Reactions of Low-spin Iron(II) Complexes with Hydroxide Ion in Aqueous Methanol: The Effect of Ligand on Rates of Reaction

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Rate laws and rate constants are reported for reactions of several low-spin iron(II) complexes with hydroxide ion in methanol–water solutions. The dependence of the form of the rate law and of reactivity on ligand type and on substituent nature is discussed. The pattern of reactivity for a range of compounds with hydroxide ion in methanol–water mixtures is compared with the reactivity pattern for analogous reactions in dimethyl sulphoxide–water mixtures.

LOW-SPIN iron(II) complexes containing ligands such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), or their derivatives react with hydroxide ion in solution according to the general rate law shown in equation (1).[1]

$$-\mathrm{d}[\text{complex}]/\mathrm{d}t = (k_1 + k_2[\mathrm{OH}^-] + k_3[\mathrm{OH}^-]^2 + \ldots)\,[\text{complex}] \quad (1)$$

Under normal conditions of hydroxide-ion concentration the k_2 term is dominant, at least in aqueous solution and in water-rich binary aqueous mixtures. We have investigated the variation of k_2 for the reaction of the $[\mathrm{Fe(bipy)_3}]^{2+}$ cation with hydroxide ion,[2] and for the analogous reaction with cyanide ion,[2,3] with solvent composition in a wide variety of binary aqueous solvent mixtures. In almost all cases it was possible to rationalise the observed reactivity trends for these second-order reactions in terms of a dominant effect of the change in chemical potential with solvent of the small hydroxide or cyanide ion.[2,3] The rationalisation assumed that the chemical potentials of the $[\mathrm{Fe(bipy)_3}]^{2+}$ cation and of the transition state either varied little, or varied in a compensatory manner, with solvent composition. The subsequent publication of estimated Gibbs free energies of transfer for the $[\mathrm{Fe(phen)_3}]^{2+}$ cation from water into mixed solvents[4] suggested that the latter explanation was more likely. We therefore wished to establish what effect varying the ligand in low-spin iron(II) complexes of this type has on the reactivity with nucleophiles, and have examined the effects of ligand variation on the reaction with hydroxide ion in methanol–water mixtures. We report the kinetics of this reaction for the cations $[\mathrm{Fe(bipy)_3}]^{2+}$, $[\mathrm{Fe(5Br\text{-}phen)_3}]^{2+}$, $[\mathrm{Fe(4,7Me_2\text{-}phen)_3}]^{2+}$, $[\mathrm{FeL_3}]^{2+}$ (L = mpa or cpa), and $[\mathrm{Fe(bpdo)}]^{2+}$.† With this selection of complexes, and results available for the

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† mpa = 4-Methyl-*N*-[phenyl(2-pyridyl)methylene]aniline, cpa = 4-chloro-*N*-[phenyl(2-pyridyl)methylene]aniline, bpdo = 1,8-bis[phenyl(2-pyridyl)methyleneamino]-3,6-diazaoctane.

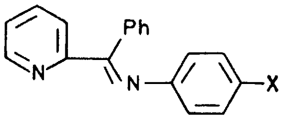
[1] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

[2] M. J. Blandamer, J. Burgess, J. G. Chambers, R. I. Haines, and H. E. Marshall, *J.C.S. Dalton*, 1977, 165.

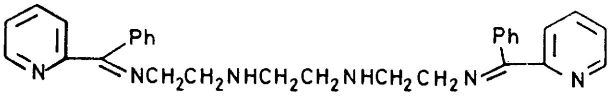
[3] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.

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

analogous reaction of the $[Fe(phen)_3]^{2+}$ cation,[5] we can examine the effects of ligand denticity, skeleton, and substituents on reactivity trends. In particular, we can establish the effects of the hydrophobic or hydrophilic natures, or of the electron-releasing or -withdrawing powers, of ligand substituents. We describe below how the nature of the ligand affects the rate law for these reactions, and how the nature of the ligand substituents affects reactivity.



mpa X = Me
cpa X = Cl



bpdo

TABLE 1

Mean observed first-order rate constants, $k_{obs.}$, for the reaction of (substituted) 1,10-phenanthroline and 2,2′-bipyridyl complexes of Fe^{II} with hydroxide ion in methanol–water mixtures at 298.2 K; $I = 0.167$ mol dm^{-3} (NaCl). Included are values of k_1 and k_2 [*cf.* text, equations (2) and (3)] derived from these $k_{obs.}$ values

