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Acid Aquation of the *tris*-2,2′(bipyridyl)iron(II) Cation. Activation Parameters and the Spin State of Intermediate Species

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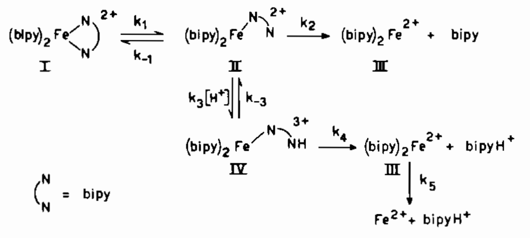
Activation parameters for the fission of the first iron–nitrogen bond in the acid aquation of $Fe(bipy)_3^{2+}$ have been determined. Available evidence suggests that there is a spin change associated with the fission of the first iron–nitrogen bond and that only the reactant is low-spin. Mechanisms of some related reactions of $Fe(bipy)_3^{2+}$ are discussed.

Introduction

In the presence of sufficient strong acid, $Fe(bipy)_3^{2+}$ and related low-spin d^6 substitution inert iron(II) complex cations dissociate. The rate of aquation of $Fe(bipy)_3^{2+}$ increases with acid concentration until a rate limit is reached[1] at *ca.* 2N. This has been interpreted[2] in terms of a mechanism involving species containing protonated 2,2′-bipyridyl as a monodentate ligand (see scheme – for clarity, solvent molecules are omitted).



The spin state of intermediates containing five coordinated nitrogen atoms is of interest because the reactant complex is low-spin, while complexes of the type $Fe(bipy)_2X_2$ are generally[3] high-spin*. Even though there has been discussion about the mechanism of this reaction, it is not known when the spin change takes place, and quoted activation parameters have uncomfortably large uncertainty limits. Here, considerably higher precision activation parameters for fission of the first iron–nitrogen bond are reported, and these, together with other results, are used to discuss the spin state of the species containing five coordinated nitrogen atoms.

* Low-spin complexes are obtained with X = high field ligand such as CN^-.

Experimental

Aquation of $Fe(bipy)_3^{2+}$ was monitored spectrophotometrically using a Perkin Elmer 204 u.v./visible instrument equipped with a thermostatted cell holder. Temperature was measured to $\pm$ .02° C with a mercury in glass thermometer, and variations in a cell at a set temperature were about $\pm$ .05° C.

Each kinetic run was started by adding 0.05 ml of concentrated $Fe(bipy)_3^{2+}$ solution to 3.00 ml of sulphuric solution (3.99N) contained in a 1 cm quartz cell that had reached thermal equilibrium in the thermostatted cell holder. After quickly shaking the stoppered cell, the change in optical density, initially *ca.* 1.3 and zero at the end of the reaction, at 525 nm was followed with respect to time. Rate constants were obtained from plots of log(optical density) versus time. These were linear for at least 95% of the reaction.

Results and Discussion

Equation (1) is obtained[2] by assuming stationary state kinetic conditions for II of the reaction scheme in the presence of excess acid if $k_{-3} < k_3[H^+]$ and k_4, k_5 are fast.

$$k_{obs} = \frac{k_1(k_2 + k_3[H^+])}{k_{-1} + k_2 + k_3[H^+]} \tag{1}$$

This expression produces an increase of observed rate constant with increasing $[H^+]$ of the type observed. By including a k_{-3} term (putting $k_3/k_{-3} = K_3$) and assuming stationary state kinetics for II and IV, equation (2) is obtained[4]:

$$k_{obs} = \frac{k_1(k_2 + K_3k_4[H^+])}{k_{-1} + k_2 + K_3k_4[H^+]} \tag{2}$$

This equation produces the same form of acid dependence as (1) and both equations have the same limiting observed rate constant at high $[H^+]$ (k_1) and the same extrapolated rate at zero $[H^+]$: $k_1k_2/(k_{-1} + k_2)$. Our kinetic data for aquation of $Fe(bipy)_3{}^{2+}$ in 3.9N H_2SO_4, together with derived activation parameters, are given in Table I. Rate constants at two temperatures (17° C and 35° C) calculated from these data agree well with limiting values obtained by Baxendale and George[1] (2.1×10^{-4}, $3.5 \times 10^{-3}s^{-1}$; calculated 2.3×10^{-4}, $3.4 \times 10^{-3}s^{-1}$), confirming that the concentration of acid used was sufficient to produce limiting rates over the experimental temperature range. Our results therefore refer to fission of the first iron–nitrogen bond in the dissociation process.

