Kinetics of Peroxodisulphate Oxidation of Low-spin Iron(II) Complexes in Binary Aqueous Mixtures

By **Michael J. Blandamer, John Burgess,* Philip P. Duce,** and **Robert I. Haines,** Department of Chemistry, University of Leicester, Leicester LE1 7RH

The kinetics of oxidation of two low-spin iron(II) complexes by peroxodisulphate in binary aqueous mixtures have been investigated. Rate constants for the oxidation of the $[Fe(phen)_3]^{2+}$ cation (phen = 1,10-phenanthroline) are reported in mixtures containing up to 60% acetone or 40% dimethyl sulphoxide. Rate constants for the oxidation of the $[Fe(bqdo)]^{2+}$ cation (bqdo = the sexidentate Schiff base derived from quinoline-2-carbaldehyde and triethylenetetramine) are reported in mixtures containing up to 40% acetone or dimethyl sulphoxide. Reactivity trends are discussed in terms of the variation of the chemical potentials of the reactants and of the transition state with solvent composition.

THERE have been many kinetic studies of the oxidation of low-spin iron(II) complexes of the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ † type in aqueous solution. Oxidation by substitution-inert metal complexes, *e.g.* $[IrCl_6]^{2-}$, is fast,[1] but oxidation by oxo-anions is often slow. Examples of kinetic studies of reactions with oxo-anions include those with chlorite and chlorate [2] and with peroxodiphosphate.[3] The most commonly studied oxo-anion oxidant has been peroxodisulphate,[4-8] but the mechanism is still not unequivocally established. Variously reported rate laws for various complexes have been interpreted in terms of ion-pair participation or parallel dissociation and oxidation as well as simple bimolecular oxidation with appropriate interference from radicals generated during the course of the reaction. It is clear that for the peroxodisulphate oxidation of $[Fe(X\text{-}phen)_3]^{2+}$ cations, where X = an electron-withdrawing substituent such as nitro or sulphonato, the observed rate-limiting step is composite [rate law as in equation (1)] with terms corresponding to rate-determining dissociation and to rate-determining oxidation.[7]

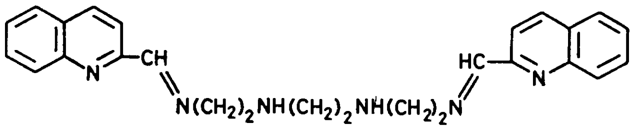
$$-d[\text{complex}]/dt = (k_1 + k_2[S_2O_8^{2-}])[\text{complex}] \quad (1)$$

This scheme is the same as that demonstrated for peroxodisulphate oxidation of the $[Fe(CN)_5(SO_3)]^{5-}$ anion.[9] Peroxodiphosphate oxidation represents the extreme of this dissociative contribution, for here the rate-determining step is entirely dissociative; redox processes are all subsequent.[3] Despite these complications, there appears to be a genuine bimolecular redox contribution to the reactions of complexes of the $[Fe(bipy)_3]^{2+}$ type with peroxodisulphate. Presumably such a reaction involves outer-sphere electron transfer, a hypothesis supported by the reported variation of redox rate constant with substituent for a series of these complex cations.[6] It is difficult to see how these redox reactions could proceed by the ligand-attack route proposed for reactions of these di-imine–iron(II) complexes with hydroxide, cyanide, or alkoxide ions.[10]

We have been interested for some time in the kinetics of substitution reactions of inorganic complexes in binary aqueous mixtures. Recently we have investigated some bimolecular examples, for instance the reactions of the $[Fe(bipy)_3]^{2+}$ and related cations with cyanide or hydroxide ion,[11] of $[Pt(bipy)Cl_2]$ with thiourea,[12] and of $[Re(CO)_5I]$ with cyanide ion.[13] We now extend our studies to the bimolecular redox reactions between low-spin iron(II) complexes and peroxodisulphate, to see how observed reactivity trends can be rationalised in terms of variations of solvation and of chemical potential of reactants and of the transition state.

