# Kinetics of Aquation of the Complex Tris[3-(2-pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine]iron(II) and its Reactions with Hydroxide, Cyanide, and Peroxodisulphate Ions

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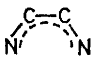
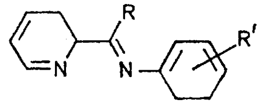
The kinetics of the reactions of the complex tris[3-(2-pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine]iron(II) in acid solution, and with hydroxide, cyanide, and peroxodisulphate ions, and hydrogen peroxide, have been investigated. The dependence of the observed rate constants on reagent concentration has been established for the reactions in acid, and with hydroxide and peroxodisulphate ions, at 35·0 °C. For the reaction with cyanide ions, the rate law has been established and, from measured rate constants over a range of cyanide-ion concentrations and over the temperature range 25·3—44·1 °C, activation parameters both for cyanide-ion attack and for complex dissociation have been estimated. The variation of the rate of cyanide-ion attack with solvent composition has been determined for ethanol–water mixtures containing up to 30% ethanol. Patterns of reactivity for this complex are compared with those previously established for other low-spin iron(II) chelate complexes.

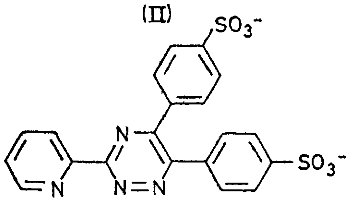
MOST iron(II) complexes are high spin, $t_{2g}^4e_g^2$, in configuration and kinetically labile. A few ligands interact sufficiently strongly with this metal centre to force spin pairing and give the kinetically inert $t_{2g}^6$ configuration. Such ligands include cyanide ion and a series of aromatic nitrogen bases containing the chelating unit (I). Several complexes containing such ligands as 2,2′-bipyridine and 1,10-phenanthroline and their derivatives, and Schiff bases of formula (II) have been intensively studied, with kinetic results reported for a variety of reactions including aquation and reaction with hydroxide or cyanide ions.[1]



(I)



(II)



(III)

Recently the preparation and characterisation of a new complex of this type, tris[3-(2-pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine]iron(II), containing the ligand (III), has been reported.[2] We are interested in comparing the kinetic behaviour and reactivity of complexes of ligands containing the chelating unit (I). We have therefore investigated the kinetics of reaction of the complex tris(ppsa)iron(II) [ppsa = 3-(2-pyridyl)-5,6-bis-(4-phenylsulphonato)-1,2,4-triazine] in acid, hydroxide, cyanide, and peroxodisulphate solutions, and in this paper compare our results with analogous information on similar iron(II) complexes, particularly the structurally most closely related complex tris(2,2′-bipyridine)iron(II).

## RESULTS AND DISCUSSION

*Aquation.*—In acid solution the complex $[Fe(ppsa)_3]^{2+}$ [ppsa = 3-(2-pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine] dissociates into aquated iron(II) and protonated ligand molecules. The aquation follows first-order kinetics up to at least 80% of complete reaction. Rate constants for aquation at various concentrations of hydrochloric and sulphuric acid, at 35·0 °C and constant ionic strength, are reported in Table 1. Aquation rates increase with increasing hydrogen-ion concentration, though the dependence is not linear. Such behaviour is reminiscent of that of the complexes $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) or $[Fe(5\text{-}NH_2phen)_3]^{2+}$ (5-$NH_2$-phen = 5-amino-1,10-phenanthroline), though not of $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) the rate of aquation of which is very nearly pH independent. The dependence of the rates of aquation of the complex $[Fe(bipy)_3]^{2+}$ on acid concentration arises from equilibrium formation of an intermediate species containing a monodentate monoprotonated 2,2′-bipyridine ligand.[3] The dependence of aquation rate on pH for the $[Fe(5\text{-}NH_2phen)_3]^{2+}$ cation arises differently, from the pH dependent protonation of the amino-substituent.[4]

TABLE 1

First-order rate constants ($k$) for aquation of the tris(ppsa)iron(II) complex in aqueous solution at 35·0 °C

| | | | | |
|---|---|---|---|---|
| HCl/M [a] | 0·017 | 0·033 | 0·066 | 0·099 |
| $10^4k/s^{-1}$ | 1·16 | 1·27 | 1·49 | 1·66 |
| HCl/M [a] | 0·132 | 0·165 | 0·231 | 0·333 |
| $10^4k/s^{-1}$ | 1·69 | 1·74 | 1·92 | 2·02 |
| $H_2SO_4$/M [b] | 0·011 | 0·044 | 0·077 | 0·110 |
| $10^4k/s^{-1}$ | 0·98 | 1·53 | 1·78 | 1·96 |

[a] $I = 0·333$M (NaCl). [b] $I = 0·333$M ($K_2SO_4$).

