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Hexachloroiridate(IV) Oxidation of Benzenediols in Binary Aqueous Solvent Mixtures: Solvation and Reactivity

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Abstract

Kinetic parameters are reported for hexachloroiridate(IV) oxidation of t-butyl-catechol (4-t-butylbenzene-1,2-diol), hydroquinone (benzene-1,4-diol) and its 2-t-butyl derivative in binary aqueous mixtures containing methanol, ethanol, t-butyl alcohol, acetone, dimethyl sulfoxide, or dimethylformamide. Solubilities are reported, and transfer chemical potentials thence derived, for hydroquinone in a range of such media and for catechol, 2,4-bis(t-butyl)catechol, methylhydroquinone and t-butylhydroquinone in methanol–water mixtures. On the basis of a selection of these kinetic and thermodynamic results we have analysed reactivity trends for several of these hexachloroiridate(IV) oxidations into initial state and transition state contributions.

Introduction

The analysis of solvent effects on reactivity into their initial state and transition state contributions has been carried out for a range of organic reactions [1] and for a representative cross section of substitutions at inorganic complexes [2, 3]. There have been rather few applications to redox reactions involving inorganic species [3, 4], though such reactions as $[Co(phen)_3]^{3+}$ oxidation of ferrocene [5], peroxodisulfate oxidation of several cobalt(III) complexes [6] and hexachloroiridate(IV) oxidation of iodide [7] may be cited as recent examples of such investigations in binary aqueous solvent media. In the present paper we report the results of an extensive study of solvent effects on reactivity for hexachloroiridate(IV) oxidation of a selection of benzenediols (catechols and quinols) in binary aqueous media. From this kinetic data, and measured solubilities of $K_2[IrCl_6]$, we have been able to build up a picture of initial state and transition state solvation effects, a preliminary indication of which was published earlier [7].

Our choice of the benzenediol–$[IrCl_6]^{2-}$ system was based on several factors. These reactions closely obey second-order kinetics in aqueous media, proceeding via outer-sphere electron transfer [8–11]. Both oxidant and reductants have been well studied in relation to redox kinetics. Thus kinetics of $[IrCl_6]^{2-}$ oxidation [12] have been reported for, e.g. iodide [7, 13], thiocyanate [13, 14], thiosulfate [13], tetraphenylboronate [15], ascorbate [16], oxalate [17], malonate [18] and organic amines [13]. In all these cases, with the exception of oxalate and perhaps of thiocyanate, second-order rate laws were obeyed. Complementarily, kinetics of oxidation of benzenediols have been established for e.g. nickel(IV) oximates [19], the mixed-valence $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation [20], manganese(III) [21], cerium(IV) [22], copper(II)–phenanthroline complexes [23], hexacyanoferrate(III) [24] and ternary iron(III)–diimine–cyanide complexes [25]. Our selected substrates thus seem an appropriate choice for a study of solvation and its effect on reactivity for a centrally important and fully documented redox system.

Experimental

Materials

Sodium hexachloroiridate(IV) was supplied by Merck; the spectra of fresh solutions agreed with literature data [26]. Other inorganic chemicals and solvents (perchloric acid, acetic acid and sodium acetate, sodium phosphate monobasic and dibasic) were analytical grade reagents and were supplied by Merck. The stability over more than 6 h of 1×10^{-4} mol dm^{-3} solutions of organic substrates in 0.01 M

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$HClO_4$ confirms that perchloric acid was free from oxidising impurities. Acetate buffers were prepared by adding acetic acid to aqueous solutions of sodium acetate, diluting to obtain a proper analytical concentration and then measuring the final pH with a calibrated pH meter (Metrohm model 605).

Benzenediols (K & K and Merck) were purified by recrystallisation; stock solutions were prepared daily in acidic media (typically pH 2 ($HClO_4$)) and protected from direct sunlight. Purity of reagents and solvents was checked by UV spectra.

Apparatus

The UV–Vis absorption spectra were recorded on a Cary 219 Varian spectrophotometer. Kinetic experiments were carried out on a Hi-Tech (Salisbury, U.K.) stopped-flow spectrophotometer equipped with an Apple II Europlus personal computer, a fast gain programmable 8-bit Analog to Digital converter and a locally-written program for date acquisition and on-line calculation of the observed rate constants. The reaction progress was followed at the wavelength of maximum absorbance of $IrCl_6^{2-}$ (487 nm, $\epsilon = 3950$ dm^3 mol^{-1} cm^{-1} [27]). Typically, the initial concentrations of reactants were $[IrCl_6]^{2-} = 1 \times 10^{-5}$ mol dm^{-3} and excess organic substrate in the range of $1–3 \times 10^{-4}$ mol dm^{-3}. Good first-order kinetics (the benzenediol is always present in large excess) were observed for all water–solvent compositions and initial reagent concentrations for two or more half-lives, except in the limit of very high content of organic cosolvents (measurements not reported). The second-order kinetic constants are obtained by averaging several independent measurements obtained at at least four different organic substrate concentrations (mean standard deviations 3–5%). The kinetic experiments were all performed at 298.2 ± 0.1 K, except where otherwise indicated.

