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Kinetics of Reaction of Substituted Tris-(1,10-phenanthroline)iron(II) Complexes with Cyanide

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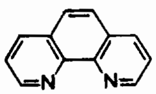
The kinetics of reaction of a series of substituted tris-(1,10-phenanthroline)iron(II) complexes with cyanide in aqueous solution and in 50% (v/v) aqueous ethanol have been investigated. For all the complexes studied the mechanism is predominantly associative in character. Second-order rate constants for reaction with cyanide vary in the expected manner with the nature of the ligand substituents; these rate constants correlate with the respective second-order rate constants for hydroxide attack.

Introduction

Several years ago Margerum and Morgenthaler[1] reported the kinetics of reaction, in aqueous solution, of the tris-(1,10-phenanthroline)iron(II) cation (ligand I) with cyanide. This reaction produces the previously characterised mixed ligand complex bis-(1,10-phenanthroline)biscyanoiron(II):[2]

$$\mathrm{Fe(phen)_3^{2+} + 2CN^- \longrightarrow Fe(phen)_2(CN)_2 + phen} \qquad (1)$$

Recently we have investigated the effect of ligand substituents on reaction rates for the analogous reaction of iron(II) complexes of the Schiff base ligands II in aqueous alcohols.[3] To link these two studies we now report the kinetics of reaction of a series of substituted tris-(1,10-phenanthroline)iron(II) complexes with cyanide in water and in 50% (v/v) aqueous ethanol.



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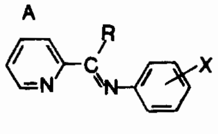

II

Results

In all runs cyanide was present in large excess and first-order kinetics were observed up to at least 85% of complete reaction. The products, Fe(X-phen)$_2$-(CN)$_2$, were characterised by their visible absorption spectra.[4] Further reaction to Fe(X-phen)(CN)$_4^{2-}$ was negligible under the conditions of this investigation. Observed first-order rate constants (k_{obs}) for reaction in aqueous solution are reported in Table I, for reaction in 50% aqueous ethanol in Table II. In all cases plots of k_{obs} against cyanide concentration are linear; in most cases the plot passes through the origin within experimental uncertainty, though in a few cases there is a small positive intercept on the rate axis. The significance of this intercept is discussed below. A typical k_{obs} against cyanide concentration plot is shown in Figure 1. The general rate law of the reaction is thus:

$$-d[\mathrm{Fe(X\text{-}phen)_3^{2+}}]/dt = \{k_1 + k_2[\mathrm{CN^-}]\}[\mathrm{Fe(X\text{-}phen)_3^{2+}}] \qquad (2)$$

with k_1 generally much smaller than $k_2[\mathrm{CN^-}]$. From the observed first-order rate constants reported in Tables I and II second-order rate constants k_2, as defined by equation (2) above, were determined graphically; the results are also included in Tables I and II. These tables contain one further set of data, second-order rate constants for attack by hydroxide,[5-7] which are relevant to the following discussion.

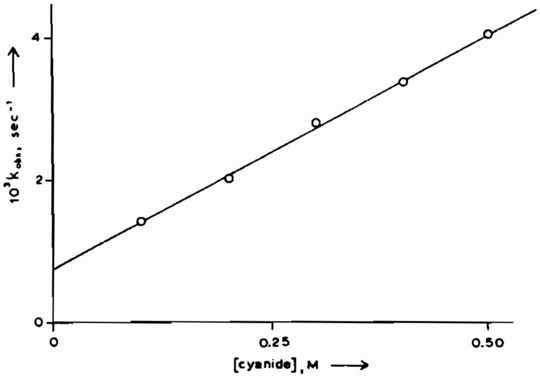

Figure 1. The dependence of observed first-order rate constants (k_{obs}) on total cyanide concentration for tris-(3,5,6,8-tetramethyl-1,10-phenanthroline)iron(II) in aqueous solution at 35.0°C.