Complex	Methanol (% v/v)[a]	[NaOH]/mol dm^{-3}					10^3k_1/s^{-1}	10^3k_2/dm^3 mol^{-1} s^{-1}
		0.033	0.067	0.100	0.133	0.167		
		$10^3k_{obs.}$/s^{-1}						
$[Fe(bipy)_3]^{2+}$	33.3	0.43	0.88	1.43	1.89	2.5		15.4[b]
	50.0	0.64	1.40	2.2	3.3	4.9		31
	66.7	1.29	2.9	4.7	7.5	11.4		74
$[Fe(4,7Me_2\text{-}phen)_3]^{2+}$	0	0.036	0.057	0.084	0.124	0.153	0.02	0.9
	33.3	0.032	0.071	0.117	0.159	0.192	0.01_5	1.2
	50.0	0.059	0.124	0.195	0.30	0.39	0.01	2.5
	70.0	0.126	0.27	0.42	0.68	0.95	0.01	6.1
$[Fe(5Br\text{-}phen)_3]^{2+}$	0	2.2	5.0	8.1	10.8	12.9	0.2_5	81
		[NaOH]/mol dm^{-3}						
		0.003 3	0.006 7	0.010 0	0.013 3	0.016 7		
$[Fe(5Br\text{-}phen)_3]^{2+}$	33.3	0.77	1.22	1.78	2.3	3.0	0.5	163
	50.0	1.85	3.4	5.0	5.9	7.5	0.9	414
	66.7	6.2	9.9	13.2	16.5		1.4	1 020

[a] Here and elsewhere in this paper percentage compositions are by volume before mixing. [b] In water, $k_2 = 7.0 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} [J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061].

EXPERIMENTAL

The complexes $[Fe(bipy)_3]^{2+}$ and $[Fe(X\text{-}phen)_3]^{2+}$ (X = 5Br or $4,7Me_2$) were prepared in solution by the reaction of AnalaR ammonium iron(II) sulphate with very slightly more than the stoicheiometric quantity of ligand (from B.D.H. or the G. F. Smith Chemical Co., Columbus, Ohio). The complexes $[FeL_3]^{2+}$ (L = mpa or cpa)[6] and $[Fe(bpdo)]^{2+}$ (ref. 7) were prepared by published methods. Sodium hydroxide and sodium chloride were AnalaR materials; concentrations of solutions of the former were checked by standard analytical procedures. Methanol was dried, using magnesium and iodine, and distilled before use. Reactions were monitored spectrophotometrically, at the respective wavelengths of maximum absorption of the complexes, in the thermostatted cell compartment of a Unicam SP 800A or SP 1800 or Beckman DK2 spectrophotometer.

RESULTS AND DISCUSSION

In all the runs hydroxide was present in large excess, and the disappearance of the iron(II) complex followed first-order kinetics over at least three to four half-lives. Observed first-order rate constants for the bipy and phen complexes are reported in Table 1, for the Schiff-base complexes in Table 2.

The $[Fe(X\text{-}phen)_3]^{2+}$ *and* $[Fe(bipy)_3]^{2+}$ *Cations.*—In each solvent mixture the dependence of $k_{obs.}$ [equation (2)] on sodium hydroxide concentration can be expressed by equation (3). Values of k_1 and k_2 defined by this equation were computed by a standard unweighted least-mean-squares procedure; they are included in Table 1.

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

$$k_{obs.} = k_1 + k_2[OH^-] \qquad (3)$$

The k_1 values correspond to rate-determining dissociation of the complex (*cf.* aquation in acidic media). They will be considered no further, except to say that their variation with solvent methanol content is consistent with trends observed for these and related complexes in other alcohol–water mixtures.[8]

The k_2 values of equation (3) and Table 1 correspond to bimolecular attack of hydroxide at the complex.

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[5] M. J. Blandamer, J. Burgess, and D. L. Roberts, unpublished work.

[6] J. Burgess, *J. Chem. Soc. (A)*, 1968, 497.

