4
20	0.10 M $HClO_4$–0.90 M $NaClO_4$	−19.2 ± 1.1
21	0.10 M $HClO_4$–0.90 M $LiClO_4$	−21.4 ± 0.6
22	1.0 M HCl	−21.5 ± 1.2
23	0.50 M HNO_3–0.50 M KNO_3	−15.6 ± 0.7
24	0.10 M HCl–0.90 M KCl	−15.2 ± 1.3

[a] Concentrations for each series of experiments are given as footnotes in ESI Supplementary Table S3. Temperatures: runs 1–13 and 20–23 at 25.0 °C, 14–19 at 10.0 °C and 24 at 5.4 °C.

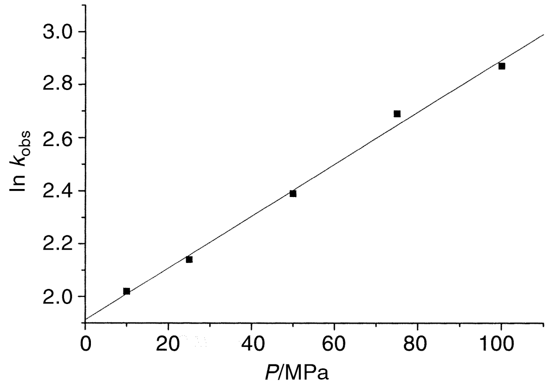

Fig. 2 Plot of ln k_{obs} *versus* pressure (MPa) for the reaction of $IrCl_6^{2-}$ with I^- at 25.0 °C in 0.10 M HCl–0.90 M NaCl (Run 13 of Table 4). The volume of activation derived from this plot is −24.3 ± 1.0 cm^3 mol^{-1}.

Fig. 2 is an example of a plot (ln k_{obs} *versus p* in MPa) used to calculate the volume of activation. The values range from −15 to −29 cm^3 mol^{-1}. Volume reduction is greater in acidic solution when no salts are added. For example, $\Delta V^‡$ is −27, −26 and −22 cm^3 mol^{-1} when the reaction mixture is 0.50 M H_2SO_4, 0.050 M H_2SO_4, and 0.050 M H_2SO_4 together with 0.45 M Na_2SO_4, respectively. The volume decrease is similarly smaller when a mixture of $HClO_4$ and $NaClO_4$ is present compared with the value for reaction in a solution of $HClO_4$ of the same ionic strength. However, these trends are not always as clear cut since the value of $\Delta V^‡$ for reaction in 0.10 M $HClO_4$ is also reduced by about 4 cm^3 mol^{-1} from that for reaction in 1.0 M $HClO_4$. Furthermore added $LiClO_4$ results in a value of $\Delta V^‡$ which is not statistically different from that obtained in 1.0 M $HClO_4$, suggesting possibly some specific influences of different cations. It is arguable that in general the differences in $\Delta V^‡$ are so modest that they are not outside of experimental error. However, the error (standard deviation) attached to most $\Delta V^‡$ values is 5 to 8% and in some cases even less. Therefore, we consider differences of 3 to 4 cm^3 mol^{-1} among values of −20 to −27 cm^3 mol^{-1} as real, although not necessarily of great significance and perhaps attributable to medium effects upon the overall large volume decrease. The latter may partly be due to increasing electrostriction of solvent caused by increasing charge density as the transition state for electron transfer is achieved.

Reaction mechanism

The two term rate law cited above is consistent with the reaction scheme, (2)–(4), and subsequent steps, which has been postulated previously.[3a] Both pathways manifest themselves at higher $[I^-]$ values; but under the conditions of the experiments reported here only the first term of the right hand side of eqn. (8) is applicable. Hence, kinetic parameters and derived activation parameters, and discussion of them, refer to steps (2) to (4) in the mechanistic scheme. In the first reported kinetic study[3a] of the oxidation of I^- by $IrCl_6^{2-}$ the electron transfer step was considered to be rate-determining. Marcus theory was applied to the presumed outer sphere electron transfer in which the encounter complex resulting from the two reactant ions is converted into the successor complex. The electron is transferred to the iridium species from the iodide ion, resulting in an iodine radical as the partner of the $IrCl_6^{3-}$ ion.

