

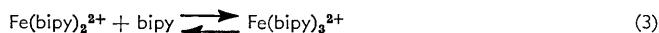
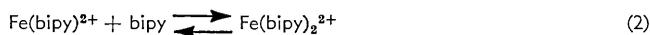
1132. Kinetics of Reactions of Ligand-substituted Tris-(2,2'-bipyridyl)iron(II) Complexes

By J. BURGESS and R. H. PRINCE

The kinetics of several reactions of the tris-(2,2'-bipyridyl)iron(II) cation and its 4,4'-dimethyl, 5,5'-dimethyl, and 4,4'-diphenyl derivatives have been studied. The reactions were those of ligand dissociation in presence of hydrogen and hydroxide ions, oxidation in presence of hydrogen peroxide, and reaction with fluoride ion. In the case of hydrogen peroxide, reaction with several tris-(1,10-phenanthroline)iron(II) complexes has also been investigated. Kinetics of reactions of the iron(II) complex of the related ligand 2,2':6',2''-terpyridyl are reported and compared with the 2,2'-bipyridyl case.

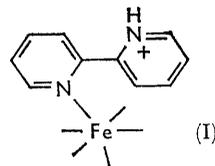
THE kinetics of reactions of the iron(II) tris-complexes of 2,2'-bipyridyl and of 1,10-phenanthroline form an interesting comparison. Thus, although the kinetics of ligand replacement in sodium hydroxide solution are similar for the two complexes, kinetics of reactions in acid solution are different.^{1,2} Kinetic results for several reactions of iron(II)-bipyridyl complexes are reported here, together with results for the iron(II) complex of the related ligand 2,2':6',2''-terpyridyl.

Previous work on the formation and dissociation equilibria of the iron(II)-2,2'-bipyridyl complexes showed that these equilibria are similar to those of the iron(II)-1,10-phenanthroline complexes.^{1,3}*



Equilibria (1) and (2) are rapidly attained, equilibrium (3) relatively slowly. As in the case of the iron(II)-1,10-phenanthroline complexes, there is a change of spin type associated with reaction (3).⁴

Acid Fission.—The difference in behaviour between the tris-2,2'-bipyridyl and 1,10-phenanthroline complexes of iron(II) in acid solution lies in the large effect of acid concentration on the rate of the former and the small effect on the latter.^{1,2} Protonated intermediates have been suggested to explain the acid dependence in the bipyridyl case;^{2,5} they are more likely with the flexible 2,2'-bipyridyl ligand, in which structures such as (I) are possible, than with the rigid 1,10-phenanthroline. Spectroscopic evidence for protonated intermediates has been presented,⁶ and disputed.⁷



We have found that the rates of acid fission for all the tris-bipyridyl complexes studied, over the concentration range 0—0.24N (sulphuric acid), are given by the expression

$$\text{Rate} = k_1 + k_2[\text{H}^+] \quad (4)$$

This dependence is illustrated for the unsubstituted tris-(2,2'-bipyridyl)iron(II) complex

* Co-ordinated water, though of undoubted importance (A. F. Richards, J. H. Ridd, and M. L. Tobe, *Chem. and Ind.*, 1963, 1737), is ignored in these equations.

¹ J. H. Baxendale and P. George, *Nature*, 1948, **162**, 777.

² J. H. Baxendale and P. George, *Trans. Faraday Soc.*, 1950, **46**, 736.

³ T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596.

⁴ F. Basolo and F. P. Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454; L. A. Welo, *Phil. Mag.*, 1928, [7], **6**, 481.

⁵ P. Krumholz, *Nature*, 1949, **163**, 724; J. H. Baxendale and P. George, *ibid.*, p. 725.

⁶ F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807.

⁷ A. A. Schilt, *J. Amer. Chem. Soc.*, 1963, **85**, 904.

in Figure 1. A more complicated dependence of rate on hydrogen-ion concentration has been observed over a wider concentration range.⁶ Average first-order rate constants are given in Table 1, with values of k_1 and k_2 obtained graphically.

The rate expression (equation 4) implies a mechanism consisting of two simultaneous reactions, one involving direct participation of hydrogen ion in the rate-determining step, the other not. The ratio of k_1 to k_2 (cf. Table 1) is approximately the same for all the complexes studied, so that substituent effects are similar in the two reactions.

Spectroscopic data on methyl substitution in 2,2'-bipyridyl and the biphenyl systems are relevant to an interpretation of its effect on acid fission. As pyridine and its derivatives exhibit spectroscopic behaviour similar to that of the corresponding benzene compounds, results for the more fully studied biphenyl system can be applied to the corresponding bipyridyl compounds.