[7] E. R. Gardner, F. M. Mekhail, and J. Burgess, *Internat. J. Chem. Kinetics*, 1974, **6**, 133.

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

There is at present some controversy on mechanistic details, in particular as to whether the hydroxide attacks a complex of this type initially at the iron atom or at the co-ordinated ligand.[9] The latter seems more likely; fortunately the site of attack is of secondary concern in the following discussion of our kinetic results.

TABLE 2

Mean observed first-order rate constants, $k_{obs.}$, for reaction of iron(II)–Schiff-base complexes with hydroxide ion in methanol–water and in dioxan–water mixtures

			[NaOH]/mol dm^{-3}			
			0.001 3	0.002 7	0.004 0	0.005 3
Complex	Conditions *	Co-solvent (% v/v)	$10^3k_{obs.}/s^{-1}$			
$[Fe(mpa)_3]^{2+}$	307.9 K, $I = 0.005\ 3$ (NaCl)	Methanol 10	0.31	0.56	0.95	1.10
		20	0.45	0.84	1.32	2.2
		40	1.15	1.78	2.4	3.9
		60	2.0	2.7	3.3	4.2
		70	2.5	3.4	4.9	6.5
$[Fe(cpa)_3]^{2+}$	307.9 K, $I = 0.005\ 3$ (NaCl)	Methanol 20	0.84	1.87	2.6	3.3
		40	1.11	2.4	4.4	6.5
		60	2.9	5.2	10.5	15.0
		70	3.4	9.2	23	40

			[NaOH]/mol dm^{-3}					
			0.033	0.067	0.133	0.20	0.27	0.33
			$10^3k_{obs.}/s^{-1}$					
$[Fe(bpdo)]^{2+}$	298.7 K, $I = 0.33$ (NaCl)	Methanol 50			0.018	0.034	0.096	0.161
		75		0.038	0.076	0.134	0.21	0.35
		Dioxan 30	0.084		0.34	0.55	0.90	1.40
		50	1.41	2.7	4.9	13.5	25	

* Values for I are in mol dm^{-3}.

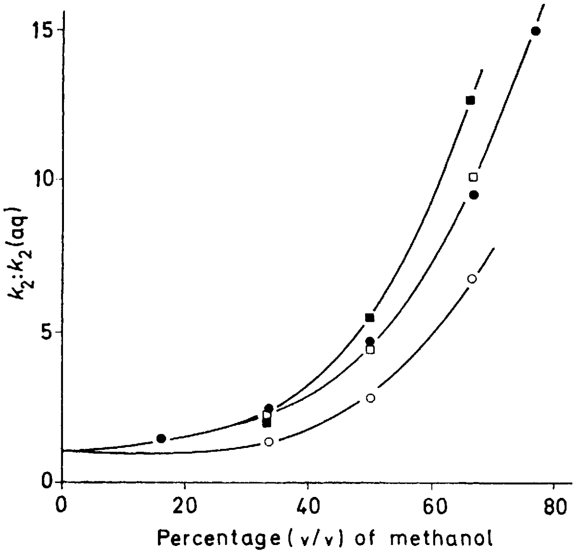

FIGURE 1 Variation of the ratios of second-order rate constants for reaction with hydroxide in methanol–water mixtures (k_2) to those in water [k_2(aq)] with solvent composition (% v/v MeOH). Complex: (□) $[Fe(bipy)_3]^{2+}$; (●) $[Fe(phen)_3]^{2+}$; (■) $[Fe(5Br\text{-}phen)_3]^{2+}$; (○) $[Fe(4,7Me_2\text{-}phen)_3]^{2+}$

