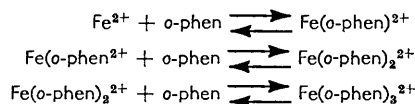


1097. *Substituent Effects on Acid Fission of Ferroins.*

By J. BURGESS and R. H. PRINCE.

Rate constants for the dissociation in acid solution of some substituted tris-1,10-phenanthroline complexes of ferrous iron have been determined spectrophotometrically at several temperatures. From these rate constants activation energies and frequency factors have been calculated and correlated with electron-donating and -accepting properties, and with steric effects, of the substituents.

THE formation and dissociation of the tris-1,10-phenanthrolineiron(II) ("ferroin") cation were first investigated by Lee, Kolthoff, and Leussing.¹ They showed that the dissociation was of the first order in the complex in an excess of acid and independent of the acid concentration; and that formation of the complex was of the fourth order overall. These results were accounted for by suggesting stepwise formation of the complex involving three equilibria (co-ordinated water is ignored):



In acid the equilibria are displaced to the left by protonation of the ligand molecules.

¹ Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596.

The rate-determining step was shown to be the addition or dissociation of the third molecule of ligand, *i.e.*, the last step in the series above.

Later workers showed that variation of acid concentration and addition of salts had a small but significant effect.² In view of this the work reported in this paper has been performed at constant acid concentration, with no added salts.

There has been one kinetic study of substituent effects in acid dissociation of ferriols.³ Rate constants, at 25°, for dissociation of four 5-substituted ferriols were reported. We have extended this work in two ways; first, by examining a wider range of substituents in several positions in the 1,10-phenanthroline nucleus, and, secondly, by determining activation energies and frequency factors for all substituents. Activation energies are correlated with mesomeric, inductive, and field effects of substituents;⁴ frequency factors can show when steric factors are important.

The effect of substituents on activation energies is small in this series, and it has not proved possible to arrange the substituents in an unequivocal order according to the size of their effects on activation energy. However, if the complexes studied are arranged in groups of related compounds it is informative to compare values within each group. The groups are as follows: (1) 5-substituents: nitro, chloro, methyl, and phenyl; (2) methyl substituents: 5-methyl, 5,6-dimethyl, 4,7-dimethyl, and 3,5,6,8-tetramethyl; (3) 5-methyl-6-nitro: comparison with 5-methyl and 5(6)-nitro; (4) 4,7-dihydroxy.

First-order rate constants for acid dissociation were determined at least three times at each of five temperatures, *viz.*, 20°, 25°, 30°, 35°, and 40°, except for the two dimethyl complexes where the reactions rates at 20° were too slow to be followed accurately. Values for the rate constants were calculated by computer (EDSAC 2), which also gave the standard deviation for each result. Standard deviations were in almost every case less than 1%. The average values obtained for the rate constants are given in Table 1.

TABLE 1.

First-order rate constants (in min.⁻¹) for dissociation of ferriols in acid.

Subst.	Initial concentration of complex in all cases, $5.0 \times 10^{-5}M$.				
	20°	25°	30°	35°	40°
None	0.00182	0.0044	0.0098	0.0227	0.049
5-Nitro	0.0125	0.0292	0.065	0.138	0.290
5-Chloro	0.0060	0.0143	0.033	0.074	0.155
5-Methyl	0.00088	0.00211	0.0050	0.0113	0.0246
5-Phenyl	0.00201	0.0048	0.0113	0.0239	0.052
5-Methyl-6-nitro	0.0194	0.044	0.094	0.189	0.36
5,6-Dimethyl	—	0.00067	0.00152	0.0035	0.0074
4,7-Dimethyl	—	0.00134	0.0031	0.0065	0.0134
3,5,6,8-Tetramethyl	0.00273	0.0069	0.0159	0.034	0.071
4,7-Dihydroxy	0.0211	0.035	0.060	0.100	0.152

Good straight-line plots of logarithms of rate constants against reciprocal temperature were obtained. The computer was used to obtain the slope of the best straight line, its standard deviation, and the value of the intercept, for the graph corresponding to each complex. Hence activation energies (E_A), their standard deviations (σ), and frequency factors ($\log_{10} A$) were calculated, and are recorded in Table 2.

