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# Kinetics and Mechanisms of Dissociation of Metal Chelates. II[1]. The Acid-catalyzed Dissociation of Tris(pyridine-2-acetaldehyde-N-Methylimine)iron(II)[2]

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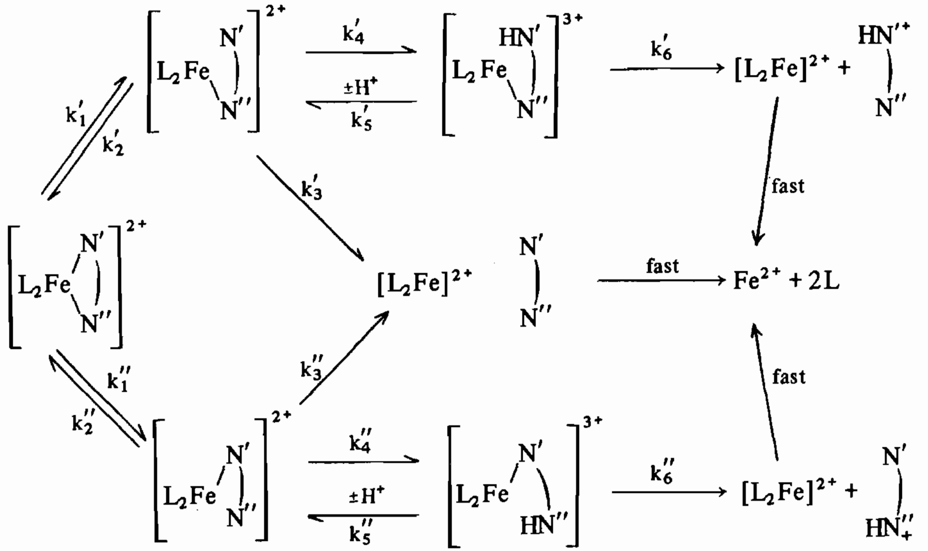
*The kinetics of the acid-catalyzed dissociation of tris(pyridine-2-acetaldehyde-N-methylimine)iron(II) were investigated photometrically in 2M HCl–LiCl mixtures, ranging from 2 × $10^{-5}$ to 2M in HCl. The rate of dissociation was shown to be first order in complex. Experimental rate data are in agreement with a mechanism previously suggested for related iron-diimine complexes with unsymmetric ligands. The mechanism consists of two simultaneous reaction paths differing by the sequence in which the bonds between the metal atom and the two different moieties of the ligand are broken. Values for the rate constants and activation parameters of the rate-determining step were estimated and compared with the values reported for related iron-diimine complexes. The influence of the methyl group, present in the chromophore, on the bonding ability of the ligand is discussed on the basis of these values.*

## Introduction

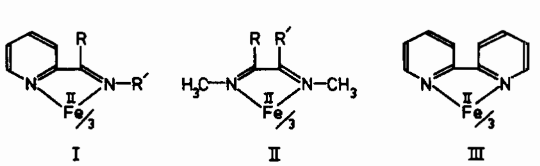
In a previous paper [1] we discussed the results of an investigation of the kinetics of the acid-catalyzed dissociation of iron(II) complexes of the pyridinalimine ligands pyridine-2-carbaldehyde-N-methylimine, pmi (I, R = H, R′ = Me) and pyridine-2-carbaldehyde-N-propylimine, ppi (I, R = H, R′ = Pr$^n$). The proposed mechanism follows the scheme of Basolo *et al.* [3, 4] for the decomposition of metal chelates, involving stepwise rupture of the metal–ligand bonds. Since the ligands studied are unsymmetric, two dissociation paths were recognized, differing by the sequence in which the bonds between the metal atom and the two different moieties of the ligand are broken.



L = N′–N″; N′ = aliphatic imine nitrogen; N″ = pyridine nitrogen

The rate law is expressed in equation 1,

$$\frac{-d\,[\mathrm{FeL_3^{2+}}]}{dt} = k_d\,[\mathrm{FeL_3^{2+}}] = \left[\frac{k_o'k_c' + k_\infty'[\mathrm{H^+}]}{k_c' + [\mathrm{H^+}]} + \frac{k_o''k_c'' + k_\infty''\,[\mathrm{H^+}]}{k_c'' + [\mathrm{H^+}]}\right][\mathrm{FeL_3^{2+}}] \qquad (1)$$



