Kinetics of Substitution at Bis(2,2′-bipyridyl)biscyanoiron(II) †

By J. Burgess, Chemistry Department, University of Leicester, Leicester LE1 7RH

The kinetics of reaction of $Fe(bipy)_2(CN)_2$ with 1,10-phenanthroline have been investigated in water and in mixed aqueous solvents. Logarithms of rate constants for this reaction, and for the analogous reaction of a Schiff base complex $Fe(SB)_2(CN)_2$, where SB = *N*-(2-pyridylmethylene)-3,4-dimethylaniline, correlate linearly with Grunwald–Winstein solvent *Y* values. Reaction of $Fe(bipy)_2(CN)_2$ with hydroxide follows a first-order rate law with rates independent of hydroxide concentration.

We are currently interested in investigating the effect of solvent composition on rates of substitution at octahedral transition-metal complexes in mixed aqueous solvents. The main purpose is to determine whether variation of rate constants with solvent composition can, as in organic chemistry, be used as diagnostic of mechanism. The most satisfactory solvent parameter for such rate correlation appears to be the Grunwald–Winstein *Y* parameter,[1] for this is an empirical kinetic index of the solvating power of pure and mixed solvents, based on solvent effects on reactivity in S_N1(lim) solvolysis of t-butyl chloride.‡ This approach has been used for several cobalt(III) complexes, *trans*-$[Co(en)_2Br(NO_2)]^+$,[3] and *cis*-[4] and *trans*-[3] isomers of $[Co(en)_2Cl_2]^+$. We now report the extension of this approach to another d^6 centre, low-spin iron(II) in $Fe(bipy)_2(CN)_2$ and related compounds. This type of compound is particularly suited to such investigations since they are, like the organic substrates first treated by Grunwald and Winstein but unlike the cobalt(III)–halide complexes mentioned above, uncharged species.

Compounds of the formula $Fe(LL)_2(CN)_2$, where LL = dinitrogen base such as bipy or phen, were first reported in 1934,[5] and rediscovered decades later by Schilt.[6] After some discussion, their stereochemistry is now generally accepted as *cis*. Redox potentials[7] and charge-transfer spectra,[8] which prove to be markedly solvent sensitive, have been reported. Kinetic studies have included aquation in aqueous acid media[9] and peroxodisulphate oxidation.[10] We now describe further kinetic studies, principally of substitution at $Fe(bipy)_2(CN)_2$ in neutral mixed aqueous solvents.

RESULTS AND DISCUSSION

The basic reaction in this work is that of $Fe(bipy)_2(CN)_2$ with 1,10-phenanthroline (phen) in neutral solution. The reaction product is the cation $Fe(phen)_3{}^{2+}$ characterised by its visible absorption spectrum, which, unlike that of the $Fe(bipy)_2(CN)_2$ starting material, is invariant with solvent composition, and precipitation as its perchlorate salt. This reaction (1) goes in the direction

$$Fe(bipy)_2(CN)_2 + 3\,phen \longrightarrow Fe(phen)_3{}^{2+} + 2bipy + 2CN^- \quad (1)$$

indicated mainly due to the greater stability of phen complexes compared to bipy complexes [compare *e.g.* $Fe(bipy)_3{}^{2+}$, $\log \beta_3 = 17{\cdot}5$, with $Fe(phen)_3{}^{2+}$, $\log \beta_3 = 21{\cdot}2$ (ref. 11)].

Presumably the rate-determining step is loss of the first bipyridyl molecule. The evidence in favour of this is two-fold. Firstly the rate of reaction is, within experimental error, independent of the concentration of 1,10-phenanthroline over *ca.* a five-fold concentration ratio [$1{\cdot}6$ to $8{\cdot}2 \times 10^{-3}$M§; concentration of $Fe(bipy)_2(CN)_2$ $1{\cdot}0 \times 10^{-4}$M]. Secondly the reaction rate is independent of the nature of the incoming ligand (Table 1). It is not possible to tell whether it is the breaking of the first or the second iron–nitrogen bond which is rate-determining. While several mechanisms involving intermediates containing one-end-bonded 2,2′-bipyridyl or 1,10-phenanthroline have been proposed, there is no preparative evidence for stable low-spin compounds of the type FeN_5O. Thus, model compounds of the type $Fe(bipy)_2(py)(OH_2)^{2+}$ have not been isolated,