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[1] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, *84*, 706 (1962).
[2] G. A. Barbieri, *Atti accad. Lincei*, *20*, 273 (1934); A. A Schilt, *J. Amer. Chem. Soc.*, *79*, 5421 (1957); *82*, 3000 (1960).
[3] J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R D. Wyvill, *J. Chem. Soc.*, (A), 44 (1971).
[4] J. Burgess, *Spectrochim. Acta* (A), *26*, 1369, 1951 (1970).
[5] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 4697 (1965).
[6] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 6061 (1965)
[7] J. Burgess, *J. Chem. Soc.* (A), 431 (1967).

Table I. Observed first-order rate constants (k_{obs}) and derived second-order rate constants ($k_2(CN^-)$)for cyanide attack at substituted tris-(1,10-phenanthroline)- and tris-(2,2'-bipyridyl)-iron(II) complexes in aqueous solution at 35.0°C, ionic strength 0.50 *M*. Second-order rate constants $k_2(OH^-)$) for hydroxide attack are also included for comparative purposes

		10^3k_{obs}, sec^{-1}						
				[KCN], *M*			k_2 (CN^-)	k_2 (OH^-)
	Subst.	0.10	0.20	0.30	0.40	0.50	M^{-1} sec^{-1}	M^{-1} sec^{-1}
phen								
	none	4.7	8.3	12.0	15.6	18.8	0.034	0.039 [a]
	5—Cl	11	20	29	39	46	0.10	0.18 [a]
	5—Me	1.7	3.2	4.7	6.4	7.9	0.016	0.015 [a]
	5,6—diMe	0.47	0.85	1.16	1.66	2.12	0.0042	0.0021 [a]
	4,7—diMe	0.9	1.5	2.1	2.4	3.4	0.006 [d]	0.0029 [a]
	3,5,6,8—tetraMe	1.4	2.0	2.9	3.3	4.0	0.007	0.0023 [a]
	3—SO_3^-	9.5	14	17	22	26	0.042	0.20 [b]
	5—SO_3^-	2.7	4.6	6.5	7.6	9.4	0.017	0.066 [b]
bipy								
	4,4'—diMe	3.7	4.9	6.8	8.5	10.4	0.018	0.015 [c]

			[KCN], *M*			
		0.033	0.067	0.100		
phen						
	$5NO_2$	20	37	53	0.51	0.29 [a]

[a] From reference 5. [b] From reference 7. [c] From reference 6. [d] Approximate value *cf.* text.

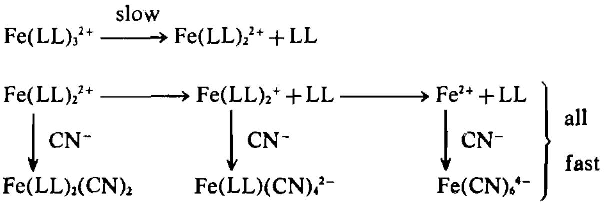
Table II. Observed first-order rate constants (k_{obs}) and derived second-order rate constants ($k_2(CN^-)$) for cyanide attack at substituted tris-(1,10-phenanthroline)iron(II) complexes in 50% aqueous ethanol at 35.0°C, ionic strength 4.0×10^{-3} *M*

					10^3 k_{obs}, sec^{-1}				
					10^4[KCN], *M*				$k_2(CN^-)$
	Subst.	4.0	8.0	12.0	16.0	24.0	32.0	40.0	M^{-1} sec^{-1}
phen									
	none	1.3	1.8	3.1	4.8	6.0			2.7
	5—NO_2	32	51	70	120				70
	5—Me				1.7	2.5	3.4	4.4	
	5,6—diMe				0.21	0.30	0.37	0.50	0.12
	4,7—diMe		0.16		0.35	0.56	0.68	0.85	0.21
	5—SO_3^-		0.27		0.30	0.34	0.40	0.44	0.06
	5—Ph				6.1	9.0	10	14	3.0
	4,7—diPh				1.7	2.2	2.7	3.9	0.8

There were several difficulties in determining the kinetics in aqueous solution. Results for the 4,7-dimethyl complex are approximate as the product started to crystallise out of solution before completion of reaction. It was therefore necessary to use an estimated value for final optical density. No kinetic results could be obtained for the 5-phenyl complex since the product started to precipitate at an early stage of the reaction, nor for the 4,7-diphenyl complex since in this case the starting tris-complex is insoluble in water.