I, R = H, R′ = $Pr^n$ : $[Fe(ppi)_3]^{2+}$
I, R = H, R′ = Me : $[Fe(pmi)_3]^{2+}$
I, R = R′ = Me : $[Fe(pai)_3]^{2+}$
II, R = R′ = H : $[Fe(gmi)_3]^{2+}$
II, R = H, R′ = Me : $[Fe(mmi)_3]^{2+}$
II, R = R′ = Me : $[Fe(bmi)_3]^{2+}$
III : $[Fe(bipy)_3]^{2+}$

Figure 1. The iron(II) tris-diimine complexes discussed in this work.

where $k'_o = k'_1k'_3/(k'_2 + k'_3)$ and $k''_o = k''_1k''_3/(k''_2 + k''_3)$ are the limiting rate constants at $[H^+] = 0$, $k'_\infty = k'_1$ and $k''_\infty = k''_1$ the limiting rate constant at infinite $[H^+]$, $k'_c = [(k'_2 + k'_3)/k'_4] + [k'_5(k'_2 + k'_3)/k'_4k'_6]$ and $k''_c = [(k''_2 + k''_3)/k''_4] + [k''_5(k''_2 + k''_3)/k''_4k''_6]$.

Diimine ligands containing aliphatic imine groupings are unstable species. Thus, thermodynamic equilibrium data are not easily available for the complexes of these ligands. In such a case kinetic parameters for the dissociation of the complex species may provide some information on the strength of the metal–ligand bonds. A comparison of the kinetic constants and activation parameters obtained for some of the elementary reaction steps in the acid-catalyzed dissociation of $[Fe(pmi)_3]^{2+}$ [1] and those reported for the iron(II) complexes of the symmetric ligands 2,2′-bipyridine *bipy* (III) [3, 5, 6] and glyoxalbismethylimine, *gmi* (II, R = R′ = H) [7], suggested that the differences between the metal–pyridine and metal–aliphatic imine bond strength are significantly reduced on passing from *bipy* and *gmi* to the mixed ligand *pmi*. In order to know if the mechanism described above, and applicable to the dissociation of $[Fe(pmi)_3]^{2+}$ and $[Fe(ppi)_3]^{2+}$ [1], can be extended to the dissociation of related iron(II) diimine complexes with unsymmetric ligands, and to investigate the relationships between the kinetics and the structure of those complexes, we decided to extend the studies to the iron(II) complexes of pyridylketoimine ligands. In the present paper we discuss the results obtained for the acid-catalyzed dissociation of tris(pyridine-2-acetaldehyde-N-methylimine)iron(II) complex (I, R = R′ = $CH_3$). Figure 1 shows the complexes referred to in this paper.

## Results

The acid-catalyzed dissociation of $[Fe(pai)_3]^{2+}$ is first-order in complex. The rate constants were obtained in the usual way and refined by a least-squares treatment. Duplicate runs were reproducible to better than 1%. Plots of $k_d$ *vs.* $|H^+|$ resulted in the curves shown in Figure 2. These curves can be resolved into two calculated curves, corresponding to each of the dissociation paths, as expressed in equation 1. Equation 2, where $k^o_o = k'_o + k''_o$, $k'_x = k'_\infty - k'_o$ and $k''_x = k''_\infty - k''_o$, was derived from equation 1 and used in the calculations.

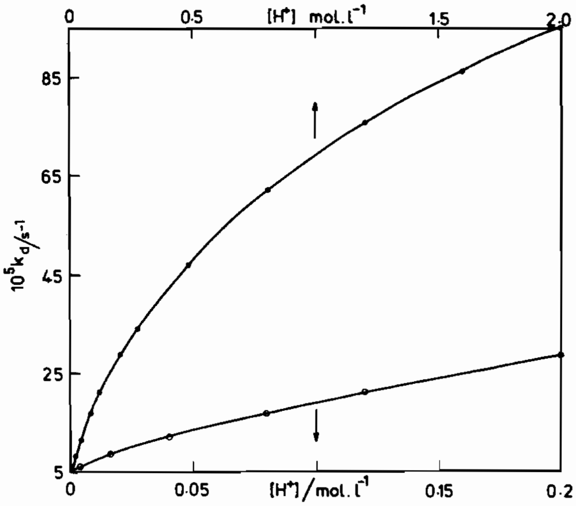


Figure 2. Dependence of the first order dissociation rate constant ($k_d$) of $[Fe(pai)_3]^{2+}$ on $[H^+]$, at 61.23 °C and I = 2.00 *M* (HCl–LiCl).