Recently, the kinetics of the reaction between $Fe(bipy)_3{}^{2+}$ and CN^- have been studied[5] under pseudo first order conditions (excess CN^-, ionic strength $0.1M$), over a fairly wide temperature range. The observed pseudo first order rate constant for this reaction forming $Fe(bipy)_2(CN)_2$, is given by:

$$k_{obs} = k_1' + k_2'[CN^-]$$

Available evidence[5,6] suggests that the second order term results from the bimolecular attack of CN^- on I.

The mechanism of the CN^- independent path could be similar to that for acid aquation, with CN^- becoming bound to the iron rather than to the ligand as with H^+ (II→IV). The extrapolated rate at zero reactant concentration (k_1') would then be $k_1k_2/(k_{-2} + k_2)$. This is the case. At 25° C the value of k_1' for reaction with cyanide ion is close to the extrapolated rate of acid aquation[7] at zero $[H^+]$. However, plots of pseudo first order rate constant *vs.* $[CN^-]$ are linear and show no superimposed curvature due to the k_1' term rising in value to k_1, even though this increase, if present, should be readily detected. This indicates that in the reactions with CN^- $k_2 > (k_3'k_4'/k_{-3}')[CN^-]$ and only in the reaction involving rapid protonation is $k_2 \approx (k_3k_4/k_{-3})[H^+]$ at experimentally convenient reactant concentrations. This is best explained in terms of II being a reactive high-spin complex (see below).

TABLE I. Kinetic Data for Aquation of $Fe(bipy)_3{}^{2+}$ in Sulphuric Acid.[a]

Temp./° C	k_{obs}/s^{-1}	k_{calc}/s^{-1} [b]
41.6	8.31×10^{-3}	8.37×10^{-3}
41.6	8.35×10^{-3}	8.37×10^{-3}
41.6	8.32×10^{-3}	8.37×10^{-3}
35.75	3.68×10^{-3}	3.73×10^{-3}
35.75	3.79×10^{-3}	3.73×10^{-3}
30.2	1.69×10^{-3}	1.68×10^{-3}
30.2	1.71×10^{-3}	1.68×10^{-3}
27.6	1.16×10^{-3}	1.15×10^{-3}
27.6	1.17×10^{-3}	1.15×10^{-3}
25.0	7.71×10^{-4}	7.77×10^{-4}
25.0	7.67×10^{-4}	7.77×10^{-4}
25.0	7.78×10^{-4}	7.77×10^{-4}
25.0	7.77×10^{-4}	7.77×10^{-4}
22.9	5.49×10^{-4}	5.64×10^{-4}
22.9	5.58×10^{-4}	5.64×10^{-4}
20.6	4.02×10^{-4}	3.96×10^{-4}
20.6	3.96×10^{-4}	3.96×10^{-4}

Activation parameters[c]: $\Delta H^{\neq} = 26.1 \pm .1$ kcal mol^{-1}
$\Delta S^{\neq} = 14.8 \pm .3$ cal mol^{-1}K^{-1}

[a] H_2SO_4 concentration = 3.92N. [b] Calculated from the derived activation parameters. [c] Error limits are standard deviations, uncorrected for degrees of freedom.

Since the temperature dependences of k_1' and k_1 are available, the variation of the ratio $k_2/(k_{-1} + k_2)$ with temperature may be calculated. In doing this, some caution is necessary because values of k_1 and k_1' were not obtained at the same ionic strength. Although it is not possible directly to determine k_1 at low ionic strengths, it is unlikely that its value will be drastically changed by ionic strength effects. Published[5] results suggest that k_1' for the cyanide reaction decreases slightly on increasing the ionic strength (at 27° C $\mu = 0.1$, $k_1' = 2.5 \pm .6 \times 10^{-4}s^{-1}$; $\mu = 0.8$, $k_1' = 1.6 \pm 1 \times 10^{-4}s^{-1}$) but the error limits are rather large. Values of k_1' at zero ionic strength for acid aquation at 25.0° C are $1.27 \pm .03 \times 10^{-4}s^{-1}$ in H_2SO_4 (calculated from data in ref. 7) and $1.2 \times 10^{-4}s^{-1}$ in HCl (ref. 2a). For reaction with hydroxide ion* $k_1' = 1.4 \pm 1 \times 10^{-4}s^{-1}$ (ref. 7). These values are somewhat lower than for reaction with CN^- at 25.3° C with $\mu = 0.1$ (see Table II). Since ionic strength factors are likely to remain fairly constant over our temperature range, it is worthwhile calculating values of $k_2/(k_{-1} + k_2)$ to see if the difference in the enthalpies of activation associated with k_2 and k_{-1} is large. These data are contained in Table II. Because of the low precision of the k_1' values ($k_2'[CN^-] > k_1'$, only four points at each temperature), the $k_2/(k_{-1} + k_2)$ ratios are similarly not very precise. None the less, it is clear that this ratio is not strongly temperature dependent and suggests that k_{-1} and k_2 have similar enthalpies of activation, which is best rationalised by II being high-spin (see below).