TABLE 1
First-order rate constants (min.^{-1}) for acid fission of tris-(2,2'-bipyridyl)iron(II) complexes at 25.0°

Substituent	Sulphuric acid concentration					k_1 (min.^{-1})	k_2 ($\text{l. mole}^{-1} \text{ min.}^{-1}$)
	0.049N	0.097N	0.146N	0.194N	0.243N		
None	0.0105	0.0134	0.0164	0.0190	—	0.0077	0.11
4,4'-Dimethyl	0.034	0.050	0.063	0.075	—	0.022	0.56
5,5'-Dimethyl	0.0154	0.0205	0.0249	0.0303	—	0.011	0.20
None (25% MeOH)	0.0060	0.0074	0.0097	0.0109	0.0141	0.0043	0.08
4,4'-Diphenyl (25% MeOH)	0.021	0.025	0.034	0.045	0.056	0.016	0.30

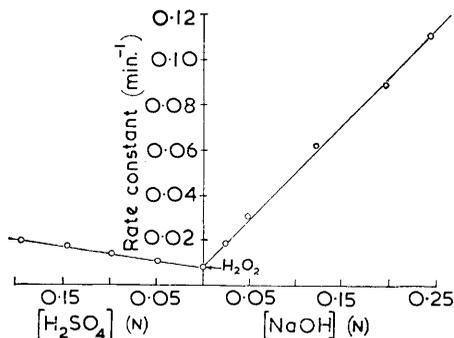


FIGURE 1. Kinetic summary for the ligand dissociation of the unsubstituted tris-(2,2'-bipyridyl)iron(II) complexes at 25° in presence of acid, alkali, and hydrogen peroxide. The point marked "H₂O₂" was obtained at a hydrogen peroxide concentration of 0.45M

Molecular orbital⁸ and valence bond⁹ theories of the biphenyl molecule forecast some double-bond character in the inter-ring (1,1') bond; there is ultraviolet spectroscopic evidence for some π -character in this bond. Ultraviolet spectroscopic results for 2,2'-bipyridyl imply some double-bond character in the inter-ring (2,2') bond of this compound also, but the extent of π -bonding appears to be less in the bipyridyl than in the biphenyl molecule.¹⁰

Methyl substitution in the 4- and 4'-positions of biphenyl increases the intensity of the conjugation band, a result ascribed to increased double-bond character in the inter-ring bond.¹¹ We have found a similar effect in the 2,2'-bipyridyl system; 5,5'-dimethyl substitution appears to increase markedly the degree of π -bonding in this bond, 4,4'-dimethyl substitution has a smaller effect. Spectral details are listed in Table 2. Similar effects were found in the spectra of the iron(II) tris-complexes of these ligands. Greater

⁸ C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188; H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, 1963, p. 389 *et seq.*

⁹ G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, 1944, p. 114.

¹⁰ P. E. Fielding and R. J. W. Le Fèvre, *J.*, 1951, 1811.

¹¹ G. H. Beaven and E. A. Johnson, *Spectrochim. Acta*, 1959, **14**, 67.

TABLE 2
Spectroscopic properties of unsubstituted and methyl-substituted 2,2'-bipyridyls
and their iron(II) tris-complexes

Substituent	Ligand u. v.		Complex		u. v. $\lambda_{\max.}$
	$\lambda_{\max.}$ (m μ)	ϵ	$\lambda_{\max.}$ (m μ)	ϵ	
None	280	12,900	522	8650	297
4,4'-Dimethyl	281	14,100	529	8470	295
5,5'-Dimethyl	289	18,300	510	8310	303

inter-ring double-bonding in the 5,5'-dimethyl complex should lead to more delocalisation in the chelate ring and hence to greater stability of the iron(II) complex.

Methyl substitution in the tris(bipyridyl)iron(II) complex causes the rate of acid fission to increase; the effect is greater for 4,4'- than for 5,5'-substitution. The methyl groups in the 4,4'-complex are *para* to the nitrogen atoms, so their electron-releasing effect will exert a greater influence on the iron-nitrogen bonding than will that of 5,5'-methyl groups. This explanation is consistent with the experimental results, and the spectroscopic evidence, which forecasts greater stability and stronger bonding in the 5,5'- than in the 4,4'-dimethyl complex. Greater chelate stabilisation in the 5,5'-complex lowers the initial-state energy and so gives a larger activation energy if the effect on the energy of the looser transition state is less; the larger activation energy is reflected in the slower rate of reaction for the 5,5'-dimethyl complex.

