Kinetics and Mechanism of Dissociation of Tris(pyridine-2-carbaldehyde-*N*-propylimine)- and Tris(pyridine-2-carbaldehyde-*N*-methylimine)-iron-(II)[1]

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The rate of dissociation of tris(pyridine-2-carbaldehyde-*N*-propylimine)iron(II), $[Fe(ppi)_3]^{2+}$, has been reinvestigated and the studies extended to tris(pyridine-2-carbaldehyde-*N*-methylimine)iron(II), $[Fe(pmi)_3]^{2+}$. Experimental rate data are in agreement with a mechanism consisting of two simultaneous reaction paths in which the order of bond breaking between the central metal atom and each of the different moieties of the ligand is reversed. Approximate values of rate constants and activation parameters of some of the elementary reaction steps have been obtained for these paths. Comparison with values reported for the complexes of 2,2′-bipyridine, $[Fe(bipy)_3]^{2+}$, and glyoxalbismethylimine, $[Fe(gmi)_3]^{2+}$, suggests that the differences between metal–pyridine and –aliphatic imine bond strengths are significantly reduced on passing from bipy and gmi to the ' mixed ' ligands pmi and ppi.

It has been shown that acid-catalysed dissociation of tris(2,2′-bipyridine)iron(II),[2,3] $[Fe(bipy)_3]^{2+}$, follows a rate law (1) where k_0 and k_∞ are limiting rate constants

$$-\frac{d[FeL_3^{2+}]}{dt} = k_d[FeL_3^{2+}] = \frac{k_0k_c + k_\infty[H^+]\,[FeL_3^{2+}]}{k_c + [H^+]} \quad (1)$$

at zero and infinite $[H^+]$, respectively. Acid-catalysed dissociation of tris(glyoxalbismethylimine)iron(II), $[Fe(gmi)_3]^{2+}$, follows the same rate expression.[4] The most likely mechanism compatible with equation (1) has been proposed by Basolo *et al.*[5] According to this mechanism the bonds between the central metal atom and the bidentate ligand are broken stepwise. Acid catalysis is explained on the basis of protonation of the free nitrogen atom of the half-bonded stationary intermediate. Another mechanism compatible with the experimental rate law, which postulates protonation of the original complex,[3] has been ruled out by equilibrium measurements.[6]

Iron(II) complexes of pyridine-2-carbaldehydeimine ligands might be expected to exhibit a similar rate expression and mechanism. However, Murmann and Healy [7] could not use equation (1) as such for acid dissociation of tris(pyridine-2-carbaldehyde-*N*-propylimine)iron(II), $[Fe(ppi)_3]^{2+}$. A quadratic term in $[H^+]$ had to be included in the numerator of the expression for k_d in equation (1) in order to obtain agreement with experiment. Moreover, k_d did not converge to a constant value at high acidities. The proposed mechanism involves participation of mono- and di-protonated species in equilibria with the original complex. The principal evidence put forward in favour of the mechanism is the decrease in absorbance of the complex with increasing acid ($HClO_4$) concentration. However, it has been shown [8] that this is due to a change in oxidation state of the metal rather than protonation of the complex.

Seeking a mechanistic explanation more in line with the aforementioned results for bipy and gmi iron(II) complexes, and in as much as available kinetic data [7] were insufficient, we decided to reinvestigate the rate of dissociation of tris(pyridine-2-carbaldehyde-*N*-propylimine)iron(II). The present paper discusses the results of this reinvestigation and an extension to tris(pyridine-2-carbaldehyde-*N*-methylimine)iron(II).

EXPERIMENTAL

Materials.— Tris(pyridine-2-carbaldehyde-*N*-propylimine)iron(II) perchlorate was prepared from pyridine-2-carbaldehyde, n-propylamine, and iron(II) sulphate in water–ethanol and precipitated with sodium perchlorate.[7] The crude product was treated with enough water at 15 °C (*ca.* 150 $cm^3\ g^{-1}$) to dissolve *ca.* two thirds of the material. Careful addition of $Na[ClO_4]$ to the filtered solution resulted in precipitation of *ca.* 50% of the dissolved material. The precipitate was dissolved in cold water and enough $Na[ClO_4]$ was added to precipitate again *ca.* 50% of the complex. The fractional precipitation was repeated. The last two fractions to precipitate differed by at most 0.3% in their rates of dissociation.† The purity of n-propylamine was checked by gas chromatography.

Tris(pyridine-2-carbaldehyde-*N*-methylimine)iron(II) perchlorate was prepared and purified in the same way. Methylamine was used instead of n-propylamine. The rates of dissociation of the different fractions were almost identical within the limits of experimental error.

Kinetics.—Kinetic measurements were carried out in 2.00M-HCl–LiCl mixtures to minimize variations of activity coefficients with varying composition of the solutions.[6] Acidity was varied from *ca.* 2×10^{-5} (0.005 mol dm^{-3} acetate buffer) to 2 mol dm^{-3}. The concentration of the complexes was 4×10^{-5}—10×10^{-5} mol dm^{-3}. The rate of

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† We isolated from the first undissolved fraction a product which differed from the final fraction by *ca.* 10% in the rate of dissociation (0.3M-HCl). The absorption spectra of the different fractions in the range 300—700 nm were practically identical, suggesting that two possible geometrical isomers of $[Fe(ppi)_3]^{2+}$ are present in the crude product.