Subsequently, it was proposed on the basis of analyses of a linear free energy relationship for a series of appropriately selected redox reactions, and of application of Marcus theory, that diffusive separation of the partners of the successor complex to form products, *i.e.* eqn. (4), is the rate-determining step. The latter proposal is still compatible with the observed second-order kinetics. It was indicated that when diffusive separation of the partners of the successor complex is rate determining, then $k_1 = K_{os}k_{ET}k_{1d}/k_{-ET}$ which is also equal to $K_{eq}k_{-1d}$, where K_{eq} is the equilibrium constant for the overall reaction. Overall here means from the reactants of eqn. (2) up to and including the products of eqn. (4). k_{-1d} is the rate constant for diffusion of $IrCl_6^{3-}$ and $I^{\bullet}$ **together** to form the successor complex.

Therefore, there are two studies of this reaction in which different rate determining steps have been proposed.[3a,10] The mechanism has also been discussed in an investigation of solvation influences upon the reaction.[11] A combination of thermodynamic data obtained from solubility measurements on K_2IrCl_6 and literature values for I^-, in aqueous mixtures, led to the following results and conclusions. The transition state in mixed solvents is more destabilised than are the reactants, considered together, relative to aqueous solution. A corollary is then that the transition state in water is more favourably solvated than are the reactants, indicating that the activated complex has a high charge density. It was proposed that the $IrCl_6^{3-}$ ion, based upon solubility measurements on K_3IrCl_6 in water and in aqueous mixtures, is more destabilised than is the activated complex upon transfer from water to the aqueous mixtures. In turn, this indicates that the transition state has a lower charge density than the iridium(III) product ion, confirming an expectation that the iodine component of the transition state occupies a significant volume. This implies that the transition state could be either between the encounter complex and the successor complex, with the electron of the iodide ion partially transferred to the iridium(IV) ion, or between the successor complex and separated products, *i.e.* $[IrCl_6^{3-} \cdots I^{\bullet}]$, since both of these would have lower charge density than would $IrCl_6^{3-}$. In an effort to decide which step is rate determining, these authors[11] considered the probable magnitudes of the individual rate constants or made estimates from appropriate properties. The quotient k_{ET}/k_{-ET} was given as 4×10^{-8} M^{-1}. The initial electron transfer is followed by competing reactions: separation of the successor complex partners, or reverse electron transfer. It was argued that k_2 is equal to 0.5 k_{ET}. This can only be valid if the quantity 0.5 refers to K_{OS} and has units of M^{-1}, since k_2 and k_{ET} are respectively second and first order rate constants. The overall analysis pointed to the redox step as rate determining.[11]

In principle, the activation parameters can be used to help to distinguish between these mechanistic pathways. The measured values represent composites of contributing terms for either pathway. For the mechanism in which the redox step is rate determining there are two contributing terms, the reaction volume for the formation of the encounter complex and the activation volume for the electron transfer step itself. In the second mechanism in which the rate determining step is diffusive separation of the partners of the successor complex there are three contributing terms. The first is the same as for the former mechanism, the second term is the reaction volume for conversion of the encounter complex into the successor complex, and the third is the volume of activation for the rate determining step of separation of the partners of the successor complex. Even without attributing numerical contributions to these individual components, it is clear on the basis of intrinsic properties alone that both $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ will be less negative for the latter than for the former mechanism. (The initial ordering of species is partly reversed if the diffusion apart of the partners of the successor complex is significantly advanced in the transition state.) Calculations are fraught with the difficulty of knowing exactly what molecular/ionic form the intermediates or the transition states assume, given the strong possibility of counter ion presence, when the ionic strength is in the region of 1.0 M. Indeed an attempt to partition quantitatively the observed $\Delta S^{\ddagger}$ or $\Delta V^{\ddagger}$ values into their component parts is not practicable.

