Kinetics of Aquation of Tris(1,10-phenanthroline)iron(II) Complexes in Aqueous Dioxan

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The dependence of rate constants for aquation of the complexes $[FeL_3]^{2+}$ [L = 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (5-NO_2phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), and 3-sulphonato-1,10-phenanthroline (3-SO_3phen)] on solvent composition and the nature and concentration of the acid added is described for water–dioxan solvent mixtures with compositions in the range 0—60% (by volume) dioxan.

The kinetics of aquation of the tris(phen)- and tris(bipy)-iron(II) cations (phen = 1,10-phenanthroline and bipy = 2,2′-bipyridine), and of their ligand-substituted derivatives, have been much studied in aqueous solution and in aqueous-organic solvent mixtures. From investigations of the variation of aquation rate constants with solvent composition, it has proved possible to make suggestions about the mechanisms of these aquation reactions and the importance of solvation in determining reactivity. Aquation of these complexes is generally carried out in acid solution in order to displace the equilibrium $[FeL_3]^{2+} \rightleftharpoons Fe^{2+} + 3L$ to the right by protonating the free ligand L. It is known that the anions thus introduced have some effect on aquation rates both in aqueous[1] and in aqueous-organic[2-4] solutions. We now report the results of a study of the aquation reactions of tris(phen)iron(II) complexes in dioxan–water mixtures, in which the effects both of solvent composition variation and of added acids have been systematically studied. From the kinetic results in the various acids in each solvent mixture, it is possible to extrapolate to zero acid concentration; it is thus possible to determine the effect of solvent composition on reactivity in the absence of added ion effects.

RESULTS AND DISCUSSION

In all the solvent mixtures and acids studied the disappearance of the iron(II) complex followed first-order kinetics to at least 70% of complete reaction. Observed first-order rate constants for aquation of the complexes $[FeL_3]^{2+}$ [L = 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (5-NO_2phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), and 3-sulphonato-1,10-phenanthroline (3-SO_3phen)], in the presence of various acids in a range of dioxan–water mixtures, are reported in Tables 1—4. The general pattern of dependence of reactivity on the nature and concentration of added acid is illustrated in Figure 1 for the tris(phen)iron(II) complex in 60% (by volume) dioxan. In 20 and 40% dioxan, and for the ligand-substituted derivatives in 60% dioxan, the pattern was similar, though with a smaller range of aquation rate constants over the range of acids in 20 and 40% dioxan. For the unsubstituted complex in all three solvent mixtures, and for the 5-NO_2phen and 4,7-Me_2phen complexes in 60% dioxan, the order of decreasing rate constant was usually, within the limits of experimental uncertainty, $H_3PO_4 > HCl > Cl_3CCO_2H > H_2SO_4 > HClO_4$. In all cases phosphoric and hydrochloric acids tended to increase reactivity, sulphuric and perchloric