The relative sensitivity of these reactions to solvation changes is illustrated in Figure 1. Here the ratios of k_2 in a given methanol–water mixture to k_2 in water are plotted against solvent composition. There is a divergence of the curves for the hydrophilic, electron-withdrawing, bromo-substituted complex and for the hydrophobic, electron-releasing, methyl-substituted complex from the curve common to the parent $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ cations. Differences in substituent do therefore lead to differences in relative reactivity, presumably through differences in the initial states and in transition states. That differences in the initial states may be important is suggested by the established differences between the solubility trends for the perchlorates of the $[Fe(5NO_2\text{-}phen)_3]^{2+}$ and $[Fe(4,7Me_2\text{-}phen)_3]^{2+}$ cations in t-butyl alcohol–water mixtures.[10] It is noteworthy that the 5Br-phen and 4,7Me$_2$-phen complexes have curves lying on opposite sides of the parent complex in Figure 1. The method for estimating Gibbs free energies of transfer of the $[Fe(phen)_3]^{2+}$ cation used by Van Meter and Neumann,[4] based as it is on a simple Born assumption, would lead either to a forecast that ligand substituents in $[Fe(phen)_3]^{2+}$ would make no difference or would cause the curves for the larger substituted cations to be on the same side of the curve for unsubstituted $[Fe(phen)_3]^{2+}$. The similarity of the curves for the $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ cations, and the sequence from $[Fe(5Br\text{-}phen)_3]^{2+}$ through $[Fe(phen)_3]^{2+}$ to $[Fe(4,7Me_2\text{-}phen)_3]^{2+}$, suggest to us that the periphery of the complex and its solvation are the important factors in determining the observed reactivity trends.

Reactivity trends for our iron(II) complexes are compared with those for reactions of some organic substrates with hydroxide ion in Figure 2. Base hydrolysis of methyl iodide[11] follows a similar trend to the iron(II) complexes, but base hydrolysis of the esters methyl

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[9] See, for example, R. D. Gillard, *Inorg. Chim. Acta*, 1974, **11**, L21; *Co-ordination Chem. Rev.*, 1975, **16**, 67.

[10] J. Burgess, *J. Chem. Soc.* (*A*), 1968, 2728.

[11] J. Murto, *Ann. Acad. Sci. Fennicae*, 1962, **AII**, 117.

acetate and ethyl acetate [12] follows a very different trend. The pattern for methanol–water mixtures shown in Figure 2 may be compared with that for a similar, although more extensive, range of base hydrolyses in dimethyl sulphoxide–water mixtures [Figure 3(*a*) of ref. 2 is directly comparable].[2] Interestingly, the lines for the iron(II) complexes in these Figures are close to that for methyl iodide, but well removed from those for esters, in both mixed-solvent series. There are disappointingly fewer entries on the methanol–water graph than on that for dimethyl sulphoxide–water. In particular, there appear to be no relevant data for cobalt(III), chromium(III), or similar complexes. The only cobalt(III) complex for which kinetic data for reaction with hydroxide exist in methanol–water mixtures is the *trans*-$[Co(py)_4Cl_2]^+$ cation (py = pyridine); [13] here there are no second-order rate constants since the S_N1-(CB) mechanism cannot operate.[14]

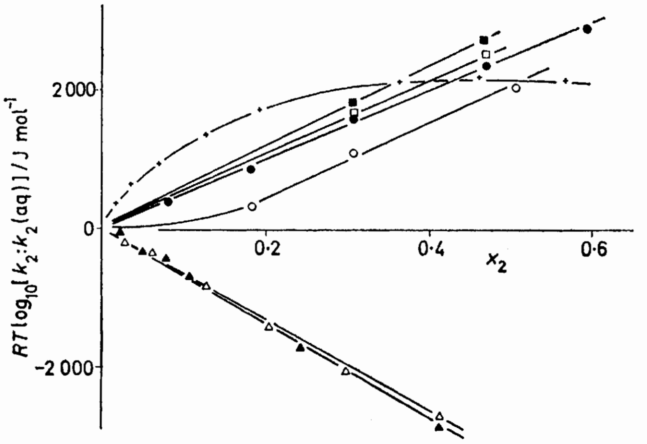

FIGURE 2 Variation of the ratios of second-order rate constants in methanol–water mixtures (k_2) to those in water [k_2(aq)] with mole fraction of methanol (x_2). Compounds: (□) $[Fe(bipy)_3]^{2+}$; (●) $[Fe(phen)_3]^{2+}$ (■) $[Fe(5Br\text{-}phen)_3]^{2+}$; (○) $[Fe(4,7Me_2\text{-}phen)_3]^{2+}$; (+) MeI; (▲) $MeCO_2Me$; (△) $MeCO_2Et$

We would have liked to extend our investigation in methanol–water mixtures to further substituted complexes, in particular to the $[Fe(5NO_2\text{-}phen)_3]^{2+}$ cation where the substituent is highly hydrophilic and electron-withdrawing. Unfortunately, the kinetics of the reaction of this cation with hydroxide ion are known to be complicated, corresponding to consecutive reactions.[15] We therefore extended our study to related Schiff-base complexes in an attempt to gain supporting evidence and extend the range of complexes covered.