Results and Discussion

By means of spectrophotometeric measurements with $IrCl_6^{2-}$ in excess, the overall eqn. (1) was derived, where H_2Q represents the benzenediols and Q the corresponding quinones

$$2IrCl_6^{2-} + H_2Q \longrightarrow 2IrCl_6^{3-} + Q + 2H^+ \qquad (1)$$

The spectra of the final products of the reaction showed the typical maximum absorption pertaining to the *o*- and *p*-quinones [28]. Thus, the reaction scheme can be represented by eqns. (2) and (3), where SQ represents the semiquinone radical

$$IrCl_6^{2-} + H_2O \rightleftharpoons IrCl_6^{3-} + SQ \qquad (2)$$

$$IrCl_6^{2-} + SQ \longrightarrow IrCl_6^{3-} + Q \qquad (3)$$

As previously reported [8], application of the steady state treatment to SQ and the absence of the effect of Ir(III) species leads to $k_{app} = 2k_2$. Deviations from this mechanism are observed at the highest molar ratio of organic cosolvents. Specific second-order rate constants (k_2) are listed in Tables 1 to 4. Table 1 documents solvent and temperature effects on oxidation of t-butyl-catechol, while Table 2 documents solvent effects on oxidation of hydroquinone (six solvents) at 298.2 K. Table 3 lists rate constants for oxidation of t-butyl-hydroquinone in methanol–water mixtures. Finally Table 4 shows the effect of pH on oxidation of t-butyl catechol in aqueous solution at 298.2 K. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) derived from the observed rate constants are included in Table 1. Where relevant, results in Tables 1 and 2 are consistent with earlier published results; substitution of methyl or of t-butyl results in a small but significant increase in rate constant, as one might expect from the incorporation of such electron-releasing groups. Activation parameters do not change dramatically with solvent composition. There is no evidence for marked extrema in $\Delta H^{\ddagger}$, $T\Delta S^{\ddagger}$ versus solvent composition plots which might correspond to solvent structural effects. In this respect these redox reactions differ notably from complex formation reactions of nickel(II) [29]. However there is a small but real increase in $\Delta H^{\ddagger}$ and in the magnitude of $\Delta S^{\ddagger}$ as the proportion of the organic cosolvent rises (Table 1).

The effects of added cosolvents on reactivity are illustrated in Figs. 1 and 2. There is a similar pattern of Gibbs free energies of activation increasing (rate constants decreasing) with increasing proportion of organic cosolvent for oxidation of both 4-t-butyl-catechol and of hydroquinone, and indeed for oxidation of iodide [7]. The effects of added alcohols increase in the expected order MeOH < EtOH < t-BuOH and, as so often, acetone and the dipolar aprotic solvents DMSO and DMF have considerably greater effects than the alcohols. In order to discuss these trends more fully we need to carry out an initial state–transition state dissection [2, 3]. Before we can do this we need to establish transfer chemical potentials for the substrates. The necessary solubilities, plus additional values to establish an overall picture of solvation trends, are reported in the next paragraph.

Measured solubilities of hydroquinone in binary aqueous solvent mixtures, and some substituted benzenediols in methanol–water mixtures, are reported in Tables 5 and 6; only solubilities of the unsubstituted benzenediols in water seem to be available in the literature [30]. These Tables also include transfer chemical potentials, in all cases from water, calculated from these solubilities on the assumption that the ratio of activity coefficients in water and in the mixed solvent is in

TABLE 1. Specific second-order rate constants and enthalpies and entropies of activation for hexachloroiridate(IV) oxidation of t-butyl-catechol in binary aqueous solvent mixtures at pH 2.0 ($HClO_4$)