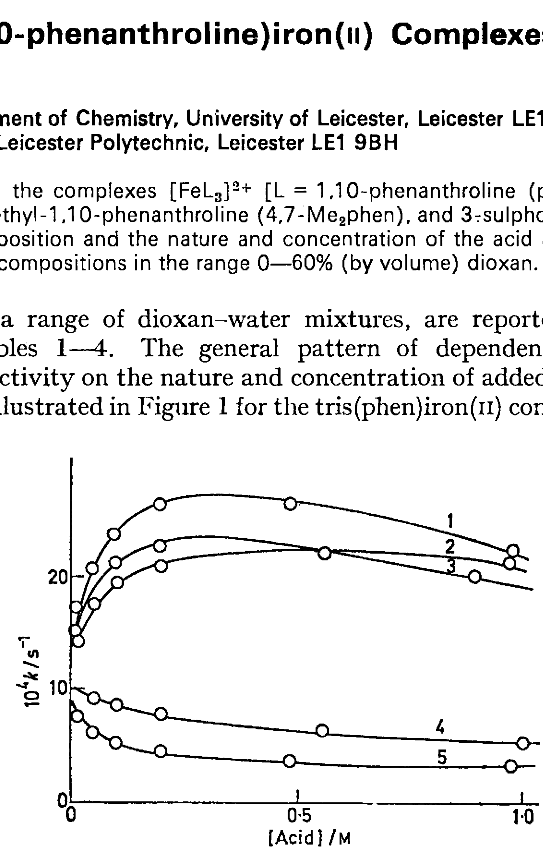

FIGURE 1 Dependence of rate constants for the aquation of the complex $[Fe(phen)_3]^{2+}$ on the nature and concentration of the acid, in 60% dioxan at 35·0 °C; (1), H_3PO_4; (2), HCl; (3), CCl_3CO_2H; (4), H_2SO_4; and (5), $HClO_4$

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

[2] J. Burgess, *J. Chem. Soc.* (*A*), 1968, 1085.

[3] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.

[4] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2351.

TABLE 1

First-order rate constants (k) for the aquation of the complex tris(1,10-phenanthroline)iron(II) in aqueous dioxan (composition by volume quoted) at 35·0 °C

20% Dioxan

HCl/M	0·01	0·05	0·10	0·20	0·57	0·95
$10^4k/\mathrm{s}^{-1}$	4·3	4·3	4·7	4·6	4·6	4·3
H_3PO_4/M	0·01		0·10		0·49	0·98
$10^4k/\mathrm{s}^{-1}$	4·4		4·7		4·7	4·3
H_2SO_4/M	0·01		0·10		0·56	1·11
$10^4k/\mathrm{s}^{-1}$	4·2		4·3		3·8	3·3
$HClO_4$/M	0·01		0·10		0·49	0·98
$10^4k/\mathrm{s}^{-1}$	3·5		3·1		2·5	1·85
CCl_3CO_2H/M	0·01		0·10		0·45	0·90
$10^4k/\mathrm{s}^{-1}$	4·2		4·2		3·3	2·2

40% Dioxan

HCl/M	0·01	0·02				0·10	0·20	0·50	0·56	0·95	1·13
$10^4k/\mathrm{s}^{-1}$	6·4	6·5				7·0	7·1	8·0	7·6	7·7	7·6
H_3PO_4/M	0·01	0·02	0·03	0·04	0·06	0·10	0·20	0·50		0·98	
$10^4k/\mathrm{s}^{-1}$	6·2	6·9	7·0	7·3	7·6	8·1	8·5	8·2		7·9	
H_2SO_4/M	0·01					0·10			0·56		1·11
$10^4k/\mathrm{s}^{-1}$	5·8					5·7			5·0		3·8
$HClO_4$/M	0·01					0·10		0·49		0·98	
$10^4k/\mathrm{s}^{-1}$	5·3					4·2		3·2		2·4	
CCl_3CO_2H/M	0·01					0·10		0·45		0·90	
$10^4k/\mathrm{s}^{-1}$	6·5					7·2		7·6		7·2	

60% Dioxan

HCl/M	0·01	0·05	0·10	0·20	0·57	0·95
$10^4k/\mathrm{s}^{-1}$	15·0	17·6	19·4	20·7	21·8	22·4
H_3PO_4/M	0·01	0·05	0·10	0·20	0·49	0·98
$10^4k/\mathrm{s}^{-1}$	17·0	20·6	23·6	26·4	26·7	21·9
H_2SO_4/M	0·01	0·05	0·10	0·20	0·56	1·11
$10^4k/\mathrm{s}^{-1}$	9·2	9·0	8·7	8·3	6·7	5·3
$HClO_4$/M	0·01	0·05	0·10	0·20	0·49	0·98
$10^4k/\mathrm{s}^{-1}$	7·4	5·9	5·5	5·3	4·4	3·3
CCl_3CO_2H/M	0·01		0·10	0·20		0·90
$10^4k/\mathrm{s}^{-1}$	14·3		21·2	22·3		20·2
$MeCO_2H$/M						1·00
$10^4k/\mathrm{s}^{-1}$						12
HBr/M						1·00
$10^4k/\mathrm{s}^{-1}$						6·4