Activation energies are high. The rate-determining step in these reactions involves the loss of the third ligand molecule, which loss is accompanied by a change of spin type from the low-spin tris-complex⁵ to the high-spin state common to the aquated ferrous ion and its mono- and bis-complexes with 1,10-phenanthroline. If there is a loss of ligand-field stabilisation energy in reaching the transition state (as is likely for a transition state

² Dickens, Basolo, and Neumann, *J. Amer. Chem. Soc.*, 1957, **79**, 1286.

³ Brandt and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532.

⁴ Dewar and Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539.

⁵ Cambi and Cagnasso, *Gazzetta*, 1933, **63**, 767.

of increased or reduced co-ordination number formed from a d -low-spin state^{6,7}) then high activation energies are to be expected.

Dissociation of phenanthroline molecules from iron atoms in ferroins involves breaking two iron-nitrogen bonds. Electron-donating or -accepting properties of substituents will be transmitted across the phenanthroline nucleus to affect the strength of the iron-nitrogen bonds. The types of interaction which may exist between a substituent and

TABLE 2.
Arrhenius parameters for dissociation of ferroins in acid.

Subst.	E_A (kcal. mole ⁻¹)	σ (kcal. mole ⁻¹)	$\log_{10} A$ (min. ⁻¹)	Subst.	E_A (kcal. mole ⁻¹)	σ (kcal. mole ⁻¹)	$\log_{10} A$ (min. ⁻¹)
None	29.9	0.2	19.6	5-Methyl-6-nitro ...	26.8	0.2	18.3
5-Nitro	28.6	0.2	19.4	5,6-Dimethyl	29.9	0.2	18.7
5-Chloro	29.7	0.1	19.9	4,7-Dimethyl	28.4	0.3	18.0
5-Methyl	30.4	0.2	19.6	3,5,6,8-Tetramethyl	29.7	0.2	19.6
5-Phenyl	29.6	0.1	19.3	4,7-Dihydroxy	18.3	0.3	11.9

a reaction centre have recently been discussed.⁴ Effects on both σ - and π -bonding between iron and nitrogen must be considered; π -bonding is especially significant in complexes, such as those of 1,10-phenanthroline, where there are available π -orbitals of low energy.⁸ Quantitative estimates of the degree of $d_{\pi}-p_{\pi}$ back-donation of electrons from iron are not available, though nuclear magnetic resonance work on some nickel complexes have shown metal-to-ligand transfer of 1/10, 1/10.7, and 1/60, of an electron in three cases.⁹ The relations between spectra, stabilities, and degrees of π -bonding in complexes are not, however, simple.¹⁰ A substituent which is electron-withdrawing will tend to weaken the iron-nitrogen σ -bond, formed by electron-pair donation from nitrogen to iron, but to strengthen the π -bonding, involving back-donation from iron to nitrogen; and conversely for an electron donor. The relative magnitudes of these two opposing effects will depend on whether the substituent affects primarily σ - or π -bonds.

5-Substitution.—The activation energies for dissociation of the 5-methyl- and 5-nitro-substituted and unsubstituted complexes are significantly different and can be explained satisfactorily in terms of the substituents effects on the iron-nitrogen σ -bond. The electron-donation from the methyl group serves to increase the σ -bond strength and thus to give a higher activation energy; electron-withdrawal by the nitro-group leads to a weaker σ -bond and lower activation energy.

Halogen substituents exert both inductive (electron-withdrawing) and mesomeric (electron-releasing) effects, illustrated, for instance, by the further electrophilic substitution in chlorobenzene. The activation energy for the dissociation of the 5-chloro-complex is only slightly lower than that for unsubstituted ferroin, but the dissociation rate is significantly greater. This is consistent with the inductive effect of the chloro-substituent weakening the iron-nitrogen σ -bond and mesomeric electron-release, primarily a π -effect, weakening the π -bonding.