Cosolvent	vol.%	$10^{-3} \times k_2$ ($dm^3 mol^{-1} s^{-1}$)			$\Delta H^{\ddagger}$ [b] (kJ mol^{-1})	$\Delta S^{\ddagger}$ [c] (J $K^{-1} mol^{-1}$)
		283.2 K	298.2 K	313.2 K		
Water		6.0	12.9	22.0		
Methanol	5	4.4	7.8	12.8	28.4	−75
	10	3.3	5.5	9.3	27.6	−81
	20	1.9	3.2	5.3	27.4	−86
	30	1.0	1.5	2.7	26.1	−97
	40	0.43	0.75	1.29	29.6	−91
	50	0.18	0.33	0.58	30.6	−94
	60[a]	0.08	0.14	0.23	30.4	−103
	70[a]	0.027	0.050	0.082	29.2	−115
Ethanol	5	4.3	7.0	12.0	27.6	−79
	10	3.3	5.5	9.4	28.2	−79
	20	1.9	3.2	5.5	27.6	−86
	30	1.0	1.7	2.8	27.1	−93
	40	0.42	0.68	1.17	27.6	−98
	50	0.17	0.31	0.55	31.6	−92
	60[a]	0.08	0.16	0.30	35.5	−84
DMSO	5	3.3	5.8	9.2	27.2	−82
	10	1.8	3.1	5.1	27.7	−86
	20	0.57	0.95	1.62	29.1	−90
	30	0.15	0.27	0.47	31.8	−92
	40	0.023	0.045	0.89	36.2	−92
	50[a]	0.0037	0.0078	0.017	39.1	−97

[a] Rate constants in these media were estimated from the early stages of the reaction, before significant deviations from first-order kinetics became apparent. [b] Uncertainties are between ±1.3 to 2.2 kJ mol^{-1}. [c] Uncertainties are between ±4 to 6 J K^{-1} mol^{-1}.

TABLE 2. Specific second-order rate constants for hexachloroiridate(IV) oxidation of hydroquinone in binary aqueous solvent mixtures[a] at pH 2.0 ($HClO_4$), 298.2 K

Cosolvent (vol.%)	$10^{-3} \times k_2$ ($dm^3 mol^{-1} s^{-1}$)					
	MeOH	EtOH	t-BuOH	Me_2CO	DMSO	DMF
10	28	25	27	16	15	14
20	15	13	14	5.5	4.3	4.1
30	6.0	[b]	[b]	1.8	1.2	1.1
46	2.2	[b]	[b]	0.27	0.15	0.08
60	0.7	[b]	[b]	0.04[c]	0.02[c]	0.01[c]

[a] $k_2 = 4.7 \times 10^4$ $dm^3 mol^{-1} s^{-1}$ in water, pH 2.0 ($HClO_4$), 298.2 K. [b] Not first-order kinetics. [c] Rate constant estimated from early stages of reaction.

TABLE 3. Specific second-order rate constants for hexachloroiridate(IV) oxidation of t-butyl-hydroquinone in methanol–water mixtures at pH 2.0 ($HClO_4$), 298.2 K

MeOH (vol.%)	0	10	20	30	46	60
$10^{-4} \times k_2$ ($dm^3 mol^{-1} s^{-1}$)	27	16	10	6.0	2.0	0.9

TABLE 4. Specific second-order rate constants for hexachloroiridate oxidation of t-butyl-catechol in aqueous buffer solution at 298.2 K

Buffer	pH	$10^{-4} \times k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)
None (0.01 mol dm^{-3} $HClO_4$)	2.0	1.3
0.01 mol dm^{-3} acetate	4.10	1.5
0.01 mol dm^{-3} acetate	5.02	1.8
0.01 mol dm^{-3} acetate	5.50	3.0
0.01 mol dm^{-3} phosphate	6.34	6.1

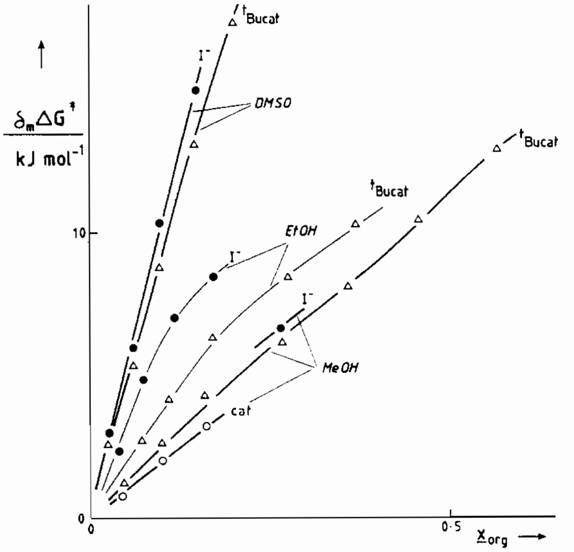

Fig. 1. Gibbs free energies of activation (298.2 K) for hexachloroiridate(IV) oxidation of catechol, t-butyl-catechol and iodide in binary aqueous mixtures as a function of mole fraction of organic solvent.