EXPERIMENTAL

Solutions containing the $[Fe(phen)_3]^{2+}$ cation were prepared by the addition of a very slight excess of AnalaR 1,10-phenanthroline (B.D.H.) to a neutral aqueous solution of AnalaR ammonium iron(II) sulphate. Complex concentrations were checked spectrophotometrically.[14] The preparation and characterisation of the iron complex $[Fe(bqdo)]^{2+}$ of the Schiff base bqdo is reported elsewhere.[15] Potassium peroxodisulphate was either AnalaR material, or prepared by electrolysis of potassium sulphate solution.[16] Solvents were either AnalaR grade and used as received, or purified by standard procedures.[17]



bqdo

Kinetic runs were carried out in 10-mm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. In view of possible difficulties arising from the presence of traces of impurities causing catalytic decomposition of the peroxodisulphate, we have in some cases confirmed reproducibility of rate constants both for samples of potassium peroxodisulphate from different sources and for runs in which a trace of the disodium salt of ethylenediaminetetra-acetate had been included in the reactant solution.

Potassium peroxodisulphate solubilities were determined by equilibrating an excess of the solid with the appropriate solvent in a thermostatted vessel. Concentrations of peroxodisulphate were estimated iodimetrically.

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† Abbreviations: bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline; bqdo = 1,8-bis[(2-quinolyl)methyleneamino]-3,6-diazaoctane. The iron(II) complex of bqdo was reported in *J.C.S. Dalton*, 1978, 1001; in the footnote on page 1001 the ligand was incorrectly named as the bis(phenyl) derivative.

RESULTS

As is usual in peroxodisulphate oxidations, the kinetic behaviour becomes progressively complicated by the contribution of radical intermediates as the reaction proceeds. In the presence of oxidisable organic cosolvents, such deviations may be so marked as to vitiate the determination of rate constants for peroxodisulphate oxidation of the $[\mathrm{Fe(phen)_3}]^{2+}$ cation. We have carried out runs in selected binary aqueous solvent mixtures, in the presence and absence of allyl acetate to act as radical scavenger,[18] in order to assess the possibilities of obtaining reasonably reliable rate constants for the $[\mathrm{Fe(phen)_3}]^{2+}$–$\mathrm{S_2O_8}^{2-}$ reaction. Solvent mixtures that gave either kinetic plots deviating from first-order behaviour (large excess of peroxodisulphate) early in a run, or in which the presence of small amounts of allyl acetate resulted in marked differences in rate constants, were eliminated from our investigation. Only aqueous acetone and aqueous dimethyl sulphoxide proved satisfactory media.

In water, aqueous acetone, and aqueous dimethyl sulphoxide the kinetics conformed, in the presence of a large excess of peroxodisulphate, to first-order behaviour [equation (2)] up to 50—60% of complete reaction.

$$-\mathrm{d[complex]}/\mathrm{d}t = k_{\mathrm{obs.}}\mathrm{[complex]} \qquad (2)$$

Observed first-order rate constants, $k_{\mathrm{obs.}}$, are reported in Tables 1 and 2. The dependence of these $k_{\mathrm{obs.}}$ values on peroxodisulphate concentration is linear for both complexes studied and for all solvent mixtures. The general rate law is shown in equation (1), with $k_{\mathrm{obs.}}$ of equation (2) being equal to $(k_1 + k_2[\mathrm{S_2O_8}^{2-}])$ of equation (1). For oxidation of $[\mathrm{Fe(phen)_3}]^{2+}$, k_1 tends to be negligible in water-rich mixtures, but to assume greater importance as the proportion of organic cosolvent increases. For $[\mathrm{Fe(bqdo)}]^{2+}$, the k_1 (dissociative) term is negligible under all the conditions we have investigated. Values of k_1 (where appropriate) and k_2, computed by a standard unweighted least-mean-squares program, are also given in Tables 1 and 2.