Spin States of II and IV

Kinetic consequences of the spin state of the species concerned are now considered in terms of the simple crystal field stabilisation approach.[8] Quoted values of ΔDq are based on dissociative mechanisms, but similar conclusions are obtained for associative mechanisms.

Low-Spin

If II is low-spin, k_1 will not be very large ($\Delta Dq \approx 4$) while k_2 is expected to be small ($\Delta Dq \approx 20$). Complex

* The reaction with OH^-, like that with CN^-, obeys a two-term rate law.

TABLE II. Limiting Rate Constants for Acid Aquation of $Fe(bipy)_3^{2+}$ and Rate Constant Ratios at Various Temperatures.

Temp./° C	k_1/s^{-1} [a]	k'_1/s^{-1} [b]	R [c]
25.3	8.13×10^{-4}	$2.08 \pm .21 \times 10^{-4}$	$0.26 \pm .03$
27.0	1.05×10^{-3}	$2.45 \pm .62 \times 10^{-4}$	$0.23 \pm .23$
28.0	1.22×10^{-3}	$2.94 \pm .21 \times 10^{-4}$	$0.24 \pm .02$
29.5	1.52×10^{-3}	$3.47 \pm .85 \times 10^{-4}$	$0.23 \pm .06$
32.0	2.18×10^{-3}	$5.62 \pm .73 \times 10^{-4}$	$0.26 \pm .03$
33.3	2.63×10^{-3}	$7.18 \pm .26 \times 10^{-4}$	$0.27 \pm .01$
35.0	3.35×10^{-3}	$8.40 \pm .45 \times 10^{-4}$	$0.25 \pm .13$
37.4	4.69×10^{-3}	$1.17 \pm .09 \times 10^{-3}$	$0.25 \pm .02$
40.0	6.72×10^{-3}	$1.87 \pm .07 \times 10^{-3}$	$0.28 \pm .01$
41.8	8.58×10^{-3}	$2.61 \pm .49 \times 10^{-3}$	$0.30 \pm .06$
42.9	9.95×10^{-3}	$3.02 \pm .48 \times 10^{-3}$	$0.30 \pm .05$
46.0	1.50×10^{-2}	$3.62 \pm .48 \times 10^{-3}$	$0.24 \pm .03$

[a] Calculated from data in Table I. [b] Calculated from data given in ref. 5 using a weighted least mean squares treatment in which each rate constant is assumed to have a constant percentage error. Quoted error limits are standard deviations corrected for the appropriate number of degrees of freedom such that doubling them produces 95% confidence limits. [c] $R = k_2/(k_{-1} + k_2)$, quoted errors as for b neglecting errors associated with k_1.

II would have kinetic stability. However, spectra obtained in the 350–600 nm region during our acid aquation experiments failed to produce any evidence for such intermediates, and there are no pH dependent changes in the visible spectrum during acid aquation.[2] With II being low-spin, k_{-1} might be expected to be faster than k_2 since the latter reaction involves a spin change, and indeed k_{-1} is faster than k_2 ($k_{-1} \approx 3k_2$, see Table II), but this difference is not temperature dependent and cannot be attributed to a significantly large value of $\Delta\Delta H^{\neq}$ for the two reactions. The comparatively small reactivity difference is therefore perhaps best interpreted in terms of a proximity chelate effect.

High-Spin

With II high-spin, k_1 is expected to be very slow ($\Delta Dq \approx 20$) and because II and III are likely to have similar spin states, no detectable quantities of these complexes are expected since $k_1 < k_2$, k_4, k_5. As found experimentally, $\Delta H_{-1}^{\neq}$ and $\Delta H_2^{\neq}$ are expected to be similar (reactions of a high-spin complex) and the rate determining step will be fission of the first iron–nitrogen bond (k_1). In agreement with this proposal, the reaction of $Fe(bipy)_3^{2+}$ with CN^- (and OH^-) provide evidence (see above) that complex II is a highly reactive short-lived species.

Finally, it is noteworthy that there is no preparative evidence for simple low-spin compounds of the type $Fe(bipy)_2N(H_2O)^{2+}$ (N = nitrogen donor).

Conclusions

From the arguments presented above, it seems likely that II and IV of the reaction scheme are high-spin complexes. The spin change occurs during the fission of the first iron–nitrogen bond.

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