[1] Presented in part in *Proc. 3rd Symp. Co-ordination Chem.*, Debrecen, Hungary, 1970, p. 357.

[2] J. H. Baxendale and P. George, *Nature*, 1948, **162**, 777; *Trans. Faraday Soc.*, 1950, **46**, 736.

[3] P. Krumholz, (*a*) *Nature*, 1949, **163**, 724; (*b*) *Anais Acad. brasil Cienc.*, 1950, **22**, 263.

[4] P. Krumholz, *Proc. 7th Internat. Conf. Co-ordination Chem.*, Stockholm, 1962, p. 280.

[5] (*a*) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807; (*b*) F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 218.

[6] P. Krumholz, *J. Phys. Chem.*, 1956, **60**, 87.

[7] R. K. Murmann and E. A. Healy, *J. Amer. Chem. Soc.*, 1961, **83**, 2092.

[8] A. A. Schilt, *J. Amer. Chem. Soc.*, 1963, **85**, 904.

dissociation was followed photometrically, at 560 nm for $[Fe(ppi)_3]^{2+}$ and 551 nm for $[Fe(pmi)_3]^{2+}$, using a Hitachi–Perkin-Elmer model 139 spectrophotometer equipped with a thermostatted cell compartment and digital readout. Kinetic runs were made at 30.15, 35.06, and 40.06 °C for $[Fe(ppi)_3]^{2+}$ and 43.12 and 56.60 °C for $[Fe(pmi)_3]^{2+}$. The temperature of the solutions was maintained to within ±0.01 °C or less. The reactions were followed for at least two half-lives. Within the experimental error, the rates of reaction were first order in complex concentration. Rate constants were obtained in the usual way and refined by a least-squares treatment. Duplicate runs were reproducible to within *ca.* ±0.2%.

RESULTS AND DISCUSSION

Kinetic Results.—Table 1 presents the values of k_d obtained for $[Fe(ppi)_3]^{2+}$ and $[Fe(pmi)_3]^{2+}$. It can be seen, in agreement with Murmann and Healy,[7] that equation (1) does not predict correctly the acid dependence of k_d for acidities greater than *ca.* 0.1 mol dm^{-3}. Values of k_d for $[Fe(ppi)_3]^{2+}$ against $[H^+]$, at 30.15 °C, are plotted in Figure 1. The curve obtained suggests that we are dealing with two superposed kinetic processes. In one, k_d tends to approach a steady value at $[H^+] = 0.1$ mol dm^{-3} [*cf.* equation (1)], whereas in the other k_d increases gradually up to the highest acidities. The curve of k_d against $[H^+]$ for $[Fe(pmi)_3]^{2+}$ follows the same pattern.

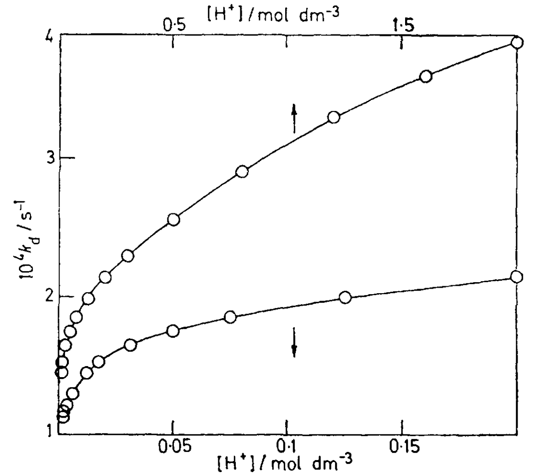


FIGURE 1 Dependence of the first-order dissociation rate constant (k_d) of $[Fe(ppi)_3]^{2+}$ on $[H^+]$ at 30.15 °C and $I = 2.00$M (HCl–LiCl)

This kinetic behaviour can be rationalized if the unsymmetric nature of the pyridine-2-carbaldehydeimine ligands is considered. The mechanism of Basolo *et al.*[5] leads one to predict two parallel dissociation paths differing by the sequence in which bonds between the metal atom and the two different moieties of the ligand are broken. The expression for k_d then takes form (2).

$$k_d = \frac{k_0'k_c' + k_\infty'[H^+]}{k_c' + [H^+]} + \frac{k_0''k_c'' + k_\infty''[H^+]}{k_c'' + [H^+]} \quad (2)$$

$$k = k_d - k_0^0 = \frac{k_x'[H^+]}{k_c' + [H^+]} + \frac{k_x''[H^+]}{k_c'' + [H^+]} = k' + k'' \quad (3)$$