TABLE 1

Observed first-order rate constants, $k_{\mathrm{obs.}}$, and derived rate constants k_1 and k_2 (*cf.* text) for peroxodisulphate oxidation of the $[\mathrm{Fe(phen)_3}]^{2+}$ cation in binary aqueous mixtures at 298.2 K and I = 0.01 mol dm^{-3} ($\mathrm{K_2[SO_4]}$)

		$[\mathrm{K_2S_2O_8}]$/mol dm^{-3}					
		0.004	0.006	0.008	0.010		
Solvent *		$10^4k_{\mathrm{obs.}}$/s^{-1}				10^4k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
5	% Acetone	3.0	4.9	6.5	7.8		0.080
10		1.7	3.0	3.6	4.8		0.050
15		0.90	1.3	1.8	2.2		0.022
20		0.70	1.1	1.4	1.6		0.015
30		0.53	0.76	0.96	1.13	0.15	0.010
40		0.60	0.84	0.96	1.11	0.3	0.008
50		0.86	1.00	1.07	1.20	0.7	0.005
60		1.15	1.11	1.25	1.30	1.0	0.003
10	% Dimethyl sulphoxide	3.0	4.5	6.3	7.2		0.072
20		0.9	1.3	1.5	2.1		0.019
30		0.9	1.3	1.5	1.9		0.015
40		0.37	0.58	0.83	1.04		0.011

* Solvent compositions are by volume before mixing.

TABLE 2

Observed first-order rate constants, $k_{\mathrm{obs.}}$, and derived rate constants k_2 (*cf.* text) for peroxodisulphate oxidation of the $[\mathrm{Fe(bqdo)}]^{2+}$ cation in binary aqueous mixtures at 298.2 K and I = 0.003 mol dm^{-3} ($\mathrm{K_2[SO_4]}$)

		$10^4[\mathrm{K_2S_2O_8}]$ mol dm^{-3}				
		2.5	5.0	7.5	10.0	k_2/dm^3 mol^{-1} s^{-1}
Solvent *		$10^3k_{\mathrm{obs.}}$/s^{-1}				
Water		4.8	9.7	15.2	20.0	20.0
10	% Acetone	1.8	3.6	5.6	7.4	7.6
20		0.6	1.1	1.7	2.3	2.3
30		0.19	0.41	0.59	0.80	0.8
40		0.02	0.05	0.08	0.10	0.1
10	% Dimethyl sulphoxide	2.0	4.9	6.4	8.7	8.7
20		0.7	1.3	2.2	2.9	3.0
30		0.3	0.5	0.8	1.0	1.0
40		0.1	0.2	0.3	0.4	0.4

* Solvent compositions are by volume before mixing.

DISCUSSION

Dissociation and Oxidation.—It has previously been demonstrated that the balance between the dissociative and redox paths for reaction of $[\mathrm{Fe(Xphen)_3}]^{2+}$ cations [the k_1 and k_2 paths of equation (1)] in aqueous solution depends on the nature of X.[7] The dissociative path is important for strongly electron-withdrawing substituents such as nitro and sulphonato, but is insignificant for methyl-substituted complexes. Now the results in Table 1 show that the k_1 *vs.* $k_2[\mathrm{S_2O_8}^{2-}]$ balance is affected by solvent composition, at least for the parent $[\mathrm{Fe(phen)_3}]^{2+}$ cation. The rate constant for dissociation of this cation increases gently with increasing proportion of organic cosolvent, but the rate constant for direct peroxodisulphate oxidation drops sharply with increasing proportion of organic cosolvent. These opposite trends explain how the balance between the k_1 and k_2 terms changes from predominance of the latter in water to predominance of the former in, say, 60% acetone (Table 1). The increasing rate of dissociation of the $[\mathrm{Fe(phen)_3}]^{2+}$ cation in increasingly organic mixtures is consistent with trends of dissociation rates for this and related complexes reported for other series of binary aqueous mixtures.[19]

