873. *Substituent Effects on Alkali Fission of Ferroins*

By J. Burgess and R. H. Prince

The kinetics of the reaction between several substituted tris-1,10-phenanthroline complexes of iron(II) and sodium hydroxide have been studied in aqueous solution. They are similar to those for the unsubstituted complex, with the exception of the 5-nitro-compound, the exceptional behaviour of which is described in detail. Activation energies and frequency factors have been determined for hydroxide attack on these tris-1,10-phenanthroline-iron(II) complexes.

THE decomposition of the tris-1,10-phenanthroline iron(II) (" ferroin ") cation has been studied much less extensively in alkaline media than in acid; all the work reported has been on the unsubstituted complex. It has long been known that the colour of ferroin solutions fades at high pH values but no kinetic investigation was published until 1957.[1] Further work, with a suggested mechanism for the reaction, has appeared in outline,[2] and subsequently in detail.[3]

Whereas the rate of dissociation of the complex in acid solution is nearly independent of the hydrogen-ion concentration [4] the rate of dissociation in alkali was found by Margerum to be dependent on hydroxide-ion concentration. There is not a simple first-order dependence; the overall rate constant, k_0, was related to the hydroxide-ion concentration in the range 0—5N by the equation:

$$k_0 = k_1 + k_2[\mathrm{OH}^-] + k_3[\mathrm{OH}^-]^2 + k_4[\mathrm{OH}^-]^3$$

It was pointed out that the last term may not be kinetically significant and may be ascribable to a specific salt effect at high concentrations. Significant upward curvature of the $k_0/[\mathrm{OH}^-]$ plot was observed even in the range 0—0·1M-hydroxide ion; this is in contrast with our results which show a linear $k_0/[\mathrm{OH}^-]$ plot in this concentration range. The rate constants k_2 and k_3 were related to a mechanism of nucleophilic attack by hydroxide ion at the iron atom. This work was carried out using potassium chloride to maintain constant ionic strength and it may be relevant that chloride ion has a substantial effect on the acid dissociation rate of ferroins.[5] It may be noted that in the reaction with hydroxide ion no mixed iron–phenanthroline hydroxide species have been detected spectrophotometrically; when cyanide ion is the nucleophile mixed species have been identified.[6] In alkali fission no oxidation of ferroin to the ferric complex occurs.[1]

We have studied the kinetics of alkali fission of several substituted ferroins and have found that, with the striking exception of the 5-nitro-complex, there is a similar dependence of rate on hydroxide-ion concentration for the substituted complexes as for ferroin itself. Typical plots of first-order rate constants (sodium hydroxide is in large excess) against hydroxide concentration are shown in Figure 1; comparable values for ferroin are shown in Figure 2. The exceptional results for 5-nitroferroin are plotted in Figure 3. Average values of the first-order rate constants for reaction with sodium hydroxide at varying concentrations for all the complexes investigated are collected in Table 1.

Within the limits of experimental uncertainty all the straight-line plots conform to the the law:

$$\text{Rate} = k_1 + k_2[\mathrm{OH}^-]$$

The simplest interpretation of this rate expression implies a reaction mechanism involving two simultaneous reactions, one involving direct participation of hydroxide ion in the

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[1] D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728.

[2] D. W. Margerum and L. P. Morgenthaler, in " Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 481.

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

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

[5] J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1957, **79**, 1286.

[6] A. A. Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 3000; cf. also ref. 3.

rate-determining step or a pre-equilibrium, and the other not. The latter, hydroxide-independent, part may be explained by reference to the stepwise equilibria for the formation of the ferroin cation:[*,4]

$$\mathrm{Fe^{2+} + o\text{-}phen \rightleftharpoons Fe(o\text{-}phen)^{2+}}$$
$$\mathrm{Fe(o\text{-}phen)^{2+} + o\text{-}phen \rightleftharpoons Fe(o\text{-}phen)_2{}^{2+}}$$
$$\mathrm{Fe(o\text{-}phen)_2{}^{2+} + o\text{-}phen \rightleftharpoons Fe(o\text{-}phen)_3{}^{2+}}$$

