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Oxidation of benzenediols by the iron(III) tetracyano bipyridyl ion: a high pressure stopped-flow kinetics study

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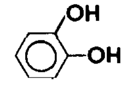
Abstract

The iron(III) tetracyano 2,2-bipyridyl ion, $[Fe(CN)_4(bpy)]^-$, readily oxidizes the benzenediols, catechol (1,2-dihydroxybenzene), 4-tertiary butyl catechol (1,2-dihydroxy-4-t-Bu-benzene), and methyl hydroquinone, (2-methyl-1,4-dihydroxybenzene) in aqueous solution. The kinetics have been studied by stopped-flow spectrophotometry in the pH range 2.5–6. At the lower end of this region the reactions are pH independent, and yield second order rate constants at 298.2 K of 50, 68 and 477 $mol^{-1}\ dm^3\ s^{-1}$ for the three diols, respectively. In the pH dependent region (3–6) the rates, in buffered solution, vary due to the presence of differently protonated species of the iron(III) complex. Application of pressure, up to 1 kbar, gives rise to more rapid oxidation, and within experimental error, the volume of activation, ΔV^* is substrate independent ($\Delta V^* = -18\ cm^3\ mol^{-1}$). The values of ΔS^* are compatible with this finding. Kinetic and activation parameters are treated within the framework of an outer-sphere electron transfer mechanism.

Introduction

Although a wide variety of methods [1] have been used and countless redox systems have been studied [2] the mechanism of many electron transfer processes, involving a metal centre, remains incompletely understood. The Hush theory [3] was adapted by Stranks [4], for consideration of both redox and non-redox reactions at elevated pressures. This treatment has been applied to a number of redox systems particularly where both reactants are charged [4, 5]. This experimental approach in which kinetic parameters are acquired for both temperature and pressure variation, can be most effective in delineating the details of reaction mechanism [6]. The reactions reported in this communication are reductions of an iron(III) cyanodiimine complex, specifically, $[Fe(CN)_4(bpy)]^-$, where bpy ≡ 2,2′-bipyridine, by catechol (1,2-dihydroxybenzene) (**1**), 4-tertiary butyl catechol (1,2-dihydroxy-4-t-Bu-benzene) (**2**) and methylhydroquinone (2-methyl-1,4-dihydroxy-benzene) (**3**).



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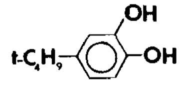

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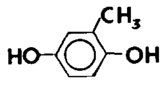

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Our choice of this iron complex as an oxidizing agent is a consequence of our general interest in several aspects of iron diimine chemistry; in particular we have examined the dissociation kinetics of several iron(II) diimine complexes, both aquation in acid solution [7, 8] and nucleophilic dissociation [9, 10], and have recently described [11] the influence of solvation, in the peroxodisulfate oxidation of iron(II)–diimine–cyano complexes. (The latter conclusion was obtained from a high pressure

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kinetic study.) There have been reports [12] recently on solvation effects and reactivity trends in oxidation of various benzenediols by the hexachloroiridate ion, $IrCl_6^{2-}$, and these studies have prompted our selection of catechols as reducing agents.

The overall reaction (1) is anticipated, from other work [13], to have a 2:1 stoichiometry as the one electron oxidant, $[Fe(CN)_4(bpy)]^-$ requires two ions per molecule of substrate:

$$2[Fe(CN)_4(bpy)]^- + QH_2 \rightarrow 2[Fe(CN)_4(bpy)]^{2-} + Q + 2H^+ \quad (1)$$

where QH_2 is the diprotonated benzenediol. The increase in acidity, predicted from this equation is observed. Consequently, the reaction was studied in buffered solutions and at constant ionic strength. Since an initial study [14], at atmospheric pressure, of the reaction kinetics involving the two catechols has been presented, and aromatic diols have been the focus of many redox reaction studies, [15] determination of the activation parameters, as a means to probe the mechanism is in order.

Experimental

Materials

The iron(III) complex was synthesized by the Schilt method [16] as $HFe(CN)_4(bpy)$, and it exhibited the characteristic UV–Vis spectrum. Benzenediols were high grade commercial products. Materials used for buffer reagents and maintaining ionic strength (sodium chloride) were reagent grade.