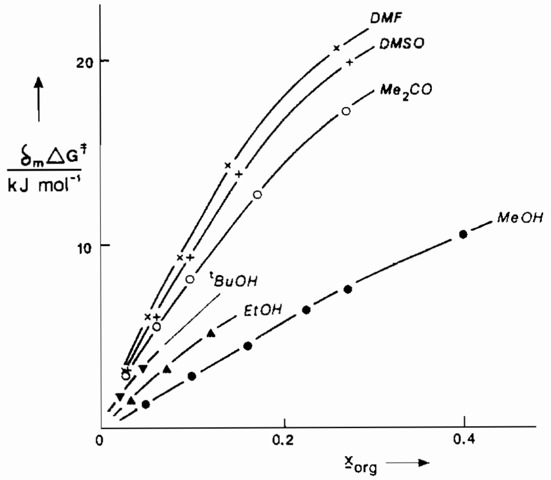

Fig. 2. Gibbs free energies of activation (298.2 K) for hexachloroiridate(IV) oxidation of hydroquinone in binary aqueous mixtures as a function of mole fraction of organic solvent.

every case unity. Unfortunately, in view of its importance in our kinetic studies, t-butyl-catechol gave problems in the attempted solubility determinations. Thus in 10% or more methanol, ethanol, or DMSO, two liquid layers were obtained, while at higher alcohol contents the t-butyl-catechol appeared indefinitely soluble. Presumably this indicates complete mutual miscibility of water, alcohol and liquid 4-t-butyl-catechol (whose melting point is only 328–331 K [31]).

TABLE 5. Solubilities (mol dm^{-3}) and transfer chemical potentials (kJ mol^{-1}, on the molar scale) for hydroquinone in binary aqueous solvent mixtures[a] at 298.2 K

	Vol.%									
	10	20	30	40	50	60	70	80	90	100
Methanol										
Solubility	0.8	0.99	1.24	1.65	2.0	2.4	2.6	2.9	2.9	3.0
$\delta_m\mu^\theta$	−0.6	−1.0	−1.6	−2.3	−2.8	−3.2	−3.4	−3.7	−3.7	−3.8
Ethanol										
Solubility	0.95	1.34	1.38	2.2	2.6	2.7	3.0	2.9	3.1	2.9
$\delta_m\mu^\theta$	−0.9	−1.8	−1.9	−3.0	−3.4	−3.5	−3.8	−3.7	−3.9	−3.7
i-Propanol										
Solubility	0.96	1.32	1.8	1.9	2.3	2.1	2.2	2.1	2.2	1.6
$\delta_m\mu^\theta$	−0.9	−1.7	−2.5	−2.6	−3.1	−2.9	−3.0	−2.9	−2.7	−2.2
t-Butyl alcohol										
Solubility	0.63	0.54	0.62	0.78	0.91	1.0	1.1	1.1	0.71	0.18
$\delta_m\mu^\theta$	0.0	+0.3	0.0	−0.5	−0.9	−1.2	−1.4	−1.4	−0.3	+3.0
Acetone										
Solubility	1.2	1.9	2.5	3.2	3.1	3.1	3.1	3.0	2.6	1.4
$\delta_m\mu^\theta$	−1.6	−2.8	−3.5	−4.1	−4.0	−4.0	−4.0	−3.9	−3.5	−2.0

[a] Measured solubility in water: 0.64 mol dm^{-3} (cf. 0.6 mol dm^{-3} in ref. 30).

TABLE 6. Solubilities (mol dm^{-3}) and transfer chemical potentials (kJ mol^{-1}, on the molar scale) for benzenediols in methanol–water mixtures at 298.2 K

	MeOH (vol.%)										
	0	10	20	30	40	50	60	70	80	90	100
Catechol											
Solubility	3.7[a]	4.6	5.0	5.1	5.3	5.6	5.4	5.5	5.6	5.5	5.3
$\delta_m\mu^\theta$		−0.6	−0.8	−0.8	−0.9	−1.1	−1.0	−1.0	−1.1	−1.0	−0.9
2,4-Bis-(t-butyl)catechol											
Solubility	3.6[b]	4.1[b]	6.3[b]	0.010	0.017		2.5		3.1		3.4
$\delta_m\mu^\theta$		−0.3	−1.4	−2.5	−3.9		−16.2		−16.8		−17.0
Methylhydroquinone											
Solubility	0.58		1.4		2.7		3.8		4.8	4.3	4.1
$\delta_m\mu^\theta$			−2.3		−3.8		−4.7		−5.2	−5.0	−4.8
t-Butylhydroquinone											
Solubility	0.023		0.089		0.086		2.9		3.9	4.0	3.6
$\delta_m\mu^\theta$			−3.3		−8.9		−12.0		−12.7	−12.8	−12.5

[a] cf. 4 mol dm^{-3} in ref. 30. [b] ×10^3.