In the case of acid fission, protonation of the ligand molecules causes the equilibria to be displaced to the left; in alkali fission the formation of sparingly soluble ferrous hydroxide will displace the equilibria to the left, resulting in dissociation of the tris-complex. In fact the iron is in the form of ferric hydroxide at the end of the reaction [1] owing to the ready oxidation of ferrous hydroxide. The amount of ferric hydroxide formed in reaction mixtures where the initial concentration of complex is 5×10^{-5}M imparts only a very slight brown tinge to the solution and does not affect spectrophotometric observations of the rate of disappearance of the complex.

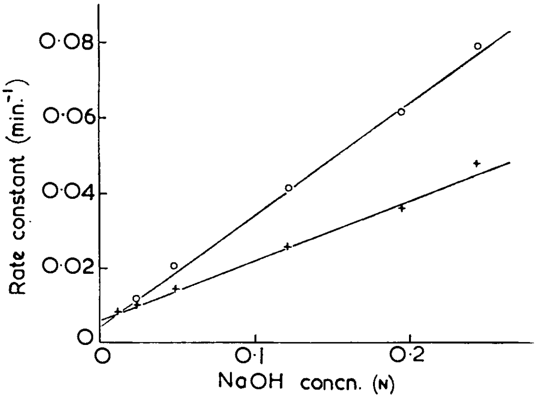

FIGURE 1. Effect of sodium hydroxide concentration on the rate of fission of ferroins: (O), 5-phenylferroin at 25°; (+), 4,7-dimethylferroin at 35°

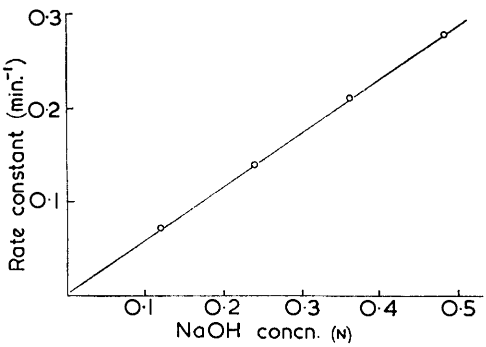

FIGURE 2. Effect of sodium hydroxide concentration on the rate of fission of unsubstituted ferroin

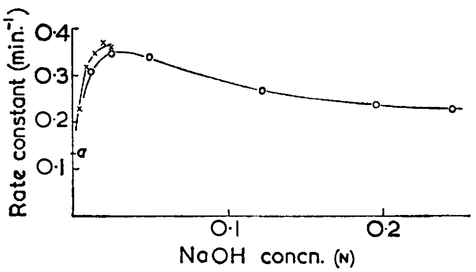

FIGURE 3. Effect of sodium hydroxide concentration on the rate of fission of 5-nitroferroin: graph of first-order rate constant against [NaOH]. Point *a* on the ordinate is the rate of fission in presence of acid. [Complex] ~5×10^{-5}M; ionic strength (×), 0·024M; (O), 0·243M

In Table 2, k_1 values for alkali fission, estimated from the intercepts of graphs similar to Figures 1 and 2, are compared with dissociation rates of the same complexes in acid at the same temperature.[7] The alkali and acid experiments were performed at different ionic strengths, but we have shown that the difference in rates of acid fission that this causes is less than 5%. Alkali, k_1, and acid-fission rate constants are approximately equal for the

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[*] Co-ordinated water molecules are ignored, though these are undoubtedly important (cf. ref. 15).

[7] J. Burgess and R. H. Prince, *J.*, 1963, 5752.