Equation (2) can be conveniently expressed as (3) where $k_0^0 = k_0' + k_0''$, $k_x' = k_\infty' - k_0'$, and $k_x'' = k_\infty'' - k_0''$. It is obvious that kinetics can only provide values for the parameters k_0^0, k_x', k_x'', k_c', and k_c''. The values of k_0' and k_0'' are undetermined within the numerical value of k_0^0. The latter is easily obtained by extrapolating experimental values of k_d to $[H^+] = 0$. Approximate values for k_x' and k_c' and for k_x'' and k_c'' were obtained from values of k_d at $[H^+] < 0.1$ and > 0.5 mol dm^{-3}, respectively. The 'best' set of values of the parameters was obtained by successive approximations in order to minimize the average deviation between the experimental values of k_d and those calculated from equation (3). The results are shown in Table 2. The fitting procedure is rather sensitive to small variations in the ratio $k_x : k_c$, but less sensitive to variations in the absolute values of the parameters. Nevertheless, variations of k_x', k_c', k_x'', and k_c'' by 2(3), 2(3), 4(3), and 4(6)%, respectively, for $[Fe(ppi)_3]^{2+}$($[Fe(pmi)_3]^{2+}$) impair significantly the agreement between experimental and calculated values of k. The excellent agreement between experimental values of k and those calculated from equation (3) using the set of parameters given in Table 2 is demonstrated in Table 3. Experiment and theory agreed within an average deviation of 0.1% for $[Fe(ppi)_3]^{2+}$ and 0.2% for $[Fe(pmi)_3]^{2+}$. The maximum deviation was 0.3% for $[Fe(ppi)_3]^{2+}$ and 0.6% for $[Fe(pmi)_3]^{2+}$. In Figure 2, the two acid-dependent terms for $[Fe(ppi)_3]^{2+}$, at 30.15 °C, are plotted against $[H^+]$, separately and as a sum.

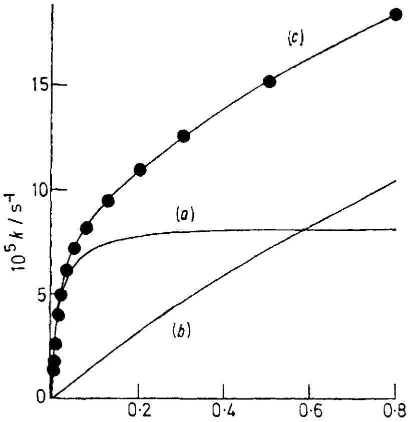


FIGURE 2 Plots of the acid-dependent kinetic terms in equation (3) against $[H^+]$ at 30.15 °C and $I = 2.00$M (HCl–LiCl): (*a*) $k = k_x''[H^+]/(k_c'' + [H^+])$; (*b*) $k = k_x'[H^+]/(k_c' + [H^+])$; (*c*) sum of (*a*) and (*b*) points are values of $k_d - k_0^0$

Figure 3 shows the dependence on $[H^+]$ of the apparent Arrhenius activation energy related to the first-order dissociation constants, k_d, of $[Fe(ppi)_3]^{2+}$ and $[Fe(pmi)_3]^{2+}$. This rather peculiar dependence reflects again the dual nature of the dissociation process. The initial steep decrease of $E^\ddagger$ with $[H^+]$ is enhanced by the increase in k_c' with temperature.

Mechanism.—The mechanism of dissociation of

TABLE 1

Pseudo-first-order rate constants for acid dissociation of $[Fe(ppi)_3]^{2+}$ and $[Fe(pmi)_3]^{2+}$

$[Fe(ppi)_3]^{2+}$ 30.15 °C $\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4k_d}{s^{-1}}$	$[Fe(ppi)_3]^{2+}$ 35.06 °C $\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4k_d}{s^{-1}}$	$[Fe(ppi)_3]^{2+}$ 40.06 °C $\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4k_d}{s^{-1}}$	$[Fe(pmi)_3]^{2+}$ 43.12 °C $\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4k_d}{s^{-1}}$	$[Fe(pmi)_3]^{2+}$ 52.60 °C $\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4k_d}{s^{-1}}$
ca. 2×10^{-5}	1.05	*ca.* 2×10^{-5}	2.31	*ca.* 2×10^{-5}	5.01	*ca.* 2×10^{-5}	0.435	*ca.* 2×10^{-5}	1.89
6.7×10^{-4}	1.08			6.5×10^{-4}	5.03	7.5×10^{-4}	0.443	7.6×10^{-4}	1.93
1.3×10^{-3}	1.11	1.3×10^{-3}	2.42	1.3×10^{-3}	5.22	1.4×10^{-3}	0.452	1.4×10^{-3}	1.95
2.5×10^{-3}	1.17			2.5×10^{-3}	5.40	2.7×10^{-3}	0.470	2.7×10^{-3}	2.01
3.8×10^{-3}	1.22	3.75×10^{-3}	2.61	3.7×10^{-4}	5.56	3.8×10^{-3}	0.484	3.9×10^{-3}	2.05
6.2×10^{-3}	1.30			6.2×10^{-3}	5.87	6.4×10^{-3}	0.516	6.4×10^{-3}	2.15
0.012	1.44	0.012	3.04	0.013	6.38	0.013	0.590	0.013	2.37
0.019	1.54			0.019	6.78	0.019	0.653	0.019	2.60
0.031	1.66	0.031	3.49	0.031	7.28	0.031	0.764	0.031	2.98
0.050	1.77			0.050	7.75	0.050	0.901	0.050	3.42
0.075	1.86	0.075	3.91	0.075	8.17	0.076	1.04	0.075	3.94
0.125	1.99			0.125	8.72	0.125	1.26	0.125	7.73
0.20	2.14	0.20	4.45	0.20	9.29	0.20	1.49	0.20	5.56
0.30	2.30			0.30	9.91	0.30	1.72	0.30	6.43
0.50	2.57	0.50	5.32	0.50	10.9	0.50	2.06	0.50	7.70
0.80	2.91			0.80	12.2	0.80	2.41	0.80	8.96
1.2	3.29	1.2	6.68	1.2	13.5	1.2	2.75	1.2	10.3
1.6	3.60			1.6	14.7	1.6	3.01	1.6	11.2
2.0	3.86	2.0	7.82	2.0	15.6	2.0	3.23	2.0	12.0