In the present case of the tris(ppsa)iron(II) complex, the observed variation of rate with acid concentration could arise from either or both these effects. The ligand ppsa could be protonated at one of the unco-ordinated triazine nitrogen atoms (protonation of a

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[1] See, for example, 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1971, vol. 1, p. 176; 1972, vol. 2, p. 168; C. H. Langford and V. S. Sastri, 'Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, M.T.P. Internat. Rev. Sci., vol. 9, Butterworths, London, series 1, 1971, p. 252, and references therein.

[2] L. L. Stookey, *Analyt. Chem.*, 1970, **42**, 779.

[3] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn., pp. 218—219.

[4] J. Burgess, *J. Chem. Soc.* (*A*), 1967, 431.

sulphonato-group is unlikely [4]). Alternatively, the flexible ppsa ligand, like flexible bipy but unlike inflexible phen, could permit the intermediacy of monodentate protonated ppsa complexes. In fact it is not possible to tell from our kinetic results which situation obtains, for the facts that plots, both of rate constants against acid concentration and of reciprocal rate constants against reciprocal hydrogen-ion concentration,[3,5] are curved could be consistent with either mechanism. However, u.v.-visible spectra of solutions of the tris(ppsa)iron(II) complex in water (pH 7) and in 1M-HCl are identical, which suggests that equilibrium ligand protonation, as for the 5-$NH_2$phen complex, is the less probable explanation for the pH dependence of aquation rates of the ppsa complex. From plots of the aquation rate constant against the logarithm of the hydrogen-ion concentration, it is possible to estimate that the rate constant for aquation in neutral solution at 35·0 °C is $0{\cdot}8 \times 10^{-4}$ $s^{-1}$, by extrapolation from the sulphuric acid results, $1{\cdot}0 \times 10^{-4}$ $s^{-1}$ from the hydrochloric acid results.

*Other Reactions.—With hydrogen peroxide.* For complexes of the type $[FeL_3]^{2+}$ [L = 2,2′-bipyridine, 1,10-phenanthroline,[6] or a Schiff base of formula (II) [7]], a method of estimating rate constants for aquation at zero acid concentration and very low ionic strength has been found using the reaction with hydrogen peroxide. The observed rate law (1), with its zero-order dependence on

$$-\mathrm{d}[FeL_3]^{2+}/\mathrm{d}t = k[FeL_3]^{2+} \qquad (1)$$

hydrogen peroxide concentration, corresponds to rate-determining dissociation of the complex $[FeL_3]^{2+}$ followed by rapid reaction of $[FeL_2]^{2+}$ and L with the hydrogen peroxide. We therefore attempted to determine rate constants for aquation of the complex tris(ppsa)iron(II) in a similar manner. Unfortunately, whereas the complexes $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ are relatively poor catalysts for the decomposition of hydrogen peroxide, the tris(ppsa)iron(II) complex is a fairly efficient catalyst. Nonetheless, it was obvious that rate law (1) does not apply to the reaction of the tris(ppsa)iron(II) complex with hydrogen peroxide, for the reaction rate increased markedly with increasing initial concentration of hydrogen peroxide. This dependence of the rate of reaction on hydrogen peroxide concentration may arise from some reaction of the co-ordinated ligand with hydrogen peroxide (see also below). From a plot of our approximate initial rates against hydrogen peroxide concentration, a rough estimate of $k \simeq 10^{-4}$ $s^{-1}$ for dissociation of the tris(ppsa)iron(II) complex in neutral solution at 35·0 °C can be made, which compares satisfactorily with that from the rate constants determined in acid media quoted in the previous paragraph.