Methods

Solution pH values were measured using a Radiometer PHM 64 instrument. Spectra of reactants and product solutions were obtained using a Shimadzu UV250 spectrophotometer, maintained when necessary at constant temperature (298.15 K) by a thermostatted cell holder. Kinetics at atmospheric pressure were studied using a Durrum D 110 stopped-flow spectrophotometer with a 0.020 m Kel-F flow path, which was thermostatted in the temperature range (293.15–313.15 K) by circulating fluid from a Haake thermostat. High pressure kinetics were measured using a purpose built, high-pressure stopped-flow spectrophotometer, described in detail elsewhere [17], which was thermostatted at 298.15 K. The latter instrument can hold sufficient of each reactant solution to be able to measure the reaction rate at each chosen pressure without refilling the drive syringes. Therefore, the volume of activation is determined efficiently from kinetic parameters all obtained from the same solutions and at exactly the same temperature. Typically twenty minutes were allowed to elapse after initial pressurization or after subsequent changes in pressure in order that thermal equilibrium in the system is reestablished. All variable pressure kinetics were carried out at a pH in the range 2.6–2.8 where the rate constant is independent of acid strength.

Solutions needed for measurement of spectra and kinetic purposes were always made up immediately before use. The kinetics were run with the condition of large excess of benzenediol which yields pseudo first order kinetics, the reaction being first order in iron(III) complex concentration. As found previously [14], the increase in absorbance at 480 nm, which is due to the difference between the high molar absorptivity of the iron(II) complex product and the relatively colourless iron(III) reactant species, gave excellent first order plots for at least three half lives. Rate constants, k_{obs}, were obtained using a software program [18] written for use on an Apple IIe computer connected to the Durrum and high-pressure stopped-flow instruments. Tabulated values of k_{obs}, are the average of at least four determinations and usually five to eight values. Kinetic and activation parameters derived from primary results were obtained using standard least-squares programmes on Atari and Apple microcomputers.

Results

A 2.0×10^{-3} mol dm^{-3} aqueous solution of $H[Fe(CN)_4(bpy)]$ gave a pH of close to pH 2.6. Addition of sodium hydroxide solution yields a point of inflection with an equimolar base concentration. These facts support the formula attributed to the iron(III) complex ion. Spectra of the complex, recorded at different pH values in the range 2–10 show a slight shift in the maximum, $\lambda = 415$ nm, with a small increase in absorbance as the pH is raised above 6. A pK value of about 8 is suggested by these observations. A proposal has been offered previously [14] that atmospheric kinetics data (k_{obs} increases significantly with increase in pH (>3.5) for fixed concentrations of iron(III) complex and catechol) can be explained by a conjugate acid–base reaction of the iron(III) complex ion. The diols used have no ionizable groups [19] that would give rise to mixtures of species in the pH range (2–6) of the kinetics measurements. Consequently as reactants, each diol solution is regarded as containing only H_2Q species. As noted earlier [14] **1** and **2** are

TABLE 1 Reaction of methyl-1,4-hydroquinone with $[Fe(CN)_4(bpy)]^-$ at 298 15 K[a]

pH	$10^{-2} \times k'_2$ (mol^{-1} dm^3 s^{-1})
2 6	4 39
2 85	6 75
3 02	7 74
3 57	9 19
3 6	9 85
3 75	10 3
4 92	65 6
5 4	100 6

[a] Ionic strength 0 1 mol dm^{-3} (NaCl), atmospheric pressure, $[Fe(CN)_4(bpy)]^- = 2$ 0 × 10^{-4} mol dm^{-3}

both oxidized at an almost constant rate in the pH range 2 5–3 5, however, the reaction rate constant increases significantly at values of pH > 3 5 This trend is repeated with the more labile methyl-1,4-hydroquinone The results for the latter, compiled as second order rate constants, k'_2, are given in Table 1 Second order rate constants are obtained from plots of k_{obs} *versus* $[H_2Q]$ Normally these values were obtained with a complex concentration of 2 50 × 10^{-4} mol dm^{-3} and a catechol concentration range of 2 5 × 10^{-3} mol dm^{-3} to 2 5 × 10^{-2} mol dm^{-3}, at an ionic strength of 0 1 mol dm^{-3} and with the pH adjusted by hydro-