Iron(II)-*Schiff-base Complexes plus Hydroxide.*—First-order rate constants for these reactions are recorded in Table 2, and plotted against sodium hydroxide concentration in Figure 3. In contrast to the bipy and phen complexes discussed above, the dependence of $k_{obs.}$ on hydroxide concentration is not linear, except for the complexes derived from mpa and cpa at low methanol concentrations. Indeed it has already been reported that the plot of $k_{obs.}$ against sodium hydroxide concentration is not linear even in water for the $[Fe(bpdo)]^{2+}$ cation.[7] The plots shown in Figure 2 can be fitted to a rate law of the form shown in equation (1), with terms in k_1, k_2, and k_3 for the complexes of ligands mpa and cpa, and terms in k_2 and k_3 for the $[Fe(bpdo)]^{2+}$ cation.

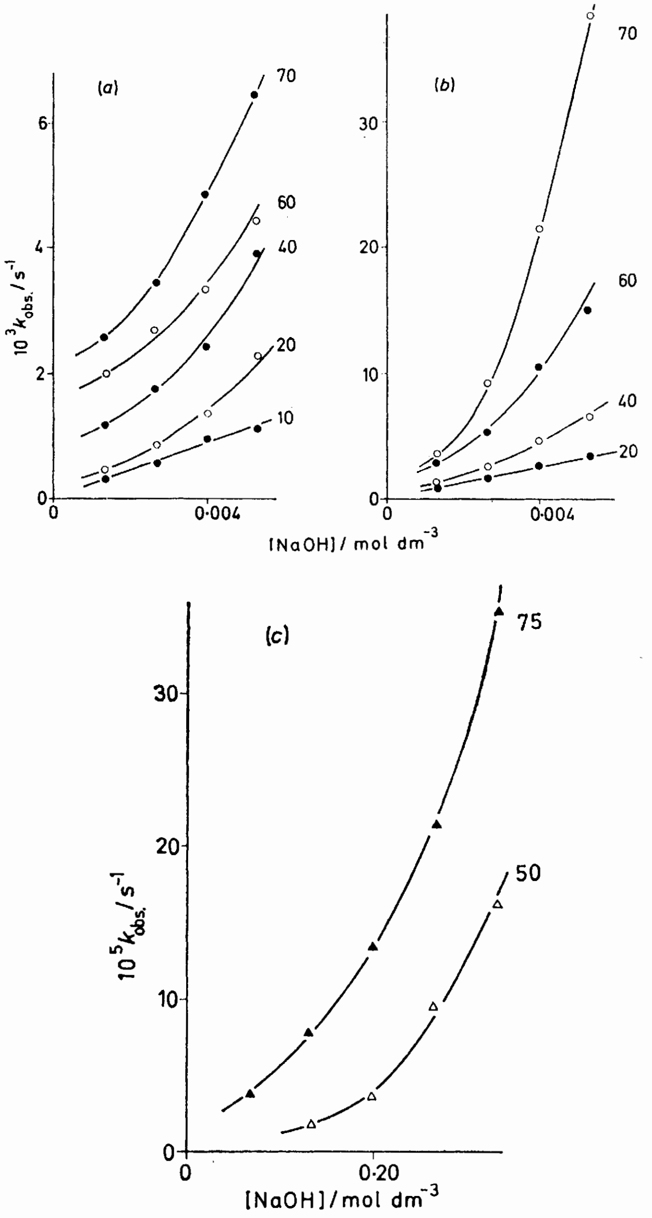

FIGURE 3 Dependence of observed first-order rate constants ($k_{obs.}$) on sodium hydroxide concentration in methanol–water mixtures (numbers are % v/v MeOH). The iron(II) complexes are (*a*) $[Fe(mpa)_3]^{2+}$ (307.9 K), (*b*) $[Fe(cpa)_3]^{2+}$ (307.9 K), and (*c*) $[Fe(bpdo)]^{2+}$ (298.7 K)

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[12] E. Tommila, A. Koivisto, J. P. Lyyra, K. Antell, and S. Heimo, *Ann. Acad. Sci. Fennicae*, 1952, **AII**, part 1; E. Tommila and S. Mattamo, *Suomen Kem.*, 1955, **B28**, 118.