*With hydroxide ions.* The rate law for the reaction of the complex $[Fe(phen)_3]^{2+}$ with hydroxide ion, over the range 0—5M, is as in equation (2).[6] The rate law for the

$$-\mathrm{d}[Fe(phen)_3]^{2+}/\mathrm{d}t = (k_1 + k_2[OH^-] + k_3[OH^-]^2 + k_4[OH^-]^3)[Fe(phen)_3]^{2+} \qquad (2)$$

reaction of a variety of iron(II) complexes *containing* the chelating unit (I) with hydroxide ion in dilute solution is as in equation (3).[7-9] In both these equations the $k_1$

$$-\mathrm{d}[FeL_3]^{2+}/\mathrm{d}t = (k_1 + k_2[OH^-])[FeL_3]^{2+}] \qquad (3)$$

terms are ascribed to rate-determining ligand dissociation followed by rapid formation and oxidation of iron(II) hydroxide.[10] The $k_2$ terms correspond to direct nucleophilic attack of hydroxide ion on the iron; the $k_3$ and $k_4$ terms probably reflect both nucleophilic attack by hydroxide ion and salt effects.

TABLE 2

Average first-order rate constants ($k$) for the reaction of the tris(ppsa)iron(II) complex with hydroxide ions in aqueous solution at 35·0 °C. $I = 0{\cdot}333$M ($KNO_3$, NaCl, $K_2SO_4$, or $NaClO_4$)

| | $10^4k/s^{-1}$ | | | |
|---|---|---|---|---|
| [NaOH]/M | $KNO_3$ | NaCl | $K_2SO_4$ | $NaClO_4$ |
| 0·017 | 4·2 | | | |
| 0·033 | 7·9 | 9·5 | 11 | 2·5 |
| 0·050 | 12·2 | | | |
| 0·067 | 15·2 | | | |
| 0·083 | 18·3 | | | |
| 0·100 | 22 | | | |
| 0·133 | 29 | 29 | 30 | 13 |
| 0·167 | 31 | | | |
| 0·200 | 36 | | | |
| 0·233 | 42 | 41 | 42 | 26 |
| 0·267 | 46 | | | |
| 0·300 | 48 | | | |
| 0·333 | 50 | | | |

Plots of observed first-order rate constants (Table 2) for reaction of the tris(ppsa)iron(II) complex with hydroxide ion in aqueous solution were somewhat curved. This curvature is in the opposite sense for perchlorate as added ion to that with chloride, nitrate, or sulphate ion. Our results thus indicate a rate equation of type (2), with $k_3$ of different sign for the perchlorate systems to that of the other systems; the precision of our results is insufficient to assess a $k_4$ term contribution. We estimate an upper limit of $2 \times 10^{-4}$ $s^{-1}$ for $k_1$ at 35·0 °C, so the $k_1$ term can be assigned as usual to rate-determining ligand dissociation [rate constant = $1 \times 10^{-4}$ $s^{-1}$ (see above)]. From the rate constants determined in 0·33M-NaOH, we estimate $k_2$ as 0·015 l $mol^{-1}$ $s^{-1}$ at 35·0 °C. For comparison, $k_2$ values at 35·0 °C for $[Fe(phen)_3]^{2+}$ derivatives range from 0·0021 to 0·38 l $mol^{-1}$ $s^{-1}$, with $k_2$ = 0·20 l $mol^{-1}$ $s^{-1}$ for the 3-$SO_3$phen and 0·066 l $mol^{-1}$ $s^{-1}$ for the 5-$SO_3$phen complexes (3-$SO_3$phen = 3-sulphonato-1,10-phenanthroline and 5-$SO_3$phen = 5-sulphonato-1,10-phenanthroline).[4]

*With cyanide ions.* The rate law for the reaction of low-spin iron(II) complexes with cyanide ion is as in

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[5] R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1172.

[6] D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728.

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

[8] J. Burgess, *J. Chem. Soc. (A)*, 1967, 955.

[9] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4497.

[10] G. Nord and T. Pizzino, *Chem. Comm.*, 1970, 1633.

equation (4).[11-14] As in the reaction with hydroxide ions,

$$-\mathrm{d}[\mathrm{FeL}_3]^{2+}/\mathrm{d}t = (k_1 + k_2[\mathrm{CN}^-])[\mathrm{FeL}_3]^{2+} \quad (4)$$

the $k_1$ term corresponds to rate-determining ligand loss, the $k_2$ term to nucleophilic attack by cyanide ion on the iron. Plots of first-order rate constants for the reaction of the tris(ppsa)iron(II) complex with cyanide ion * (Table 3) are linear, so the rate law corresponds to equation (4). From computed $k_1$ and $k_2$ values (Table 3), activation parameters for both dissociation and cyanide-ion attack were derived (Tables 4 and 5).