TABLE 2 Reaction of diols with $[Fe(CN)_4(bpy)]^-$ at 298 15 K, pH 2 6[a]

Diol	[diol] × 10^2 (mol dm^{-3})	k_{obs}(s^{-1})	k'_2 (mol^{-1} dm^3 s^{-1})
Catechol	0 25	0 295(6)	53 ± 4
	0 625	0 484(7)	
	0 90	0 629(9)	
	2 50	1 40(5)	
Catechol	0 25	0 233(13)	44 ± 2
	0 50	0 331(9)	
	1 0	0 536(16)	
	1 5	0 787(13)	
	2 5	0 853(11)	
4-t-Bu-catechol	0 50	0 326(6)	67 7 ± 1 1
	0 75	0 501(7)	
	1 0	0 637(10)	
Methyl-1,4-hydroquinone	0 25	1 30 (6)	477 ± 34
	0 50	2 09 (6)	
	0 75	3 29 (6)	
	1 25	5 98 (6)	

[a] $[Fe(CN)_4(bpy)]^- = 2$ 0 × 10^{-4} mol dm^{-3}, the pH of both reactants was adjusted to 2 6 and the ionic strength made up to 0 1 mol dm^{-3} (NaCl)

TABLE 3 Effect of temperature on the reaction between benzenediols and $[Fe(CN)_4(bpy)]^-$ at pH 2 6[a]

Diol	T(K)	k'_2 (mol^{-1} dm^3 s^{-1})	ΔH* (kJ mol^{-1})	ΔS* (J mol^{-1} K^{-1})
Catechol	293 15	44	33 ± 3	−101 ± 11
	298 15	50 4		
	303 15	74 9		
	308 15	88		
	313 15	107		
4-t-Bu-catechol	298 15	74	32 9 ± 3	−101 ± 10
	303 15	89		
	308 15	109		
	313 65	149		
Methyl-1,4-hydroquinone	298 15	443	13 2 ± 1 5	−150 ± 5
	302 65	503		
	307 15	533		
	310 15	572		
Methyl-1,4-hydroquinone[b]	298 15	413	16 8 ± 1 5	−138 ± 5
	303 35	474		
	308 15	564		
	313 45	606		
	318 45	680		

[a] $[Fe(CN)_4(bpy)]^- = 2$ 0 × 10^{-4} mol dm^{-3}, [diol] = 5 0 × 10^{-3} mol dm^{-3}, ionic strength 0 1 mol dm^{-3} (NaCl), atmospheric pressure

[b] pH 2 8

chloric acid or by buffers Kinetic data at 298 15 K and atmospheric pressure are assembled in Table 2 The effect of the t-butyl substituent is in the direction of facilitating oxidation with k_2 for catechol being 50 mol^{-1} dm^3 s^{-1}, and 74 mol^{-1} dm^3 s^{-1} for the substituted 1,2-diol However, since the error on k'_2 is typically ±10%, this difference may not be very significant By contrast methyl-1,4-hydroquinone is oxidized almost an order of magnitude faster, and in fact at the upper pH range becomes too labile even for the stopped-flow method Kinetic runs over a range of temperature, usually 293 15–313 15 K, and pressures (1 bar to 1 kbar at 298 15 K), were carried out and these results and derived parameters, ΔH^*, ΔS^* and ΔV^* are presented in Tables 3 and 4, respectively Figures 1, 2 and 3 show sample plots for derivation of second order rate constants, enthalpy and entropy of activation, and the volume of activation, respectively

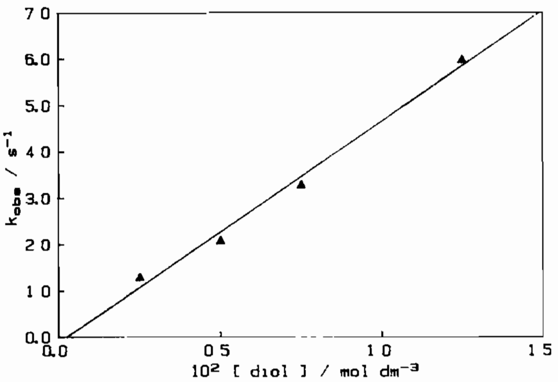

Fig 1 Oxidation of **3** by $[Fe(CN)_4(bpy)]^-$, at pH 2 6 and 298 2 K k_{obs} *vs* [diol]