TABLE 1

First-order rate constants (min.$^{-1}$) for alkali fission of ferroins at various sodium hydroxide concentrations

		Sodium hydroxide concentration			
Substituent	Temp.	0·121N	0·243N	0·364N	0·485N
None	25·0°	0·0738 0·0733 0·0709	0·134 0·141 0·143	0·209 0·208 0·213	0·270 0·283 0·278

(Ionic strength 0·485M)

		Sodium hydroxide concentration					
		0·012N	0·024N	0·049N	0·121N	0·194N	0·243N
5-Methyl	35·0		0·0320 0·0311	0·0532 0·0552	0·115 0·114 0·117 0·116 0·118 0·118	0·173 0·181	0·224 0·231 0·229
5-Chloro	25·0		0·0850 0·0859	0·180 0·174	0·414 0·411	0·676 0·688	0·853 0·950
5-Phenyl	25·0		0·0113 0·0118	0·0203 0·0197	0·0398 0·0410 0·0423	0·0610 0·0612	0·0776 0·0794
5-Methyl 6-nitro.........	20·0		0·114 0·115	0·220 0·226	0·482 0·495	0·721 0·720	0·893 0·910
5,6-Dimethyl	35·0	0·00502 0·00477	0·00628 0·00628 0·00647	0·00952 0·00940 0·0101	0·0173 0·0179	0·0250 0·0251 0·0263	0·343 0·0343 0·0310 0·0303 0·0359 0·0353
4,7-Dimethyl	35·0	0·00820 0·00870	0·0102 0·0102	0·0143 0·0142	0·0257 0·0250	0·0352 0·0357	0·0486 0·0478 0·0467 0·0455 0·0498
3,5,6,8-Tetramethyl ...	35·0	0·0301 0·0287	0·0321 0·0313	0·0374 0·0357 0·0362	0·0444 0·0444	0·0544 0·0544	0·0694 0·0696 0·0708
5-Nitro	20·0		0·0445 0·0444 0·0435 0·0423	0·0408 0·0412 0·0452	0·0315 0·0310 0·0290 0·0296	0·0282 0·0267 0·0258 0·0256	0·0265 0·0265 0·0266
	25·0		0·0876 0·0875 0·0878 0·0874	0·0810 0·0812 0·0802 0·0814	0·0580 0·0665 0·0652 0·0644 0·0619	0·0560 0·0572 0·0531 0·0524	0·0549 0·0541 0·0540 0·0534
	30·0		0·165 0·165 0·178 0·179	0·157 0·158 0·171 0·167	0·130 0·133 0·136 0·138	0·115 0·112 0·122 0·118	0·114 0·113 0·113
	35·0	0·296 0·325	0·331 0·329 0·369 0·369	0·335 0·341 0·339 0·330 0·343	0·268 0·282 0·276 0·269 0·271	0·245 0·234 0·253 0·254	0·235 0·228

(Ionic strength 0·243M)

		Sodium hydroxide concentration				
		0·0048N	0·0097N	0·0146N	0·0194N	0·0243N
5-Nitro	25·0	0·059 0·058	0·089 0·090	0·097 0·096	0·093 0·092	0·108 0·106
	35·0	0·249 0·236	0·317 0·315	0·357 0·351	0·367 0·366	0·353 0·361
5-Methyl 6-nitro.........	25·0	0·0722 0·071	0·119 0·118	0·169 0·167	0·243 0·249	0·286 0·289

(Ionic strength 0·0243M)

complexes listed in Table 2, and it is concluded that the explanation of the hydroxide-independent part of the alkali fission reaction, displacement of the formation equilibria by removal of ferrous ions as insoluble hydroxide, is reasonable.

Possible mechanisms for the hydroxide-dependent part of the reaction have been discussed by Margerum and his co-workers.[1-3] It is the effect of substituents on this part of the reaction which this Paper describes. Rate constants and Arrhenius parameters, obtained as described in the Experimental section, are listed in Tables 3 and 4.

The activation energies and frequency factors are discussed in two groups, 5-substituted ferroins and methyl-substituted ferroins, followed by the 5-methyl-6-nitro- and 4,7-dihydroxy-complexes. Finally, the exceptional case of the 5-nitro-compound is described in detail.