TABLE 2

Kinetic parameters in equation (3) for dissociation of $[Fe(ppi)_3]^{2+}$ and $[Fe(pmi)_3]^{2+}$ in 2M-HCl–LiCl

Complex	$\frac{\theta_c}{°C}$	$\frac{10^4k_0{}^0}{s^{-1}}$	$\frac{10^4k_x{}'}{s^{-1}}$	$\frac{10^4k_x{}''}{s^{-1}}$	$\frac{10^2k_c{}'}{mol\ dm^{-3}}$	$\frac{k_c{}''}{mol\ dm^{-3}}$
$[Fe(ppi)_3]^{2+}$	30.15	1.04	0.84 ± 0.01	4.75 ± 0.15	1.48 ± 0.02	2.8 ± 0.15
	40.06	5.01	3.48 ± 0.05	17.8 ± 0.7	2.06 ± 0.04	3.0 ± 0.2
$[Fe(pmi)_3]^{2+}$	43.12	0.434	1.00 ± 0.04	3.37 ± 0.08	0.85 ± 0.04	1.7 ± 0.2
	52.60	1.89	3.7 ± 0.2	12.5 ± 0.35	1.03 ± 0.05	1.8 ± 0.2

TABLE 3

Values of k, experimental ($k = k_d - k_0{}^0$) and calculated from equation (3) ($k' + k''$); δ is the relative % deviation calculated from $\delta = 100[k - (k' + k'')]/k_d$

$[Fe(ppi)_3]^{2+}$, 30.15 °C

$\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4(k' + k'')}{s^{-1}}$	$\frac{10^4k}{s^{-1}}$	$\frac{10^4k_d}{s^{-1}}$	$\frac{\delta}{\%}$
ca. 2×10^{-5}	0.001	0.002	1.05	+0.03
6.7×10^{-4}	0.037	0.037	1.08	−0.02
1.3×10^{-3}	0.070	0.070	1.11	+0.02
2.5×10^{-3}	0.126	0.127	1.17	+0.06
3.8×10^{-3}	0.175	0.178	1.22	+0.19
6.2×10^{-3}	0.256	0.256	1.30	+0.01
0.012	0.401	0.401	1.44	0
0.019	0.495	0.496	1.54	+0.03
0.031	0.617	0.618	1.66	+0.07
0.050	0.726	0.723	1.76	−0.14
0.075	0.819	0.819	1.86	−0.02
0.125	0.947	0.945	1.99	−0.10
0.20	1.09	1.10	2.14	+0.13
0.30	1.25	1.26	2.30	+0.25
0.50	1.53	1.53	2.57	+0.05
0.80	1.874	1.87	2.91	−0.15
1.2	2.25	2.25	3.29	−0.09
1.6	2.55	2.55	3.60	0
2.0	2.81	2.82	3.86	+0.25
				$\Sigma\lvert\delta\rvert$ 1.60

$[Fe(pmi)_3]^{2+}$, 43.12 °C

$\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^4(k' + k'')}{s^{-1}}$	$\frac{10^4k}{s^{-1}}$	$\frac{10^4k_d}{s^{-1}}$	$\frac{\delta}{\%}$
ca. 2×10^{-5}	0	0.001	0.435	+0.24
7.5×10^{-4}	0.010	0.009	0.443	−0.32
1.4×10^{-3}	0.019	0.018	0.452	−0.21
2.7×10^{-3}	0.036	0.036	0.470	+0.05
3.9×10^{-3}	0.052	0.051	0.484	−0.24
6.4×10^{-3}	0.082	0.082	0.516	−0.02
0.013	0.154	0.156	0.590	+0.25
0.019	0.219	0.219	0.653	+0.08
0.031	0.331	0.330	0.764	−0.09
0.050	0.468	0.467	0.901	−0.09
0.075	0.612	0.608	1.04	−0.36
0.125	0.826	0.826	1.26	+0·01
0.20	1.06	1.06	1.49	+0.03
0.30	1.28	1.29	1.72	+0.39
0.50	1.62	1.62	2.06	+0.27
0.80	1.98	1.98	2.41	−0.07
1.2	2.33	2.31	2.75	−0.42
1.6	2.58	2.58	3.01	0
2.0	2.76	2.80	3.23	+0.58
				$\Sigma\lvert\delta\rvert$ 3.72