Rate constants, activation energies, and frequency factors, are not significantly different for the 5-phenyl and the unsubstituted complex. The phenyl group can act as an electron-acceptor or -donor, depending on environment. This ambivalent behaviour is shown by

⁶ Basolo and Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454; Broomhead and Dwyer, *Austral. J. Chem.*, 1961, **14**, 250.

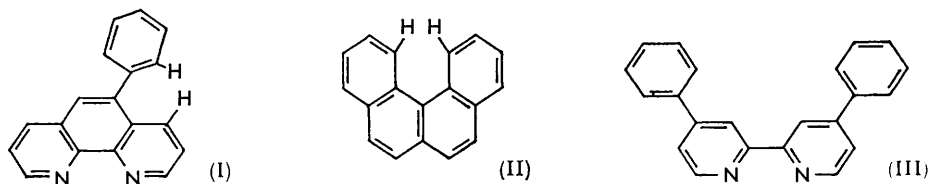
⁷ Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 108.

⁸ Sutton, *J. Inorg. Nuclear Chem.*, 1958, **8**, 31.

⁹ (a) Eaton, Josey, Phillips, and Benson, *J. Chem. Phys.*, 1962, **37**, 347; (b) Lalancette, Eaton, Benson, and Phillips, *J. Amer. Chem. Soc.*, 1962, **84**, 3968; (c) Eaton, Josey, Benson, Phillips, and Cairns, *ibid.*, 1962, **84**, 4100.

¹⁰ Williams, *J.*, 1956, 8.

pK_a measurements on phenyl-1,10-phenanthrolines.¹¹ A Catalin model of 5-phenyl-1,10-phenanthroline indicates that it is not possible to make the phenyl group coplanar with the phenanthroline nucleus. There is overcrowding of the hydrogen atoms as shown in the diagram (I).¹² The situation here is similar to that in benzo[*c*]phenanthrene (II),



where overcrowding of the hydrogen atoms marked results in this molecules' adopting a spiral rather than a planar configuration.¹³ If the phenyl group cannot become coplanar with the phenanthroline nucleus, then interaction, which is a function of the cosine of the interplanar angle,¹⁴ will be reduced, with a corresponding reduction in the electron-donating or -accepting effect of the phenyl substituent on the iron-nitrogen bond strength.

There is some ultraviolet spectral evidence for inhibition of interaction with the phenyl group in phenyl-1,10-phenanthroline. Wavelengths of maximum absorption and molar extinction coefficients for 5-phenyl- and 4,7-diphenyl-1,10-phenanthrolines, and for the unsubstituted ligand, are given in Table 3, together with data for 4,4'-diphenyl-2,2'-bipyridyl and unsubstituted 2,2'-bipyridyl. There is no overcrowding in the diphenyl-bipyridyl compound (III); whereas there is overcrowding in both phenylphenanthrolines. Table 3 shows that phenyl-substitution in the bipyridyl case has a much greater effect than 5- or 4,7-phenyl substitution in 1,10-phenanthroline.

TABLE 3.

Data from ultraviolet spectra.

	$\lambda_{\max.}$	ϵ		$\lambda_{\max.}$	ϵ
1,10-Phenanthroline	264	32,000	2,2'-Bipyridyl	282	14,300
5-Phenyl-1,10-phenanthroline	269	34,300	4,4'-Diphenyl-2,2'-bipyridyl	249	46,400
4,7-Diphenyl-1,10-phenanthroline	273	39,000			

It has been shown that Hammett σ -constants,¹⁵ which reflect substituent effects on free-energy differences in many organic systems, can also be applied to the reactivity of metal complexes.¹⁶ The 5-position in 1,10-phenanthroline is *meta* to one iron-nitrogen bond and *para* to the other. The logarithms of rate constants at 25° have been plotted against both *meta*- and *para*- σ -constants. There is no linear relation between $\log k$ and *meta*- σ -constants; there is a linear relation with *para*- σ -constants over a limited range but the σ -value for the nitro-group is apparently too large (or the rate too small) for linearity over an extended range. These graphs illustrate the possibility of applying Hammett σ -values to reactions of metal complexes, but do not permit an unequivocal choice of *meta* or *para* as a description of the 5-position in this connection.