TABLE 2

First-order rate constants (k) for the aquation of the complex tris(5-nitro-1,10-phenanthroline)iron(II) in 60% dioxan at 35·0 °C

HCl/M	0·001	0·01	0·10	0·20	0·33	0·40	0·57	0·80	1·13
$10^3k/\mathrm{s}^{-1}$	14·6	26	34	39	43	45	48	41	55
$HClO_4$/M	0·001	0·01		0·10	0·20	0·49	0·82		0·98
$10^3k/\mathrm{s}^{-1}$	5·7	4·3		2·4	1·6	1·2	0·84		0·59
H_2SO_4/M	0·001	0·01		0·10	0·20	0·55	0·89		1·10
$10^3k/\mathrm{s}^{-1}$	17·3	12·7		11·8	9·9	8·1	6·8		6·7
H_3PO_4/M	0·001								
$10^3k/\mathrm{s}^{-1}$	49								

TABLE 3

First-order rate constants (k) for the aquation of the complex tris(4,7-dimethyl-1,10-phenanthroline)iron(II) in 60% dioxan at 35·0 °C

HCl/M	0·001	0·010	0·066	0·10	0·20	0·40	0·57	0·77	1·15
$10^5k/\mathrm{s}^{-1}$	5·8	7·3	8·5	8·5	8·5	8·4	8·6	8·5	7·8
H_2SO_4/M	0·001	0·010	0·066	0·10	0·20	0·55	0·77	1·11	
$10^5k/\mathrm{s}^{-1}$	5·5	5·6	5·2	5·1	4·6	3·8	3·4	2·8	
H_3PO_4/M	0·001	0·010	0·066	0·10	0·20	0·40	0·49	0·65	0·97
$10^5k/\mathrm{s}^{-1}$	6·3	7·7	8·6	8·6	8·8	8·6	8·7	7·7	6·1

acids to decrease reactivity. It was thus straightforward to extrapolate the rate constant against acid concentration plots back to a common point at zero acid concentration for each complex and solvent mixture. This situation is thus different from, and more favourable than, the more common situation where rates decrease with decreasing anion concentration for all anions, making extrapolation of reactivity trends to zero anion

TABLE 4

First-order rate constants (k) for the aquation of the complex tris(3-sulphonato-1,10-phenanthroline)iron(II) in acids (1M) and 60% dioxan at 35·0 °C

Acid	$10^3k/\mathrm{s}^{-1}$
H_3PO_4	3·3
HCl	2·9
H_2SO_4	1·7
$HClO_4$	0·99

concentration difficult or impossible.[5] Aquation rate constants estimated at zero acid concentration are collected in Table 5. Whether the anion was added in the form of an acid or predominantly * as a salt did not affect dissociation rates to a significant extent. This is shown by a comparison of the results in Table 6 with their respective analogues in Tables 1—3.

TABLE 5

First-order rate constants (k) for aquation of tris(1,10-phenanthroline)iron(II) complexes in aqueous dioxan, extrapolated to zero acid concentration at 35·0 °C

	% Dioxan (v/v)			
	0	20	40	60
Complex	$10^4k/s^{-1}$			
$[Fe(phen)_3]^{2+}$	3·7 [a]	4·0	5·5	11·0
$[Fe(5\text{-}NO_2phen)_3]^{2+}$	23·0 [b]			150
$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$	1·1 [b]			0·55

phen = Phenanthroline, 5-NO_2phen = 5-nitro-1,10-phenanthroline, 4,7-Me_2phen = 4,7-dimethyl-1,10-phenanthroline.

[a] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752.
[b] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.

TABLE 6

First-order rate constants (k) for the aquation of tris(1,10-phenanthroline)iron(II) complexes in solutions containing acids and their respective potassium salts, in 60% dioxan at 35·0 °C

Complex	$[H^+]$/M	[Anion]/M	$10^4k/s^{-1}$
$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$	0·03	0·40 (Cl^-)	0·90
	0·03	0·76 (Cl^-)	0·95
	0·01	0·06 (PO_4^{3-})	0·98
	0·01	0·12 (PO_4^{3-})	1·00
$[Fe(5\text{-}NO_2phen)_3]^{2+}$	0·03	0·40 (Cl^-)	380
	0·03	0·76 (Cl^-)	480

4,7-Me_2phen = 4,7-Dimethyl-1,10-phenanthroline, 5-NO_2-phen = 5-nitro-1,10-phenanthroline.