$[Fe(ppi)_3]^{2+}$ and $[Fe(pmi)_3]^{2+}$ can be pictured as in the Scheme. According to this reaction scheme and applying the steady-state approximation to the half-bonded intermediates, the experimental rate constant, k_d, will be given by the equation (4) which is mathematically equivalent to (2), where $k_c' = (k_2' + k_3')(k_5' + k_6')/k_4'k_6'$ and $k_c'' = (k_2'' + k_3'')(k_5'' + k_6'')/k_4''k_6''$. At low $[H^+]$, $k_d = k_0{}^0 = [k_1'k_3'/(k_2' + k_3')] + [k_1''k_3''/(k_2'' + k_3'')] = k_0' + k_0''$. At high $[H^+]$, $k_d = k_\infty = k_1' + k_1''$

$$k_d = k_1'\left\{\frac{k_3'(k_5' + k_6') + k_4'k_6'[H^+]}{(k_2' + k_3')(k_5' + k_6') + k_4'k_6'[H^+]}\right\} + k_1''\left\{\frac{k_3''(k_5'' + k_6'') + k_4''k_6''[H^+]}{(k_2'' + k_3'')(k_5'' + k_6'') + k_4''k_6''[H^+]}\right\} \quad (4)$$

$= k_\infty' + k_\infty''$. The constant k_0^0 refers to total loss of the first ligand; k_∞' (or k_∞'') refers to breaking of the first metal–nitrogen bond in the original complex, which could be either the metal–pyridine or the metal–aliphatic di-imine bond. Assignment of k_∞' and k_∞'' can be made by comparing the ratio k_∞''(pmi) : k_∞'(pmi) $\approx 3 : 1$ with k_∞(bipy)/k_∞(gmi) $\approx 10^3 : 1$.* In spite of the drastic reduction of this ratio in the complex of the 'mixed' ligand, pmi, it is improbable that an inversion in the reactivities of the aliphatic and aromatic nitrogen atoms will occur on passing from $[Fe(bipy)_3]^{2+}$ and $[Fe(gmi)_3]^{2+}$ to $[Fe(pmi)_3]^{2+}$. It follows that the constant k_∞' refers to the reaction path in which the bond between the metal and the aliphatic imine nitrogen is broken first, while k_∞'' refers to that in which the metal–pyridine bond is broken first. The same conclusion holds for $[Fe(ppi)_3]^{2+}$ ($k_\infty'' : k_\infty' \approx 5 : 1$). A comparison of the values of the constants k_c' and k_c'' of $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ and those of k_c for $[Fe(bipy)_3]^{2+}$ and $[Fe(gmi)_3]^{2+}$ (see below) corroborates this assignment.

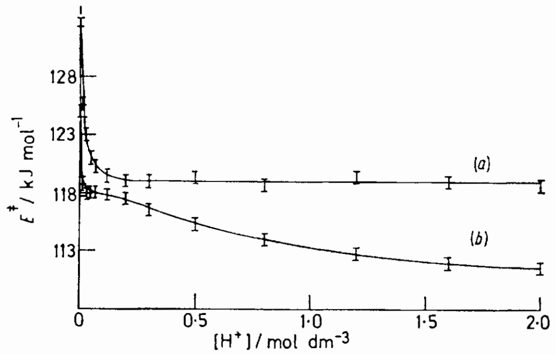
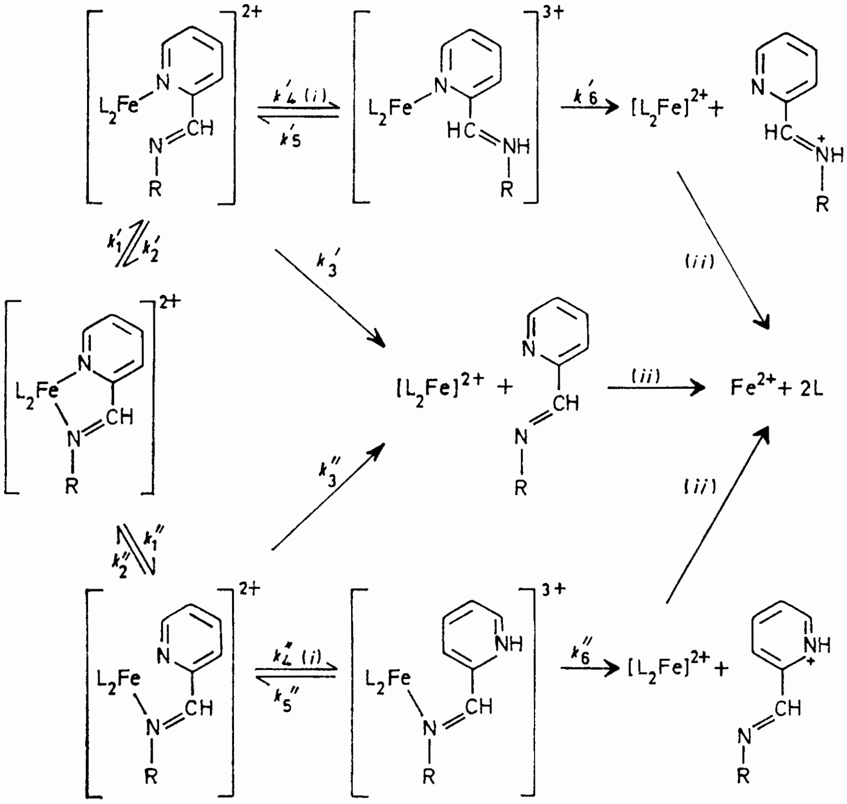