Frequency factors are all approximately equal for the range of 5-substituents studied. This implies similarity of mechanism throughout; steric factors should not be important

¹¹ Schilt and Smith, *J. Phys. Chem.*, 1956, **60**, 1546.

¹² James, D.Phil. Thesis, Oxford, 1960, p. 49.

¹³ Herbstein and Schmidt, *J.*, 1954, **3302**; Hirschfeld, Sandler, and Schmidt, *J.*, 1963, 2108; Hirschfeld, *J.*, 1963, 2126.

¹⁴ Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3349.

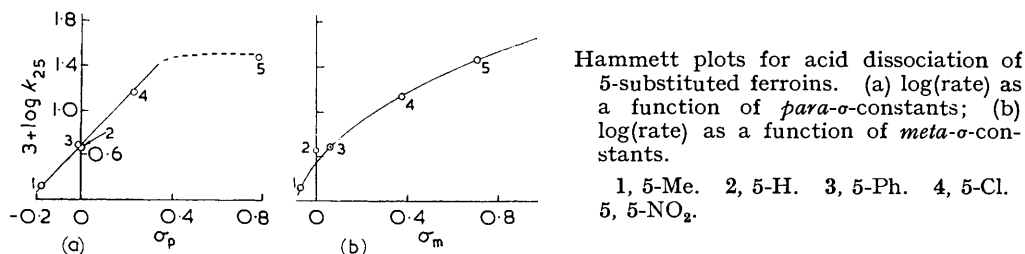
¹⁵ Bunnett, Ch. 6, "Investigation of Rates and Mechanisms of Reactions, Techniques of Organic Chemistry," Vol. 8, Part I, ed. by Weissberger, Interscience, New York, 1962.

¹⁶ Ellis, Hogg, and Wilkins, *J.*, 1959, 3308.

since the substituents are not interfering at the reaction centre and the degree of structure-loosening in the transition state is similar for all substituents.

5-Methyl-6-nitroferroin.—The activation energy for acid fission of this complex (26.8 kcal. mole⁻¹) is less than those for the 5-methyl (30.4 kcal. mole⁻¹), the 5-nitro (28.6 kcal. mole⁻¹), or the unsubstituted (29.9 kcal. mole⁻¹) complex. The value might have been expected to lie between those for the 5-methyl and 5-nitro-complexes, or, if the mesomeric effect of the nitro-group had been dominant, to be roughly equal to the 5-nitro-value. The low value actually obtained implies that some additional effect must be considered.

A model of 5-methyl-6-nitro-1,10-phenanthroline shows that the methyl group prevents the adjacent nitro-group from becoming coplanar with the phenanthroline nucleus without upsetting its geometry. Three forms of distortion are possible. First, the nitro-group may be twisted out of coplanarity with the phenanthroline nucleus, thereby reducing the



degree of interaction; secondly, the 5,6-carbon-carbon bond could become lengthened; or, thirdly, the phenanthroline nucleus could become bent. The last two cases permit greater resonance interaction between the nitro-group and the phenanthroline nucleus at the cost of some loss of resonance stabilisation of the latter.

There is infrared, ultraviolet, and electron spin resonance (e.s.r.) evidence relating to distortion in *o*-nitrotoluene, the simplest structure comparable to 5-methyl-6-nitro-1,10-phenanthroline. The infrared¹⁷ and ultraviolet¹⁸ results were explained by non-coplanarity of the nitro-group with the benzene ring, but the e.s.r. work¹⁹ was interpreted in terms of twisting of the nitro-group about an axis lying in the ring. The latter can best be used to explain the low activation energy for acid fission of 5-methyl-6-nitroferroin. Reduction of nitrophenanthroline resonance cannot explain the effect observed, but distortion of the system would result in strain which could be relieved in the transition state, leading to a low activation energy for the reaction.

The infrared spectra of 5-methyl-6-nitro- and of 5-nitro-1,10-phenanthrolines have been run (Nujol mull, Perkin-Elmer Infracord spectrophotometer); the N-O stretching frequency is shifted from 1356 cm.⁻¹ in the 5-nitro-complex to 1382 cm.⁻¹ in the 5-methyl-6-nitro-compound, a shift which could be due to distortion in the molecule.