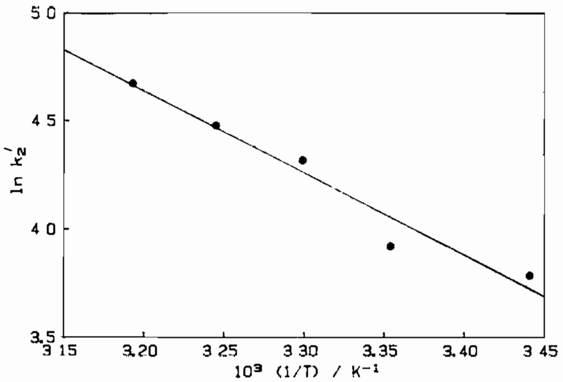

Fig 2 Temperature dependence of oxidation of **1** by $[Fe(CN)_4(bpy)]^-$ at pH 2 6 Plot of derived second order rate constant, k'_2 *vs* reciprocal of temperature

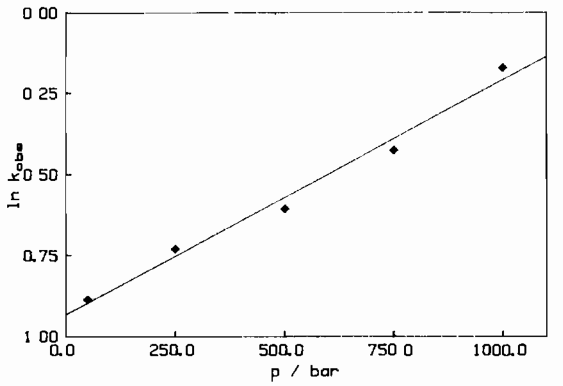

Fig 3 Pressure dependence of reaction of $[Fe(CN)_4(bpy)]^-$ with **2** at 298 2 K and pH 2 6 Plot of ln k_{obs} *vs* pressure

TABLE 4 Effect of pressure on the reaction between benzenediols and $[Fe(CN)_4(bpy)]^-$ at pH 2 6 and 298 15[a]

P (bar)	k_{obs}(s^{-1})			
	Catechol		t-Bu-catechol[d]	Methyl-1,4-hydroquinone[d]
	I[b]	II[c]		
50	0 513	0 256	0 412	3 05
250	0 578	0 344	0 482	3 47
500	0 679	0 409	0 546	4 21
750	0 838	0 480	0 654	5 19
1000	1 03	0 530	0 844	5 62
ΔV^* (cm^3 mol^{-1})	$-18\ 3 \pm 0\ 8$	$-18\ 3 \pm 2\ 5$	$-18\ 0 \pm 1\ 3$	$-16\ 7 \pm 1\ 1$

[a] Ionic strength 0 1 mol dm^{-3}, $[Fe(CN)_4(bpy)]^- = 2\ 0 \times 10^{-4}$ mol dm^{-3} [b] [catechol] = $1\ 75 \times 10^{-2}$ mol dm^{-3} [c] [catechol] = $5\ 0 \times 10^{-3}$ mol dm^{-3} [d] [diol = $7\ 5 \times 10^{-3}$ mol dm^{-3}

Discussion

Kinetics

The second order rate law at atmospheric pressure, and the appearance of the pH-rate constant profiles found here for the three benzene diols confirm the findings previously noted [14]. In the present study values of k'_2 are slightly less than those for reaction (1) reported earlier, but hardly outside the experimental error range. The values of about 50, 68 and 477 $\mathrm{mol^{-1}\ dm^3\ s^{-1}}$ for **1**, **2** and **3**, respectively at 298.2 K (Table 2), in the pH independent region establish an order of reactivity. Before the detailed mechanism is discussed, reactivity can be analyzed in a simple way to indicate that an electron donating group has a slight accelerating effect on the electron transfer reaction and that diol oxidation is markedly facilitated by *para* hydroxy groups compared with *ortho* diols. These effects have also been noted for oxidation of benzene diols by cobalt(III) species [13] and by the hexachloroiridate (IV) ion [12, 15], in an aqueous perchloric acid medium (pH 2).