4,4'-Diphenyl substitution causes an increase in the rate of dissociation in acid solution. Comparison of the pK_{NH^+} values (in 50% dioxan) of 4,4'-diphenyl (pK 3.25) and unsubstituted (pK 3.62) 2,2'-bipyridyls¹² shows that the phenyl substituents decrease the availability of the lone pairs on the nitrogen atoms in the free ligand. This implies weaker iron-nitrogen σ -bonding in the phenyl-complex, which is consistent with the easier dissociation of the 4,4'-diphenyl complex.

Alkali Fission.—The kinetics of alkali fission of tris-(2,2'-bipyridyl)iron(II) complexes are analogous to those of ferroins.¹³ They can be represented (Figure 1) over the range of hydroxide concentrations studied (up to 0.243M-sodium hydroxide) by the expression

$$\text{Rate} = k_1 + k_2[\text{OH}^-] \quad (5)$$

Average first-order rate constants for alkali fission at various excess sodium hydroxide concentrations at 25.0° are given in Table 3. Alkali fission of the 4,4'-diphenyl complex has not been studied since it is not soluble in water.

TABLE 3
First-order rate constants (min.⁻¹) for alkali fission of tris-(2,2'-bipyridyl)iron(II)
complexes at 25.0

Substituent	Sodium hydroxide concentration								k_1 (min. ⁻¹)	k_2 (l. mole ⁻¹ min. ⁻¹)
	0.012M	0.024M	0.049M	0.073M	0.097M	0.121M	0.194M	0.243M		
None	—	0.0185	0.0302	—	—	0.061	0.089	0.111	0.009	0.42
4,4'-Dimethyl	—	0.047	0.074	0.089	0.111	—	—	—	0.016	0.36
5,5'-Dimethyl	0.0138	0.0201	0.0302	—	—	0.058	0.077	0.096	0.013	0.34

Equation (5) implies that alkali fission of tris-(2,2'-bipyridyl)iron(II) complexes, like alkali fission of the similar 1,10-phenanthroline compounds, occurs by a mechanism involving two simultaneous reactions, one with direct participation by hydroxide ion, the other not. In the case of the 1,10-phenanthroline complexes it was shown that the hydroxide-independent part of alkali fission was analogous to acid fission; the formation-dissociation equilibria for the tris-complex were pulled in the direction of dissociation by

¹² B. R. James, D.Phil. Thesis, Oxford, 1960.

¹³ J. Burgess and R. H. Prince, *J.*, 1965, 4697.

protonation of ligand molecules in acid and by formation of sparingly soluble ferrous hydroxide in alkali. As these two processes have a common rate-determining step (loss of one ligand molecule from the tris-complex) the equality of rate constants is explained. The bipyridyl case is complicated by the dependence on acid concentration of the rate of acid fission, but if the acid-independent rate constant (k_1 in equation 4) for each complex is compared with the hydroxide-independent rate constant (k_1 in equation 5) for each complex (Table 4), striking similarities are apparent. In each case acid and alkali values can be said to be equal within experimental error. There is thus a dissociative contribution common to acid and alkali fission of tris-(2,2'-bipyridyl)iron(II) complexes, just as has been demonstrated for tris-(1,10-phenanthroline)iron(II) complexes.

The effect of methyl substitution on the k_1 (alkali-independent) rate constants is, as expected, the same as on the k_1 (acid-independent) rate constants in the acid fission reaction of these complexes. Rate constants for hydroxide attack (k_2 in equation 5) on both dimethyl complexes are lower than for hydroxide attack on the unsubstituted bipyridyl complex. This is consistent with electron release by the methyl groups to the nitrogen and iron atoms across the conjugated ring system, thereby increasing electron density in the vicinity of the iron atom and discouraging nucleophilic attack by the hydroxide ion. The difference between the rate constants for hydroxide attack on the 4,4'- and 5,5'-dimethyl complexes is not large enough to be significant.

TABLE 4

Concentration-independent rate constants for acid and alkali fission of tris-(2,2'-bipyridyl)iron(II) complexes at 25.0

Substituent	k_1 (alkali) (min. ⁻¹)	k_1 (acid) (min. ⁻¹)
None	0.009	0.008
4,4'-Dimethyl	0.016	0.022
5,5'-Dimethyl	0.013	0.011

Reaction with Hydrogen Peroxide.—Hydrogen peroxide reacts with bipyridyl and phenanthroline complexes of iron(II), but with no detectable formation of the respective blue iron(III) complexes, in contrast with true oxidation by, for instance, peroxydisulphate or cerium(IV) compounds. The rate of the decomposition with hydrogen peroxide is first-order with respect to the complex, but it is nearly independent of hydrogen peroxide concentration (Table 5). First-order rate constants were obtained for the reaction of several bipyridyl and phenanthroline complexes of iron(II); average values are given in Table 6. These rate constants were obtained using almost neutral hydrogen peroxide solution prepared as described in the Experimental section. Table 6 also contains average values [k_1 (acid)] for acid fission at the same temperature.¹⁴ For the bipyridyl complexes the acid-independent rate constant is quoted in the Table.