FIGURE 3 Dependence on [H$^+$] of the apparent Arrhenius activation energy ($E^\ddagger$) for dissociation of $[Fe(pmi)_3]^{2+}$ (*a*) and of $[Fe(ppi)_3]^{2+}$ (*b*)



SCHEME R = Me (L = pmi) or Pr^n (ppi): (*i*), ±H$^+$; (*ii*), fast.

The Ratio $k_\infty : k_0$ *and Estimation of* k_∞' *and* k_∞''.—According to the mechanism pictured above, $k_\infty/k_0 = 1 + (k_2/k_3)$ for both paths. Thus, $k_\infty' : k_0'$ (and $k_\infty'' : k_0''$) will depend on the ratio of the rates of reclosure of the chelate ring (k_2) and breaking of the second metal–nitrogen bond in the half-bonded intermediate (k_3). The rates of closure of chelate rings are mainly governed by highly positive entropies of activation[9] that will not be too different in different iron–di-imine complexes. On the other hand, breaking of the iron–unidentate di-imine bond will depend strongly on the environment of the nitrogen atom attached to the metal atom. Thus it is reasonable to expect that k_3 will be much more influenced by the nature of the di-imine ligand than will k_2. This means that $k_\infty : k_0$ reflects primarily the strength of the iron–unidentate di-imine bond in the half-bonded intermediates. For $[Fe(bipy)_3]^{2+}$ and $[Fe(gmi)_3]^{2+}$ k_∞ :

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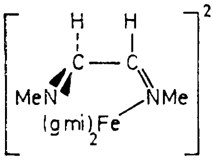
* Values of k_∞(bipy) and k_∞(gmi) were obtained from refs. 3 and 4, respectively, and corrected to the same temperature.

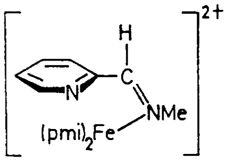
[9] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn.

k_0 * is *ca.* 7 (2.2M-HCl–LiCl) and 25 : 1 (0.5M-HCl–LiCl), respectively. The larger value of this ratio for $[Fe(gmi)_3]^{2+}$ compared with $[Fe(bipy)_3]^{2+}$ must be due to the greater basicity of the aliphatic imine nitrogen.

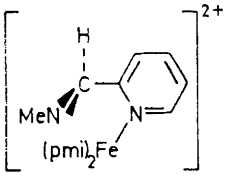
For $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ kinetics can only provide lower and upper limits for the rate constants, and consequently for the ratios $k_\infty' : k_0'$ and $k_\infty'' : k_0''$. The uncertainty in the ratios and in the constants can be reduced using for $[Fe(pmi)_3]^{2+}$, at 43 °C, a lower limit of $k_\infty' : k_0' = 7 : 1$ {the value of $k_\infty : k_0$ for $[Fe(bipy)_3]^{2+}$}; the upper limit was obtained from the condition that $k_\infty' : k_0' \leqslant k_\infty'' : k_0''$. Thus the estimated ratios were $k_\infty' : k_0' = 7$—11 and $k_\infty'' : k_0'' = 11$—13.5 : 1. From the above results one can conclude that k_∞ (bipy) : k_0 (bipy) $< k_\infty'$ (pmi) : k_0' (pmi) $< k_\infty''$ (pmi) : k_0'' (pmi) $< k_\infty$ (gmi) : k_0 (gmi). This trend can be rationalized on the basis of steric effects operating in the half-bonded intermediates (I)—(IV). The metal–nitrogen bond would be weaker in (II) than in (I) due to the greater steric hindrance of the pyridine ring compared with the CH:NMe group. The inverse effect would operate in (III) and (IV) and the metal–nitrogen bond would be stronger in (III). Thus k_3 would increase in the order (I) < (II) < (III) < (IV), in agreement with the trend observed for $k_\infty/k_0 = 1 + (k_2/k_3)$.