Discussion

Mechanism. The general rate law reported in the previous section (equation (2)) is the same as that reported for the unsubstituted complex by Margerum and Morgenthaler.[1] The values for the second-order rate constants from the two investigations are in reasonable agreement. The two-term rate law of equation (2) indicates two parallel reaction pathways. The first, k_1, term is independent of cyanide concentration, which suggests a mechanism involving rate determining loss of a phenanthroline ligand. There are several likely subsequent fast reactions, between which it is not possible to choose due to product characterisation difficulties arising from the paucity of chemical and spectroscopic information available on the mixed ligand complexes:



The nature of the initial slow step is confirmed by comparison of k_1 values for reaction in the presence of cyanide with known k_1 values for aquation of the respective complexes. For the three cases where the k_1 term of equation (2) is not negligible in comparison with $k_2[CN^-]$ there is acceptable agreement. Thus for the reaction of the 3,5,6,8-tetramethyl complex k_1 for the cyanide reaction is 0.0007 sec^{-1}, whereas k_1 for acid aquation[8] is 0.0006 sec^{-1}, at 35 °C.

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(8) J. Burgess and R. H. Prince, *J. Chem. Soc.*, 5752 (1963).

For the 3-sulphonato complex the values are 0.005 and 0.004[7] sec^{-1} respectively, while for the 4,4′-dimethyl-2,2′-bipyridyl analogue the values are 0.0010 and 0.008[6] sec^{-1} respectively.

The second, and dominant, term in the rate law is first-order in cyanide and thus suggests bimolecular attack at the complex, despite the high electron density in the t_{2g} orbitals which the incoming cyanide must penetrate. At the concentrations used in the experiments in aqueous solution the cyanide will be present almost entirely as the simple anion; the concentration of HCN will account for less than 1.5% of the total cyanide.[10] However in the runs in 50% ethanol the cyanide concentration is lower, and the dielectric constant of the solvent is also lower, so the proportion of cyanide present as HCN rather than as CN^- will increase considerably. It is, unfortunately, impossible to estimate the $HCN:CN^-$ ratio in 50% ethanol since the requisite thermodynamic parameters for ionisation of HCN in mixed aqueous alcoholic solvents are not available. Nor are they readily available by experiment or interpolation in view of the complicated nature of the interactions between the various components in acidic mixed aqueous solvents.[11] Nonetheless the rate law of equation (2) still holds in 50% ethanol, with $[CN^-]$ standing for total concentration of cyanide. Whether this should be interpreted as parallel attack of CN^- and of HCN at the complex, or as attack only of CN^- with corresponding adjustments to the apparent second-order rate constants to allow for inactive HCN, cannot be decided on the currently available evidence. The correspondence of k_1 in cyanide solution with k_1 for acid aquation still applies in 50% ethanol, for instance for the 5-sulphonato complex the respective values are 2.0 and 2.5×10^{-4} sec^{-1}.

Substituent effects. The effects of ligand substituents on cyanide attack (*i.e.* k_2 in equation (2)) are as anticipated from the known electron -releasing and -withdrawing properties of the various substituents. Thus nitro or chloro groups withdraw electrons, reduce the electron density in the vicinity of the iron atom and thus facilitate nucleophilic attack; electron-releasing methyl groups have the opposite effect.

