Kinetics of Reaction of Tris(2,2′-bipyridyl)iron(II) with Cyanide in Aqueous Solution

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

The kinetics of the reaction between the tris(2,2′-bipyridyl)iron(II) cation and cyanide ion have been investigated, and activation parameters for this reaction determined.

MARGERUM and MORGENTHALER reported the rate law, rate constants, and activation parameters for the reaction of tris(1,10-phenanthroline)iron(II) with cyanide ion in aqueous solution.[1] We have investigated the effects of solvent composition and ligand substitution on reaction rates of a series of substituted tris(1,10-phenanthroline)iron(II) [2] and of analogous Schiff base–iron(II) [3] complexes. We now report the results of our kinetic investigation into the reaction of the tris(2,2′-bipyridyl)-iron(II) cation with cyanide ion.

RESULTS AND DISCUSSION

The reaction of primary interest taking place is [4] (1).

$$\mathrm{Fe(bipy)_3}^{2+} + 2\mathrm{CN}^- = \mathrm{Fe(bipy)_2(CN)_2} + \mathrm{bipy} \quad (1)$$

The iron(II) product was characterised by its visible absorption spectrum.[4,5] All kinetic runs were conducted in the presence of a considerable excess of cyanide; under these conditions first-order kinetics were observed up to at least 85% of complete reaction. The experimental rate law is thus (2). There was no evidence

$$-\mathrm{d}[\mathrm{Fe(bipy)_3}^{2+}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Fe(bipy)_3}^{2+}] \quad (2)$$

that the subsequent reaction (3) was taking place to a significant extent.

$$\mathrm{Fe(bipy)_2(CN)_2} + 2\mathrm{CN}^- = [\mathrm{Fe(bipy)(CN)_4}]^{2-} + \mathrm{bipy} \quad (3)$$

The dependence of observed first-order rate constants on cyanide-ion concentration * and on temperature is shown in Table 1. At each temperature the dependence of k_{obs} on cyanide concentration takes the form (4) to

$$k_{\mathrm{obs}} = k_1 + k_2[\mathrm{CN}^-] \quad (4)$$

$$-\mathrm{d}[\mathrm{Fe(bipy)_3}^{2+}]/\mathrm{d}t = \{k_1 + k_2[\mathrm{CN}^-]\}[\mathrm{Fe(bipy)_3}^{2+}] \quad (5)$$

give a rate law (5). Values of k_1 and k_2, estimated graphically, are in Table 1. This rate law for reaction

---

* Concentrations of free cyanide ion were calculated from the known amount of potassium cyanide added and the known values of the pK_a of HCN over the temperature range of these experiments (R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *Inorg. Chem.*, 1962, **1**, 828).

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

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

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

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

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

TABLE 1

Observed first-order rate constants (k_{obs}) and derived rate constants k_1 and k_2 (*cf.* text) for reaction of $Fe(bipy)_3^{2+}$ with cyanide in aqueous solution; ionic strength 0·100M, maintained by potassium chloride

	$10^4k_{obs}/s^{-1}$					
	$[CN^-]$/M					
Temp./°C	0·025	0·050	0·075	0·100	$10^4k_1/s^{-1}$	10^4k_2/ l mol^{-1} s^{-1}
25·3	4·0	6·1	7·9	9·8	2·0	77
27·0	4·8	7·7	9·7	12·0	2·7	93
28·0	5·6	8·3	11·1	13·5	3·0	107
29·5	6·8	10·4	14·2	16·5	3·5	135
32·0	10·1	15·2	19·2	23·8	5·8	179
33·3	12·7	18·0	23·6	29·2	7·1	220
35·0	15·6	19·2	28·0	35·7	8·0	280
37·4	21	31	40	49	11·5	380
40·0	31	43	55	68	18·0	500
41·8	39	55	69	78	25	570
42·9	46	66	80	95	30	670
46·0	62	92	115	141	38	1040

with cyanide closely resembles that (6) for reaction with hydroxide [6] over the same concentration range (up to 0·1M). Although over the range of acidities up to 5N

$$-d[Fe(bipy)_3^{2+}]/dt = \{k_1 + k_2[OH^-]\}[Fe(bipy)_3^{2+}] \tag{6}$$

the rate law for reaction of $Fe(bipy)_3^{2+}$ in acid solution is more complicated [it approximates to (7)] up to an acid