In general the activation energies and frequency factors for hydroxide attack are lower than those for acid fission. Activation energies for reaction of ferroin with cyanide and with azide [3] are yet lower than with hydroxide. Nucleophilic attack seems to occur more easily than ligand dissociation for ferroin. Reduced frequency factors indicate that a greater degree of order is required in the transition state, compared with the initial state, of the reaction with alkali than is true of acid fission.

TABLE 2

Comparison of rate constants for alkali and acid fission of substituted ferroins

Substituent	Temp.	k_1 (alkali) (min.$^{-1}$)	k_1 (acid) (min.$^{-1}$)	Substituent	Temp.	k_1 (alkali) (min.$^{-1}$)	k_1 (acid) (min.$^{-1}$)
None	25·0°	0·004	0·0044	5-Methyl-6-nitro	20·0°	0·040	0·020
5-Methyl	35·0	0·010	0·0113	5,6-Dimethyl	35·0	0·0033	0·0035
5-Chloro	25·0	0·010	0·0143	4,7-Dimethyl	35·0	0·006	0·0065
5-Phenyl	25·0	0·005	0·0048	3,5,6,8-Tetramethyl	35·0	0·028	0·034

TABLE 3

Average second-order rate constants (l.mole^{-1}. min.$^{-1}$) for alkali fission of ferroins: temperature variation

Substituent	[NaOH] (M)	Temperature 20·0°	25·0°	30·0°	35·0°
None	0·121	0·334	0·65	1·26	2·35
5-Methyl	0·243	0·121	0·238	0·48	0·89
5-Chloro	0·024	1·50	3·03	5·9	11·0
5-Phenyl	0·121	0·149	0·302	0·58	1·10
5,6-Dimethyl	0·243	0·0137	0·030	0·061	0·124
4,7-Dimethyl	0·243	0·0187	0·043	0·088	0·173
3,5,6,8-Tetramethyl	0·243	0·0146	0·0313	0·069	0·139
5-Methyl-6-nitro	0·0048	2·5	5·2	11·0	22·6
5-Nitro	0·0048	3·3	5·6	10·1	17·4

TABLE 4

Arrhenius parameters for alkali fission of substituted ferroins

Substituent	E_A (kcal. mole^{-1})	σ (kcal. mole^{-1})	$\log_{10} A$ (min.$^{-1}$)
None	23·6	0·1	17·1
5-Methyl	24·1	0·2	17·0
5-Chloro	23·9	0·5	18·0
5-Phenyl	23·9	0·2	17·0
5,6-Dimethyl	26·2	0·3	17·7
4,7-Dimethyl	26·6	0·3	18·1
3,5,6,8-Tetramethyl	27·1	0·3	18·4
5-Methyl-6-nitro	26·6	0·5	20·1
5-Nitro	20·2	0·5	15·6

There are three effects which a substituent may have on the activation energies for reaction with hydroxide ion, changes in the σ- and π-bonding between iron and nitrogen and change in the electron density around the iron atom, depending on the electron-withdrawing or -donating properties of the substituents. Greater electron withdrawal by a substituent, leaving the iron more positive, should facilitate attack by the negatively charged hydroxide ion. Substituent effects on the σ- and π-bonding have already been considered in an earlier Paper on acid fission.[7]

5-*Substitution*.—The activation energy for reaction of the 5-chloro-complex is not significantly different from that for unsubstituted ferroin. The reason for the large standard deviation is explained in the Experimental section. However, the second-order rate constants for the 5-chloro-complex are larger than those for ferroin itself (see Table **3**). Faster reaction is consistent with inductive electron withdrawal by the chloro-group reducing the electron density in the vicinity of the iron atom and making nucleophilic attack easier.

The 5-methyl complex has a significantly higher activation energy than ferroin itself. Electron release by the methyl group has been found in the case of acid fission to increase the strength of the iron–nitrogen bond; it will also increase electron density around the iron atom and thereby discourage hydroxide attack. Both effects should hinder reaction and are consistent with the higher activation energy observed.