TABLE 5

First-order rate constants (min.⁻¹ × 10³) at 25.0° for reaction of hydrogen peroxide with ferroin and with tris-(4,4'-dimethyl-2,2'-bipyridyl)iron(II) complex (no added salts)

[H ₂ O ₂] (M)	0.45	0.90
<i>o</i> -Phenanthroline	3.94, 4.00	4.25, 4.17, 4.18
4,4'-Dimethyl-2,2'-bipyridyl	16.8, 17.0, 17.4	19.0, 18.2

The equality of acid fission and hydrogen peroxide reaction rates which is demonstrated by Table 6 implies that the two reactions have a common rate-determining step. The rate-determining step in acid fission is the loss of one ligand molecule from the tris-complex; subsequent loss of ligand molecules is much more rapid. In the iron(II)-2,2'-bipyridyl system it has been found that the bis- and mono-complexes react quickly with hydrogen

¹⁴ J. Burgess and R. H. Prince, *J.*, 1963, 5752.

TABLE 6

Average first-order constants for decomposition with hydrogen peroxide, and for acid fission, of tris-(2,2'-bipyridyl)iron(II) and tris-(1,10-phenanthroline)iron(II) complexes. Hydrogen peroxide concentration, 0.45M

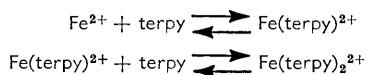
Ligand	Temp.	k_1 (H ₂ O ₂) (min. ⁻¹)	k_1 (acid) (min. ⁻¹)
Bipyridyl	25.0	0.0080	0.0081
4,4'-Dimethyl	25.0	0.017	0.022
5,5'-Dimethyl	25.0	0.0090	0.0110
<i>o</i> -Phenanthroline	25.0	0.0040	0.0044
5-Nitro	25.0	0.029	0.029
	35.0	0.151	0.142
5-Methyl	25.0	0.0022	0.0021
	25.0	0.015	0.014
5-Chloro	35.0	0.081	0.074
	25.0	0.0039	0.0048
5-Phenyl	25.0	0.046	0.044
5-Methyl-6-nitro	35.0	0.0050	0.0065
4,7-Dimethyl	35.0	0.029	0.034
3,5,6,8-Tetramethyl	35.0		

peroxide, and that hydrogen peroxide oxidises 2,2'-bipyridyl at a significant rate.¹⁵ Hence, reaction of iron(II) bipyridyl and phenanthroline complexes with hydrogen peroxide occurs by rate-determining loss of one ligand molecule followed by rapid reaction of the bis- and mono-complexes, and of the ligand, with hydrogen peroxide.

The rate of decomposition of these complexes with hydrogen peroxide is approximately equal to that of acid fission, and is therefore equal to that for the hydroxide-independent part of alkali fission (cf. above and ref. 13). The dissociation behaviour of an iron(II)-bipyridyl or -phenanthroline complex in acid, neutral, and alkaline media can be summarised graphically as in Figure 1. The rate constant for ligand exchange at pH 7 of the tris-(2,2'-bipyridyl)iron(II) complex is 0.008 min.⁻¹¹⁶ and is the same as that for the decomposition with hydrogen peroxide (0.008 min.⁻¹), k_1 (acid) (0.008 min.⁻¹), and k_1 (alkali) (0.009 min.⁻¹). Loss of one ligand molecule from the tris-complex seems to be the rate-determining step in all four cases.

Reaction with Fluoride Ion.—The tris-(2,2'-bipyridyl)iron(II) complex reacts slowly with aqueous sodium fluoride solution, whereas the tris-(1,10-phenanthroline)iron(II) complex does not. The rate of reaction of the bipyridyl complex is much slower than the rate of acid fission, indicating that the reaction with fluoride does not take place by a simple ligand-dissociation mechanism. The reaction was too slow to be followed with the spectrophotometric apparatus available. However, comparison of the 4,4'-dimethyl and unsubstituted complexes at 90° shows that the former reacts with fluoride ion much more rapidly than the latter. The nature of the reaction remains to be investigated.