[13] C. N. Elgy and C. F. Wells, personal communication.

[14] R. Pearson, P. M. Henry, and F. Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5382.

[15] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

(The non-appearance of a significant k_1 term for this last complex can be explained by the very low rate of its dissociation in neutral solution.[7]) The accuracy of k_2 values estimated by such curve fitting is rather low, so it is not possible to construct a graph analogous to Figure 1 for these Schiff-base complexes. However, it is possible to gain an idea of the relative effects of substituents for the complexes derived from the bidentate ligands mpa and cpa by plotting $k_{obs.}$ at a given concentration of sodium hydroxide against solvent composition (Figure 4). This plot has a similar appearance to Figure 1, with the halogeno-derivative more sensitive to solvent change than the methyl derivative.

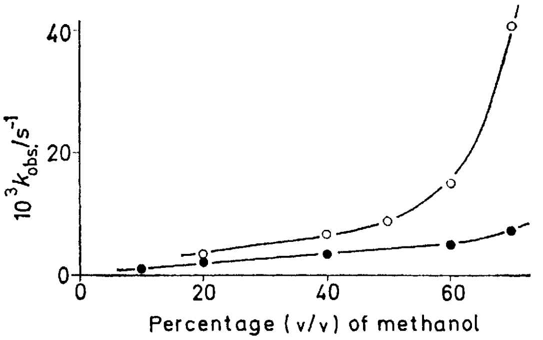

FIGURE 4 Variation of observed first-order rate constants for the reactions of Schiff-base complexes of Fe^{II} with hydroxide ion at $[NaOH] = 0.005\ 3\ mol\ dm^{-3}$, 307.9 K, with solvent composition in methanol–water mixtures (% v/v MeOH). Complex: (●) $[Fe(mpa)_3]^{2+}$; (○) $[Fe(cpa)_3]^{2+}$

It is not clear why the $k_3[OH^-]^2$ term of equation (1) is important for these Schiff-base complexes but not, under similar conditions, for the $[Fe(phen)_3]^{2+}$ series of complexes. The simplest suggestion for the mechanism of this reaction path, for which there are precedents in ruthenium(II) chemistry,[16] is that rate-determining hydroxide attack takes place at an intermediate in which hydroxide has already been added to one of the ligand molecules in a fast pre-equilibrium step.

TABLE 3

Variation of $k_2 : k_2(aq)$ with solvent composition for bimolecular reactions of low-spin iron(II) complexes with hydroxide ion in aqueous methanol at 298.2 K

	Methanol (% v/v)					
Complex	0	16.7	33.3	50.0	66.7	76.7
$[Fe(bipy)_3]^{2+}$	1		2.2	4.4	10.1	
$[Fe(phen)_3]^{2+}$	1	1.5	2.3	4.7	9.5	14.9
$[Fe(4,7Me_2\text{-}phen)_3]^{2+}$	1		1.3	2.8	6.7	
$[Fe(5Br\text{-}phen)_3]^{2+}$	1		2.0	5.4	12.6	

Table 2 shows that the reaction of the $[Fe(bpdo)]^{2+}$ cation with hydroxide follows the same rate law in dioxan–water as in methanol–water mixtures; rates increase more dramatically in the former series, reflecting the more rapid increase in the chemical potential of the hydroxide ion.[17]

We thank the Royal Society for the provision of a Grant-in-aid for the purchase of one of the spectrophotometers, and the S.R.C. for support.

[7/1883 *Received, 27th October,* 1977]

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[16] See, for example, R. D. Gillard, C. T. Hughes, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 51; R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *ibid.*, 1977, **2**, 12; *J.C.S. Dalton*, 1977, 1039.

[17] D. Feakins and D. J. Turner, *J. Chem. Soc.*, 1965, 4986; H. P. Bennetto, D. Feakins, and K. G. Lawrence, *J. Chem. Soc.* (*A*), 1968, 1493.