TABLE 1

Observed first-order rate constants (*k*) for reaction of $Fe(bipy)_2(CN)_2$ with 1,10-phenanthrolines in neutral solution at 35·0 °C. Initial $[Fe(bipy)_2(CN)_2]$ $1{\cdot}0 \times 10^{-4}$M; initial [phen] between 1·6 and $8{\cdot}2 \times 10^{-3}$M

	10^6k/s		
Solvent	phen	4,7-Me_2phen	5-$SO_3{}^-$-phen
Water	2·8		3·0
40% MeOH	0·5	0·6	0·5
40% EtOH	1·1	0·9	

---

† A preliminary report has appeared in *Chem. Comm.*, 1969, 1422.

‡ Though t-butyl chloride is the accepted standard for S_N1(lim) solvolysis, recent work suggests that solvolysis of 1-adamantyl halides would provide a better standard for the S_N1(lim) reference.[2]

§ Higher concentrations of 1,10-phenanthroline cannot be achieved, at least in water-rich conditions, owing to solubility restrictions.[12]

[1] 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.

[2] D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1970, **92**, 5977.

[3] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.

[4] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2703.

[5] G. A. Barbieri, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1934, **20**, 273.

[6] A. A. Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 3000.

[7] A. A. Schilt and J. Bacon, *Analyt. Chem.*, 1969, **41**, 1669.

[8] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329; J. Burgess, *Spectrochim. Acta* (*A*), 1970, **26**, 1369, 1957.

[9] V. Balzani, V. Carassiti, and L. Moggi, *Inorg. Chem.*, 1964, **3**, 1252.

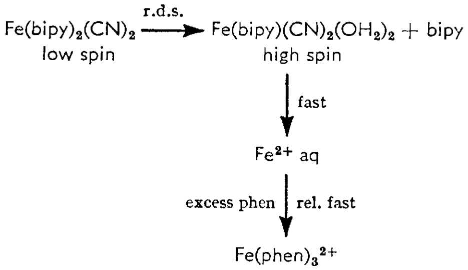
[10] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2114.

[11] H. Irving and D. H. Mellor, *J. Chem. Soc.* (*A*), 1962, 5222.

[12] R. G. Pearson and O. A. Gansow, *Inorg. Chem.*, 1968, **7**, 1373.

and we have not obtained evidence in favour of Fe(5,5′-Me_2bipy)(terpy)$(OH_2)^{2+}$ in the reaction of Fe(5,5′-Me_2bipy)$_3^{2+}$ with terpy. This last reaction has a unique rate-determining step; a sequence of spectra recorded during a run shows a clear isosbestic point at 523 nm.

The proposed mechanism for the reaction of equation (1) is thus:



Solvent Effects.—First-order rate constants for substitution according to equation (1) in a variety of mixed aqueous solvents are reported in Table 2. The average value for substitution in water is $2{\cdot}8 \times 10^{-6}$ s^{-1} at 35·0 °C, which compares satisfactorily with a value of 30×10^{-6} s^{-1} at 50·0 °C, pH 7, extrapolated from results reported for aquation in acid aqueous solutions.[9] A large increase in rate with increasing temperature is to be anticipated since activation energies for substitution at low-spin iron(II) complexes tend to be high, for example for aquation of Fe(phen)$_3^{2+}$ the activation energy is 30 kcal mol^{-1} (ref. 13), for aquation of Fe(bipy)$_3^{2+}$ in neutral solution 26 kcal mol^{-1} (ref. 14).