While the oxidation is accelerated with an increase of the pH, this feature of the reactivity is much more dramatic when the iron(III) complex is the oxidant. For example, the rate enhancement is a factor of 25 when the pH increases from 2.6 to 5.4 for the reaction of the iron(III) complex (Table 1), whereas the rate constant is only slightly more than doubled for a parallel pH increase, for the $\mathrm{IrCl_6}^{2-}$ ion [12]. It is therefore concluded that the iron(III) species has a pH dependent composition and that one or more high pH forms of the complex are very labile. It has been proposed [20] that protonation of the $[\mathrm{Fe(CN)_4(bpy)}]^-$ ions occurs at the nitrogen of a cyano moiety, and at each one in sufficiently acidic solution. Since the incipient iron(II) complex with a higher negative charge will have a greater affinity for hydrogen ions, an uncharacterized set of conjugate acid–base species will be part of the overall reaction scheme in the pH dependent region. Consequently, the kinetic and activation parameters obtained in the pH independent region form the basis for further discussion.

A mechanism similar to that suggested for oxidation of benzene diols by the $\mathrm{IrCl_6}^{2-}$ species is appropriate

$$[\mathrm{Fe(CN)_4(bpy)}]^- + \mathrm{QH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe(CN)_4(bpy)}]^{2-} + \mathrm{QH_2}^+$$

$$[\mathrm{Fe(CN)_4(bpy)}]^- + \mathrm{QH_2}^+ \xrightarrow{k_2} [\mathrm{Fe(CN)_4(bpy)}]^{2-} + \mathrm{Q} + 2\mathrm{H}^+$$

These two consecutive processes account for the reaction stoichiometry and the second order kinetics in evidence when k_{obs} is plotted against diol concentration, and from considering the following. If a rate law is based on use of the steady state approximation for $\mathrm{QH_2}^+$, and then simplified, the rate of loss of iron(III) complex can be expressed by

$$\frac{-\mathrm{d}}{\mathrm{d}t}[\mathrm{Fe(CN)_4(bpy)}]^- = \frac{2k_1k_2[\mathrm{Fe(CN)_4(bpy)}]^{2-}[\mathrm{QH_2}]}{k_{-1}[\mathrm{Fe(CN)_4(bpy)}]^{2-} + k_2[\mathrm{Fe(CN)_4(bpy)}]^-}$$

whereupon if $k_{-1}[\mathrm{Fe(CN)_4(bpy)}]^{2-} \ll k_2[\mathrm{Fe(CN)_4(bpy)}]^-$ the equation reduces to

$$\frac{-\mathrm{d}}{\mathrm{d}t}[\mathrm{Fe(CN)_4(bpy)}]^- = 2k_1[\mathrm{Fe(CN)_4(bpy)}]^-[\mathrm{QH_2}]$$

with $k_{\mathrm{obs}} = 2k_1[\mathrm{QH_2}]$, when $[\mathrm{QH_2}] \gg [\mathrm{Fe(CN)_4(bpy)}]^-$ and plots of k_{obs} *versus* $[\mathrm{QH_2}]$ are reasonably linear (as for example in Fig. 1). Second order rate constants, k'_2, are equal to $2k_1$ according to this scheme. If this mechanistic scheme applies it would imply that increasing acidity would favour the reverse step of semiquinone formation and complicate the release of protons, from the diol or other intermediate species. However, this would be evident with other oxidizing agents if it pertained. The pH independence of the reaction in the range 2–3 argues against rate retardation by a reverse reaction. Thus $\mathrm{QH_2}^+$ must react rapidly with a second Fe(III) molecule.