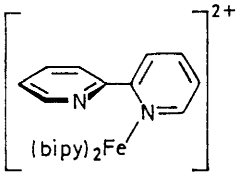
(I)



(II)



(III)



(IV)

TABLE 4

Values of the kinetic constants for dissociation of $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ in 2M-HCl–LiCl

Complex	$\frac{\theta_c}{°C}$	$k_\infty' : k_0'$	$\frac{10^5 k_0'}{s^{-1}}$	$\frac{10^4 k_\infty'}{s^{-1}}$	$k_\infty'' : k''$	$\frac{10^5 k_0''}{s^{-1}}$	$\frac{10^4 k_\infty''}{s^{-1}}$
$[Fe(pmi)_3]^{2+}$	43.12	9 ± 2	1.35 ± 0.35	1.14 ± 0.08	12.25 ± 1.25	3.0 ± 0.4	3.67 ± 0.13
	52.60	7.75 ± 1.75	5.8 ± 1.5	4.25 ± 0.35	10.25 ± 0.75	13.1 ± 1.5	13.8 ± 0.5
$[Fe(ppi)_3]^{2+}$	30.15	7.5 ± 3.5	1.8 ± 1.0	1.0 ± 0.1	6.6 ± 0.6	8.6 ± 1.2	5.57 ± 0.23
	40.06	6.5 ± 3.0	9 ± 5	4.4 ± 0.5	5.75 ± 0.25	45 ± 10	22.4 ± 1.7

Since pertinent data referring to the aliphatic *N*-propylimine derivative are not available, wide limits were used for $[Fe(ppi)_3]^{2+}$ (from $k_\infty' : k_0' = 2\, k_\infty'' : k_0''$ to $k_\infty'' : k_0'' = 2\, k_\infty' : k_0'$). At 40 °C, $k_\infty' : k_0' = 3.5$—9.5 and $k_\infty'' : k_0'' = 4.5$—5.9 : 1 were the estimated ratios. Table 4 gives the values of the ratios $k_\infty' : k_0'$ and $k_\infty'' : k_0''$ and the constants k_0', k_∞', k_0'', and k_∞'' for $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$, at different temperatures. The values of $k_0'(k_0'')$ and $k_\infty'(k_\infty'')$ were estimated by substitution of $k_\infty' = k_x' + k_0'$ $(k_\infty'' = k_x'' + k_0'')$ into $k_\infty'/k_0'(k_\infty''/k_0'')$. The error limits quoted for the constants were estimated by taking into account the uncertainties in the ratios $k_x' : k_0'$ $(k_x'' : k_0'')$ (see above) and in the parameters k_x' (k_x'') (see Table 2).

The Constant k$_c$.—Equation (5) can be obtained from (4). In equation (5), which is valid for both dissociation

$$k_c = \frac{k_2 + k_3}{k_4} + \frac{K(k_2 + k_3)}{k_6} \qquad (5)$$

paths (k_c' and k_c''), K $(= k_5/k_4)$ is the acid-dissociation equilibrium constant of the half-bonded protonated intermediate. A comparison of the values of k_c' and k_c'' of $[Fe(pmi)_3]^{2+}$ (Table 2) with the estimated values of k_c of $[Fe(gmi)_3]^{2+}$ (0.1, at 50—60 °C in 0.5M-HCl–LiCl) [4] and of $[Fe(bipy)_3]^{2+}$ (0.4, at 25 °C in 2.2M-HCl–LiCl) [3] shows the order $k_c' < k_c$(gmi) $< k_c$ (bipy) $< k_c''$.

For the acid hydrolysis of $[Fe(bipy)_3]^{2+}$, Basolo *et al.*[5] made the assumption that $k_6 \gg k_5$. Equation (5) then reduces to $k_c = (k_2 + k_3)/k_4$. From published data on the kinetics of formation of $[Fe(bipy)_3]^{2+}$,[6,10] one can conclude that $k_2 \approx 10^5$—10^6 and $k_3 \approx 10^4$—10^5 s^{-1}. On the other hand, rates of protonation of nitrogen are in general close to the limiting diffusion-controlled values,[11] $k_4 \approx 10^{10}$—10^{11} dm^3 mol^{-1} s^{-1}. Thus Basolo's assumption leads to $k_c \approx 10^{-4}$—10^{-6} mol dm^{-3}, which disagrees with the experimental values of k_c. It seems, therefore, that the values of k_c will depend essentially on the second term in equation (5).†

Since $k_2 \gg k_3$, and k_2 does not vary greatly for the different di-imine complexes, the differences in k_c will largely depend on differences in K/k_6. In terms of the basicities of the free nitrogen atom in the half-bonded intermediates (I)—(IV), a probable order of K(I) $\approx$ K(III) $\ll$ K(II) $\approx$ K(IV) can be assumed. Since k_6 increases in the order (I) < (II) < (III) < (IV), one can predict the order k_c(III) $< k_c$(I) $< k_c$(IV) $< k_c$(II) which corresponds qualitatively with the experimental order.

Kinetic Parameters for Acid Dissociation of Iron(II) *Di-imine Complexes.*—Table 5 presents kinetic data for

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* Extrapolated to 40 °C from data of refs. 3 and 4.

† This assumption is implicit in the interpretation of the rate data for dissociation of nickel(II), oxovanadium(IV), and beryllium pentane-2,4-dionates (R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 1966, **5**, 1223 and 1228).

[10] R. H. Holyer, C. P. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1965, **4**, 929.