Effects of Added Anions.—There are three notable features of the dependences of dissociation rates on the nature and concentration of added anions. First there is a significant effect for all the complexes studied. Secondly the effects are greatest for the 5-NO_2phen complex, considerably smaller for the phen complex, and smaller still for the 4,7-Me_2phen and 3-SO_3phen complexes. Thirdly rates of dissociation increase on the addition of, for example, chloride or phosphate ions, but decrease on adding perchlorate or sulphate ions. There would seem to be two possible ways in which added anions can have a differential effect on reactivities: (i) through ion-pair formation and (ii) less directly through modification of the solvent activity, the effect of this on solvation and consequently on the reactivity either of the free complex or of an ion-pair.

The usual result of ion-pair formation between a complex cation and a simple anion is an increase in substitution rates of the former. In the present case, however, aquation rates *decreased* as the concentration of perchloric or sulphuric acid was increased. We feel that these observed reductions in the aquation rate should be ascribed primarily to the decreasing activity of water as the acid concentration increases. It may be that the curvature in the plot of aquation rate against acid concentration for aquation in perchloric acid results solely from such a decrease in water activity but, in view of recent reports of ion association between transition-metal complex cations and the perchlorate ion,[6] it is not possible to rule out ion-pairing in the present situation. Thus the curve corresponding to zero ion-pairing may well lie somewhere below that for perchloric acid in Figure 1 and in comparable plots for other conditions. It seems unwarranted to use even perchlorate ion as an ' inert ' anion for maintaining ionic strengths in our reactions. This conclusion unfortunately precludes the investigation of effects of varying the concentration of other added ions at constant ionic strength, though, of course, valid comparisons of the effects of various anions at constant ionic strength can be made at any fixed acid concentration. It is thus possible to assess the kinetic consequences of the nature of added anions, but not of their concentration.

If the observed decrease in reactivity with increasing concentration of perchloric or sulphuric acid can indeed be ascribed to activity and solvation changes, then the curves for the various acids in Figure 1 can be interpreted in terms of effects of formation of more reactive ion-pairs superimposed on the basic ' activity-controlled ' curve corresponding to, or below, that of perchloric acid. The estimation of ion-pairing constants is not possible, for two reasons. First the position of the base line, the ' activity-controlled ' curve, is not known; secondly there is a great paucity of data pertaining to pK values for acids in aqueous dioxan, which prevents the estimation of anion concentrations. As stated earlier, rates of dissociation of the 5-NO_2phen complex are much more sensitive to the nature and concentration of added acids than are those of the phen complex, the dissociation rates of which are more sensitive than those of the 4,7-Me_2phen or 3-SO_3phen complexes. For instance, the ratio of the rate constant for aquation in 1M-phosphoric acid to that in 1M-perchloric acid is over 100 : 1 for the 5-NO_2phen complex, 7 : 1 for the phen complex, 3·3 : 1 for the 3-SO_3phen complex, and probably also *ca.* 3 : 1 for the 4,7-Me_2phen complex. It is noteworthy that dissociation rates for the 3-SO_3phen complex do vary with the nature of the anion, for the overall charge on this complex is 1—, even in fairly strong acid. The small dependences of aquation rates on the anion nature observed for this complex, and also therefore those for the 4,7-Me_2phen complex, may arise solely from solvation differences. Ion-pairing may thus only be significant for the phen and

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* There must, of course, be some acid present to force the dissociation reaction to go to completion.

[5] See for example, K. W. Bowker, E. R. Gardner, and J. Burgess, *Trans. Faraday Soc.*, 1970, **66**, 2065; 1971, **67**, 3076; J. Burgess, E. R. Gardner, and F. M. Mekhail, *J.C.S. Dalton*, 1972, 487.

