

Solvent and Pressure Effects on Intramolecular Electron Transfer Rates Within a Binuclear Cobalt(III)–Pyrazine Carboxylate–Iron(II) Anion

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Abstract

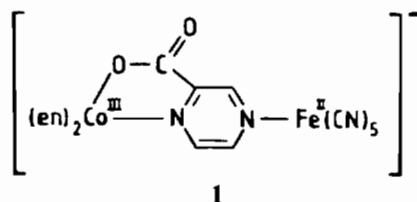
Rate constants are reported for intramolecular electron transfer within the pyrazine carboxylate bridged dinuclear complex $[(en)_2Co(pzc)Fe(CN)_5]^-$ in aqueous methanol, 0 to 80% (by volume) methanol. Activation volumes for this process in water and in 60% methanol are +24 and +7 $cm^3 mol^{-1}$ respectively. Rate constant trends and activation volumes are discussed in terms of medium dielectric properties and of solvation of the initial state and of the activated complex for electron transfer.

Introduction

Patterns of solvation effects on reactivities for outer-sphere redox reactions between pairs of transition metal complexes are now becoming established. For many such reactions, including $[Ru(hfac)_3]^{0/-}$ [1] and $[Cr(biphenyl)_2]^{+/0}$ [2] electron exchange and $[Co(terpy)_2]^{2+}$ reduction of $[Co(bipy)_3]^{3+}$ [3], the Marcus–Hush theory [4] holds, but for such systems as $[Mn(cyclohexylisocyanide)_6]^{2+/+}$ [5] and ferrocinium/ferrocene [6] electron exchange, specific solvation effects result in a lack of the correlation of rate constants with the dielectric parameter $(1/D_{op}) - (1/D_s)$ predicted by the Marcus–Hush theory. It is more difficult to establish a solvation-reactivity pattern for inner-sphere redox reactions, since medium effects reflect solvation changes during precursor complex formation as well as those associated with the actual electron transfer step [7]. This has been illustrated in iron(II) reduction of the $[Co(NH_3)_5Cl]^{2+}$ cation [8]. The electron transfer step within an inner-sphere transition state can be modelled with mixed valence (MV) binuclear complexes [9]. For such complexes as $[(CH_3N)_5Ru(4,4'-bipy)Ru(NH_3)_5]^{5+}$, electron transfer rate

constants, k_{et} , estimated from near-infrared spectroscopic data correlate well with $(1/D_{op}) - (1/D_s)$ [10]. Similarly satisfactory correlations can be demonstrated for intervalence charge-transfer within unsymmetrical MV species such as $[(H_3N)_5Ru(pyrazine)RuCl(bipy)_2]^{4+}$, once due allowance has been made for solvent effects on the overall Gibbs free energy change [11]. Unfortunately the derivation of k_{et} values for these fast intramolecular electron transfers from spectroscopic data involves rather drastic assumptions, particularly in relation to activation entropies [9]. It is therefore desirable to attempt to establish solvent effects on reactivities in systems where electron transfer is much slower, so that conventional kinetic monitoring is possible.

Electron transfer within binuclear complexes is generally only slow when the electron has to be transferred into an e_g rather than a t_{2g} orbital. Cobalt(III), t_{2g}^6 , is the obvious example. In this paper we report solvent effects on k_{et} in aqueous methanol (0 to 80% by volume) for the pyrazine carboxylate bridged species (1) [12, 13]. Neither the Marcus–Hush theory nor simple solvation considerations explain adequately the observed increase then decrease in k_{et} as the methanol content of the solvent increases. Activation volumes, from high pressure kinetic measurements in 0 and 60% methanol, show that solvation must play an important role in determining reactivity. This is also shown by the relation of the reactivity trend to the estimated transfer chemical potential trend for 1, estimated from solubility measurements on $[Co(en)_2(pzc)](ClO_4)_2$ and published data for the hexacyanoferrate(III) anion.



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TABLE I. Solvatochromism of the Binuclear Mixed Valence Complex and of the Iron(III) Product, $[\text{Fe}(\text{CN})_5(\text{pzc})]^{3-}$

Solvent ^a	λ_{max} (nm)	$[\text{Fe}(\text{CN})_5(\text{pzc})]^{3-}$	
		$[(\text{en})_2\text{Co}(\text{pzc})\text{Fe}(\text{CN})_5]^-$	Reaction product
Water	636		462
Methanol 20%	630		468
40%	624		472
60%	616		475
80%			477
Acetone 40%	597		(ca. 495 ^c)
t-Butyl alcohol 40%	605		485
			490

^aCompositions are volume (%) before mixing. ^b $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{pzc})]$ prepared by bromine oxidation of $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{pzc})]$ prepared by reaction of $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ with pzc^- . ^cVcry broad band.

