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The Chemistry of theTris(2,2′-bipyridyl)iron(II) Cation in Strongly Acidic Media

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Tris*(2,2′-bipyridyl)iron(II) perchlorate is completely dissociated in concentrated hydrochloric acid to mono-protonated bipyridyl and chloroferrate. The pale blue solutions given by* $[Fe(bipy)_3](ClO_4)_2$ *in concentrated nitric, sulphuric or perchloric acids are attributed to the formation of iron(III) species, including possibly a* bis*(2,2′-bipyridyl) complex. A solid of composition* $[Fe(bipy)_2(NO_3)_2](ClO_4)$ *has been isolated from the nitric acid solutions which both magnetic and Mössbauer data show to contain low spin iron (III). The species generates* $[Fe(bipy)_3]^{2+}$ *rapidly when dissolved in water in the presence of light, but is stable in solutions o fconcentrated oxidising acids.*

Introduction

Several years ago Healy and Murmann[1] reported that the familiar deep red tris(2,2′-bipyridyl)iron(II) cation slowly produced a pale blue solution (λ_{max} = 620 nm, E = 15) when dissolved in 8-12 *M* $HClO_4$. The solution was paramagnetic (μ_{eff} = 5.2 B.M.) but partially reverted to the $Fe(bipy)_3^{2+}$ complex on dilution with 1 *M* $HClO_4$. Similar behaviour was observed in sulphuric acid. The observations were explained by involving a protonated form of the cation and some degree of dissociation to Fe^{2+}. Some related complexes underwent similar changes, and the observations were of importance at the time in connection with attempts to explain the acid dependence of the dissociation of the complex cations.[2,3]

We have now observed that, in concentrated nitric acid, the rate of production of an identical blue complex is much more rapid and more complete than in $HClO_4$. Subsequent isolation of a solid material from the nitric acid medium leads us to believe that an iron(III) rather than an iron(II) species is responsible for the blue colour in strongly acid media.

Results and Discussion

(a) *Solution of* $[Fe(bipy)_3](ClO_4)_2$ *in concentrated Hydrochloric Acid.* The *tris*(2,2′-bipyridyl)iron(II) complex as perchlorate is soluble in concentrated hydrochloric acid to afford a yellow solution the ultraviolet spectrum of which is consistent with the presence of protonated bipyridyl. The peak maximum of 298 nm suggested mainly mono-protonated bipyridyl molecules to be present since bipy H^+ has a characteristic band at 301 nm.[4,5] The spectrum of bipyriyl in 12 *M* $HClO_4$, which might reasonably be expected to contain a considerable concentration of $[bipyH_2]^{2+}$ ions, gives a maximum at 288 nm. In addition to bands attributable to protonated bipyridyl, the spectrum contains a band at 370 nm which is also present in the spectrum of solutions of ferrous chloride in concentrated hydrochloric acid and which is attributed to an anionic chloro-complex of iron. It is clear that virtually complete dissociation of the *tris*(2,2′bipyridyl)iron(II) complex occurs in this medium.

(b) *Solutions of* $[Fe(II)(bipy)_3](ClO_4)_2$ *in concentrated nitric, sulphuric and perchloric acids.* In close agreement with Healy and Murmann[1] we find that, in 60% $HClO_4$, the familiar deep red colour of the $[Fe^{II}(bipy)_3]^{2+}$ ion slowly gives way to a pale blue colour (λ_m = 610 nm, E apparent = 15). However in concentrated nitric acid the development of the blue colour is much more rapid (λ_m = 610 nm) and the final value of E apparent is now 160 mol^{-1} cm^{-1}. In concentrated (98%) sulphuric acid the rate of production of the blue colour is again slow but the limiting value for E app. is 90. Addition of small quantities of water to the sulphuric acid solution did not alter E app., thus the intensity of the blue colour achieved does not appear to be related to the H_3O^+ concentration; indeed addition of large quantities of water resulted in all three cases to partial regeneration of $[Fe^{II}(bipy)_3]^{2+}$. In our experiments the regeneration of the ferrous complex was 25% (HNO_3), and 10% (H_2SO_4 and $HClO_4$) as determined colourimetrically and based on the quantity of $[Fe(bipy)_3](ClO_4)_2$ initially introduced.