[6] L. Heck, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 701; H. Yoneda, M. Muto, T. Baba, and T. Miura, *Bull. Chem. Soc. Japan*, 1971, **44**, 689.

the 5-NO_2phen complexes. It seems that both solvation-activity effects and ion-pairing contribute to determining the observed reactivities in these systems.

The variation of the rate constant for aquation of the complex $[Fe(phen)_3]^{2+}$ in perchloric acid–phosphoric acid mixtures of constant total molarity, in 60% dioxan, is illustrated in Figure 2. The shape of this plot suggests that the strengths of these two acids are such that ionisation of phosphoric acid is suppressed by perchloric acid, except at low concentration of the latter. Thus formation of the more reactive $H_2PO_4^-$ ion-pairs only occurs in $H_3PO_4 : HClO_4$ mole ratios of greater than *ca.* 5 : 1.

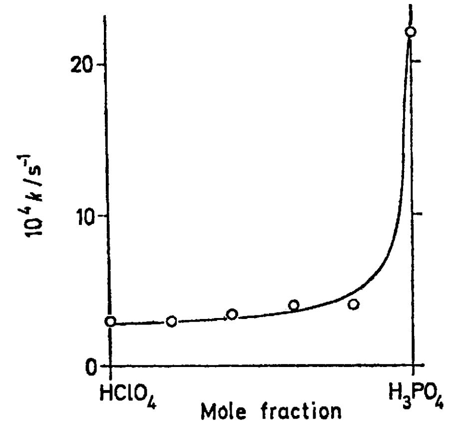

FIGURE 2 Dependence of rate constants for aquation of the complex $[Fe(phen)_3]^{2+}$ on composition of a $HClO_4$–H_3PO_4 mixture, of constant overall molarity, in 60% dioxan, at 35·0 °C

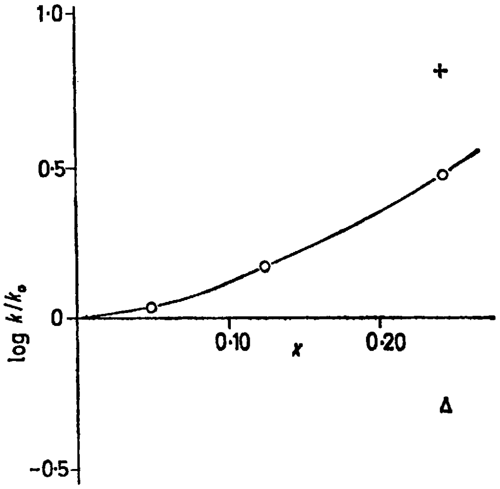

FIGURE 3 Logarithms of ratios of the first-order rate constants, extrapolated to zero acid concentration, in aqueous dioxan (k) (x = mole fraction dioxan) to those in water (k_0) for aquation of the complexes $[Fe(phen)_3]^{2+}$ (○), $[Fe(5\text{-}NO_2\text{-}phen)_3]^{2+}$ (+), and $[Fe(4,7\text{-}Me_2phen]_3]^{2+}$ (Δ) at 35·0 °C in various water–dioxan solvent mixtures

Solvent Effects.—Dioxan–water. The variation of rate constants for aquation, extrapolated to zero concentration of added acid, is shown for each complex in Figure 3. Both the phen and the 5-NO_2phen complexes aquate more rapidly as the proportion of dioxan increases, but the rate of aquation of the 4,7-Me_2phen complex is less in 60% dioxan than in water. This marked difference in behaviour between the complexes may be due to differences in mechanism or in solvation of the ligands and the leaving groups. The addition of dioxan to water tends to disrupt the structure of the latter,[7] which could make aquation by an associative mechanism easier in dioxan–water than in water itself. If aquation takes place by an essentially dissociative mechanism, then reactivities will be controlled by solvation of the complexes in their initial and transition states. This solvation will depend to some extent on the nature of the ligand; for example, whether it contains a strongly hydrophilic substituent like sulphonate, a mildly hydrophilic group like nitro, or a hydrophobic group like methyl.