Comparison with hydroxide attack. There is an obvious parallel between the bimolecular attack of cyanide proposed here and the bimolecular attack by hydroxide previously demonstrated for these complexes.[1,5,12*] If indeed both reactions simply involve direct bimolecular attack of cyanide or of hydroxide at the central iron atom then one might expect a direct correlation of rate constants. This hypothesis is tested in Figure 2, wherein are plotted the logarithms of the respective second-order rate constants (data from Table I). There is a good linear correlation for all but three complexes, and moreover the rate constants for hydroxide and for cyanide attack are of comparable magnitude. The 5-nitro complex probably lies off the correlation line by reason of its mechanism of reaction with hydroxide, whose peculiarities[5] have yet to be satisfactorily resolved.[13] The other two deviant points are for the two sulphonato complexes. These complexes have two distinctive, and probably closely connected characteristics — that they contain charged ligands (the substituent is $-SO_3^-$ in neutral solution[7]) and are very much more readily solvated by water[14] than the other complexes in this study. The anomalously low rate constants for cyanide attack at the sulphonato complexes might therefore be attributed to solvation effects. Whereas the cyanide must penetrate the solvation shell of the complex to approach the iron, a hydroxide ion can be generated in close proximity to the iron by proton transfer from one of the water molecules lying between the planar ligands[15] to bulk solvent. The point for the 4,4′-dimethyl-2,2′-bipyridyl complex lies on the correlation line of Figure 2. There is thus no difference between the phenanthroline and bipyridyl series of complexes. It is not possible to include tris-Schiff base (ligand II above) complexes in the correlation since they are insoluble in water, and rates of hydroxide attack in aqueous al-

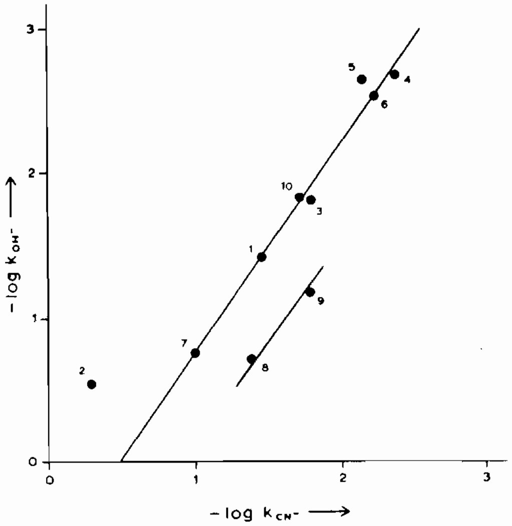

Figure 2. Correlation of logarithms of second-order rate constants for cyanide attack (k_{CN^-}) with those for hydroxide attack (k_{OH^-}) for substituted tris-(1,10-phenanthroline)iron(II) (points 1-9) and substituted tris-(2,2′-bipyridyl)iron(II) (point 10) cations. Substituents: 1, none; 2, 5-nitro; 3, 5-methyl; 4, 5,6-dimethyl; 5, 3,5,6,8-tetramethyl; 6, 4,7-dimethyl; 7, 5-chloro; 8, 3-sulphonato; 9, 5-sulphonato; 10, 4,4′-dimethyl.

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(9) F. Basolo and F. P. Dwyer, *J. Amer. Chem. Soc.*, *76*, 1454 (1954); L. Cambi and A. Cagnasso, *Gazz. Chim. Ital.*, *63*, 767 (1933); *64*, 772 (1935).

(10) H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 2332 (1931).

(11) F. Franks and D. J. G. Ives, *Quart. Rev.*, *20*, 1 (1966).

(12) D. W Margerum, *J. Amer. Chem. Soc.*, *79*, 2728 (1959).

(*) Recent work on the reaction of the tris-(1,10-phenanthroline)- and tris-(2,2′-bipyridyl)-iron(II) cations with hydroxide (G. Nord and T. Pizzino, *Chem. Comm.* 1633 (1970)) has indicated that the presence of oxygen is necessary for reaction to proceed. However as the proposed mechanism involves rapid oxidation subsequent to rate-determining hydroxide attack it is still possible to compare observed secondorder rate constants for cyanide and hydroxide attack at iron in these complexes.

(13) R. D. Gillard, personal communication.

(14) J. Burgess, *J. Chem. Soc.* (A), 2728 (1968).

(15) A. Jensen, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, *80*, 2354 (1958); L. Seiden, F. Basolo, and H. M. Neumann, *ibid.*, *81*, 3809 (1959).

cohols (ROH) are inaccessible due to the possibility of parallel OH^- and OR^- attack.