Experimental

$[\text{Co}(\text{en})_2(\text{pzc})](\text{ClO}_4)_2$ was prepared by the published method [12]. Sodium nitroprusside was treated with concentrated aqueous ammonia to yield $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)]$ [14], which on dissolution in water immediately gives the $[\text{Fe}(\text{CN})_5(\text{OH}_2)]^{3-}$ anion. On mixing aqueous solutions containing 2×10^{-4} M $[\text{Co}(\text{en})_2(\text{pzc})](\text{ClO}_4)_2$ and 2×10^{-4} M $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{OH}_2)]$, the binuclear complex **1** is fully formed within a matter of seconds [12]. Repeat scan spectra in the visible region (the $\text{Fe} \rightarrow \text{pzc}$ MLCT in **1** is at 635 nm, with $\epsilon = 9500 \text{ M}^{-1} \text{ cm}^{-1}$) then give k_{et} for electron transfer from iron to cobalt within **1**; the successor complex rapidly dissociates to $[\text{Fe}(\text{CN})_5(\text{pzc})]^{3-}$, Co^{2+} aq, and ethane-1,2-diamine. The repeat scan spectra showed an excellent isosbestic point at 527 nm. Analogous procedures were used to obtain k_{et} values in methanol–water mixtures; rates of formation of the binuclear species and the position of the isosbestic point varied somewhat with solvent composition. The latter results from the solvatochromic behaviour of the $[\text{Fe}(\text{CN})_5(\text{pzc})]^{3-}$ product (Table I). Indeed comparison of final spectra for the k_{et} runs with spectra from an authentic sample of this iron(III) complex (prepared by bromine oxidation of $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{pzc})]$) provided the required product characterisation. The range of methanol–water compositions which could be studied was limited to 0 to 80% (by volume previous to mixing) by the very low solubility of **1** at high percentages of methanol. The dependence of k_{et} on pressure was determined using the apparatus and methods described earlier [15].

Results

The kinetic results, both at atmospheric and at high pressure, are collected in Table II. Values of

TABLE II. First-order Rate Constants for Intramolecular Electron Transfer Within the $[(\text{en})_2\text{Co}(\text{pzc})\text{Fe}(\text{CN})_5]^-$ Anion in Methanol–Water Mixtures^a at 298.2 K; Initial Concentration of Binuclear Complex = 1.0, 1.5, or 2.0×10^{-4} mol dm⁻³

	Volume (%) methanol ^b				
	0	20	40	60	80
$10^5 k$ (s ⁻¹) at $P = 0.001$ kbar	10.4	12.5	12.3	7.6	1.7
	0.34	7.6		6.9	
	0.68	5.1		6.3	
ΔV^\ddagger (cm ³ mol ⁻¹)	+24		+7		

^a $k_{\text{et}} = 9.6 \times 10^{-5} \text{ s}^{-1}$ and $1.5 \times 10^{-5} \text{ s}^{-1}$ in 40% acetone, 40% t-butyl alcohol respectively, at 298.2 K and 1 atmosphere pressure. ^bPercentages by volume before mixing.

k_{et} were obtained at more than one initial concentration of binuclear complex, *i.e.* of $[\text{Co}(\text{en})_2(\text{pzc})](\text{ClO}_4)_2$ and $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)]$ solutions, in most solvent mixtures. This was done to check the independence of k_{et} of initial concentration – a variation of apparent k_{et} with initial concentration would suggest that at lower concentrations formation of **1** might not be complete by the time that monitoring of $-\text{d}[\text{binuclear species } \mathbf{1}]/\text{d}t$ started. The initial formation reaction is presumably first-order in each reactant, so its half-life will increase steeply as initial concentrations are lowered. There could also be a marked decrease in rate as the methanol content of the media increased. Indeed there are indications that the formation reaction is not kinetically distinct from the subsequent electron transfer step when initial concentrations of 0.5×10^{-4} mol dm⁻³ of each reactant are used in methanol-rich mixtures.