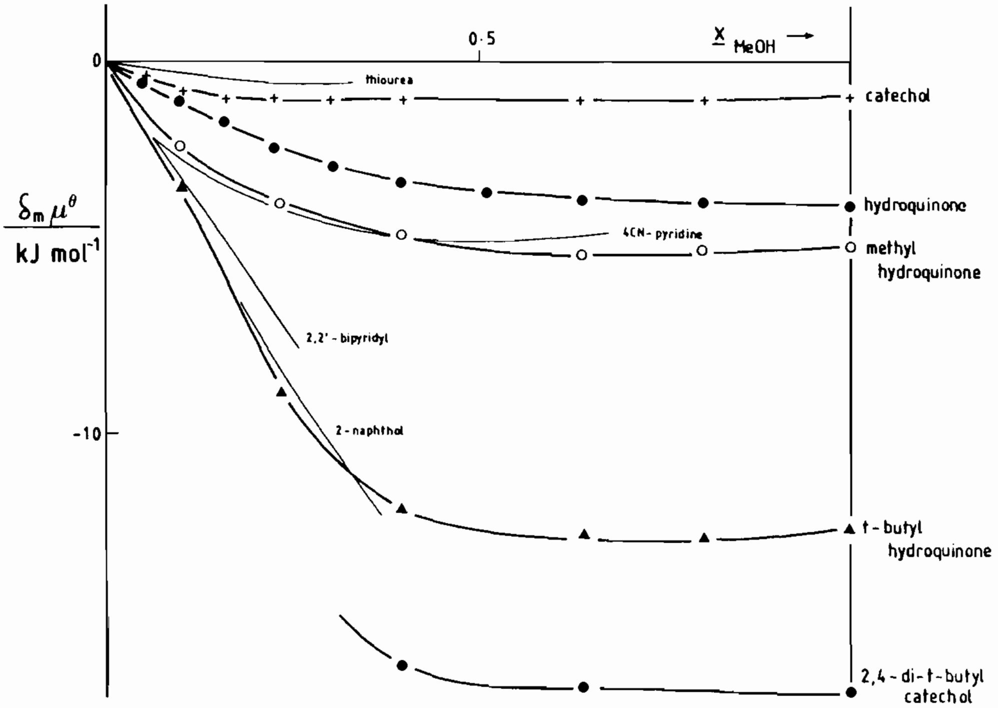

Fig. 3. Transfer chemical potentials (molar scale; 298.2 K) for methanol–water mixtures as a function of mole fraction of methanol.

Transfer chemical potentials for (substituted) benzenediols are plotted as a function of mole fraction methanol in Fig. 3, which includes a limited selection of other organic solutes of interest to inorganic chemists for the purposes of comparison. The curvatures of the plots in this Figure confirm the expected marked preferential solvation of (substituted) benzenediols by methanol. The magnitudes of $\delta_m\mu^\theta$ values for the methyl and t-butyl derivatives reflect the hydrophobic properties of these groups. Figure 4 shows how transfer chemical potentials for hydroquinone depend on the nature and proportion of the cosolvent. The plots for methanol and ethanol as cosolvents are very similar to the plots in Fig. 3, suggesting simple preferential solvation by these alcohols. However the plots for acetone and for t-butyl alcohol show marked minima, implying significant stabilisation in appropriate solvent

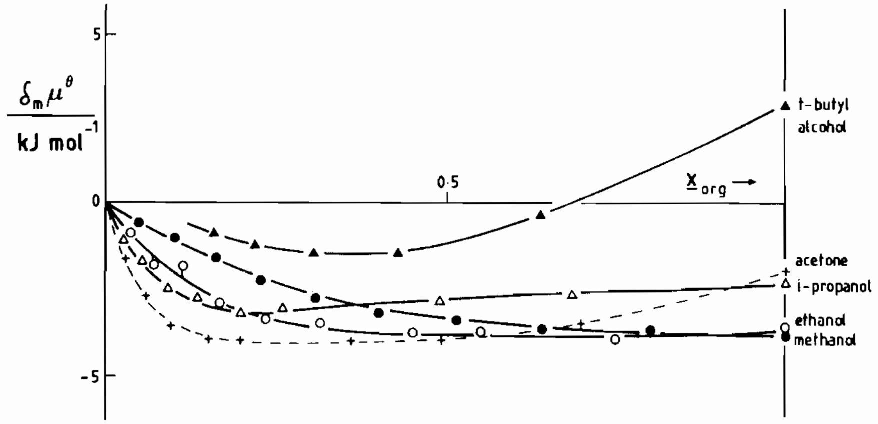

Fig. 4. Transfer chemical potentials (molar scale; 298.2 K) for hydroquinone in binary aqueous solvent mixtures as a function of mole fraction of organic solvent.