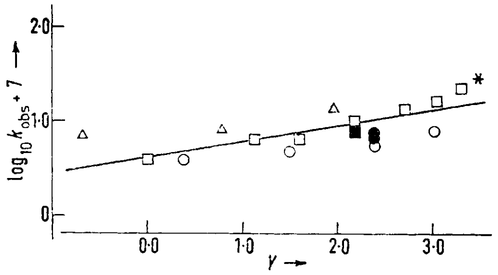


FIGURE 1 Correlation of logarithms of rate constants (k_{obs}) for reaction of Fe(bipy)$_2$(CN)$_2$ with 1,10-phenanthroline and its derivatives in mixed aqueous solvents with solvent *Y* values. Nonaqueous component: ○, methanol; □, ethanol; △, acetone; ✱, water. Open symbols correspond to reaction with unsubstituted 1,10-phenanthroline, filled symbols to reaction with the 4,7-dimethyl or 5-sulphonato-derivative

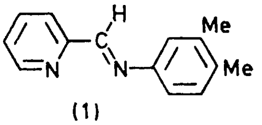
TABLE 2

Observed first-order rate constants (*k*) for reaction of Fe(bipy)$_2$(CN)$_2$ with 1,10-phenanthroline in mixed aqueous solvents at 35·0 °C. Initial [Fe(bipy)$_2$(CN)$_2$] $1{\cdot}0 \times 10^{-4}$M; initial [phen] $4{\cdot}2 \times 10^{-3}$M

Volume % non-aq. component	10^6k/s		
	EtOH	MeOH	Me_2CO
10	2·2		
20	1·6	0·8	1·5
30	1·3		
40	1·1	0·5	0·9
50	0·7		
60	0·7	0·5	0·8
80	0·4	0·4	

Decadic logarithms of rate constants for substitution at Fe(bipy)$_2$(CN)$_2$ are plotted against solvent *Y* values[1] in Figure 1. The best straight line has a slope (*m*) of *ca.* 0·2.

The similar reaction of the Schiff base complex Fe(SB)$_2$(CN)$_2$ [SB = *N*-(2-pyridylmethylene)-3,4-dimethylaniline (1)] with 1,10-phenanthroline, which again produces Fe(phen)$_3^{2+}$ as ultimate product, has been investigated over the solvent composition range 50—90% ethanol [more aqueous solvent mixtures are precluded by low solubilities of Fe(SB)$_2$(CN)$_2$] at 15·0 °C. Rate constants are reported in Table 3; a plot of their logarithms against solvent *Y* values has a slope of zero.



(1)

TABLE 3

Observed first-order rate constants (*k*) for reaction of Fe(SB)$_2$(CN)$_2$, SB = Schiff base (1) in text, with 1,10-phenanthroline in aqueous ethanol at 15·0 °C

% EtOH	*k*/s	% EtOH	*k*/s
50	0·06	80	0·04
60	0·04	90	0·05
70	0·05		

Thus aquation rates for these Fe(LL)$_2$(CN)$_2$ complexes are fairly insensitive to solvent composition and, moreover, the *mY* plot for the compound with LL = bipy is a poorer approximation to a straight line than the *mY* plot for *cis*-[Co(en)$_2$Cl$_2$]$^+$.[4] Small values of *m* are consistent with relatively small changes in solvation with solvent variation, which could be consistent with a relatively small degree of solvation of the large leaving group, bipy, and the large moiety remaining, Fe(bipy)(CN)$_2$. For a small leaving group (chloride) but a large remaining moiety [Co(en)$_2$Cl[4] or Ir(en)$_2$Cl[15]] *m* values of *ca.* 0·25 to 0·3 have been reported. However a small value of *m* may also, by analogy with organic systems, be associated with some degree of associative character in the mechanism (for methyl bromide *m* = 0·22, in contrast to *m* = 1·00 for t-butyl chloride). The scatter of the points in the *mY* plot of Figure 1 is also consistent with some degree of associative character. Unfortunately it is not possible to determine rate constants for aquation of Fe(LL)$_2$(CN)$_2$ in aqueous formic acid or aqueous acetic acid, which for a reaction of significant associative character would be expected to be much lower than in aqueous alcohols of comparable

---

[13] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752; and references therein.

[14] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, 1950, **46**, 736.

[15] F. Mekhail, E. R. Gardner, and J. Burgess, *J.C.S. Dalton*, in the press.