[11] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell, Oxford, 1964, pp. 66, 244, and 263.

dissociation of the iron(II) di-imine complexes discussed above. $E_0^‡$ Refers to the parameter k_0, which for $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ contains contributions from both dissociation paths. $E_\infty^‡$ Refers to the parameter k_∞ and its values for $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ were calculated from k_∞' and k_∞'' using equation (6), where

$$E_\infty^‡ = R\left(\frac{T_2T_1}{T_2 - T_1}\right)\ln\frac{k_{\infty 2}}{k_{\infty 1}} \qquad (6)$$

$k_{\infty 1}$ and $k_{\infty 2}$ are constants at temperatures T_1 and T_2, respectively. The errors in $E_\infty^‡$ for $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ are the sum of those from two different sources: the uncertainties in $k_0'(k_0'')$ and in $k_x'(k_x'')$. The contribution of the first was taken as the difference in the values $E_\infty'(E_\infty'')$ obtained using first the upper limits and secondly the lower limits of $k_{\infty 2}'(k_{\infty 2}'')$ and $k_{\infty 1}'(k_{\infty 1}'')$. The contribution of the uncertainty in $k_x'(k_x'')$ was calculated by a standard method.[12]

TABLE 5

Activation parameters for dissociation of iron di-imine complexes

Complex	$-\log k_\infty$ at 40 °C	$E_0^‡$ / kJ mol^{-1}	$E_\infty^‡$ / kJ mol^{-1}	$\Delta S_0^‡$ / J K^{-1} mol^{-1}	$\Delta S_\infty^‡$ / J K^{-1} mol^{-1}
$[Fe(gmi)_3]^{2+}$ [a]	5.13	140 ± 2	128 ± 4	67 ± 7	64 ± 13
$[Fe(bipy)_3]^{2+}$ [b]	2.10	123 ± 2	109 ± 8	80 ± 7	62 ± 27
$[Fe(pmi)_3]^{2+}$	4.14 [c] 3.64 [d]	133 ± 2	119 ± 7, [c] 118 ± 4 [d]	95 ± 7	59 ± 20, [c] 67 ± 13 [d]
$[Fe(ppi)_3]^{2+}$	3.36, [c] 2.66 [d]	124 ± 2	117 ± 3, [c] 109 ± 4 [d]	80 ± 7	63 ± 8, [c] 51 ± 13 [d]

[a] From ref. 4. [b] From refs. 3*a*, 5*a*, and R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341. [c] Iron(II)–aliphatic imine bond broken first. [d] Iron(II)–pyridine bond broken first.

When comparing data in Table 5 one has to consider that the probability of breaking one single metal–ligand bond in the complex of a symmetrical ligand, *e.g.* bipy, is twice that of breaking the equivalent bond (*i.e.* metal–pyridine) in complexes of the unsymmetrical ligands pmi and ppi. With this in mind one notices that in $[Fe(pmi)_3]^{2+}$ k_∞' increases with respect to k_∞ of $[Fe(gmi)_3]^{2+}$ and k_∞'' decreases with respect to k_∞ of $[Fe(bipy)_3]^{2+}$ by the same factor, *i.e.* 18. The mean of $-\log k_\infty'$ and $-\log k_\infty''$ is 3.59 in agreement with the mean of $-\log k_\infty$ for $[Fe(gmi)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$, *i.e.* 3.62. The difference between the activation free energies, $\Delta(\Delta G^‡)$, of $[Fe(gmi)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ is 18 kJ mol^{-1} while the same difference for the two dissociation paths of $[Fe(pmi)_3]^{2+}$ is only 3 kJ mol^{-1}. This disparity is too large to be explained by differences in activation entropies, which are equal within experimental error. In fact, without taking into account the experimental errors in Arrhenius activation energies, one obtains the differences $E_\infty^‡[Fe(gmi)_3{}^{2+}] - E_\infty^‡[Fe(bipy)_3{}^{2+}] \approx 19$ kJ mol^{-1} and $E_\infty^‡[Fe(pmi)_3{}^{2+}] - E_\infty^‡[Fe(pmi)_3{}^{2+}] \approx 0$. Thus it is apparent that the differences in bond strengths of M–N (aliphatic imine) and M–N (pyridine) in complexes of the two symmetric ligands are substantially reduced on passing to the complex of the unsymmetrical (mixed) ligand pmi. The reasons for such behaviour are under investigation. Within the limits of experimental error, the means of both $E_0^‡$ and $E_\infty^‡$ of $[Fe(gmi)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ (131.8 and 118.0 kJ mol^{-1}) are close to $E_0^‡ = 132.6$ kJ mol^{-1} and the mean of $E_\infty^{‡\prime}$ and $E_\infty^{‡\prime\prime}$ (119.2 kJ mol^{-1}) obtained for $[Fe(pmi)_3]^{2+}$.

Though pertinent data referring to (glyoxalbispropylimine)iron(II) are not available, it is possible to assume that for this complex k_∞ and $E_\infty^‡$ are respectively larger and smaller than the values for $[Fe(gmi)_3]^{2+}$. The reverse probably holds for $[Fe(bipy)_3]^{2+}$. Thus it is to be expected that values of k_∞' and k_∞'' for $[Fe(ppi)_3]^{2+}$ are larger than those for $[Fe(pmi)_3]^{2+}$. The reverse should be valid for $E_\infty^‡$.

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[12] H. Margenau and G. M. Murphy, 'The Mathematics of Physics and Chemistry,' D. Van Nostrand, Princeton, 1967, 2nd edn., p. 515.