TABLE 7. Initial state–transition state analysis of reactivity trends for hexachloroiridate(IV) oxidation of hydroquinone in binary aqueous solvent mixtures. All values are at 298.2 K; transfer chemical potentials are on the molar scale and TATB (TPTB for methanol) single ion assumption

	Cosolvent (vol.%)				
	MeOH		EtOH	Me_2CO	Me_2SO
	20	40	40	40	40
$\delta_m \Delta G^\ddagger$	2.9	6.4[a]	7.0[b]	13.8[a]	14.8[a]
$\delta_m \mu^\theta$ (hq)	−1.0	−2.3	−3.0	−4.1	−5.6[c]
$\delta_m \mu^\theta$ ($IrCl_6^{2-}$)	3.9	5.4	8.4	16.6	7.0
$\delta_m \mu^\theta$ (is)	2.9	3.1	5.4	12.5	1.4
$\delta_m \mu^\ddagger$	5.8	9.6	13	26	16

[a] Interpolated from Table 2 results. [b] Extrapolated from Table 2 results. [c] Solubility of hydroquinone in 40% DMSO is 6.1 mol dm^{-3} (this work).

mixtures. This suggests that solvation is heaviest when there is both water present to solvate the hydroxyl substituents and acetone or t-butyl alcohol present to solvate the lipophilic aromatic ring. Such stabilisation in mixed solvents has been described for, for example, $Fe(CN)_2(bipy)_2$ in a similar range of mixed solvents [25]. Here water solvates the hydrophilic cyanide ligands, but a fattier solvent is needed to solvate the lipophilic exposed region of the 2,2′-bipyridyl ligands. Similar minima in solvent mixtures, arising from similar reinforcement of specific solute segment–solvent interactions, have been described for a number of organic solutes in binary aqueous solvent mixtures, for instance for such sulfa drugs as sulfathiazole (1) [32], sulfacetamide (2) [32] and sulfanilamide (3) [33].

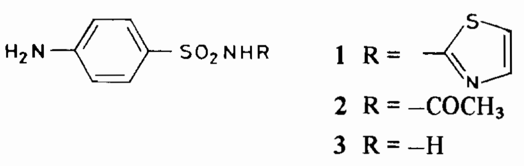

TABLE 8. Initial state–transition state analysis of reactivity trends for hexachloroiridate(IV) oxidation of t-butyl-hydroquinone in methanol–water mixtures. All values are at 298.2 K; transfer chemical potentials are on the molar scale and TPTB single ion assumption

	MeOH (vol.%)	
	20	40
$\delta_m \Delta G^\ddagger$	2.9	6.4
$\delta_m \mu^\theta$ (tbhq)	−3.3	−8.9
$\delta_m \mu^\theta$ ($IrCl_6^{2-}$)	3.9	5.4
$\delta_m \mu^\theta$ (is)	0.6	−4.5
$\delta_m \mu^\ddagger$	3.5	−1.9

[a] Interpolated from Table 3 results.

Initial state–transition state analyses of reactivity trends are set out in Tables 7 and 8, and the results depicted in Figs. 5 and 6. We have included our earlier results on the hexachloroiridate(IV) oxidations of catechol and of iodide [7] in Fig. 5 for the purposes of comparison. These present versions differ