However it is the redox component of these reactions which is of major interest here, and which will be the subject of the remainder of this paper. The first and most general point to make is that the trend of decreasing rate constant with increasing proportion of organic cosolvent is the same as that reported for several other redox reactions of this type; this trend seems to operate regardless of the sign or magnitude of the charge product of the reactants. Relevant examples which exhibit this stated reactivity trend include the redox reactions between $[\mathrm{Fe(bipy)_2(CN)_2}]$ and $\mathrm{S_2O_8}^{2-}$ (ref. 20) and between hydrazine and $[\mathrm{Fe(CN)_6}]^{3-}$ (ref. 21) in methanol-water mixtures, and between formaldehyde and $\mathrm{Ce[SO_4]_2}$ in non-aqueous solvents.[22] The electron-exchange rates between pairs of complexes of the type $[\mathrm{M(phen)_3}]^{2+}$ and $[\mathrm{M'(phen)_3}]^{3+}$ in non-aqueous solvents are also very much less than in water.[23]

Ion Pairing and the Transition State.—In one discussion of the mechanism of peroxodisulphate oxidation of the $[\mathrm{Fe(phen)_3}]^{2+}$ cation, involvement of a stable ion pair has been suggested.[6] A similar proposal has been made for peroxodisulphate oxidation of the $[\mathrm{Co(bipy)_3}]^{2+}$

TABLE 3

Transfer parameters $\delta_m\mu^\ominus$(reactants), $\delta_m\Delta G^\ddagger$, and $\delta_m\mu^\ddagger$, defined in the text, for peroxodisulphate oxidation of the [Fe(phen)$_3$]$^{2+}$ cation at 298.2 K

Percentage of acetone in solvent [a]	$\delta_m\mu^\ominus$ (reactants)/kJ mol^{-1}					$\delta_m\Delta G^\ddagger$/kJ mol^{-1}	$\delta_m\mu^\ddagger$/kJ mol^{-1}	
		$S_2O_8^{2-}$		Total				
	[Fe(phen)$_3$]$^{2+}$ [b]	*c*	*d*	*c*	*d*		*c*	*d*
10	−14	+4.7	+2.1	−9.3	−11.9	+3.4	−6	−8
20	−24	+10.1	+4.7	−13.9	−19.3	+6.4	−8	−13
30	−30	+15.2	+9.3	−14.8	−20.7	+7.4	−7	−13
40	−34	+19.8	+13.4	−14.2	−20.6	+7.9	−6	−13

[a] By volume before mixing. [b] From ref. 27. [c] From ref. 28, using $\delta_m\mu^\ominus(K^+)$ from C. F. Wells, *J.C.S. Faraday I*, 1973, 984; 1974, 694. [d] From ref. 28, using $\delta_m\mu^\ominus(K^+)$ from M. Alfenaar and C. L. de Ligny, *Rec. Trav. chim.*, 1967, **86**, 929; D. Bax, C. L. de Ligny, and A. G. Remijnse, *ibid.*, 1972, **91**, 1225.

cation.[24] However, although spectroscopic evidence has been presented for ion pairing between the iron(III) complex [Fe(phen)$_3$]$^{3+}$ and dinegative anions,[25] there is no analogous direct evidence for ion pairing involving the [Fe(phen)$_3$]$^{2+}$ cation and small dinegative anions. Indeed, the alkaline-earth metal cations Mg^{2+} to Ba^{2+} do not form ion pairs with the peroxodisulphate anion in aqueous solution.[26] Thus there is no compelling evidence for the intermediacy of a stable ion pair in the [Fe(phen)$_3$]$^{2+}$ plus $S_2O_8^{2-}$ reaction, although the transition state for electron transfer must bear a close resemblance to an ion pair.

Reactant and Transition-state Solvation.—As mentioned in the Introduction, the variation of rate constant with solvent composition has for several reactions been dissected into initial-state and transition-state components, to give a clearer idea of factors affecting reactivity. The Gibbs free energy of activation, $\Delta G^\ddagger$, is related to the chemical potentials of the reactants and of the transition state by equation (3). If one adopts aqueous solution as the reference medium, then the

$$\Delta G^\ddagger = \mu^\ddagger - \mu^\ominus\{\mathrm{Fe(phen)_3}^{2+}\} - \mu^\ominus\{S_2O_8^{2-}\} \quad (3)$$

dependence of each quantity in equation (3) on solvent composition (mole fraction of organic cosolvent, x_2) can be expressed in the form of equation (4) using the solvent operator δ_m. Standard states used here refer to a

$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ddagger - \delta_m\mu^\ominus\{\mathrm{Fe(phen)_3}^{2+}\} - \delta_m\mu^\ominus\{S_2O_8^{2-}\} \quad (4)$$

hypothetical solution having both molarity and activity coefficient of unity.