We have been able to isolate a bluish green solid from the solution of $[Fe(bipy)_3](ClO_4)_2$ in concentrated nitric acid. This material had a diffuse reflectance spectrum (20.3 kK, sh.; 16.4 kK) similar to that observed for a sample of $[Fe^{III}(bipy)_3](ClO_4)_3$ synthesised by the method of Bustall and Nyholm (21.3 K, 16.3

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[1] E.A. Healy and R.K. Murmann, *J. Amer. Chem. Soc.*, *79*, 5827 (1957).
[2] F. Basolo, J.C. Hays, and H.M. Neumann, *J. Amer. Chem. Soc.*, 76, 2807 (1954).
[3] E.A. Healy and R.K. Murmann, *J. Amer. Chem. Soc.*, *83*, 2092 (1961).
[4] K. Nakamoto, *J. Phys. Chem.*, *64*, 1420 (1960).
[5] I.R. Beattie and M. Webster, *J. Phys. Chem.*, *66*, 115 (1962).

K).[3] However both elemental analysis and, more particularly Mössbauer data suggest that it is not in fact the *tris*(2,2'bipyridyl)iron(III) complex. The analysis indicates a stoichiometry $Fe(bipy)_2(NO_3)_2(ClO_4)$. The infra-red spectrum shows the perchlorate to be ionic and also contains, bands characteristc of co-ordinated nitrate groups (1430 cm^{-1}, 1285 cm^{-1}, 1015 cm^{-1}, 810 cm^{-1}), however if KBr is used as the sampling matrix only bands due to ionic nitrate are seen (1360 cm^{-1}). The Mössbauer spectrum consists of a cleanly resolved quadrupole doublet at room temperature the chemical isomer shift (δ) being 0.32 mm sec^{-1} relative to sodium nitro-pusside and the quadrupole splitting 1.58 mm sec^{-1}; on cooling to 77 K the parameters are $\delta = 0.40$ mm sec^{-1} and $\Delta E_q = 1.75$ mm sec^{-1}. The effective magnetic moment is 2.15 B.M. at 298 K and 2.03 at 77 K. Thus the magnetic and Mössbauer data are consistent with the persence of spin paired iron(III) in a single chemical environment and give no indication of anomalous temperature behaviour (cf. data[8] for $[Fe^{III}(bipy_3](ClO_4)_3.3H_2O$, $\delta = 0.29$ (300K), 0.32 (80K)mm sec^{-1}; $\Delta E_q = 1.69$ (300 K), 1.80 (80 K)-mm sec^{-1}). The complex gives a solution in concentrated nitric acid of $\lambda_m = 610$ nm and E app = 130 and exactly similar solutions in concentrated perchloric acid ($\lambda_m = 610$ nm, E = 130) and sulphuric acid ($\lambda_m = 610$ nm, E = 120). The nitric acid solutions obey Beer's law and it would appear to be established that the species responsible for the blue colour are iron(III) compounds.

Whilst the solid material discussed above may tentatively be identified as dinitratobis(2,2'-bipyridyl)-iron(III) perchlorate with, presumably,[9], a *cis* configuration, it is less easy to identify the species in solution. *Tris*(2,2'-bipyridyl)iron(III)perchlorate also affords blue solutions of $\lambda_m = 610$ nm in nitric acid for which E = 190. This band is probably of charge transfer origin and occurs in similar positions for the *tris*- and *cis* - *bis* - complexes. The fact that the solutions prepared from the *tris*-complex show greater values of E app suggest that this may be the major species responsible for the colour, thus we need to invoke a disproportionation in solutions prepared from $Fe(bipy)_2(NO_3)_2\ ClO_4$:

$$3[Fe(bipy)_2(NO_3)_2]ClO_4 \rightleftharpoons 2[Fe(bipy)_3]^{3+} + Fe^{3+} + 6NO_3^- \qquad (1)$$