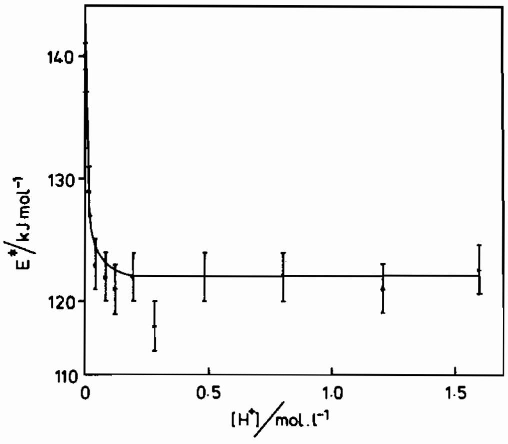


Figure 3. Dependence on $[H^+]$ of the apparent Arrhenius activation energy ($E^{\ddagger}$) for the dissociation of $[Fe(pai)_3]^{2+}$.

$$k = k_d - k^o_o = \frac{k'_x\,[H^+]}{k'_c + [H^+]} + \frac{k''_x\,[H^+]}{k''_c + [H^+]} = k' + k'' \qquad (2)$$

The values determined for the parameters of equation 2 are shown in Table I. The parameter $k^o_o$ was determined by extrapolating the experimental values of $k_d$

TABLE I. Kinetic Parameters in Equation 2 for Dissociation of $[Fe(pai)_3]^{2+}$ in 2*M* HCl–LiCl.

| Temperature, °C | $10^5$ $k_o^o$ s$^{-1}$ | $10^5$ $k'_x$s$^{-1}$ | $10^2$ $k'_c$ *M* | $10^4$ $k''_x$ s$^{-1}$ | $k''_c$ *M* |
|---|---|---|---|---|---|
| 52.85 | 1.46 ± 0.02 | 0.70 ± 0.02 | 1.63 ± 0.05 | 3.95 ± 0.05 | 0.86 ± 0.02 |
| 56.66 | 2.66 ± 0.03 | 3.3 ± 0.2 | 4.2 ± 0.2 | 7.4 ± 0.2 | 1.30 ± 0.05 |
| 61.23 | 5.38 ± 0.05 | 9.5 ± 0.6 | 6.8 ± 0.9 | 15.2 ± 0.3 | 1.77 ± 0.03 |

TABLE II. Values of k, experimental ($k = k_d$) and calculated from Equation 2 ($k = k' + k''$), for $[Fe(pai)]^{2+}$, in 2*M* HCl–LiCl.

| $[H^+]$/mol l$^{-1}$ | 52.85 °C | | $10^5$ $k_d$/s$^{-1}$<br>56.66 °C | | 61.23 °C | |
|---|---|---|---|---|---|---|
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| $2 \times 10^{-5}$ | 1.46 | 1.46 | 2.66 | 2.66 | 5.40 | 5.38 |
| $7.8 \times 10^{-4}$ | 1.52 | 1.53 | 2.78 | 2.77 | 5.58 | 5.56 |
| $1.4 \times 10^{-3}$ | 1.58 | 1.58 | 2.85 | 2.85 | 5.72 | 5.69 |
| $2.1 \times 10^{-3}$ | 1.64 | 1.64 | 2.95 | 2.94 | 5.83 | 5.84 |
| $3.4 \times 10^{-3}$ | 1.71 | 1.74 | 3.10 | 3.11 | 6.22 | 6.16 |
| 0.016 | 2.66 | 2.54 | 4.58 | 4.50 | 8.78 | 8.64 |
| 0.040 | 3.73 | 3.73 | 6.20 | 6.48 | 11.6 | 12.3 |
| 0.080 | 5.43 | 5.39 | 9.14 | 9.13 | 16.8 | 17.0 |
| 0.12 | 6.89 | 6.91 | 11.3 | 11.4 | 20.9 | 21.0 |
| 0.20 | 9.27 | 9.56 | 15.9 | 15.3 | 28.6 | 27.7 |
| 0.28 | 11.4 | 11.8 | 19.4 | 18.7 | 33.8 | 33.7 |
| 0.48 | 15.3 | 16.2 | 26.0 | 25.8 | 47.0 | 46.2 |
| 0.81 | 20.1 | 21.2 | 33.4 | 34.2 | 62.2 | 61.5 |
| 1.2 | 24.7 | 25.2 | 41.7 | 41.6 | 75.8 | 75.8 |
| 1.6 | 27.7 | 27.9 | 46.2 | 46.9 | 85.6 | 86.2 |
| 2.0 | 29.8 | 29.7 | 51.5 | 50.9 | 95.4 | 95.2 |

to $[H^+] = 0$. The "best" set of values for the parameters $k'_x$, $k''_x$, $k'_c$ and $k''_c$ was obtained by successive approximations in order to minimize the average deviation between the experimental values of $k_d$ and those calculated from equation 2. The calculation was programmed for a PDP 10 digital computer and processed in the Computation Centre of this University. Calculated and experimental values of $k_d$ are compared in Table II.