Comparison of the results for the 5-phenyl and unsubstituted complexes shows that the activation energy for the phenyl complex is probably higher, and the rate of reaction certainly less. Slower reaction could be caused either by greater delocalisation in the phenyl complex, giving stronger iron–nitrogen bonding, or by electron release by the phenyl group increasing the electron density at the iron atom. Evidence against the latter explanation is provided by the pK_{NH^+} values of 5-phenyl and unsubstituted 1,10-phenanthrolines,[8] which imply electron withdrawal by a phenyl group at position 5. However, a phenyl group can act as donor or acceptor of electrons depending on environment, and here strengthening of the iron–nitrogen π-bonding by greater delocalisation may result from π-donation from the phenyl group, which in turn would increase the electron density at the iron and further discourage hydroxide attack. In any case the smallness of the effect of 5-phenyl substitution can be attributed to steric inhibition of resonance interaction between phenyl group and phenanthroline system due to forced noncoplanarity of these two systems.[7]

Methyl Substitution.—For methyl-substituted ferroins the activation energy for hydroxide attack is in all cases higher than for unsubstituted ferroin, the activation energy increasing with increasing methyl substitution. This contrasts with acid fission, where methyl substituents can have either an activating or deactivating effect.[7] In alkali fission the magnitude of methyl-substituent effects depends on the position of substitution. This additivity of methyl-substituent effects in alkali fission parallels the effects on redox potentials for the ferrous–ferric complex couples and on pK_{NH^+} values for the ligand molecules. The effect on basicity can be explained by electron release from the methyl groups. Such electron release will, in the case of alkali fission, increase the electron density in the neighbourhood of the iron atom and make hydroxide attack more difficult. Maximum effect is observed for methyl substitution at the 4 and 7 positions, which are *para* to the nitrogen atoms.

Frequency factors for 5- and methyl-substituted ferroins are all the same within experimental error. The mechanism of the reaction should be the same for all these complexes; the substituents are well removed from the reaction centre and should therefore not interfere sterically.

5-*Methyl*-6-*nitroferroin*.—The activation energy for hydroxide attack on this complex is unexpectedly high compared with that for acid fission, in fact it is approximately equal to that for acid fission; this is the only complex in this study for which the alkali-fission

[8] A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, 1956, **60**, 1546.

activation energy is as high as the acid value. Later we shall see that the 5-nitro-substituent facilitates hydroxide attack. In the 5-methyl-6-nitro-complex the nitro-group does not seem to have any activating effect. In the discussion of acid fission of this complex[7] it was pointed out that the two substituents sterically interfered, that three forms of distortion in the molecule were possible, and that the evidence favoured non-coplanarity of the nitro-group with the phenanthroline nucleus. Such non-coplanarity would reduce the resonance interaction between the nitro-substituent and the rest of the molecule and render the electron-withdrawing properties of the nitro-group of little importance for the reactivity of the molecule. Of course, this only explains why the activation energy for the 5-methyl-6-nitro-complex is not lower than that for the 5-methyl complex; it does not explain the fact that the activation energy of the former is appreciably larger than that for the latter. The log A value for the 5-methyl-6-nitro-complex is significantly larger than those for the other complexes. This is consistent with a greater loosening of the transition state relative to the initial state for this complex compared with the others.

4,7-*Dihydroxyferroin*.—This complex is stable in saturated sodium hydroxide solution.[9] In alkali, the substituents are O^- rather than OH. The two O groups are *para* to the nitrogen atoms bonded to the iron; their large mesomeric effect can be relayed across the π-electron system of phenanthroline to give a much larger electron density at the iron atom and thus inhibit hydroxide attack. Strong field effects[10] of the substituent give the same effect. In the similar case of complexes derived from chelidamic acid stability is greatly increased by proton loss from the hydroxy-group which, as in 4,7-dihydroxyferroin, is *para* to the nitrogen atom.[11] The very large difference in stability and reactivity caused by deprotonation of hydroxyl substituents may be compared with the large differences between the reactivities of phenol and the phenoxide ion, of an aromatic carboxylic acid and the corresponding carboxylate anion, and of the anilinium ion and aniline itself.