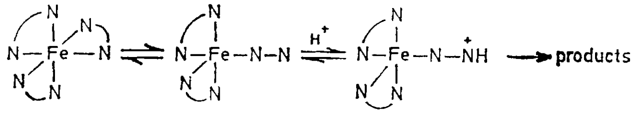
$$-d[Fe(bipy)_3^{2+}]/dt = \frac{1 + k[H^+]}{k' + k''[H^+]}[Fe(bipy)_3^{2+}] \tag{7}$$

concentration of *ca.* 0·4N this reaction too follows a rate law [7] (8) similar to that for the cyanide and hydroxide reactions. In all three reactions the k_1 term of the

$$-d[Fe(bipy)_3^{2+}]/dt = \{k_1 + k_2[H^+]\}[Fe(bipy)_3^{2+}] \tag{8}$$

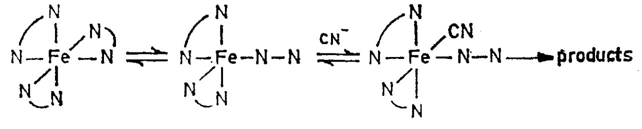
rate laws is assigned to a dissociative process, in which the loss of the first bipyridyl ligand is rate-determining. In the present cyanide reaction this assignment is based not only on the non-appearance of the cyanide concentration in this term of the rate law but also on the similarity of k_1 here to analogous k_1 values from similar rate laws for other reactions of this $Fe(bipy)_3^{2+}$ cation. Thus for the dissociation of this cation in acid solution k_1 is $1·3 \times 10^{-4}$ s^{-1} at 25·0 °C, in basic solution k_1 is $0·9 \times 10^{-4}$ s^{-1} at 25·0 °C, in neutral hydrogen peroxide k_1 is $1·4 \times 10^{-4}$ s^{-1}; in the present cyanide reaction k_1 can be estimated as $1·9 \times 10^{-4}$ s^{-1} at 25·0 °C. The fate of the transient intermediate $Fe(bipy)_2^{2+}$, or $Fe(bipy)_2(OH_2)_2^{2+}$, is uncertain. It may pick up cyanide to become $Fe(bipy)_2(CN)_2$, or may dissociate to Fe^{2+},aq and then eventually form $Fe(CN)_6^{4-}$. Comparison of initial and final optical densities suggests that both paths operate. From the k_1 values in Table 1 the activation energy for loss of the first bipyridyl from $Fe(bipy)_3^{2+}$ is 27·7 ± 0·6 kcal mol^{-1} which is, as expected, high but rather less than the value of 29·9 kcal mol^{-1} for loss of the first phenanthroline from the more stable complex $Fe(phen)_3^{2+}$.[8]

The primary interest in this paper is k_2 of rate law (5). In earlier work on this and the related reactions of $Fe(phen)_3^{2+}$ and analogous Schiff base complexes $Fe(SB)_3^{2+}$ with cyanide [1-3] this term has been assigned to direct bimolecular nucleophilic attack of cyanide at the iron atom. The k_2 term of the rate law (6) for reaction with hydroxide has similarly been ascribed to direct attack of the hydroxide at the iron atom of the complex.[6] However, there is an alternative way in which a term in cyanide concentration could arise in the rate law. In acid solution the acid-dependent part of the rate law arises from pre-equilibrium protonation of a ligand nitrogen atom in an intermediate complex containing a singly-bonded bipy ligand (Scheme 1). While there is no direct evidence in the form of isolated and characterised compounds of the type $Fe(bipy)(terpy)(OH_2)^{2+}$,[9] or $Fe(bipy)_2(py)(OH_2)^{2+}$, to support a tolerably stable intermediate (3), there are several well established chromium(III)-ethylenediamine analogues containing singly-bonded ethylenediamine.[10] An analogous mechanism should be considered for the reaction with cyanide, for although cyanide cannot add to the nitrogen of a singly-bonded bipyridyl ligand it could take up the vacant co-ordination site on the iron as shown in Scheme 2 to give a similar kinetic pattern. Intermediate (4) is likely to be a more stable species than intermediate (3) in view of the greater crystal-field stabilising effect of cyanide than of water. At first sight this seems inconsistent with the greater reactivity of cyanide ion than of hydrogen ion (Table 3), but in fact the derived k_2 values include the equilibrium constants for (2) $\rightleftharpoons$ (3) and (2) $\rightleftharpoons$ (4), which cannot be estimated.