However, determination of the magnetic moments of solutions in concentrated nitric acid does not suggest that reaction (i) is important since solutions obtained from $[Fe(bipy)_2(NO_3)_2]ClO_4$ (solution μ_{eff} = 2.4 B.M.), $[Fe(bipy)_3](ClO_4)_3$ (solution μ_{eff} = 2.3 B.M.) or $[Fe^{II}(bipy)_3](ClO_4)_2$ (solution μ_{eff} = 2.4 B.M.) all contain only low spin iron(III) whereas (1), if important, should afford a reasonable concentration of high spin iron(III). An alternative view is that the following dissociation equilibria are set up:

$$[Fe(bipy)_3]^{3+} \rightleftharpoons [Fe(bipy)_2]^{3+} + bipy \qquad (2)$$

$$[Fe(bipy)_2]^{3+} \rightleftharpoons [Fe(bipy)]^{3+} + bipy \qquad (3)$$

$$[Fe(bipy)]^{+3} \rightleftharpoons [Fe^{3+} + bipy] \qquad (4)$$

$$bipy + H^+ \underset{slow}{\overset{fast}{\rightleftharpoons}} bipyH^+ \qquad (5)$$

Thus the extra 2,2'-bipyridyl present in solutions prepared from the *tris* complex may increase the effective concentration of the low spin species. Addition of even a large excess of 2,2'-bipyridyl has no immediate effect indicating that (5) is fast. However on standing E app for the 610 nm. band increases for *all* solutions no matter how prepared. The results suggest therefore that the solutions contain both *bis* and probably some *tris* (2,2'-bipyridyl)iron-(III) species. The differing efficiency with which nitric, perchloric and sulphuric acids generate the iron(III) species from $[Fe^{II}(bipy)_3](ClO_4)$ must be related to their oxidising powers rather than to their strength as acids.

We find that when $[Fe(bipy)_2(NO_3)_2](ClO_4)$ is dissolved in water a bluish violet solution is produced which gradually becomes red. The change may be followed spectrophotometrically and can be attributed to the development of a significant concentration of $[Fe(bipy)_3]^{2+}$. In a typical experiment 25% of the iron added may be accounted for as $[Fe(bipy)_3]^{2+}$ and redox titration establishes that 33% of the iron is iron(II). However we find this reaction to require the presence of light which in turn suggests that the regeneration of the ferrous complex when solutions of $[Fe(bipy)_3]^{2+}$ in concentrated acids are diluted may also be light sensitive. It is of interest that Wehry and Ward recently demonstrated that the related *tris*(1,10-phenanthroline)iron(III) species undergoes photo reduction to $[Fe(phen)_3]^{2+}$ with the quantum yield varying from zero for 98% sulphuric acid to reach a steady maximum at 8.5*M* acid. In the phenanthroline case ultra-violet light was needed, however our experiments were carried out in a laboratory lit entirely with fluorescent strip lighting and we have previously found that the U.V. flux is sufficient to give trouble when handling any photosensitive species.

Experimental Section

U.V. and visible region spectra were recorded with a Unicam SP700 instrument. Diffuse reflectance spectra were recorded against magnesium oxide using the SP735 attachment. Infra-red spectra were obtained using a Perkin Elmer 457 spectrometer. The Mössbauer spectrum of $[Fe(bipy)_2(NO_3)_2](ClO_4)$ was recorded at 77 K using a Pd- ^{57}Co source by the PCMU, Harwell. The data at room temperature were obtained within the department also using a Pd- ^{57}Co source. Magnetic measurements were made by the Gouy method using mercuric tetraisothiocyantatocobaltate for solids and nickel chloride solutions as calibrants for solutions. Measurements at 77 K were made with a Newport variable temperature Gouy apparatus.

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Analysis for $[Fe^{II}(bipy)_3]^{2+}$ was carried out colourmetrically using a charge transfer band at 522 nm for which E = 8,650.[11] Redox titrations were with standard solutions of ceric ammonium sulphate. The acids used were commercial specimens described as "concentrated".

Tris(2,2'-bipyridyl)iron(III) perchlorate was prepared by the method of Bustall and Nyholm[7].

Dinitratobis(2,2'bipyridyl)iron(III) perchlorate. $[Fe^{II}(bipy_3](ClO_4)_2$[7] (0.5 g) was dissolved in concentrated nitric acid (5 cm^3) and evacuated over sodium hydroxide when blue-green *crystals* of the above compound were obtained. Found: C, 40.3; H, 2.8; Fe, 9.5; N, 13.7. $C_{20}H_{16}ClFeN_6O_{10}$, requires C, 40.3; H, 2.8; Fe, 9.9; N, 14.2.

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