TABLE 3

First-order rate constants ($k$) for the reaction of the tris(ppsa)iron(II) complex with cyanide ions, $I$ = 0·333M (KCl). The derived rate constants $k_1$ and $k_2$ correspond to those defined by equation (4) of the text

| Solvent | Temp./°C | [KCN]/M<br>0·017 | 0·033 | 0·066 | 0·099 | 0·132 | 0·165 | 0·198 | 0·231 | 0·264 | 0·297 | 0·333 | $10^4k_1$/s$^{-1}$ | $10^4k_2$/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $10^4k$/s$^{-1}$ | | | | | | | | | | | | |
| Water | 25·3 | | 0·7 | 1·1 | | 1·6 | 2·0 | | 2·6 | 3·1 | 3·3 | 3·5 | 0·5 | 9·4 |
| | 28·4 | 0·9 | 1·2 | 1·8 | 2·4 | 2·8 | 3·3 | 3·6 | 4·4 | 4·5 | 4·9 | 5·4 | 0·8 | 14·2 |
| | 29·9 | 1·4 | 1·6 | 2·0 | 2·7 | 3·3 | 4·1 | 4·5 | 5·2 | 6·0 | 6·7 | 7·1 | 0·9 | 18·9 |
| | 34·5 | 1·9 | 2·8 | 3·9 | 5·4 | 6·8 | 8·1 | 8·4 | 10·5 | 12·0 | 12·0 | 12·5 | 1·9 | 34 |
| | 38·8 | 3·6 | 5·3 | 7·9 | 9·8 | 11·2 | 15·2 | 16·3 | | 19·6 | 23·3 | 24·6 | 3·1 | 66 |
| | 44·1 | 7·8 | 9·8 | 14·6 | 18·5 | | 25·4 | 30·1 | 35·8 | | 42·1 | 44·1 | 6·4 | 119 |
| Ethanol 10% | 35·0 | | 2·2 | | | 6·0 | | | 9·2 | | | 13·0 | 1·0 | 36 |
| 20% | 35·0 | | 2·1 | | | 6·0 | | | 10·2 | | | 14·8 | 0·7 | 41 |
| 30% | 35·0 | | 2·3 | | | 7·7 | | | 12·9 | | | 19·3 | 0·4 | 53 |

TABLE 4

Activation parameters for dissociation of $[\mathrm{FeL}_3]^{2+}$ complexes in aqueous solution

| L | $\Delta H^\ddagger$/kcal mol$^{-1}$ | $\Delta S^\ddagger$/cal K$^{-1}$ mol$^{-1}$ | Ref. |
|---|---|---|---|
| ppsa | 25·2 ± 1·5 [a] | +6 ± 4 [a] | This work |
| bipy | 27·4 | +16 | b |
| phen | 29·3 | +31 | c |
| 3-$SO_3$phen | 21·4 | −1 | 4 |
| 5-$SO_3$phen | 26·2 | +9 | 4 |

ppsa = 3-(2-Pyridyl)-5,6-bis(4-phenylsulphanato)-1,2,4-triazine, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, 3-$SO_3$phen = 3-sulphonato-1,10-phenanthroline, and 5-$SO_3$phen = 5-sulphonato-1,10-phenanthroline.

[a] 90% Confidence limits. [b] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807. [c] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752.

