

Initial State and Transition State Solvation in the Peroxodisulphate Oxidation of Dicyanobis(2,2'-bipyridyl)iron(II)†

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Summary Solvent effects on the kinetics of peroxodisulphate oxidation of dicyanobis(2,2'-bipyridyl)iron(II), $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$, in aqueous methanol have been analysed into initial state and transition state components; the latter dominate the observed reactivity trend.

SOLVENT effects on reactivity have been analysed into initial state and transition state contributions for several substitution reactions. Both enthalpy data for *t*-butyl chloride solvolysis¹ and volume data for benzyl chloride solvolysis² show dominance of initial state solvation effects. The same conclusion has been reached (from Gibbs free energies and chemical potential data) for the Menshutkin reaction of trimethylamine with methyl iodide³ and for the reaction of tetraethyltin with mercury(II) chloride.⁴ How-

ever, initial state and transition state effects are of comparable importance in the Menshutkin reaction of *p*-nitrobenzyl chloride with methyl iodide and in reactions of tetra-alkyl-lead compounds with iodine.³ Initial state solvation effects are again dominant for the reaction of $[\text{Pt}(\text{bipy})\text{Cl}_2]$, *bipy* = 2,2'-bipyridyl, with thiourea⁵ and in the mercury(II)-catalysed aquation of the $[\text{ReCl}_6]^{2-}$ anion, but initial state and transition state solvation effects are both important in the mercury(II)-catalysed aquation of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ cation and in the reaction of the $[\text{Fe}(\text{bipy})_3]^{2+}$ cation with cyanide.⁶ Here we describe the first analysis of solvent effects into initial state and transition state components for a redox reaction of an inorganic complex, the peroxodisulphate oxidation of the low-spin iron(II) $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$.

† No reprints available.

The peroxodisulphate oxidation of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ follows second-order kinetics;⁷ second-order rate constants (k_2) in aqueous methanol and in water are shown in the Table. Gibbs free energies of transfer of the peroxo-

TABLE. Initial state and transition state contributions to reactivity in the peroxodisulphate oxidation of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ in aqueous methanol

% Methanol (volume)	0	20	40	Ref.
$10^3 k_2/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$	600	56	15	7
10^4 solubility $[\text{Fe}(\text{bipy})_2(\text{CN})_2]/\text{mol dm}^{-3}$		1.8	13.2	74.4
$\therefore \delta_m \mu^\ominus [\text{Fe}(\text{bipy})_2(\text{CN})_2]/\text{kJ mol}^{-1}$		-4.9	-9.2	
$\delta_m \mu^\ominus (\text{S}_2\text{O}_8^{2-})/\text{kJ mol}^{-1}$		+4	+9	8
$\therefore \delta_m \mu^\ominus$ (initial state)/ kJ mol^{-1}		-0.9	-0.2	
$\delta_m \Delta G^\ddagger/\text{kJ mol}^{-1}$		+5.9	+9.1	
$\therefore \delta_m \mu^\ddagger/\text{kJ mol}^{-1}$		+5.0	+8.9	

sulphate anion, $\delta_m \mu^\ominus (\text{S}_2\text{O}_8^{2-})$, have been estimated from solubilities of potassium peroxodisulphate⁸ and published values for $\delta_m \mu^\ominus (\text{K}^+)$ ⁹ (and therefore depend on the assumptions used in establishing single ion values here). Solubilities of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ in water and in methanol + water mixtures have been determined by atomic absorption spectroscopy. Hence, Gibbs free energies of transfer for this compound and for the initial state of the redox reaction have been calculated. The transfer function $\delta_m \Delta G^\ddagger$ has been calculated from the rate constant variation, and hence the transfer function for the transition state, $\delta_m \mu^\ddagger$, calculated. All these values are included in the Table, and their variation with solvent composition illustrated in the Figure.

The stabilisation of the iron(II) complex on adding methanol to aqueous solution is matched by the destabilisation of the peroxodisulphate anion. Thus, the net solvent effect on the initial state is very small. The observed marked decrease in rate constant as the proportion of methanol increases must therefore reflect a marked destabilisation of the transition state. Thus, here transition state solvation effects are much more important than initial state solvation effects. This is a novel situation; in all the substitution reactions analysed so far initial state effects are either dominant or comparable in magnitude to transition state effects.

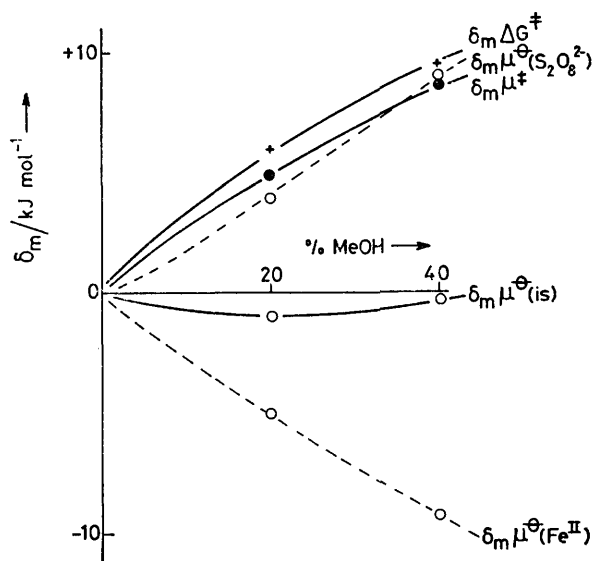


FIGURE. Analysis of the initial state and transition state solvation contributions to the peroxodisulphate oxidation of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$.

The reason for the marked destabilisation of the transition state as the proportion of methanol increases is not clear. If the outer-sphere peroxodisulphate-complex electron transfer takes place from the periphery of the bipyridyl ligand, then the increasingly favourable solvation of this hydrophobic region in increasingly methanolic mixtures would make peroxodisulphate approach, and thus transition state formation, more difficult as the proportion of methanol in the solvent medium increases. It would seem desirable to analyse solvent effects on peroxodisulphate oxidation of, say, the other members of the series $[\text{Fe}(\text{bipy})_3]^{2+}$, $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$, and $[\text{Fe}(\text{CN})_6]^{4-}$, before making final comments on solvation effects on this type of reaction.

(Received, 4th August 1978; Com. 858.)

¹ E. M. Arnett, W. G. Bentrude, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 1965, **87**, 2048; and references therein.

² S. J. Dickson and J. B. Hyne, *Canad. J. Chem.*, 1971, **49**, 2394.

³ M. H. Abraham, *Chem. Comm.*, 1969, 1307; *J.C.S. Perkin II*, 1972, 1343.

⁴ M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *Chem. Comm.*, 1969, 930; M. H. Abraham, *J. Chem. Soc. (A)*, 1971, 1061.

⁵ M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1977, 60.

⁶ M. J. Blandamer, J. Burgess, A. J. Duffield, and R. I. Haines, to be submitted to *J.C.S. Dalton*.

⁷ J. Burgess, *J. Chem. Soc. (A)*, 1970, 2114.

⁸ M. J. Blandamer, J. Burgess, and R. I. Haines, *J. Inorg. Nuclear Chem.*, accepted for publication.

⁹ C. F. Wells, *J.C.S. Faraday I*, 1973, **69**, 984.