TABLE III. Solubilities^a and Transfer Chemical Potentials^b

	Volume (%) methanol ^c				
	0	20	40	60	80
10^3 soly $[\text{Co}(\text{en})_2(\text{pzc})](\text{ClO}_4)_2$ ^d	18.1	12.3	9.4	7.6	3.9
$\delta_{\text{m}}\mu^\circ$ $[\text{Co}(\text{en})_2(\text{pzc})](\text{ClO}_4)_2$		+1.0	+1.6	+2.2	+3.8
$2 \delta_{\text{m}}\mu^\circ$ (ClO_4^-) ^e		+0.1	-0.2	+0.4	+3.2
$\delta_{\text{m}}\mu^\circ$ $[\text{Co}(\text{en})_2(\text{pzc})]^{2+}$		+0.9	+1.8	+1.8	+0.6
$\delta_{\text{m}}\mu^\circ$ $[\text{Fe}(\text{CN})_6]^{3-}$ ^e		-4.1	-3.2	-3.2	+11
$\delta_{\text{m}}\mu^\circ$ (is model) ^f		-3.2	-1.4	-1.4	+12
$\delta_{\text{m}}\Delta G^\ddagger$ ^g		-0.4	-0.4	+0.8	+4.5
$\delta_{\text{m}}\mu^\ddagger$		-3.6	-1.8	-0.6	+16

^aMol dm⁻³ at 298.2 K. ^bkJ mol⁻¹; on the molar scale at 298.2 K; TPTB assumption. ^cVolume percent before mixing.

^dDetermined spectrophotometrically. ^eRef. 25. ^f $[(\text{en})_2\text{Co}(\text{pzc})\text{Fe}(\text{CN})_5]^-$ taken as $[\text{Co}(\text{en})_2(\text{pzc})]^{2+} + [\text{Fe}(\text{CN})_6]^{3-}$.

^gFrom rate constants given in Table II.

Activation volumes calculated from the pressure dependence of k_{et} are also included in Table II. Solubilities of $[\text{Co}(\text{en})_2(\text{pzc})](\text{ClO}_4)_2$ in methanol-water mixtures are given in Table III, which gives the derivation of transfer chemical potentials from these solubilities.

Discussion

The Marcus-Hush theory of electron transfer [4] forecasts an increase in rate constant as solvent polarity decreases. The rate constants for electron transfer within the binuclear $[(\text{en})_2\text{Co}(\text{pzc})\text{Fe}(\text{CN})_5]^-$ anion conform to this expectation only over the range 0 to 20% methanol. Thereafter there is marked deviation, with a large decrease in rate constant on going from 60 to 80% methanol contrasting with the small increase expected from the Marcus-Hush approach. The dependence of k_{et} on $(1/D_{\text{op}}) - (1/D_s)$, on $1/D$, and on solvent Y values [16] is shown in the three plots in Fig. 1. Logarithms of k_{et} correlate less badly with $1/D$ than with $(1/D_{\text{op}}) - (1/D_s)$, but reactivity is clearly not controlled directly by solvent dielectric properties. The plot of $\log k_{\text{et}}$ against solvent Y values, in other words against logarithms of rate constants for *t*-butyl chloride solvolysis, is included to give an idea of the large magnitude of the solvent effect on reactivity at high methanol content.

The large positive activation volume for k_{et} in water suggests considerable desolvation of the binuclear complex in the approach to the transition state for this electron transfer. This deduction is supported by an analogous interpretation of large positive activation entropies for electron transfer within other similar $\text{Co}^{\text{III}}\text{-LL-Fe}^{\text{II}}(\text{CN})_5$ com-

plexes [13, 17]. There is probably a significant positive contribution to ΔV^\ddagger arising from cobalt-ligand bond stretching in transition state formation, but this must be small as ΔV^\ddagger in 60% methanol is only +7 cm³ mol⁻¹ (Table II). There is unlikely to be a contribution from iron-cyanide bond stretching or shortening, since iron-cyanide bond lengths are essentially equal in $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ [18]. Thus, contrary to the views expressed in relation to the positive ΔV^\ddagger reported earlier for intramolecular electron transfer within a μ -peroxodicycobalt(III) complex [19], we believe that cobalt-ligand bond stretching makes a relatively small contribution to the experimental ΔV^\ddagger . Rather, especially in water, ΔV^\ddagger is dominated by desolvation on forming the transition state. A significant contribution from partial desolvation of $[\text{Fe}(\text{CN})_6]^{4-}$ in the transition state for outer-sphere reduction of $[\text{Co}(\text{NH}_3)_5\text{L}]^{3+}$, L = water, pyridine, or dimethylsulphoxide, results in markedly positive activation volumes, +26 to +34 cm³ mol⁻¹ [20]. Similarly, the volume change (ΔV°) for $[\text{Fe}(\text{CN})_6]^{4-}$ reduction of cytochrome *c*, +37 cm³ mol⁻¹, also reflects desolvation of $[\text{Fe}(\text{CN})_6]^{4-}$ on oxidation to $[\text{Fe}(\text{CN})_6]^{3-}$ [21]. The difference in partial molar volumes between $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ is +41 cm³ mol⁻¹ [22].