Terpyridyl Complex.—2,2':6',2''-Terpyridyl acts as a terdentate ligand; the stable purple iron(II) complex contains two ligand molecules per iron atom. The formation equilibria are:



The addition or dissociation of the second ligand molecule will be rate-determining, both by analogy with the phenanthroline and bipyridyl complexes, and from a consideration of magnetic properties, for a change of spin type occurs in reaction (2).

The dependence of the rate of fission of the bis(terpyridyl)iron(II) cation on acid concentration is shown in Figure 2. The dependence is approximately linear over the concentration range studied, but extrapolation of the best straight line gives a negative intercept on the rate axis, whereas an intercept at the position of the rate of ligand exchange at pH 7

¹⁵ W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, 1955, **51**, 935.

¹⁶ R. Hogg and R. G. Wilkins, *J.*, 1962, 341.

($10^{-5} \text{ min.}^{-1}$)¹⁶ would have been expected by analogy with the behaviour of the bipyridyl complexes. The graph of rate against acid concentration is probably curved at low concentrations.

The kinetics of alkali fission are not simple, again in contrast with the behaviour of the similar bipyridyl complexes. First-order plots are curved but initial first-order rate constants can be estimated graphically. The initial first-order rate constants listed in Table 7 show that the reaction is first-order in complex; the dependence of rate on sodium hydroxide concentration is shown in Figure 2(b) which is similar to that of rate on acid concentration.

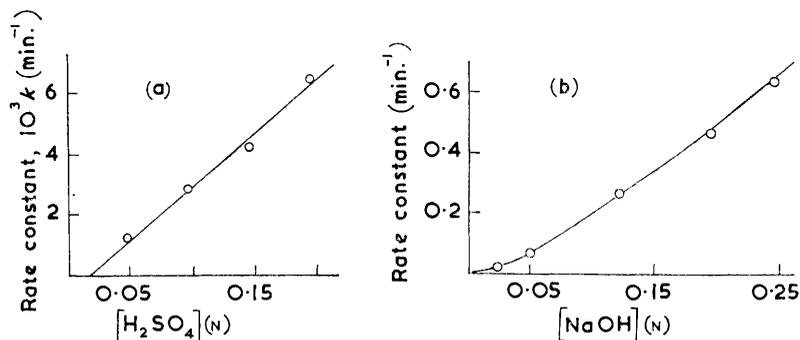


FIGURE 2. Graphs showing the ligand dissociation rate of the bis-(2,2':6',2'') terpyridyliron(II) complex (a) in acid solution and (b) in alkaline solutions. Concentration of complex, $2.6 \times 10^{-5} \text{ M}$

The bis(terpyridyl)iron(II) complex reacts very slowly with hydrogen peroxide in neutral solution, at a rate roughly equal to that of ligand exchange under similar conditions. This behaviour is the same as that of the bipyridyl complexes.

TABLE 7

Initial first-order rate constants for alkali fission of bis(terpyridyl)iron(II) complex; effect of variation of complex and sodium hydroxide concentration

(a) Variation of initial complex concentration at 25.0° . [NaOH], 0.049N; ionic strength, 0.243M.									
[Complex] ₀ × 10 ⁵ (M)	0.5	1.1	1.6	2.1	2.6	3.2	3.7	4.2	5.3
k ₁ (min. ⁻¹ × 10 ²)	5.3	5.0	5.3	4.6	5.7	5.1	4.5	4.6	4.5
(b) Variation of sodium hydroxide concentration at 35.0° . [Complex] ₀ $2.6 \times 10^{-5} \text{ M}$; ionic strength, 0.243M.									
[NaOH] (N)	0.024	0.049	0.121	0.194	0.243				
k ₁ (min. ⁻¹ × 10 ²)	2.0	6.5	26.5	46.5	64.0				

The irregular behaviour of the terpyridyl complex in acid and alkali fission may be due to the participation of particular bidentate intermediates of sufficient stability to give consecutive-reaction kinetics.

EXPERIMENTAL

The apparatus and techniques have already been described.^{13,14} AnalaR hydrogen peroxide had pH *ca.* 3, which is near the limit of the stability range of bipyridyl- and phenanthroline-iron(II) complexes in aqueous solution. To avoid any possibility of acid fission taking place, the hydrogen peroxide was treated first with calcium carbonate, which raised its pH to 5, and then with magnesium turnings, which further raised the pH to about 6. This almost neutral hydrogen peroxide was used to obtain all the kinetic results reported in this Paper.

J. B. acknowledges with thanks the award of a D.S.I.R. Studentship. We thank Dr. M. V. Wilkes for computing facilities, and Dr. R. J. P. Williams, Oxford University, for providing some of the bipyridyl ligands.