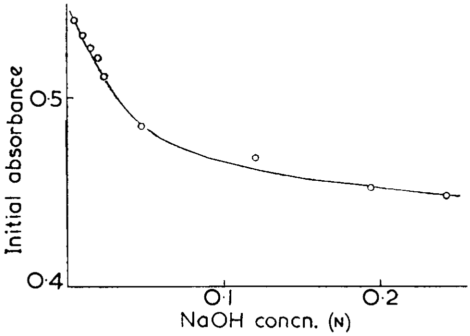

FIGURE 4. Effect of sodium hydroxide concentration on the initial absorbance of 5-nitroferroin solution

5-*Nitroferroin*.—All individual runs gave good straight-line graphs when the logarithms of optical densities were plotted against time, so all were first-order, as expected from the use of sodium hydroxide in large excess.

The dependence of overall rate on alkali concentration at 35·0° is shown in Figure 3. Table 1 shows that the dependence is similar at other temperatures. The behaviour of the 5-nitro-complex, where the rate decreases slightly with increasing hydroxide concentration in strongly alkaline media, is very different from the linear dependence found for all the other ferroins studied, illustrated in Figures 1 and 2. It is not possible to extrapolate the 5-nitro-graph accurately to zero hydroxide concentration, but the curve could well pass through the point on the axis corresponding to the rate of acid fission.

[9] A. A. Schilt, G. F. Smith, and A. Heimbuch, *Analyt. Chem.*, 1956, **28**, 809.
[10] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539.
[11] G. Anderegg, *Helv. Chim. Acta*, 1963, **46**, 1011.

Not only the rate varies unexpectedly with hydroxide-ion concentration, the initial optical-density values for the kinetic runs (at 510 mμ, wavelength of maximum absorption for 5-nitroferroin [12]) depend on the hydroxide concentration; the higher this concentration the lower the initial optical density, although the dependence is not linear. Values at 35·0° are shown in Figure 4; a similar curve was found for 20·0, 25·0, and 30·0°. The variation in initial optical density implies a rapidly established equilibrium, and the manner in which the rate of alkali fission becomes progressively slower than expected as the hydroxide concentration increases implies that whatever intermediate is formed is less reactive towards hydroxide ion than the 5-nitro-complex itself.

Solutions of 5-nitro-1,10-phenanthroline in alkali have been investigated. The ultraviolet spectra of a series of solutions of this ligand, in 10% ethanol and at various sodium hydroxide concentrations, show two peaks, at 267 and 326 mμ, and an isosbestic point (Figure 5), implying an alkali-dependent equilibrium of two species.

It is impossible to carry out analogous experiments with 5-nitroferroin itself since it dissociates too rapidly, even at 0°, for spectra to be run successfully. However, the visible absorption spectrum of a solution of 5-nitroferroin containing 0·2N-NaOH was run at 0°; the result is reproduced as Figure 6. There is a broad peak at 528 mμ; the fact that dissociation was proceeding as the spectrum was being scanned (from low to high wavelengths) means that the maximum of this peak may occur at a higher wavelength than 528 mμ. The wavelength of maximum absorption for 5-nitroferroin is 510 mμ,[12] hence this spectroscopic evidence indicates the rapid formation of significant amounts of some other species from 5-nitroferroin on the addition of sodium hydroxide.

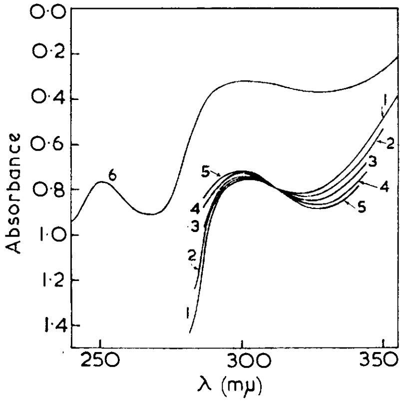

FIGURE 5. Absorption spectra in the 250—350-mμ region of 5-nitro-*o*-phenanthroline. Curves 1—5, spectra in presence of increasing concentrations of sodium hydroxide showing isosbestic point; curve 6, the spectrum of 5-nitro-*o*-phenanthroline in neutral solution (absorbance scale × 2)