Methyl-substitution.—Polymethyl-substitution has an additive effect on the redox potential of the ferrous-ferric-phenanthroline complex couple.²⁰ This additivity is also found for methyl-substituent effects on the p*K*_a value of 1,10-phenanthroline.¹¹ The case of acid fission is less simple. The 5-methyl complex has an activation energy significantly higher, the 4,7-dimethyl complex significantly lower, than that for unsubstituted ferroin, while the values for the 5,6-dimethyl and the 3,5,6,8-tetramethyl complexes are not significantly different from that for ferroin itself. The simple picture of substituent effects on the iron-nitrogen σ -bond, which was sufficient to explain the results for 5-substituted ferroins, is not capable of explaining the results for methylferroins. For these

¹⁷ Van Veen, Verkade, and Wepster, *Rec. Trav. chim.*, 1957, **76**, 801.

¹⁸ Brown and Reagen, *J. Amer. Chem. Soc.*, 1947, **69**, 1032.

¹⁹ Geske and Ragle, *J. Amer. Chem. Soc.*, 1961, **83**, 3532.

²⁰ Smith and Banick, *Talanta*, 1959, **2**, 348.

complexes substituent effects on the iron–nitrogen π - and σ -bonds, and on the electron density around the nitrogen atom, must be considered. It will also be necessary to consider the effect of hyperconjugative, as well as inductive, electron-release by the methyl group.

There is still much controversy on the subject of hyperconjugation. It is a useful concept in the present discussion, and its use can be supported by a considerable body of recent evidence. This evidence comes from ultraviolet spectroscopy of sulphur–sulphur bonded organic compounds,²¹ from nuclear magnetic resonance studies of acetylacetonate complexes of vanadium,²² of *p*-tolyl and fluorenyl derivatives of nickel–(aminotropone imine) complexes,^{9a} and of similar nickel complexes derived from salicylaldehyde,^{9b} and from e.s.r. investigations of tolu-*p*-benzosemiquinone,²³ and of methylanthracenes.²⁴

In the 4,7-dimethyl complex both π -inductive and hyperconjugative effects will be important, the latter especially so as the 4- and the 7-position are *para* to the nitrogen atoms. Both effects tend to decrease π -bonding but increase σ -bonding. As both effects are primarily of a π -nature, the decrease in π -bonding will be dominant, which is consistent with the low activation energy observed. The 5,6-dimethyl and the 3,5,6,8-tetramethyl complex will be less affected by hyperconjugative π -bond weakening; the near-equality of the activation energies for these two complexes and ferroin itself implies that π -bond weakening and σ -bond strengthening are of comparable magnitude. The larger activation energy for the acid fission of the 5-methyl-substituted complex is harder to explain in these terms. It is to be expected that the conjugative and the inductive effects will be reduced in magnitude compared with 4- and 7-methyl-substituted ligands: the slightly larger activation energy of the 5-methyl-substituted complex compared with that of the unsubstituted ligand suggests that iron–nitrogen bond strengthening is the dominant effect. It might be expected that further strengthening and a higher activation energy would be observed with the 5,6-dimethyl-substituted ligand: that such substitution leads to a lower activation energy, not significantly different from that of the unsubstituted 1,10-phenanthroline, again suggests a unique interaction of groups in 5- and 6-positions. Models show that a steric effect cannot be large, but kinetically significant “buttressing” effects have been ascribed to methyl groups adjacent to one another in the benzene nucleus.²⁵ If any distortions are relieved in the transition state, then a lowering of activation energy is possible, compensating for a potential increase of strength of the iron–nitrogen bond.