The quantity $\delta_m\Delta G^\ddagger$ of equation (4) can be calculated from the variation of the second-order rate constant with x_2. The determination of $\delta_m\mu^\ominus$ values for ions is not a straightforward matter. Appropriate results are available for the [Fe(phen)$_3$]$^{2+}$ (ref. 27) and $S_2O_8^{2-}$ (ref. 28) ions in methanol–water and acetone–water mixtures. The assumptions used in deriving these single-ion values are set out in the reference cited. Transfer chemical potentials for the $S_2O_8^{2-}$ anion from water into aqueous dimethyl sulphoxide have been derived from our measured solubilities of the potassium salt and published values for $\delta_m\mu^\ominus(K^+)$,[29] based on the assumption that $AsPh_4^+ = BPh_4^-$. Transfer chemical potentials for the [Fe(phen)$_3$]$^{2+}$ cation from water into aqueous dimethyl sulphoxide have been estimated by analogy from values for this and other ions for transfer to aqueous methanol, acetone, and dimethyl sulphoxide.

TABLE 4

Dissection of solvent effects on the [Fe(phen)$_3$]$^{2+}$–$S_2O_8^{2-}$ reaction into initial-state and transition-state contributions, for aqueous dimethyl sulphoxide at 298.2 K

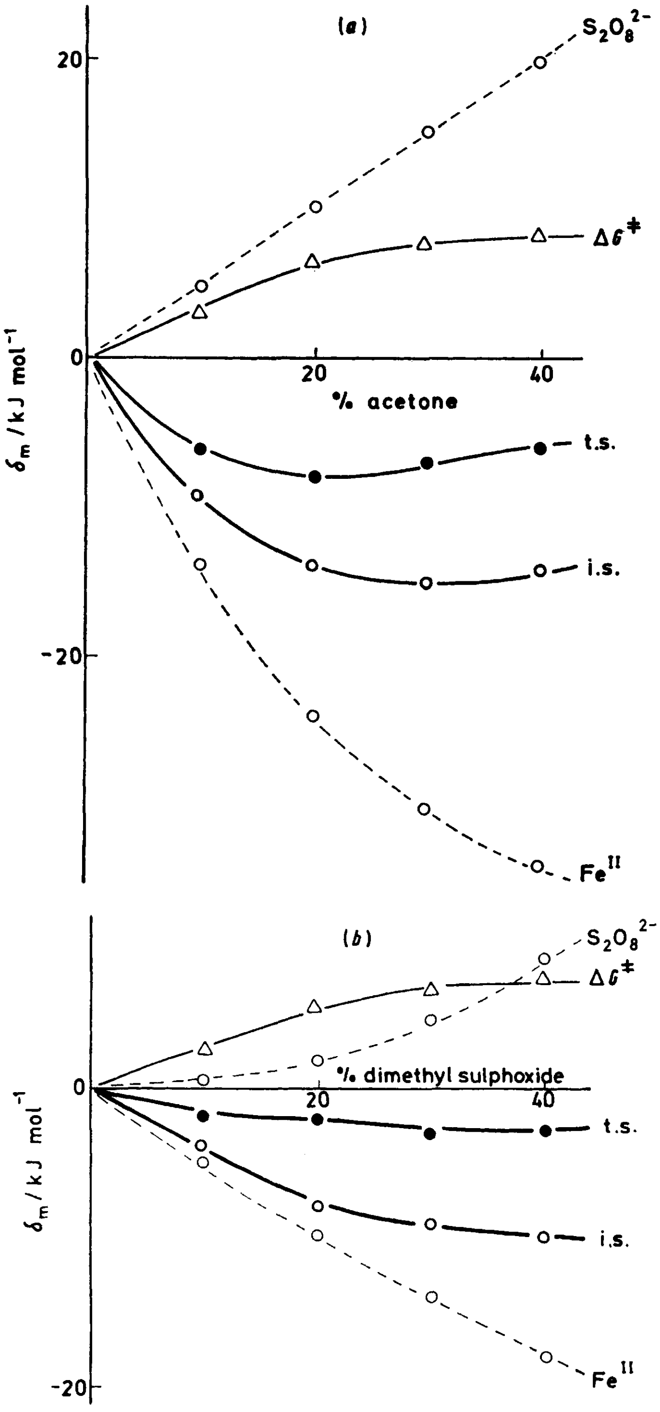
%(v/v) Dimethyl sulphoxide	0	10	20	30	40
Solubility($K_2S_2O_8$) mol dm^{-3}	0.216	0.205	0.185	0.145	0.106
∴ $\delta_m\mu(K_2S_2O_8)$/kJ mol^{-1}		0.39	1.15	2.96	5.29
$\delta_m\mu(K^+)$/kJ mol^{-1} [a]		−0.1	−0.3	−0.8	−1.5
∴ $\delta_m\mu(S_2O_8^{2-})$/kJ mol^{-1}		+0.6	+1.8	+4.6	+8.4
$\delta_m\mu\{\mathrm{Fe(phen)_3}^{2+}\}$/kJ mol^{-1} [b]		−5	−10	−14	−18
∴ $\delta_m\mu$(i.s.)/kJ mol^{-1}		−4	−8	−9	−10
$\delta_m\Delta G^\ddagger$/kJ mol^{-1}		+2.5	+5.8	+6.4	+7.2
∴ $\delta_m\mu^\ddagger$/kJ mol^{-1}		−2	−2	−3	−3