However, it is possible to attempt to assign to each step the likelihood of a positive or negative volume change and also to estimate whether a large or small volume change is reasonable. The reaction volume for the formation of the encounter complex is expected to be a small negative quantity providing there is no extensive desolvation of the reaction species upon encounter. In proceeding from the encounter complex to the successor complex, there is a transfer of one electron to the $IrCl_6^{2-}$ species as it is reduced. The other partner is now an iodine atom. To what extent the electron transfer upon the transition state being reached will determine the magnitude of the effect of charge concentration upon $\Delta V^{\ddagger}$ for this step. The contribution to $\Delta V^{\ddagger}$ will be negative. At the same time the electron is being lost from the iodide ion which would result in transfer of electrostricted solvent to bulk water. The iodide ion has a considerable radius and although capable of being surrounded by several solvating water molecules the charge density is low which may result in a relatively small positive volume contribution. Changes in electrostriction, as pointed out in the Introduction, are obviously important in understanding volume changes in electron transfer reactions. Unfortunately, it has not been possible to obtain reliable values of the partial molar volumes of the $IrCl_6^{2-}$ and $IrCl_6^{3-}$ species to quantify the difference. For the mechanism in which electron transfer is rate determining, it is concluded from this analysis that the volume of activation is negative, primarily as a result of the increasing electrostriction from charge concentration.

Two additional volume contributions must be considered for a mechanism in which the rate-determining step is diffusion apart of the successor complex partners. One is that corresponding to k_{-ET}, and the second is that related to k_{1d}. In the former step, because of the principle of microscopic reversibility, the position of the transition state must be the same as it is in the forward direction, meaning that if it were “early” in the forward direction it must be “late” in the reverse direction. There is no intrinsic volume change and the volume of activation will be determined by the solvation changes caused by charge distribution, and this will result in a positive volume contribution. However, the magnitude will depend heavily on the extent of charge change within the activated complex. The second contribution has an intrinsic component as the partners diffuse apart from the successor complex, although this will not necessarily be particularly significant as no covalent bonds are broken, but would nevertheless be thought to be a positive volume. It is not clear how intimately close the partners are in the successor complex, or whether they simply occupy a volume that is more or less the sum of the volumes of the two species. There is a possibility that the $IrCl_6^{3-}$ ion will be able completely to surround itself by solvating water upon diffusion away from the iodine radical that could result in a small volume decrease. The iodine radical would not be expected to be markedly solvated within either the successor complex or as a free species. There is regrettably, but understandably, no available value for the partial molar volume of the iodine radical. In summary then the intrinsic and electrostriction terms could be mutually cancelling.

Thus we arrive at a situation where the volume of activation for the two suggested mechanisms would rest upon the relative magnitudes of these contributions and therefore whether the value would be more negative or not for the rate determining redox step mechanism. That is, the positive contribution originating in the $k_{-\mathrm{ET}}$ step of the back reaction is negative in the overall count, but it is not possible to conclude whether this will be more than compensated for by the positive value for the $k_{1\mathrm{d}}$ step. Therefore the finding of a large or moderately large negative value of $\Delta V^{\ddagger}$ experimentally does not allow distinction between the mechanisms on this basis. If the diffusion apart step is in fact diffusion controlled kinetically, then it would not be expected to contribute to the rate determining step for a reaction conveniently measured by the stopped-flow method. It is evident though that, as noticed before, electrostriction changes contribute significantly to volume changes independent of mechanism. It should also be noted that, in so far as molecular ordering is concerned, the significantly negative entropies of activation are not compatible with a mechanism that has an unchanged number of species in the rate determining phase of the overall reaction.

Conclusion

The reaction between I^- and the $IrCl_6^{2-}$ ion is second-order (studied under pseudo first-order conditions), providing a moderate excess of iodide ion is used, thus avoiding a term that is second order in iodide ion, in aqueous acidic media. The reaction is subject to catalysis by the K^+ ion, and secondary medium effects of different magnitude were found depending on the conjugate base of the acid, or anionic component of added electrolyte. A moderate sensitivity to temperature was observed, with values that depended on the reaction medium ranging from 20 to 35 kJ mol^{-1} for the enthalpy of activation for the composite rate constant. Both $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are large negative values. Although an analysis points more toward a rate determining redox mechanism, a clear distinction between that and a mechanism containing in addition rate determination from diffusion apart of the partners of the successor complex species is not conclusively afforded by these results.

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