General. Kinetic results are now available for the aquation of the complex tris(phen)iron(II) and its 5-NO_2phen and 4,7-Me_2phen derivatives in a variety of mixed aqueous solvents: methanol–,[8] ethanol–,[3] t-butyl alcohol–,[2] acetonitrile–,[4] and formic acid–water[3] as well as dioxan–water. In most cases rate constants extrapolated to zero acid concentration are not available, but the relatively small uncertainties introduced by this variability do not seriously obscure the general pattern of reactivities for these complexes in water-rich aqueous-organic solvent mixtures. As has previously been adumbrated,[3] it is not possible to correlate rate constants for aquation of these complexes with Grunwald–Winstein solvent Y values.[9] Whether this observation indicates that there is considerable associative character to the aquation mechanisms, or whether the non-correlation is merely a result of working with phenanthroline ligands rather than the very different ligand chloride as leaving group, cannot be decided until, or unless, a Grunwald–Winstein correlation is found for solvolysis of a complex with a neutral organic ligand as leaving group.

The available kinetic results for aquation of the 5-NO_2phen and 4,7-Me_2phen complexes in mixed aqueous solvents, at 35·0 °C, are summarised in Figures 4 and 5. There is a marked contrast between the patterns for these two complexes. For the 4,7-Me_2phen complex aquation rates decrease with increasing mole fraction of organic cosolvent in all cases for which results are available. This pattern closely resembles that of, for example, aquation of cobalt(III) aminohalogeno-complexes,[10] and is not inconsistent with a predominantly dissociative mechanism. For the 5-NO_2phen complex a greater variety of reactivity trends with solvent composition behaviour is apparent. As mentioned before,[2,4] this type

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[7] R. A. Horne, 'Survey of Progress in Chemistry,' vol. 4, ed. A. F. Scott, Academic Press, London, 1968, p. 32.

[8] L. Seiden, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1959, **81**, 3809.

[9] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; P. R. Wells, *Chem. Rev.*, 1963, **63**, 171; C. Reichardt *Angew. Chem. Internat. Edn.*, 1965, **4**, 29; P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968, ch. 4.

[10] J. Burgess and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 310 and references therein.

of behaviour may arise from some associative character to the aquation mechanism for this complex. The effective positive charge on the iron in the complex containing three electron-withdrawing nitro-substituents in the ligands will be considerably greater than that in the 4,7-Me_2phen complex which contains six mildly electron-releasing ligand substituents. The order of increasing aquation rate with the nature of the cosolvent, at constant mole fraction of the organic component, is roughly in the expected order of ease of availability of water for incorporation into a transition state. Thus the minimum rate is that in aqueous formic acid, in which water is firmly bonded in the solvent structure. However, solvent structure will affect solvation of the complex. Hence it is also possible, if less attractive to the present authors, to explain the observed kinetic pattern for the 5-NO_2phen complex on the basis of a dissociative mechanism in which rates are markedly sensitive to solvation of the initial and transition states. This solvation may be greatly influenced by the availability of the components of the mixed solvent for complex solvation rather than for intra-solvent hydrogen bonding.

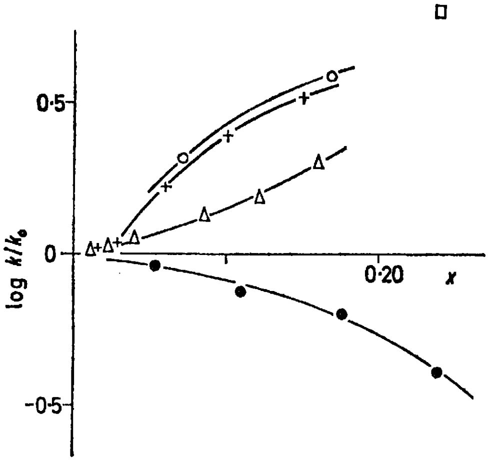

FIGURE 4 Variation of rate constants for aquation of the complex $[Fe(5\text{-}NO_2phen)_3]^{2+}$ with solvent composition (x = mole fraction of organic component), at 35·0 °C, in aqueous-organic mixed solvents: (○), EtOH; (+), Bu^tOH; (△), MeCN; (●), HCO_2H; (□), dioxan