An important role for solvation in determining the observed reactivity trend is also suggested by transfer chemical potentials. The sum of the transfer chemical potentials for $[\text{Co}(\text{en})_2(\text{pzc})]^{2+}$ and for $[\text{Fe}(\text{CN})_6]^{3-}$ can be used as an approximation for $\delta_{\text{m}}\mu^\circ$ ($[(\text{en})_2\text{Co}(\text{pzc})\text{Fe}(\text{CN})_5]^-$) (Table III). Figure 2 shows a close similarity between the plots of $\delta_{\text{m}}\mu^\circ$ (binuclear model) and of logarithms of rate constants. We are not at present able to carry out an initial state-transition state analysis of the reactivity

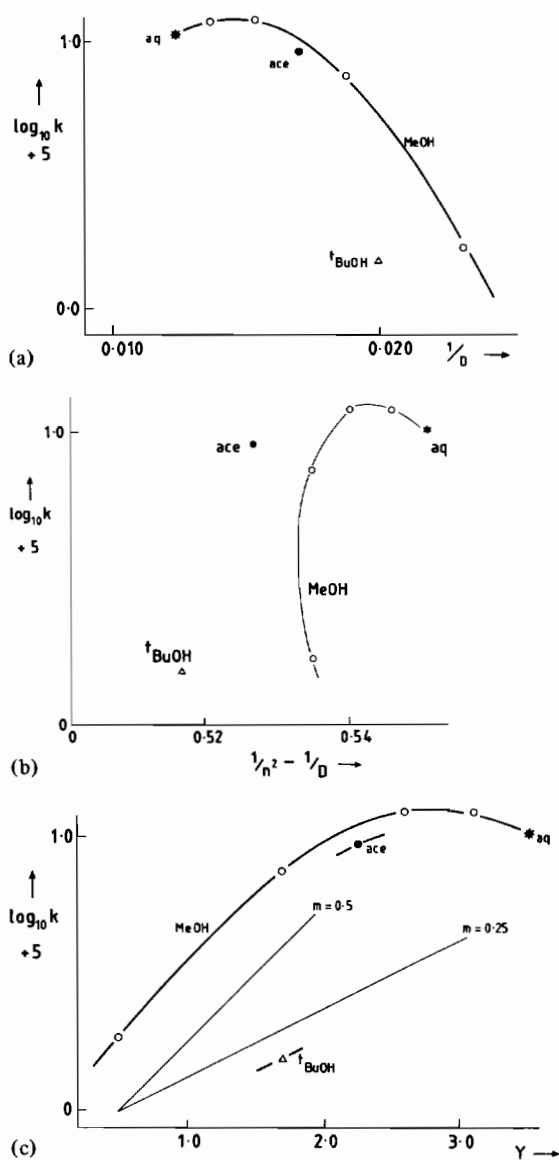


Fig. 1. The relation between intramolecular electron transfer rate constants (k) for $[(en)_2Co(pzc)Fe(CN)_5]^-$ and (a) static dielectric constants (D), (b) the dielectric function $(1/n^2) - (1/D)$, and (c) Y values for binary aqueous solvent mixtures.

trend, as we have not been able to synthesise the $[(en)_2Cr(pzc)Fe(CN)_5]^-$ anion, the obvious non-redox analogue of our $Co^{III}-pzc-Fe^{II}$ binuclear complex. Clearly it is important to assess the role of solvation as quantitatively as possible, in view of the currently increasing realisation and discussion of the role of specific solute-solvent interactions in modifying the forecasts of Marcus-Hush and other theories in relation to electron transfer in solution [23] and at the solution-solid interface, *i.e.* at electrodes [24].

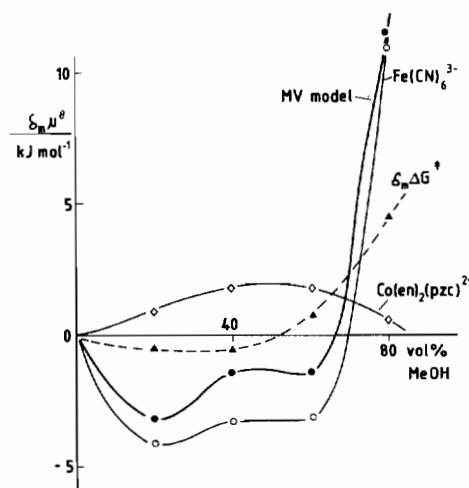


Fig. 2. The relation between the activation barrier trend ($\delta_m \Delta G^\ddagger$) for intramolecular electron transfer within $[(en)_2Co(pzc)Fe(CN)_5]^-$ and transfer chemical potentials for $[Co(en)_2(pzc)]^{2+}$, $[Fe(CN)_6]^{3-}$, and the mixed valence model (see text).

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