Activation Volumes for Peroxodisulphate Oxidation of Iron(II)–Diimine–Cyanide Complexes

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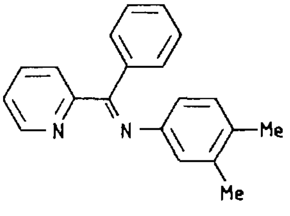
Several years ago we reported that the activation volume for the peroxodisulphate oxidation of the $[Fe(CN)_4(bipy)]^{2-}$ anion was 0 ± 1 cm^3 mol^{-1} in aqueous solution [1]. This is one of very few activation volumes reported for simple outer-sphere electron transfer [2]. The value of approximately zero for $\Delta V^{\ddagger}$ implies that the change of state of solvation in going to the transition state balances the intrinsic $\Delta V^{\ddagger}$ for formation of a bimolecular transition state, generally believed to be about −10 cm^3 mol^{-1} [3]. Our recent demonstrations that activation volumes for base hydrolysis of iron(II)–diimine complexes are largely determined by solvent electrostriction, the contribution of which depends markedly on the nature of the ligand through its effect on solvation of the complex [4], prompted us to look in more detail at peroxodisulphate oxidation of low-spin iron(II) complexes. In this letter we show how activation volumes for such reactions depend on charge, ligand nature and solvent medium.

Rate constants for peroxodisulphate oxidation of the iron(II) complexes were determined at atmospheric and at elevated pressures using the apparatus and techniques described earlier [5]. The complexes $[Fe(CN)_4(LL)]^{2-}$ (with LL = bipy or phen) were prepared by Schilt's method [6]; the analogous complex $[Fe(CN)_4(ein)]^{2-}$ (ein = the smallest diimine HN:CHCH:NH) was prepared by oxidation of the ethane-1,2-diamine complex $[Fe(CN)_4(en)]^{2-}$ [7]. The $[Fe(CN)_4(Me_2bsb)]^{2-}$ anion was prepared from $[Fe(Me_2bsb)_3]^{2+}$, itself generated from 2-benzoylpyridine and 3,4-dimethylaniline [8], by Schilt's method [6]. $[Fe(CN)_2(bipy)_2]$ was prepared by the usual method [6]. Potassium peroxodisulphate was AnalaR material; fresh solutions were made up immediately before each kinetic experiment.

All runs were carried out in the presence of a large excess of peroxodisulphate; all reaction mixtures were approximately 10^{-5} mol dm^{-3} in EDTA, so that any traces of transition metal ions would be sequestered and thereby prevented from affecting the rate of oxidation. First-order kinetics were followed closely for the first half-life and slightly less closely for the second (this is rather better kinetic behaviour than exhibited in peroxodisulphate oxidation of analogous $[Fe(diimine)_3]^{2+}$ cations). Ratios of observed first-order rate constants at high pressure to their equivalents at atmospheric pressure are reported in Table 1. Plots of logarithms of these ratios against pressure were essentially linear; activation volumes derived from the slopes of such plots (Fig. 1) are also included in the Table.



Me_2bsb

It is clear that the zero activation volume for peroxodisulphate oxidation of the $[Fe(CN)_4(bipy)]^{2-}$ anion in aqueous solution [1] represents the balance between a negative intrinsic contribution and a positive contribution from solvation and electrostriction changes on going from reactants to transition state. The important role played by complex solvation is apparent if one compares $\Delta V^{\ddagger}$ values for the $[Fe(CN)_4(diimine)]^{2-}$ anions. These range

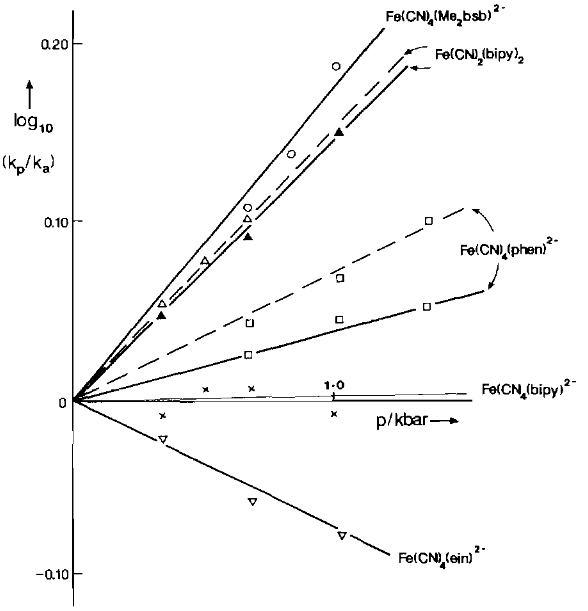


Fig. 1. Effect of pressure on rate constants for peroxodisulphate oxidation of iron(II)–diimine–cyanide complexes: (——) aqueous solution; (– – –) in 60% dimethyl sulphoxide.