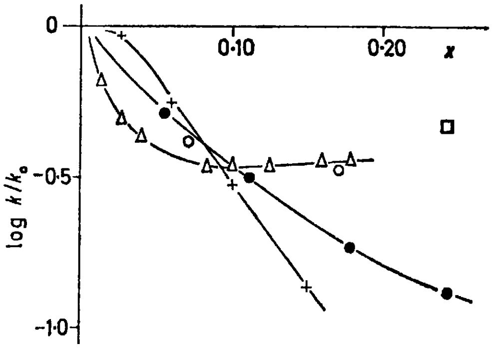

FIGURE 5 Variation of rate constants for aquation of the complex $[Fe(4,7\text{-}Me_2phen)_3]^{2+}$ with solvent composition, at 35·0 °C, in aqueous-organic mixed solvents; key as in Figure 4

Activation Parameters.—We have determined these for aquation of the 4,7-Me_2phen and 5-NO_2phen complexes in 60% dioxan, in the presence of hydrochloric or sulphuric acid. First-order rate constants are reported in Table 7; activation enthalpies and activation entropies, with their standard errors (σ), in Table 8. For each complex, the activation enthalpies in 60% dioxan in the presence of the two acids differ significantly (the 90% confidence limits, for 12 degrees of freedom, are ±1·78σ), but, whereas for the 4,7-Me_2phen complex the activation enthalpy is higher in hydrochloric acid, the reverse is the case for the 5-NO_2phen complex. Again all four activation enthalpies for reaction in 60% dioxan differ from the respective values in water, but, for the 5-NO_2phen complex in hydrochloric acid, the activation enthalpy is lower in 60% dioxan, while for the other three cases the reverse trend is observed. Thus there seems no simple pattern in the activation parameters in these systems.

TABLE 7

First-order rate constants (k) for aquation of the 5-NO_2phen and 4,7-Me_2phen complexes in aqueous dioxan (60%)

	$10^3k(5\text{-}NO_2)/s^{-1}$		$10^5k(4,7\text{-}Me_2)/s^{-1}$	
Temp./°C	0·5M-H_2SO_4	0·5M-HCl	0·5M-H_2SO_4	0·5M-HCl
25·0	1·60	9·0	0·85	1·80
26·5	2·05	10·0	0·99	2·21
27·1	2·25	11·2	1·34	2·34
29·2	3·2	15·4	1·73	3·7
30·6	4·4	23·0	2·3	5·1
31·7	4·7	23·3	2·5	6·0
33·4	6·9	35	3·6	8·0
35·0	7·5	42	4·3	8·8
37·7	12·0	51	6·8	16·1
39·3	16	71	9·6	23
40·5	18	78	11·5	28
42·0	23	97	15·4	37
32·9	28	106	16·8	41
45·0	37	140	22	55

TABLE 8

Activation parameters (with their standard errors) for the aquation of the 5-NO_2phen and 4,7-Me_2phen complexes in 60% dioxan

		$\Delta H^\ddagger$	$\Delta S^\ddagger$
Complex	Acid	kcal mol^{-1}	cal K^{-1} mol^{-1}
$[Fe(5\text{-}NO_2phen)_3]^{2+}$	H_2SO_4	29·5 ± 0·4	+28 ± 2
	HCl	26·5 ± 0·7	+21 ± 2
$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$	H_2SO_4	31·3 ± 0·5	+23 ± 2
	HCl	33·3 ± 0·5	+33 ± 2

5-NO_2phen = 5-Nitro-1,10-phenanthroline, 4,7-Me_2phen = 4,7-dimethyl-1,10-phenanthroline.

EXPERIMENTAL

Solutions of the iron(II) complexes were prepared by adding a slight excess of ligand to a neutral, freshly-prepared solution of ammonium iron(II) sulphate (AnalaR). Dioxan was of scintillation grade purity (Nuclear Enterprises Ltd.). Kinetic runs were carried out in 1 cm cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer; optical density changes were monitored at 510 nm. The initial concentration of iron(II) complex was 10^{-4}M in each run.

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