Y values,[16] since in these solvents these substrates become protonated so that the reactant is now the different compound $[Fe(LL)_2(CNH)(CN)]^+$.[17] Some degree of associative character has been suggested for aquation of $Fe(phen)_3^{2+}$ as a result of a study of aquation results in aqueous formic acid and aqueous ethanol;[18] the aqueous ethanol results indicated an m value of *ca.* −0·1 for this compound. The geometry of $Fe(LL)_2(CN)_2$ or of $Fe(phen)_3^{2+}$ is perhaps somewhat more favourable than that of most cobalt(III) complexes for some interaction between incoming water and central metal atom in the transition state for aquation, for it is possible for water molecules to approach fairly closely to the iron between the planar ligand molecules.[19] However the results discussed in this section, though consistent with some degree of associative character in the aquation mechanism for $Fe(LL)_2(CN)_2$, are equivocal. There is, unfortunately, no chance of probing the mechanism further by modifying the non-reacting cyanide ligand, for all other compounds $Fe(LL)_2X_2$, even when X = NCS, are substitution-labile.[20]

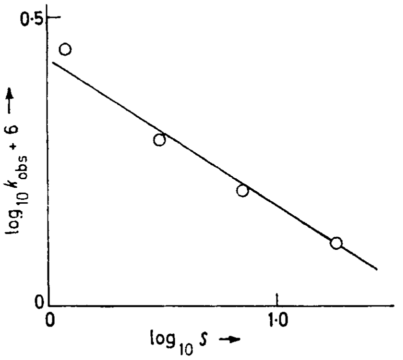


FIGURE 2 Correlation of logarithms of rate constants (k_{obs}) for reaction of $Fe(bipy)_2(CN)_2$ with 1,10-phenanthroline with logarithms of solubilities (S) of $Fe(bipy)_2(CN)_2$ in water and in aqueous ethanol (10, 20, 30% v/v ethanol); 35·0°

Solvation of $Fe(bipy)_2(CN)_2$.—To obtain further information on the importance of solvation in these reactions, we have determined the solubility of $Fe(bipy)_2(CN)_2$ in aqueous ethanol. The results are reported, with solubilities compared with kinetics by plotting logarithms of solubilities against logarithms of rate constants (equivalent to free energies of solution against free energies of activation for ideal solutions under standard conditions), in Figure 2. There is a correlation between these quantities, with rate constants much less sensitive than solubilities to solvent variation. The correspondence between decreasing rate and increasing solubility suggests that initial-state stabilisation by increasing solvation is significant in determining the pattern of reactivity in mixed aqueous solvents of increasing proportions of organic component. Detailed separation of solvation effects into initial-state and transition-state effects, as in the recent elegant and extensive studies of reactions between tetra-alkyltin compounds and mercury-(II) halides,[21] presupposes a knowledge of the mechanism of the reaction in question, and is therefore not yet possible in the present situation.

Reaction with Hydroxide.—The cations $Fe(LL)_3^{2+}$, where LL = 2,2′-bipyridyl, 1,10-phenanthroline, or one of their substituted derivatives, react with hydroxide in aqueous solution according to the rate law (2)[22]

$$d[Fe(LL)_3^{2+}]/dt = \{k_1 + k_2[OH^-]\}[Fe(LL)_3^{2+}] \qquad (2)$$

where the k_2 term derives from direct nucleophilic attack of hydroxide at the iron atom. By contrast, hydroxide attack at the analogous $Ni(LL)_3^{2+}$ cations follows the simpler rate law (3)[23] with no kinetic

$$d[Ni(LL)_3^{2+}]/dt = k_1[Ni(LL)_3^{2+}] \qquad (3)$$

evidence for bimolecular attack of hydroxide at the nickel. We have now found that the first-order rate constants for reaction of $Fe(bipy)_2(CN)_2$ with hydroxide ion (excess) in aqueous solution at 35·0 °C are constant, at a value of $2·0 \pm 0·4 \times 10^{-6}$ s^{-1} over a range of sodium hydroxide concentrations between 0·07 and 0·30M, indicating a rate law (4) which is the same as that for $Ni(LL)_3^{2+}$, see equation (3) above, rather than that for $Fe(LL)_3^{2+}$, equation (2).