[a] From ref. 29. [b] Estimated (*cf.* text).

Our analysis of reactivity trends into initial-state (i.s.) and transition-state (t.s.) contributions is set out in Tables 3 and 4, and depicted in the Figure. The patterns for aqueous acetone and for aqueous dimethyl sulphoxide are similar, with some degree of stabilisation of the initial state as the proportion of the organic cosolvent is increased resulting from rather greater stabilisation of the iron(II) cation only partly offset by destabilisation of the $S_2O_8^{2-}$ anion. The decrease in rates observed for both series of solvent mixtures arises from smaller stabilisation of the transition state than of the initial state. A similar pattern probably also applies to methanol–water mixtures, but here the analysis is unsatisfactory on two counts: the large uncertainties in rate constants because of significant interference from radical intermediates, and the relatively large differences between two sets of values for $\delta_m\mu(S_2O_8^{2-})$ which can be derived from two independent sources.

We therefore conclude that the transition state is stabilised on transfer from water into aqueous acetone or into aqueous dimethyl sulphoxide, and probably also into aqueous methanol, at least for water-rich solvent mixtures. Such a conclusion is intuitively reasonable in electrostatic terms, as transition-state formation involves charge cancellation. Also, the character of the transition state is controlled in part by the large hydrophobic groups surrounding the iron atom; the solubility of apolar solutes increases (*i.e.* $\delta_m\mu^\ominus < 0$) when an organic cosolvent is added to a solution in water. It is probably fortuitous but nevertheless noteworthy that the curve for $\delta_m\mu^\ddagger$ falls almost half-way between the curves for the two initial states, the dinegative hydrophilic peroxodisulphate and the dipositive hydrophobic iron(II) complex.

Thus the rate constant for the reaction, or $\delta_m\Delta G^{\ddagger}$, is affected both by reactant solvation changes and by transition-state solvation changes. The importance of these two factors is comparable, a situation which contrasts markedly with such reactions as those of tetra-alkyltin compounds with mercury(II) halides,[30,31] of amines with alkyl halides (Menschutkin),[32] and of [Pt(bipy)Cl_2] with thiourea.[12] Peroxodisulphate oxidation of $[Fe(phen)_3]^{2+}$ also thus differs from substitution reactions of the closely related $[Fe(bipy)_3]^{2+}$ cation, where solvent effects on reactivity are dominated by solvation and consequent chemical-potential changes at the small hydroxide or cyanide ions.[11]