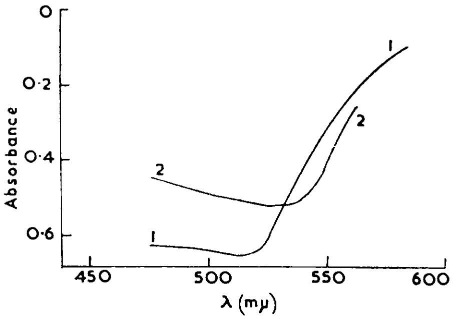

FIGURE 6. Absorption spectra of 5-nitroferroin: (1) in neutral solution; (2) with added sodium hydroxide

It has not proved possible to characterise the species formed on addition of sodium hydroxide to 5-nitroferroin solution, but the experimental data are consistent with the structure (I) in which the 5-nitroferroin has lost a proton from the 6-position, adjacent to the position of substitution of the nitro-group. The behaviour of 5-methyl-6-nitroferroin, which is not abnormal, implies that the exceptional results for the 5-nitro-complex are not due to the nitro-group itself nor to proton loss from any position other than 6. Lability

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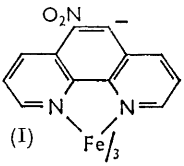
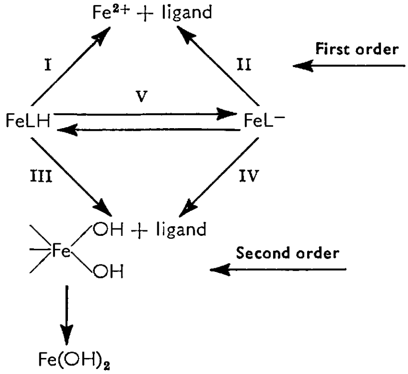
[12] M. L. Moss, M. G. Mellon, and G. F. Smith, *Analyt. Chem.*, 1942, **14**, 931.

of protons *ortho* to nitro-groups in aromatic systems has been demonstrated for *m*-dinitrobenzene.[13] This compound readily undergoes deuterium exchange which occurs mainly at the 2-position *ortho* to both nitro-groups. The presence of a negative charge at the 6-position would be expected to affect the visible absorption spectrum. The nearest related compound the spectrum of which has been studied is nitromethane, where the presence of the $CH_2NO_2^-$ ion has been demonstrated.[14] It is assumed that the mechanism of dissociation of the intermediate and of the 5-nitro-complex is the same as that for other substituted ferroins. The assumption seems reasonable and is consistent with the observed kinetics as will be shown later. There is, however, little direct experimental evidence for this assumption. The variation of the rate of fission with ionic strength, at 35·0° and with 0·049N-NaOH, is illustrated in Figure 7 for 5-nitro- and unsubstituted ferroins. The shapes of the two curves are similar but nothing definite can be deduced since it is not possible to work at the low ionic strengths required for the Debye–Hückel theory to apply accurately, and even if it were the case of the 5-nitro-compound, would be complicated by the possiblity of one, two, or three of the ligand molecules being deprotonated by the action of sodium hydroxide. The product of the ionic charges of the reactants from a corresponding $\ln k_2$ *vs.* f $(\sqrt{\mu})$ plot could lie anywhere between -2 and $+1$. The proposed reaction scheme for 5-nitroferroin (FeLH) in sodium hydroxide solution is as follows: the 6-deprotonated intermediate is represented by FeL:



(I)



This scheme contains hydroxide-independent (I and II) and hydroxide-dependent (III and IV) reactions for both the 5-nitro-complex and its conjugate base, and is therefore of the same form as the reaction scheme for alkali fission of other ferroins. Reaction V is a rapidly attained equilibrium. Reaction IV must be slower than reaction III to give the observed concentration variation of the overall reaction rate. This is reasonable; the negative charge at the 6-position will lower the rectivity of the intermediate towards hydroxide attack (cf. 4,7-dihydroxyferroin above, where negatively charged oxygen atoms cause a dramatic decrease in reactivity towards such attack).