$$d[Fe(bipy)_2(CN)_2]/dt = k_1[Fe(bipy)_2(CN)_2] \qquad (4)$$

The first-order rate constant for hydroxide attack at $Fe(bipy)_2(CN)_2$, *viz.* $2·0 \times 10^{-6}$ s^{-1}, is very similar to that for substitution in neutral solution, which is $2·8 \times 10^{-6}$ s^{-1}. It therefore seems likely that they both involve loss of the first bipyridyl molecule as the rate-determining step. Whereas fast disintegration of the suggested intermediate $Fe(bipy)(CN)_2(OH_2)_2$ is followed by trapping the Fe^{2+} with 1,10-phenanthroline in neutral solution, in the presence of hydroxide the Fe^{2+} is converted into $Fe(OH)_2$ which is presumably oxidised by dissolved oxygen into hydrated ferric oxide.[24]

EXPERIMENTAL

The compounds $Fe(bipy)_2(CN)_2$[6] and $Fe(SB)_2(CN)_2$,[25] where SB = *N*-(2-pyridylmethylene)-3,4-dimethylaniline, were prepared by published methods. $Fe(bipy)_2(CN)_2$

---

[16] See, *e.g.*, J. C. Lockhart, 'Introduction to Inorganic Reaction Mechanisms,' Butterworths, London, 1966, p. 35.

[17] See, *e.g.*, A. A. Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 5779; N. K. Hamer and L. E. Orgel, *Nature*, 1961, **190**, 439; M. F. A. Dove and J. G. Hallett, *J. Chem. Soc.* (*A*), 1969, 1204.

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

[19] A. Jensen, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1958, **80**, 2354.

[20] K. Madeja and E. König, *J. Inorg. Nuclear Chem.*, 1963, **25**, 377.

[21] *E.g.*, M. H. Abraham, F. Behbahany, M. J. Hogarth, R. J. Irving, and G. F. Johnston, *Chem. Comm.*, 1969, 117; M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *ibid.*, p. 930.

[22] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706; J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697, 6061.

[23] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 710.

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

[25] J. Burgess, *Spectrochim. Acta* (*A*), 1970, **26**, 1957; P. Krumholz, *Inorg. Chem.*, 1965, **4**, 609; J. Burgess and R. H. Prince, *J. Chem. Soc.* (*A*), 1967, 434.

requires several recrystallisations from aqueous methanol to remove the last traces of $Fe(bipy)_3^{2+}$. Organic solvents were AnalaR grade; mixed aqueous solvents of the compositions stated were made up by volume ratios before mixing.

Kinetic results were obtained using a Unicam SP800 recording spectrophotometer equipped with a thermostatted cell compartment. Usually runs were followed by repeated scans at intervals, in order to check that each (substitution) run exhibited an isosbestic point. Rates were calculated from optical densities at 510 nm, *i.e.* they were determined as the rate of appearance of the tris-(1,10-phenanthroline)iron(II) cation, since changes in optical density were greater here than at the wavelength of maximum absorption of $Fe(bipy)_2(CN)_2$. At relatively high proportions of non-aqueous components the wavelength of maximum absorption of $Fe(bipy)_2(CN)_2$ shifted sufficiently to longer wavelengths for the rate of disappearance for this compound to be determined; in these cases it was found that $-d[Fe(bipy)_2(CN)_2]/dt$ did equal $+d[Fe(phen)_3^{2+}]/dt$. Between four and six runs were performed for substitution in water, 20, 40, 60, and 80% ethanol; in other solvent mixtures either one or two runs only were performed.

Solubilities were determined directly by equilibrating thermostatted solutions with an excess of solid $Fe(bipy)_2(CN)_2$ over periods of several days; concentrations were determined spectrophotometrically, by comparison of optical densities with those of solutions of known concentration in the same solvent mixture. Five separate determinations were carried out for each solvent mixture; the standard deviations are 3 to 4%. The precision of the kinetic results is slightly lower, except in water where difficulties arising from the low solubility of $Fe(bipy)_2(CN)_2$ result in a standard deviation of as high as 10%.

I thank the Royal Society for a Grant-in-aid for the purchase of the spectrophotometer.

[1/1561 *Received, August* 26*th*, 1971]