(1) (2) (3)

SCHEME 1



(1) (2) (4)

SCHEME 2

In an attempt to choose between the two possible mechanisms, (1) $\rightleftharpoons$ (2) $\rightleftharpoons$ (4) $\longrightarrow$ products and direct nucleophilic attack by cyanide, we have conducted experiments at considerably higher cyanide concentration to see if there is any indication of the approach to a limiting rate which would indicate the former mechanism

---

[6] Ref. 1, and J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

[7] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 1st edn., Wiley, New York, 1958, pp. 152—155; J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061.

[8] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752.

[9] J. Burgess, *J.C.S. Dalton*, 1972, 203.

[10] See, *e.g.*, R. F. Childers, K. G. Van der Zyl, D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 1968, **7**, 749, 2678.

[*cf.* equation (7)]. Observed first-order rate constants were 0·0010, 0·0018, 0·0026, and 0·0036 s^{-1} for cyanide-ion concentrations of 0·20, 0·40, 0·60, and 0·80M (in all cases ionic strength was 0·80M, maintained by potassium chloride) at 27·0 °C. The linearity of this dependence of rate on cyanide-ion concentration gives no positive support for the $(1) \rightleftharpoons (2) \rightleftharpoons (4) \longrightarrow$ products mechanism, but one cannot rule out the possibility of approach to a limiting rate at experimentally inaccessibly high cyanide concentrations. The estimated second-order rate constant, k_2, at an ionic strength of 0·80M is 0·0041 l mol^{-1} s^{-1} at 27·0 °C; at an ionic strength of 0·10M, k_2 at 27· 0 °C is 0·0093 l mol^{-1} s^{-1} (Table 1). The quotient of the difference between the logarithms of these rate constants and between the square roots of the respective ionic strengths is −1·8, which is close to the value of −2·0 predicted from Debye–Hückel theory for reaction between a cation of charge +2 and an anion of charge −1.

It is impossible to be sure that the potassium chloride used to maintain ionic strengths is an inert material. Perchlorates cannot be used to maintain ionic strengths since the perchlorate of the complex cation is far too sparingly soluble in water. The best that can be done is to compare the effect of chloride and of some other anion, here nitrate, to see if there is any significant difference. At a cyanide-ion concentration of 0·20M observed first-order rate constants, at 27·0 °C, were 0·00098 and 0·00100 s^{-1} for duplicate runs in the presence of 0·60M-potassium chloride, and 0·00096 and 0·00102 s^{-1} in the presence of 0·60M-potassium nitrate.

At the high ionic strengths of the present investigation, the Debye–Hückel theory's support for the direct bimolecular cyanide attack mechanism can be considered only tentative. There are two other considerations that also tend to support the direct-attack mechanism. The first is simply the comparison of activation parameters (Table 2) for reaction of $Fe(bipy)_2^{2+}$ and cyanide with those for $Fe(phen)_3^{2+}$ with cyanide; for while the flexible bipyridyl ligand would permit intermediates of the type (4) above, the rigid phenanthroline ligand should not. Table 2 shows a fair measure of agreement between the activation parameters for the two systems. The simple electrostatic model [11] for estimating the activation entropy for a reaction between ions in solution suggests that for simple bimolecular cyanide attack, in this case involving ions of charge +2 and −1 and sum of radii between 5 and 6 Å, the activation entropy should be +6 to +8 cal mol^{-1} K^{-1}; the observed value of +9 cal mol K^{-1} is in close agreement with this. We have thus several pieces of evidence which tentatively suggest a direct bimolecular mechanism, rather than the $(1) \rightleftharpoons (2) \rightleftharpoons (4) \longrightarrow$ products mechanism, for cyanide attack at $Fe(bipy)_3^{2+}$, but this evidence is not unequivocal.