The step in the mechanism characterized by k_1, is a composite process of the encounter complex formation (formation constant, K) and a rate determining electron transfer step (first order rate constant, k), since the reaction can be thought to proceed by an outer-sphere electron transfer mechanism. Because the benzene diols are neutral the value of K is predicted to be small compared with a precursor complex formed from two oppositely charged ionic species. Therefore the reaction here can be considered as directly second order. We may assume that the oxidation of the proposed semiquinone occurs rapidly, based on this minimal mechanism. The variation in reactivity between the different diols, therefore, can be interpreted in terms of changes in either or both of K and k. For the 1,2-benzenediols, the ion–dipole interaction should be quite similar, and the electron transfer step would also be expected to be very similar in rate, particularly as the bulky tertiary butyl group is remote from the electron transfer site. With a smaller dipole moment, the 1,4-diol will form the encounter complex less well, although it is conceivable that interaction occurs directly between one polar hydroxy group and the charged oxidant, yielding an increase in K However, it would be surprising if the factor of ten in the reactivity difference resided in K Estimates of ion–dipole interactions based upon a modified form of the equation proposed by Fuoss [21] would indicate only small differences in K for different dipole strengths for the same ion It is much more likely that the electron transfer step, (k), is facilitated by the particular electronic organization where only one hydroxy group is interacting with the anion At what stage a proton is liberated or when electron abstraction occurs and whether this is different for the different diol isomers cannot be answered from our results The difficulty of interpreting kinetic results in terms of the properties of reactants is illustrated by the factor of fifteen that 4-methyl-1,2-benzenediol is oxidized faster by $IrCl_6^{2-}$ than is the unsubstituted diol [15] In earlier work [15] a correlation was observed between the reactivity of the diol substrate and the standard redox potential for reduction of the product back to the diol While we may anticipate a parallel correlation here, which would imply a similar mechanism for both oxidants, at present there are insufficient data to pursue this point or apply the Marcus theory

Activation parameters

The enthalpy of activation, ΔH^*, for **3** (~ 15 kJ mol^{-1}) is about one half that for the 1,2-diols (**1** and **2**) However, the values are in the range expected for an outer-sphere mechanism, and lower than would be anticipated for a mechanism involving bond breakage in the oxidant This markedly lower enthalpy barrier for the reaction of **3** is paired with a much greater degree of order in the transition state than occurs for **1** and **2**, as indicated from entropies of activation (Table 3) What the precise molecular organizations of the transition states are for transfer of the electron to the iron complex are not known, but the entropy of activation differences reflect differences of detail, but not of charge, since the volume of activation, ΔV^* (Table 4), is essentially invariant The large negative values of ΔS^* and ΔV^* contrast with large positive values of these parameters [5] for the reduction of cobalt(III) complexes, $[Co(NH_3)_5X]^{3+}$ where X was H_2O, pyridine or $(CH_3)_2SO$, by the $[Fe(CN)_6]^{4-}$ ion In the latter reaction an overall charge reduction occurs as the reaction proceeds giving rise to decreased electrostriction, and accounts for the increase in the volume of the system The present results, therefore, in which charge is developed during the reaction are compatible Other results for outer-sphere electron transfer, involving oxidation of iron(II) diimine complexes by peroxodisulfate ions [11, 22], have shown the importance of solvational changes as well as intrinsic changes, and draw attention to small differences of ΔV^* for similar reactions caused by the magnitudes of non-reacting ligand

The oxidation of benzenediols by $[Fe(CN)_4(bpy)]^-$ yields first an ion dipole complex for which the volume will change little as no change in charge occurs and no covalent bonds are formed, or broken In transition metal complex substitution reactions, the outer-sphere complex initially formed has a very small positive volume change estimated to be associated with it [23] Therefore, the principal factor contributing to the overall ΔV^* values of -18 cm^3 mol^{-1} is charge creation during the electron transfer step

The particular contributions are difficult to assess without the partial molar volumes of both the iron(III) reactant and iron(II) product species While a change of as much as 40 cm^3 mol^{-1}, the difference between the partial molar volumes of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, [5], is not anticipated here, incipient charge differences for this type of species give rise to large volume changes The proton has a partial molar volume of $-4\ 5$ cm^3 mol^{-1}, [24], and therefore, this would give rise to a contribution of one third to one quarter of the total change However, the extent to which the proton is removed within the transition state is not known The forming semiquinone would not be anticipated to have a significantly different molar volume than its corresponding diol, therefore the common ΔV^* reflects principally changes in charge, which are similar in all three reactions

Further systems will be needed to be studied to add to the relative scarcity of information on pressure effects on outer-sphere electron transfer reactions, before the details of the various contributing components may be quantified and better understood

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