4,7-Dihydroxyferroin.—The activation energy is low, which is consistent with the large mesomeric effects of the $\text{—}\ddot{\text{O}}\text{H}$ groups, *para* to the nitrogen atoms, weakening the iron–nitrogen π -bonding to a great extent. Once an iron–nitrogen bond has broken, it is unlikely to be reformed quickly since a structure (IV) is more likely than (V) for an inter-



mediate. The situation here is comparable to that with 4-hydroxyquinoline, which exists primarily as (VI) rather than (VII). The ratio (VI) : (VII) is 24000 : 1.²⁶ The anomalously low redox potential for the ferrous–ferric–3-carboxy-4-hydroxy-1,10-phenanthroline couple has been interpreted in terms of contributions from quinonoid structures (VIII).²⁷

²¹ Rosenthal and Oster, *J. Amer. Chem. Soc.*, 1961, **83**, 4445.

²² Forman, Murrell, and Orgel, *J. Chem. Phys.*, 1959, **31**, 1129.

²³ Ingram, “Free Radicals,” Butterworths, London, 1958, p. 153.

²⁴ Bolton, Carrington, and McLachlan, *Mol. Phys.*, 1962, **5**, 31.

²⁵ Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353.

²⁶ Albert and Phillips, *J.*, 1956, 1294.

²⁷ Perrin, *Rev. Pure Appl. Chem.*, 1959, **9**, 257.

Tautomeric equilibrium between benzenoid and quinonoid structures in 4,7-dihydroxy-1,10-phenanthroline has been suggested as the reason for the very slow formation of the ferrous complex from this ligand.²⁸

A quinonoid structure for the 4,7-dihydroxyferroin intermediate in acid fission may, by its reluctance to recombine with the iron atom, affect both activation energy and frequency factor for this reaction. Alternatively, a process involving rapid reversible loss of a proton from a hydroxyl group of the ligand followed by a slow attack of a proton on the iron-nitrogen bond is equally consistent with the kinetic results. This will be



discussed further in the next paper in this series which will deal with the fission of ferroins in alkali.

EXPERIMENTAL

Substituted Phenanthrolines.—These were, with one exception, gifts from Dr. R. J. P. Williams or Dr. R. G. Wilkins, to whom the authors are very grateful, or obtained from B.D.H. or Lights Chemical Company. 5-Methyl-6-nitro-1,10-phenanthroline was prepared by the method of Smith and Richter.²⁹ Two samples of this ligand were made, one had m. p. 267°, the other 270° (lit., 268—270°). Complex solutions derived from these two samples gave identical kinetic results. Ligands were recrystallised where necessary from ethanol or ethanol-water.

Ferrous Ammonium Sulphate.—"AnalaR" material was recrystallised as described by Vogel's method.³⁰

Ferrous-Phenanthroline Solutions.—These were prepared by adding ligand, in slight excess to avoid mono- or bis-complex formation,³¹ to ferrous ammonium sulphate solution of the required concentration. It was necessary to work with sulphates and sulphuric acid rather than perchlorates and perchloric acid as the perchlorates of many substituted 1,10-phenanthrolines are extremely sparingly soluble in water.³²

Apparatus.—A Unicam S.P. 500 spectrophotometer was fitted with a thermostat-controlled cell-holder (supplied by Unicam), through which was circulated water from a constant-temperature bath equipped with a contact thermometer and relay.

Kinetic Measurements.—1 ml. of 4.29N-sulphuric acid was added to 3 ml. of ferrous complex solution, contained in a 1 cm. cell, to start the reaction. Thus acid dissociation results have all been obtained at an overall sulphuric acid concentration of 1.07N.

Ultraviolet Absorption.—The values given in Table 3 were obtained with a Cary model 14M recording spectrophotometer. Solutions were in ethanol.

We are greatly indebted to Dr. M. V. Wilkes for permission to compute our results on EDSAC 2, and to the D.S.I.R. for a maintenance grant to J. B.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, March 26th, 1963.]

²⁸ Hawkins, Duewell, and Pickering, *Analyt. Chim. Acta*, 1961, **25**, 257.

²⁹ Smith and Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. Frederick Smith Chemical Co., Columbus, Ohio, 1944, p. 12.

³⁰ Vogel, "Quantitative Inorganic Analysis," Longmans, London, 1961, p. 282.

³¹ Kolthoff, Leussing, and Lee, *J. Amer. Chem. Soc.*, 1950, **72**, 2173.

³² See, e.g., Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313.