TABLE 2

Activation parameters for reaction of $Fe(LL)_3^{2+}$ complexes with cyanide

		$\Delta H_{\ddagger}$ kcal mol^{-1}	$\Delta S_{\ddagger}$ cal mol^{-1} K^{-1}	Ref.
$Fe(bipy)_3^{2+}$	Water	23·0 ± 0·8	+9	This work
$Fe(phen)_3^{2+}$	Water	20 ± 3	−3	1
$Fe(SB)_3^{2+}$	95% MeOH	20·4 ± 1·0	+10	3

SB = Schiff base from aniline plus pyridine-2-carbaldehyde.

TABLE 3

Comparison of second-order rate constants for reaction of $Fe(bipy)_3^{2+}$ and its methyl-substituted derivatives with cyanide, hydroxide, and acid

	$k_{308}(CN^-)$	$k_{298}(OH^-)$	$k_{298}(H^+)$
$Fe(bipy)_3^{2+}$	0·028	0·0070	0·0018
$Fe(5,5'\text{-diMebipy})_3^{2+}$		0·0057	0·0033
$Fe(4,4'\text{-diMebipy})_3^{2+}$	0·018	0·0060	0·0093

The effects of ligand substituents on reactivities is shown in Table 3. Methyl substituents in the 4- and 4′-positions affect reactivities by their electron-donating properties modifying the iron–nitrogen bond strength and the electron density around the iron. Methyl substituents in the 5- and 5′-positions will also have this effect, though to a smaller extent, and may also affect reactivities by the introduction of some steric strain (' buttressing effect ') into the initial and perhaps the transition state. The interesting features of the results in Table 3 are the parallel reactivity trends for k_2 values for cyanide and hydroxide attack and the opposite trend for k_2 values for acid aquation. This pattern is not inconsistent with a similar bimolecular attack at iron mechanism for both cyanide and hydroxide reactions and the rather different multi-intermediate path $[(1) \rightleftharpoons (2) \rightleftharpoons (3) \longrightarrow$ products] for the k_2 term for acid aquation.

In 50% ethanol the reaction of $Fe(bipy)_3^{2+}$ with cyanide is very much faster; in this solvent $k_2 = 0{\cdot}42$ l mol^{-1} s^{-1}, while k_1 is too small to detect. This behaviour closely parallels that observed in the analogous Schiff base–iron(II) complexes, where rates of bimolecular cyanide attack increase rapidly as the proportion of alcohol in the solvent increases but dissociation rates remain roughly the same and thus become swamped at high proportions of alcohol.

EXPERIMENTAL

The tris(2,2′-bipyridyl)iron(II) complex solution was prepared from AnalaR iron(II) ammonium sulphate and a slight excess of the ligand. Potassium cyanide and potassium chloride solutions were prepared from AnalaR materials. Reactions were carried out in 1 cm silica cells in the thermostatted cell holder of a Unicam SP 800A recording spectrophotometer. Optical densities were measured at 526 nm, the wavelength of maximum absorption of the starting material.

I acknowledge the award by the Royal Society of a grant-in-aid for the purchase of the spectrophotometer, and the assistance of Mr. J. A. Evans in computing (Elliott 803) activation parameters and their standard deviations.

[1/1458 *Received*, 16*th August*, 1971]

---

[11] K. J. Laidler, ' Reaction Kinetics,' vol. 2, Pergamon, Oxford, 1963, pp. 11—13.