Analysis of solvent effects on peroxodisulphate oxidation of the $[Fe(phen)_3]^{2+}$ cation in (*a*) acetone–water and (*b*) dimethyl sulphoxide–water mixtures, at 298.2 K. The plots show the dependence of transfer parameters on solvent composition for the individual reactants (– – ○ – –), the initial state (i.s., — ○ —), the Gibbs free energy of activation (— △ —), and the transition state (t.s., — ● —)

Sexidentate Schiff-base Complex.—The Figure brings out the important role of stabilisation of $[Fe(phen)_3]^{2+}$ on adding acetone to water in determining the reactivity trend for peroxodisulphate oxidation; the changing chemical potential of the iron(II) cation makes the largest single contribution to $\delta_m\Delta G^{\ddagger}$. We were therefore interested to see if similar trends were exhibited by similar iron(II) complexes, and have studied the kinetics of peroxodisulphate oxidation of the iron(II) complex of the sexidentate Schiff base bqdo derived from quinoline-2-carbaldehyde and triethylenetetramine, $[Fe(bqdo)]^{2+}$.[15] This complex has a similarly hydrophobic periphery to the $[Fe(phen)_3]^{2+}$ cation and the same charge, and its kinetic reactivity patterns for several reactions have been established.[15]

Rate constants for peroxodisulphate oxidation of the $[Fe(bqdo)]^{2+}$ cation are reported in Table 2. Observed first-order rate constants (large excess of peroxodisulphate) are proportional to the peroxodisulphate concentration. The rate law is thus simple second order. The lack of any significant rate-determining dissociative pathway is consistent with the known very slow rate of dissociation of such complexes of sexidentate ligands in neutral solution.[15,33,34] Second-order rate constants for peroxodisulphate oxidation (Table 2) decrease with increasing proportion of organic cosolvent, which parallels the behaviour of the $[Fe(phen)_3]^{2+}$ cation.

Conclusions.—Although we have deduced that initial-state and transition-state solvation effects are of comparable importance in determining reactivity trends for peroxodisulphate oxidation of the $[Fe(phen)_3]^{2+}$ cation, this conclusion is based on a limited range of results. Extension to most other organic cosolvents is ruled out by radical complications (*cf.* above). Potential oxidants such as peroxodiphosphate [3,35] and percarbonates (which are carbonates with hydrogen peroxide of crystallisation) [36] are ruled out as they react through rate-determining dissociation of cations of the $[Fe(phen)_3]^{2+}$ type.[37] Peroxodicarbonate [38] and percarboxylates [39] are expected to give complicated kinetic patterns for oxidation. For these oxidants, and organic peroxides,[40] the problems of radical interference may well recur, and determination of Gibbs free energies of transfer would prove difficult. Recent preliminary results suggest that ternary complexes of the $[Fe(phen)_2(CN)_2]$ and $[Fe(phen)(CN)_4]^{2-}$ type, which are weaker reductants than $[Fe(phen)_3]^{2+}$, may exhibit peroxodisulphate oxidation kinetics much less troubled by cosolvent-derived radical complications. However, progress may well prove most satisfactory in the area of outer-sphere electron-transfer processes between one-electron reductants and one-electron oxidants, as for instance the hexachloroiridate(IV) oxidation of iodide.

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REFERENCES

[1] J. Halpern, R. J. Legare, and R. Lumry, *J. Amer. Chem. Soc.*, 1963, **85**, 680.

[2] B. Z. Shakhashiri and G. Gordon, *J. Amer. Chem. Soc.*, 1969, **91**, 1103.

[3] A. A. Green, J. O. Edwards, and P. Jones, *Inorg. Chem.*, 1966, **5**, 1858.

[4] D. H. Irvine, *J. Chem. Soc.*, 1959, 2977.

[5] J. Burgess and R. H. Prince, *J. Chem. Soc.* (*A*), 1966, 1772.

[6] S. Raman and C. H. Brubaker, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1091.

[7] J. Burgess and R. H. Prince, *J. Chem. Soc.* (*A*), 1970, 2111.