The experimental results are in good qualitative agreement with rate equations derived from the above reaction scheme. Quantitative agreement is not to be expected, considering that six reactions may be involved, and that the effect of the variable amounts of sodium sulphate used to maintain constant ionic strength, though it should be small, may not be negligible.

In order to estimate the activation energy for hydroxide attack on 5-nitroferroin a series of runs at temperatures of 20·0, 25·0, 30·0, and 35·0° was carried out at the lowest practicable sodium hydroxide concentration (0·0048M). The second-order rate constants

[13] R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.*, 1962, 176.
[14] S. Nagakura, *Mol. Phys.*, 1960, **3**, 152.

are given in Table 3, and the Arrhenius parameters in Table 4. As the initial optical densities for these runs were indistinguishable from those for pure 5-nitroferroin solutions there can only have been a very small concentration of deprotonated intermediate present under these conditions. However, the presence of a little of the deprotonated form will have affected the results insofar as its dissociation will have made a small contribution to the observed rates of alkali fission.

In view of the experimental complications the probable error in the estimated activation energy for the 5-nitro-complex will be larger than that implied by the standard deviation given in Table 4. Even so the calculated value, 20 kcal.mole^{-1}, is much smaller than that for ferroin itself (23·6 kcal.mole^{-1}). The low activation energy is consistent with the electron-withdrawing properties of the nitro-group encouraging nucleophilic hydroxide attack at the iron atom by reducing the electron density there.

EXPERIMENTAL

The materials, apparatus, and methods were the same as those used for the study of acid fission reported previously.[7] All rates quoted in Table 1 were obtained at an ionic strength of 0·243M, AnalaR sodium sulphate decahydrate being used to maintain this value. The same compound was used to vary ionic strengths to obtain the results shown in Figure 7.

Rates, in excess of sodium hydroxide solution, conform to a first-order expression over at least 90% of reaction.

The method of obtaining activation energies and frequency factors for the hydroxide-dependent process was as follows. From the graphs of overall reaction rate against sodium hydroxide concentration a suitable alkali concentration was selected so that the reaction rates in the range 20—35° would not be too fast to follow spectrophotometrically with the apparatus available. Then at least three kinetic runs were performed at each of the four temperatures 20·0, 25·0, 30·0, and 35·0° at the chosen alkali concentration. Rates of acid fission were subtracted from the overall alkali-fission rates to give the first-order rate constants for the hydroxide-dependent reaction. Division by alkali concentration gave the second-order rate constants, from which activation energies (E_A) and their standard deviations (σ), and frequency factors ($\log_{10} A$) for hydroxide attack on each of the substituted ferroins, were computed with the aid of an EDSAC 2 computer. Results are given in Tables 3 and 4.

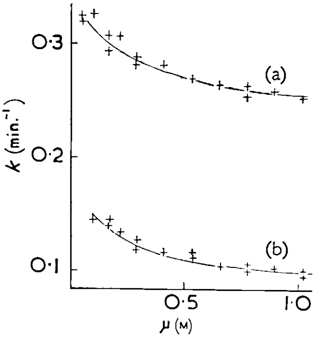


FIGURE 7. Effect of ionic strength (μ) on the rate constant (k) of the fission of ferroin (a) and 5-nitro ferroin (b) with alkali

This method for obtaining second-order rate constants works most satisfactorily when the rate of acid fission is much less than that of alkali fission. In the few cases where the rate of the hydroxide-independent reaction is comparable with that of hydroxide-dependent reaction there is greater uncertainty in the former value, which is the difference between two experimentally determined quantities, and there is a comparatively large standard deviation for the activation of energy (cf. 5-chloroferroin).

Ultraviolet and visible absorption spectra were run on a Perkin-Elmer u.v. 137 spectrophotometer.

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