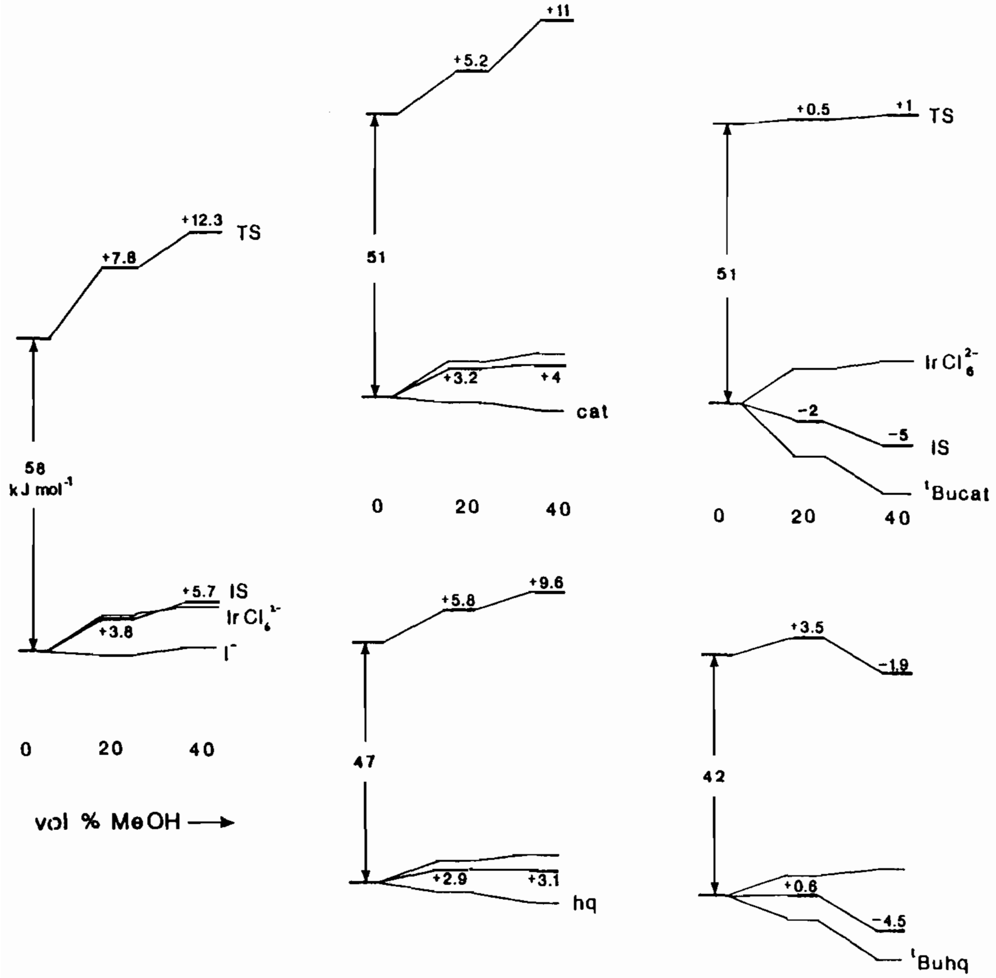

Fig. 5. Initial state–transition state analysis of reactivity trends for hexachloroiridate(IV) oxidations in methanol–water mixtures (TPTB assumption; 298.2 K; kJ mol^{-1}).

from those published earlier [7], as we have converted from Wells's single ion assumption to the TPTB single ion assumption so that all the component parts of Figs. 5 and 6 are directly comparable. Figure 5 shows how the differences in the hydrophilicity of the reactants iodide > catechol > hydroquinone ≫ t-butyl compounds affects both the initial and transition states. The very small destabilisation of iodide and the very small stabilisation of catechol or of hydroquinone on transfer from water into 40% methanol are almost negligible in comparison with the destabilisation of the strongly hydrophilic $[IrCl_6]^{2-}$ anion, so the latter dominates the initial state trend for these three reductants. On the other hand the strongly hydrophobic t-butyl group dominates over the $[IrCl_6]^{2-}$ for the other two systems. The transition state trends reflect these initial state differences, with large destabilisation of $[IrCl_6^{2-}...I^-]^{\ddagger}$, moderate destabilisation of $[IrCl_6^{2-}...cat,hq]^{\ddagger}$, and even a modest stabilisation of $[IrCl_6^{2-}...t\text{-}Bu\text{-}hq]^{\ddagger}$ on transfer to 40% methanol.

Whereas Fig. 5 illustrates the effects of varying the reductant in methanol–water mixtures, Fig. 6 illustrates the effects of varying the nature of the cosolvent, specifically for the hexachloroiridate(IV)–hydroquinone reaction. The media in Fig. 6 are also arranged in order of decreasing rate constant from left to right. There is a good correlation between the various parameters for all the so-called 'typically aqueous' [34] solvent mixtures, but the points for DMSO, a 'typically non-aqueous' cosolvent, do not fit the general pattern. In all cases the initial state is destabilised on transfer from water as destabilisation of $[IrCl_6]^{2-}$ is greater than stabilisation of the only slightly hydrophobic hydroquinone. It is the anomalously small destabilisation of $[IrCl_6]^{2-}$ on transfer to 40% DMSO that upsets the overall correlation pattern; solvation of the $[IrCl_6]^{2-}$ moiety is clearly similar in the transition state.

The contrast between the complicated patterns just described and the apparently simple pattern of rate constants decreasing as the proportion of organic

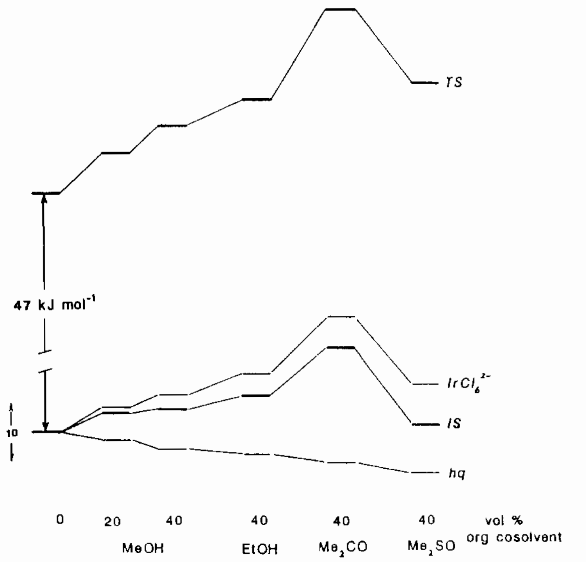

Fig. 6. Initial state–transition state analysis of reactivity trends for hexachloroiridate(IV) oxidation of hydroquinone in binary aqueous solvent mixtures (TPTB or TATB assumption; 298.2 K; kJ mol^{-1}).