[8] D. A. House, *Chem. Rev.*, 1962, **62**, 185; T. A. Turney, ' Oxidation Mechanisms,' Butterworths, London, 1965, p. 147.

[9] Y. Sulfab, *Inorg. Chim. Acta*, 1977, **22**, 35

[10] R. D. Gillard, *Co-ordination Chem. Rev.*, 1975, **16**, 67.

[11] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606; M. J. Blandamer, J. Burgess, J. G. Chambers, R. I. Haines, and H. E. Marshall, *ibid.*, 1977, 165.

[12] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1977, 60.

[13] M. J. Blandamer, J. Burgess, S. J. Cartwright, and M. Dupree, *J.C.S. Dalton*, 1976, 1158.

[14] M. L. Moss, M. G. Mellon, and G. F. Smith, *Analyt. Chem.*, 1942, **14**, 931.

[15] M. J. Blandamer, J. Burgess, R. I. Haines, F. M. Mekhail, and P. Askalani, *J.C.S. Dalton*, 1978, 1001; R. I. Haines, Ph.D. Thesis, University of Leicester, 1977.

[16] D. M. Adams and J. B. Raynor, 'Advanced Practical Inorganic Chemistry,' Wiley, London, 1965, p. 122.

[17] A. J. Gordon and R. A. Ford, ' The Chemist's Companion: A Handbook of Practical Data, Techniques, and References,' Wiley, London, 1972.

[18] See, for example, I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Amer. Chem. Soc.*, 1953, **75**, 1439; D. L. Ball, M. M. Crutchfield, and J. O. Edwards, *J. Org. Chem.*, 1960, **25**, 1599.

[19] See, for example, J. Burgess, *J. Chem. Soc.* (*A*), 1968, 1085; 1969, 1899; 1970, 2351.

[20] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2114.

[21] V. K. Jindal, M. C. Agrawal, and S. P. Mushran, *Z. Naturforsch.*, 1970, **B25**, 188.

[22] P. K. Saiprakash, B. Sethuram, and T. N. Rao, *J. Inorg. Nuclear Chem.*, 1976, **38**, 880.

[23] N. D. Stalnaker, J. C. Solenberger, and A. C. Wahl, *J. Phys. Chem.*, 1977, **81**, 601.

[24] K. Ohashi, M. Matsuzawa, E. Hamano, and K. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 2440.

[25] J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1957, **79**, 1286.

[26] F. A. Jackman and M. W. Lister, *J. Solution Chem.*, 1976, **5**, 417.

[27] F. M. Van Meter and H. M. Neumann, *J. Amer. Chem. Soc.*, 1976, **98**, 1382.

[28] M. J. Blandamer, J. Burgess, and R. I. Haines, *J. Inorg. Nuclear Chem.*, 1979, **41**, 258.

[29] B. G. Cox, R. Natarajan, and W. E. Waghorne, *J.C.S. Faraday I*, 1979, 1780.

[30] M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *Chem. Comm.*, 1969, 930.

[31] M. H. Abraham, *J. Chem. Soc.* (*A*), 1971, 1061.

[32] M. H. Abraham, *Chem. Comm.*, 1969, 1307.

[33] E. R. Gardner, F. M. Mekhail, and J. Burgess, *Internat. J. Chem. Kinetics*, 1964, **6**, 133.

[34] J. Burgess and G. M. Burton, *Rev. Latinoam. Quim.*, accepted for publication.

[35] S. Kapoor and Y. K. Gupta, *J. Inorg. Nuclear Chem.*, 1977, **39**, 1019.

[36] M. A. A. F. de C. T. Carrondo, W. P. Griffith, D. P. Jones, and A. C. Skapski, *J.C.S. Dalton*, 1977, 2323.

[37] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061.

[38] M. F. Sorokina and N. E. Khomutov, *Russ. J. Phys. Chem.*, 1976, **50**, 915.

[39] A. M. Kuliev, G. A. Agaev, and M. M. Mukhtarov, *Kinetica i Kataliz*, 1976, **17**, 1428.

[40] P. G. Cookson, A. G. Davies, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 1022.