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TABLE 1. Second-order Rate Constants at Atmospheric Pressure, Logarithms of Ratios of Second-order Rate Constants at High Pressures to Those at Atmospheric Pressure, and Activation Volumes for Peroxodisulphate Oxidation of Iron(II)–Diimine–Cyanide Complexes at 298.2 K

	$[K_2S_2O_8]$ (mol dm^{-3})	λ_{max} (nm)	k_2 (1 bar) (M^{-1} s^{-1})	$\log_{10}(k_p/k_a)$ at P (kbar)					$\Delta V^{\ddagger}$ (cm^3 mol^{-1})
				0.34	0.69	0.87	1.04	1.38	
In water									
$[Fe(CN)_4(ein)]^{2-}$	0.0100	510	0.042	−0.023	−0.062		−0.081		+4.6
$[Fe(CN)_4(phen)]^{2-}$	0.0050	470	0.050		0.023		0.040	0.049	−2.1
$[Fe(CN)_2(bipy)_2]$	0.0020	520	0.120	0.047	0.089		0.148		−7.7
$[Fe(CN)_4(Me_2bsb)]^{2-}$	0.0080	535	0.026		0.101	0.135	0.185		−10.2
In 60% DMSO									
$[Fe(CN)_4(phen)]^{2-}$	0.010	530	0.024		0.038		0.068	0.098	−3.6
$[Fe(CN)_2(bipy)_2]$	0.030	565	0.025	0.051	0.076		0.098		−8.3

from a value of −10 cm^3 mol^{-1} for the complex with the large and hydrophobic Me_2bsb ligand to +5 cm^3 mol^{-1} for ein, the smallest and least hydrophobic ligand. The former value is approximately that expected for a bimolecular process in which the solvation contribution to $\Delta V^{\ddagger}$ is negligible. The bipy and phen complexes, of medium size and hydrophobicity, have intermediate values, with the slightly larger phen complex having the anticipated slightly more negative activation volume. The importance of charge is apparent if one compares $\Delta V^{\ddagger} = -8$ cm^3 mol^{-1} for peroxodisulphate oxidation of $[Fe(CN)_2(bipy)_2]$ with the value of approximately zero for the $[Fe(CN)_4(bipy)]^{2-}$ anion [1].

The effect of changing the solvent from water to 60% (by volume) dimethyl sulphoxide is negligible for oxidation of $[Fe(CN)_2(bipy)_2]$, but significant, albeit rather small, for oxidation of the $[Fe(CN)_4(bipy)]^{2-}$ anion. This small medium effect can presumably be attributed to compensation between solvation contributions assignable to the hydrophilic cyanide ligands and the peroxodisulphate anion, and to the predominantly hydrophobic phen ligand. We hope to pursue our investigation into the role of solvation in this type of reaction by establishing transfer chemical potential [9, 10] and solvatochromism [10, 11] trends for the anionic complexes, and by carrying out initial state–transition state analyses of reactivity trends, in mixed solvents.

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References

1 J. Burgess and C. D. Hubbard, *Inorg. Chim. Acta, 64* (1982) L71.

2 T. W. Swaddle, in R. van Eldik (ed.), *Inorganic High Pressure Chemistry—Kinetics and Mechanisms*, Elsevier, Amsterdam, 1986, Ch. 5 (see p. 280).

3 T. Asano and W. J. Le Noble, *Chem. Rev., 78* (1978) 407.

4 J. Burgess and C. D. Hubbard, *J. Chem. Soc., Chem. Commun.*, (1983) 1482; *J. Am. Chem. Soc., 106* (1984) 1717.

5 N. Hallinen, P. McArdle, J. Burgess and P. Guardado, *J. Organomet. Chem., 333* (1987) 77.

6 A. A. Schilt, *J. Am. Chem. Soc., 82* (1960) 3000.

7 V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, (1972) 207.

8 P. Krumholz, *Inorg. Chem., 4* (1965) 609.

9 E. E. Abu-Gharib, M. J. Blandamer, J. Burgess, N. Gosal, P. Guardado, F. Sanchez and C. D. Hubbard, *Transition Met. Chem., 9* (1984) 306; M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A. W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C. D. Hubbard and E. E. Abu-Gharib, *J. Chem. Soc., Faraday Trans. 1, 82* (1986) 1471.

10 J. Burgess, S. Radulovic and F. Sanchez, *Transition Met. Chem., 12* (1987) 529.

11 J. Burgess, *Spectrochim. Acta, Part A, 26* (1970) 1957; J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem., 6* (1981) 145; M. Kotowski, R. van Eldik, Razak bin Ali, J. Burgess and S. Radulovic, *Inorg. Chim. Acta, 131* (1987) 225 and refs. therein.