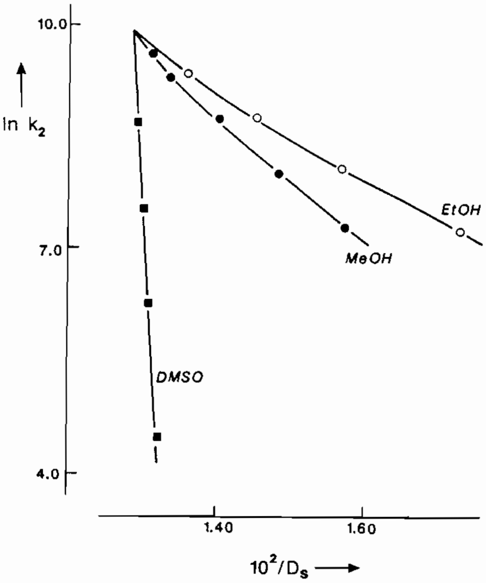

Fig. 7. Relation between reactivity and medium dielectric constant for hexachloroiridate(IV) oxidation of t-butylcatechol in binary aqueous mixtures.

cosolvent increases might suggest that in these systems reactivity might be controlled by some simple solvent parameter rather than by solvent–solute interactions. We therefore attempted to correlate reactivities with the obvious choice of solvent parameter in this context, dielectric constant. Figure 7 shows a typical product of such an exercise, and demonstrates that reactivities are not

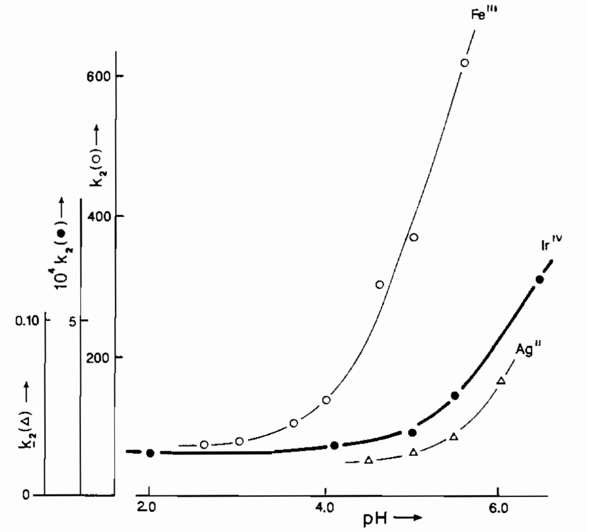

Fig. 8. Dependence of reactivity (k_2 (dm^3 mol^{-1} s^{-1})) on pH for oxidation of t-butyl-hydroquinone by $[Ir(Cl_6]^{2-}$; catechol by $[Fe(CN)_4(bipy)]^-$; 2-thiopyrimidine by $[Ag(cyclam)]^{2+}$.

simply determined by the dielectric properties of the respective solvent media (when a single straight line accommodating all solvents would have been expected).

Finally Fig. 8 compares the pH effect on this type of reaction with that for the oxidation of catechol by the iron(III) complex $[Fe(CN)_4(bipy)]^-$ [35] and of oxidation of 2-thiopyridine by the silver(II) complex $[Ag(cyclam)]^{2+}$ [36]. The much larger effect in the case of the iron complex may be ascribed to the possibility of protonation of coordinated cyanide. Acid dependences of reactivities in electron transfer reactions of these types will be discussed in more detail elsewhere, in connection with the kinetic results for oxidation by iron(III)–diimine–cyanide complexes [35]. These species, e.g. $[Fe(CN)_2(phen)_2]^+$ as well as the tetracyanoanion specified above, would be useful oxidants for continuation of the present project. They are of modest charge, which is a considerable advantage in deriving transfer chemical potentials (which are indeed available for some such species in some binary aqueous solvent mixtures [25]). They also provide the opportunity to vary the hydrophobic/hydrophilic properties of the oxidant, by varying the number of diimine and cyanide ligands and by varying the nature of the diimine [37], in a way that would be very difficult or impossible for iridium(IV) oxidants.

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