The activation enthalpy for dissociation of the tris(ppsa)iron(II) complex is, like those for dissociation of similar low-spin iron(II) complexes, high. This is as expected for a $t_{2g}{}^6$ complex, where crystal-field stabilisation and activation energies are high. The ppsa ligand differs from bipy in two ways: its inclusion of a triazine ring and its phenylsulphonato-substituents. The likely kinetic consequences of the former are impossible to assess; reference to the phen series of complexes indicates that the presence of the strongly electron-withdrawing sulphonato-group results in a considerable decrease in the activation enthalpy for dissociation. Hence the observed lower activation energy for dissociation of the ppsa complex compared with that of the bipy complex may be ascribed, at least in part, to the presence of the sulphonato-groups in the former. The lower activation entropy for dissociation of the ppsa complex compared with that of the bipy complex can also be partly ascribed to the influence of the sulphonato-substituents, again by comparison with trends in the phen series of complexes. Activation parameters for dissociation of the ppsa complex conform with the general approximately linear $\Delta H^\ddagger$–$\Delta S^\ddagger$ correlation for the dissociation of low-spin iron(II) complexes.

The activation parameters for cyanide-ion attack on the tris(ppsa)iron(II) complex are very similar to those for the tris(bipy)iron(II) complex;[14] the presence of the triazine ring and the sulphonato-substituents together do not have much effect on the ease of nucleophilic substitution at the iron(II) centre.

TABLE 5

Activation parameters for cyanide-ion attack on $[\mathrm{FeL}_3]^{2+}$ complexes in aqueous solution

| L | $\Delta H^\ddagger$/kcal mol$^{-1}$ | $\Delta S^\ddagger$/cal K$^{-1}$ mol$^{-1}$ | Ref. |
|---|---|---|---|
| ppsa | 25·2 ± 1·2 [a] | +12 ± 4 [a] | This work |
| bipy | 23·0 ± 0·6 [a] | +9 ± 2 [a] | 14 |
| phen | 20 | −3 | 11 |

[a] 90% Confidence limits.

The results in Table 3 show that, in ethanol–water mixtures, the rate of dissociation ($k_1$) of the ppsa complex decreases while the rate constant for cyanide-ion attack ($k_2$) increases, as the proportion of ethanol increases. The latter trend in $k_2$ values is similar to those reported earlier for cyanide-ion attack on the complex tris(phen)iron(II)[13] and analogous Schiff base complexes

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* Concentrations of free cyanide ion were estimated from potassium cyanide concentrations used and the published p$K_a$ values for hydrogen cyanide over the temperature range of our experiments.[15]

[11] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

[12] J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), 1971, 44.

[13] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[14] J. Burgess, *J.C.S. Dalton*, 1972, 1061.

[15] R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *Inorg. Chem.*, 1962, **1**, 828.

of iron(II).[12] Whether dissociation rates for low-spin iron(II) complexes increase or decrease with increasing non-aqueous component in aqueous-organic solvents depends both on the nature of the organic solvent and on ligand substituents. There are very few available results for complexes of sulphonato-substituted ligands, but we can point out that the trend observed here, of decreasing dissociation rate constants with increasing proportion of ethanol, is the same as that reported for the $[Fe(3\text{-}SO_3phen)_3]^{2+}$ and $[Fe(5\text{-}SO_3phen)_3]^{2+}$ complexes in water-rich aqueous acetonitrile.[16]

We have not been able to isolate the product of the reaction between the tris(ppsa)iron(II) complex and cyanide ion, but the charge-transfer spectrum suggests that it is *cis*-dicyanobis(ppsa)iron(II). The evidence * is based on comparisons of molar absorption coefficients, and of correlations of frequencies of maximum absorption with solvent $E_T$ values,[17,18] with those for similar known iron(II)–aza-aromatic ligand–cyano-complexes.[19-21]

*With peroxodisulphate ions.* First-order rate constants for the reaction of the tris(ppsa)iron(II) complex with peroxodisulphate ions (in excess) are reported in Table 6. These results indicate the rate law (5). Again the

$$-d[\text{Complex}]/dt = (k_1 + k_2[S_2O_8^{2-}])[\text{Complex}] \quad (5)$$

kinetic pattern is the same as that previously described for, *e.g.*, analogous iron(II) complexes of phen ligands.[22] The $k_1$ term corresponds to rate-determining ligand dissociation followed by rapid reaction of intermediates with peroxodisulphate ion, and the $k_2$ term corresponds to direct oxidation of the iron(II) complex to its iron(III) analogue. This assignment of mechanism for the $k_1$ term can be checked by comparing the $k_1$ value here ($1{\cdot}0 \times 10^{-4}$ s$^{-1}$ at 35 °C) with rate constants for dissociation of the complex in the presence of acid, hydrogen peroxide, or cyanide ion (see above); the agreement is satisfactory. The second-order rate constant for the reaction with peroxodisulphate ion ($k_2$ in the rate law above) is 0·0029 l mol$^{-1}$ s$^{-1}$ at 35 °C.