Figure 3 shows the Arrhenius activation energies as a function of $[H^+]$.

## Discussion

The results show that the kinetics of dissociation of tris(pyridine-2-acetaldehyde-N-methylimine)iron(II), $[Fe(pai)_3]^{2+}$ (I, R = R' = $CH_3$), can be interpreted in terms of the mechanism of Basolo *et al.* [3, 4], involving stepwise rupture of the metal–ligand bonds. The first step of the dissociation process is the rupture of a single metal–ligand bond (rate constant $k_\infty$). The half-bonded intermediate thus formed either recloses to reform the chelate ring or loses the first ligand completely (rate constant $k_o$). The loss of the further ligands is very fast and does not affect the rate law.

The dissociation rate constant at infinite $[H^+]$, $k_\infty$, reflects the strength of the metal–nitrogen bonds. In the case of the complex under study, the constant contains contributions of both dissociation paths. Values of $k'_\infty$ and $k''_\infty$ can be calculated from $k'_\infty = k'_x + k'_o$ and $k''_\infty = k''_x + k''_o$ (see equation 2). Kinetics provide values only for the parameters $k'_x$ and $k''_x$. Values for $k'_o$ and $k''_o$ can only be obtained as a sum ($k_o = k'_o + k''_o$) by extrapolating $k_d$ to $[H^+] = 0$. However, from the values shown in Table I one can see that $k''_x \gg k_o^o$ and so $k''_\infty \approx k''_x$. Estimation of $k'$ is less accurate, but can be made assuming that $k''_o > 2k'_o$ [8]. This leads to values of 0.7–1.2$\times 10^{-5}$ s$^{-1}$ at 52.85 °C, 3–4.4 $\times 10^{-5}$ at 56.66 °C and 9–12 $\times 10^{-5}$ at 61.23 °C.

A comparison between the values of $k_d$ at 52.85 °C shown in Table II and the values reported [1] for $[Fe(pmi)_3]^{2+}$ at 52.60 °C shows that the ratio $k_d$(pmi)/$k_d$(pai) decreases as $[H^+]$ increases. At low $[H^+]$ ($k_o$) the ratio is *ca.* 12 and at high $[H^+]$ it drops to *ca.* 4. The higher kinetic stability of $[Fe(pai)_3]^{2+}$

TABLE III. Rounded-off Values of Kinetic Parameters for the Dissociation of Iron Diimine Complexes. Rate Constants at 60 °C.

| Ligand | $k_o$, $s^{-1}$ | $k_\infty$, $s^{-1}$ | $-\log k_o$ | $-\log k_\infty$ | $E^\ddagger_o$, kJ | $E^\ddagger_\infty$, kJ |
|---|---|---|---|---|---|---|
| gmi[a] | $8 \times 10^{-6}$ | $1.2 \times 10^{-4}$ | 5.1 | 3.9 | 140 | 127 |
| mmi[b] | – | $3 \times 10^{-5}$ | – | 4.5 | – | – |
| bmi[b] | – | $3 \times 10^{-6}$ | – | 5.5 | – | – |
| pmi[c] | $6 \times 10^{-4}$ | $1 \times 10^{-3}$ [f]<br>$3 \times 10^{-3}$ [g] | 3.2 | 3.0<br>2.5 | 133 | 119[f]<br>117[g] |
| ppi[c] | $3 \times 10^{-3}$ | $6 \times 10^{-3}$ [f]<br>$2.5 \times 10^{-2}$ [g] | 2.5 | 2.2<br>1.6 | 124 | 117[f]<br>109[g] |
| pai[d] | $5 \times 10^{-3}$ | $1 \times 10^{-4}$ [f]<br>$1.5 \times 10^{-3}$ [g] | 4.3 | 4.0<br>2.8 | 141 | 122 |
| bipy[e] | $2 \times 10^{-2}$ | 0.15 | 1.7 | 0.8 | 123 | 109 |

[a] Reference 7. [b] Reference 9. [c] Reference 1. [d] This work. [e] References 3, 5, 6. [f] Iron–aliphatic imine bond broken first ($k'_\infty$). [g] Iron–pyridine bond broken first ($k''_\infty$).

reflected in the values of $k_d$ at low [H$^+$] should be due to the presence of the methyl group in the α-carbon, which both increases the σ-bonding ability of the ligand [9] and hinders rotation around the carbon–carbon bond in the chromophore. The decrease in the ratio as [H$^+$] increases could be explained on the basis of the protonation of the half-bonded intermediates. Due to a greater basicity of the nitrogens induced by the methyl group at the α-carbon, the $[Fe(pai)_3H]^{3+}$ protonated species must be more stable than the corresponding $[Fe(pmi)_3H]^{3+}$.