Reaction in 50% ethanol. As mentioned in the preceding paragraph no direct correlation of hydroxide and cyanide rate constants is possible in this mixed aqueous solvent. Also the lack of knowledge of $HCN:CN^-$ ratios described earlier prevents unequivocal determination of precise second-order rate constants for attack by the CN^- ion. Nonetheless some qualitative discussion of rates in 50% ethanol is possible and informative. The most obvious feature is that reaction with cyanide is very much faster in 50% ethanol than in water, which is the expected trend for reaction between oppositely charged species. Also the trend is k_2 values in 50% ethanol, *viz.*, k_2 for 5-nitro > unsubstituted > 5-methyl > 4,7-dimethyl > 5,6-dimethyl, is the same as in water, though the range of rates, like the rate constants themselves, is larger in the mixed solvent. Thus k_2(5-nitro)/k_2(5,6-dimethyl) is 130 in water, 580 in 50% ethanol. The results for the 5- sulphonato complex are again anomalous.

It was not possible, due to insolubility difficulties, to determine the effect of phenyl substituents on reactivities in aqueous solution, as reported in the Results section. Solubilities in 50% ethanol are more favourable, so kinetic results for reaction of the 5-phenyl and for the 4,7-diphenyl complex with cyanide in this solvent mixture are available. Substituent effects on reactivity are similar to those observed in other similar reactions, for instance in acid aquation of these complexes. In cyanide reaction and acid aquation a 5-phenyl group has little effect, in both cases causing a rate increase of about 10%. The figures for cyanide attack are in Table II; for acid aquation[8] the first-order rate constant for the unsubstituted complex in water at 25°C is 7.3×10^{-5} sec^{-1}, for the 5-phenyl complex 8.0×10^{-5} sec^{-1}. A slightly greater effect is produced by 4,7-diphenyl substitution, which results in a roughly threefold decrease in rates of both cyanide attack and acid aquation. Again the cyanide results are in Table II; for acid aquation, this time in 60% methanol at 25°C, rate constants are 14×10^{-5} sec^{-1} for the unsubstituted complex and 4.5×10^{-5} sec^{-1} for the 4,7-diphenyl complex.[16]

4,7-Dihydroxy complex. Attempts were made to estimate the second-order rate constant for cyanide attack on this complex. This determination would be of particular interest in assessing the reactivity of this complex to associative nucleophilic attack since a rate constant for hydroxide attack cannot be obtained. In sodium hydroxide solution the ligand substituents become $-O^-$ rather than $-OH$; moreover the rate of reaction of the 4,7-di-O^- complex with hydroxide ion is extremely slow.[17] Precise determination of k_2 for cyanide attack at the 4,7-di-OH complex is not possible, since the dithionite necessarily present in the complex solution interferes with the reaction, but initial rate estimates indicate fairly fast reacion of this complex with cyanide, with a rate constant in the region of that for the 5-chloro complex.

Experimental Section

Solutions of the substituted tris-(1,10-phenanthroline) and tris-(2,2'-bipyridyl)iron(II) complexes were made up from iron(II) ammonium sulphate and a slight excess of ligand. Potassium cyanide and potassium chloride solutions were made up directly from AnalaR material. Concentrations of reagents are indicated in the Table captions; ionic strengths were maintained by the use of potassium chloride in aqueous solution, potassium nitrate in 50% ethanol. Reactions were carried out in 1 cm silica cells in the thermostatted cell holder of a Unicam SP 800A recording spectrophotometer. Optical density readings were made at 510 mμ for the substituted 1,10-phenanthroline complexes, at 525 mμ for the 4,4'-dimethyl-2,2'-bipyridyl complex; these wavelengths are at or near the wavelengths of maximum absorption of the tris-ligand complexes.

Acknowledgements. Thanks are due to the Royal Society for a Grant-in-aid for the purchase of the spectrophotometer, and to Dr. Gwyneth Nord for providing pre-publication information on the effect of oxygen on the reactions of these iron(II) complexes with hydroxide.

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(16) J. Burgess, Ph. D. thesis, Cambridge, 1963 p. 42.

(17) A. A. Schilt, G. F. Smith, and A. Heimbuch, *Analyt. Chem.*, *28*, 809 (1956).