TABLE 6

Average first-order rate constants ($k$) for the reaction of the tris(ppsa)iron(II) complex with potassium peroxodisulphate in aqueous solution at 35·0 °C, $I$ = 0·99M ($Na_2SO_4$)

| $[K_2S_2O_8]$/M | 0·002 | 0·003 | 0·007 | 0·010 | 0·013 | 0·017 | 0·020 | 0·023 | 0·027 | 0·033 |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^4k$/s$^{-1}$ | 1·03 | 1·09 | 1·21 | 1·34 | 1·32 | 1·56 | 1·58 | 1·66 | 1·74 | 1·97 |

An outer-sphere mechanism for peroxodisulphate-ion oxidation of low-spin iron(II) complexes seem probable. There should then be a linear correlation [23] of logarithms of the second-order rate constants with the standard redox potentials of the respective iron(II)–iron(III) complex couples. In practise this test cannot be applied, for the available rate constants have been derived from a variety of inconsistent treatments of experimental results. Assumptions used include a simple bimolecular second-order model, parallel dissociation and oxidation,[22] and ion-pair participation.[24] We have determined a redox potential of +0·88 V for the iron(II)–iron(III)–ppsa couple at 4 °C (to minimise aquation) in 1M-$HClO_4$, by potentiometric titration against cerium(IV) ions. It is surprising, from a comparison of this redox potential with those reported for analogous bipy and phen couples, that the rate of the peroxodisulphate-ion oxidation of the tris(ppsa)iron(II) complex is lower than any reported for iron(II) complexes of bipy or phen ligands. The considerably slower reaction of the ppsa complex with peroxodisulphate ion than with the much weaker oxidant hydrogen peroxide strengthens our feeling (see above) that the rate-determining step with the latter is a reaction of the co-ordinated ligands rather than simple iron(II) to iron(III) oxidation.

## CONCLUSIONS

The reactivity pattern for the tris(ppsa)iron(II) complex in acid solution, and with hydroxide, cyanide, and peroxodisulphate ions is very similar to that for the closely related complex tris(bipy)iron(II) and indeed for similar complexes of (substituted) phen ligands and Schiff bases with iron(II). There are differences in detail and differences between the relative reactivity of the various complexes towards dissociation, nucleophilic attack, and oxidation, but the outline is the same for all $[FeL_3]^{2+}$ complexes studied to date.

## EXPERIMENTAL

3-(2-Pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine (ppsa) (Ferrozine) was obtained from the Hach Chemical Company, Ames, Iowa. Solutions of the tris(ppsa)iron(II) complex were prepared from the ligand ppsa and ammonium iron(II) sulphate (AnalaR); their visible absorption spectra were checked against published data.[3] Solutions of the other reagents were prepared from AnalaR grade materials; a trace of the disodium salt of ethylenediaminetetra-acetic acid was added to potassium peroxodisulphate solutions to sequester any traces of heavy metal cations.

Kinetics of reactions were followed spectrophotometrically at 562 nm, the wavelength of maximum absorption in the visible region of the tris(ppsa)iron(II) complex. Reactions were carried out in 1 cm cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Rate constants and activation energies, with their

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* Details of the spectra and $\nu_{max.}$ against $E_T$ plots are available from the authors.

[16] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2352.

[17] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1; C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[18] C. Reichardt, 'Lösungsmitteleffekte in der organischen Chemie,' Verlag Chemie, Weinheim, 1968.

[19] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329.

[20] J. Burgess and S. F. N. Morton, *J.C.S. Dalton*, 1972, 1712.

[21] J. Burgess, *Spectrochim. Acta*, 1970, **26A**, 1369, 1957.

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

[23] See, for example, I. Ruff, *Quart. Rev.*, 1968, **22**, 199 and references therein.

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

standard errors, were calculated by a least-mean-squares procedure,[25] using an Elliot 803 or 4130 computer.

We thank the Royal Society, for the award of a grant-in-aid to purchase the spectrophotometer, and J. A. Evans and M. Hacker for assistance with computing.

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[25] E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, pp. 38—42.