Table III shows the rounded-off values of the kinetic parameters for a series of diimine iron(II) complexes. Assignment of $k'_\infty$ and $k''_\infty$ for the complexes of unsymmetric ligands can be made by comparison with the values of $k_\infty$ of $[Fe(gmi)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ – $k'_\infty$ corresponds to the rupture of the iron–aliphatic nitrogen bond first and $k''_\infty$ to the iron–pyridine nitrogen bond first. Considering the aliphatic imine complexes it can be seen that each methyl group present in the chromophore decreases the constant by one order of magnitude, following an increase in the σ-bonding ability of the ligands [9]. The ratio $k'_w(pmi)/k'_w(pai)$ which corresponds to the rupture of the metal–aliphatic imine bond is *ca.* 10:1 in accordance with the introduction of a methyl group in the chromophore. The ratio $k'_\infty(pai):\frac{1}{2}k'_\infty(bmi)$ [10] is *ca.* 70:1, showing a reduction in the bonding strength on passing from the symmetric to the unsymmetric diimine ligand. The same has been observed [1] for $[Fe(pmi)_3]^{2+}$ and $[Fe(gmi)_3]^{2+}$ ($k'_\infty(pmi):\frac{1}{2}k'_\infty(gmi)$ = 17:1). The constant for the rupture of the iron–pyridine bond ($k''_\infty$) decreases in the order $[Fe(bipy)_3]^{2+}$ > $[Fe(pmi)_3]^{2+}$ > $[Fe(pai)_3]^{2+}$ (50:2:1) which is the order of increasing bond strength. The effect of the methyl group on the α-carbon is greater upon the metal–aliphatic imine bond as suggested by a comparison between the values of $k'_\infty$ and $k''_\infty$ for $[Fe(pai)_3]^{2+}$ and $[Fe(pmi)_3]^{2+}$, $k'_\infty(pmi) \approx 10k'_\infty(pai)$ and $k''_\infty(pmi) \approx 2k''_\infty(pai)$, at 60 °C.

The dependence of the apparent Arrhenius activation energy on [H$^+$] is shown in Figure 3. Since the observed rate constants are made up of sums of individual rate constants it is not possible to obtain values of $E^\ddagger_\infty$ for each independent dissociation path. However, from the values of the parameters in Table I one can infer that $k''_\infty \gg k''_o$. If this is so, $k''_2 \gg k''_3$ and $k''_o = k'_1k''_3/k''_2$, that is $k''_o/k''_\infty = k''_3/k''_2$. Since $k''_\infty \gg k'_\infty$ and assuming that $k''_o \gg k'_o$, $E^\ddagger_o - E^\ddagger_\infty \approx E^\ddagger_3 - E^\ddagger_2 \approx 20$ kJ.

It is thus apparent that the activation energy for breaking the iron–aliphatic imine bond in the half-bonded intermediate is greater than that for the ring closure at the pyridine nitrogen – as one would expect.

## Experimental

### *Materials*

Tris(pyridine-2-acetaldehyde-N-methylimine)iron(II) perchlorate was prepared from pyridine-2-acetaldehyde, N-methylimine and iron(II) chloride in water–ethanol and precipitated with sodium perchlorate [11]. The crude product (2 g) was dissolved in 1 l of water–methanol 50%. Careful addition of

$NaClO_4$ to the filtered solution at 0 °C, resulted in precipitation of *ca.* 2/3 of the complex. Addition of more $NaClO_4$ to the filtered solution precipitated a second fraction (0.15 g). The two fractions differed by less than 0.5% in their rates of dissociation.

### *Kinetics*

Kinetic measurements were carried out photometrically in 2.00 *M* HCl–LiCl mixtures. Acidity was varied from $2 \times 10^{-5}$ (0.005 *M* acetate buffer) to 2 *M*. A weighed amount of the complex was dissolved in 50 ml of the electrolyte in order to give a initial transmittance of *ca.* 20%. The concentration of the complex was *ca.* $10^{-5}$ *M*. The reactions were carried out in thermostatted water bath with the temperature maintained within ±0.03 °C. Samples were taken at appropriate time intervals and the transmittances at 558 nm measured on a Zeiss PM2D spectrophotometer. Kinetic runs were made at 52.85, 56.66 and 61.23 °C. The reactions were followed for at least two half-lives.

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