Equilibria in Complexes of *N*-Heterocyclic Molecules. Part 13.† The Racemization and Dissociation of Some Tris(1,10-Phenanthroline) and Tris(2,2'-Bipyridyl) Complexes of Iron-(II) and -(III)

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The racemization and dissociation of $[Fe(phen)_3]^{3+}$, together with the racemization of $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{3+}$, have been followed kinetically in aqueous acid solutions containing HCl, H_2SO_4, or HNO_3 up to 100% acid concentration. The rates of racemization and dissociation of $[FeL_3]^{3+}$ [L = 1,10-phenanthroline(phen) or 2,2'-bipyridyl(bipy)] are zero in 100% H_2SO_4, and the racemization of $[Fe(phen)_3]^{2+}$ reaches a limiting rate in *ca.* 11.0 mol dm^{-3} HCl. The kinetics of dissociation of $[Fe(bipy)_3]^{3+}$ are quite different from other reported complexes and a maximum rate is attained at *ca.* 3.0 mol dm^{-3} H_2SO_4. On the basis of the observations and previously reported data, a new mechanism for racemization and dissociation is proposed.

THE mechanisms of racemization and dissociation of tris complexes of 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy) with transition-metal ions have attracted the attention of many workers[1] for the last 30 years. We have shown[2] that the formation of covalent hydrates and related pseudo-bases of the complex is important in the racemization and dissociation of $[Ni(phen)_3]^{2+}$, and recently we reported[3] that the dissociation of $[Fe(bipy)_3]^{3+}$ in aqueous acid is also dependent on the formation of these now well established[4,5] species. One of us[6,7] has suggested that these phenomena are widespread in the reactions of metal complexes of these di-imine ligands. We therefore decided to extend our studies to other complexes of phen and bipy. We present here the results of studies on the racemization and dissociation of $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ in acid solutions, together with the related racemization data for $[Fe(phen)_3]^{2+}$. An amalgamation of these results with the many earlier sets provides strong support for a new mechanism.

EXPERIMENTAL

Materials.—The salt $[Fe(bipy)_3][ClO_4]_2\cdot 2H_2O$ was prepared and resolved by the method of Dwyer and Gyarfas.[8] $[Fe(phen)_3][ClO_4]_2\cdot 3H_2O$ was prepared and resolved by a method[9] similar to the above.

Kinetic Studies.—For the dissociation studies a solution of Ce^{4+} (0.01 mol dm^{-3} as the nitrate) in the appropriate solvent was thermostatted in a water-bath; Ce^{4+} was thus used to avoid formation of any iron(II) species. To this solution was added sufficient complex that the concentration of the parent cation was in the range 1.0×10^{-4}—1.2×10^{-4} mol dm^{-3}. An aliquot portion of the solution was quickly transferred to a 1 cm thermostatted (±0.1 °C) silica cell in a Beckman DK2A ratio-recording spectrophotometer, and the decrease in absorbance at 600 nm was followed with time. At this wavelength the products of the reaction have negligible absorption. Values of $k_{obs.}$ were obtained from gradients of plots of log A against time. Linear first-order kinetics were observed for greater than 3 half-lives for both $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ at all the acid concentrations. The rate constants reported are the averages from triplicate or quadruplicate runs with reproducibility ±3%.

Racemization kinetics for $[Fe(phen)_3]^{2+}$ were obtained by dissolving an appropriate amount of optically active perchlorate salt in pre-equilibrated HCl solutions of known concentration. An aliquot portion was quickly transferred to a 1-cm thermostatted (±0.1 °C) silica cell in a Roussel–Jouan Dichrographe B. The decrease in $\Delta\varepsilon$ at 540 nm was followed with time. Values of $k_{obs.}$ were obtained from gradients of plots of log $\Delta\varepsilon$ against time. Good first-order kinetics were obtained for greater than 3 half-lives at each concentration of acid. The rate constants reported are the averages from triplicate runs with reproducibility ±2%.

The racemization kinetics of optically active $[Fe(bipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ were obtained in a similar way to the above except that the solutions prepared were 0.01 mol dm^{-3} in Ce^{4+}.‡ The reactions were followed by monitoring the decrease in $\Delta\varepsilon$ with time at 600 $\{[Fe(phen)_3]^{3+}\}$ and at 620 nm $\{[Fe(bipy)_3]^{3+}\}$. Linear first-order kinetics were generally obtained for greater than 2 half-lives and the rate constants reported are also the averages from triplicate runs with reproducibility ±2%. In concentrated H_2SO_4, no racemization or dissociation of the iron(III) complexes was detected over 24 h at 25 °C. Circular dichroism (c.d.) measurements were made on Roussel–Jouan B, Cary 61, and Jasco J20 instruments. Water activity data are from ref. 10.

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† Part 12; K. H. Al-Obaidi, R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, in the press.

‡ Concentrated H_2SO_4 solutions were saturated with $Ce[NO_3]_4$.

[1] See, for example (*a*) F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. 4; (*b*) J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697; M. J. Blandamer, J. Burgess, J. G. Chambers, R. I. Haines, and H. E. Marshall, *J.C.S. Dalton*, 1977, 165 and refs. therein.

[2] R. D. Gillard and P. A. Williams, *Transition Metal Chem.*, 1977, **2**, 14.

[3] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, **2**, 47.

[4] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *J.C.S. Dalton*, 1977, 1039.

[5] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 247.

[6] R. D. Gillard, *Inorg. Chim. Acta*, 1974, **11**, L21.

[7] R. D. Gillard, *Co-ordination Chem. Rev.*, 1975, **16**, 67.

[8] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1951, **84**, 135.

[9] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1950, **83**, 263.

[10] A. J. Gordon and R. A. Ford, 'The Chemist's Companion,' Wiley, New York, 1972, pp. 65—66.

RESULTS AND DISCUSSION

(*a*) $[Fe(phen)_3]^{2+}$.—Racemization (k_r) rate constants are given in Table 1.

It has been said [11-13] that the rate of dissociation of $[Fe(phen)_3]^{2+}$ is independent of acid concentration. Another report [14] mentioned that this ion is stable in aqueous solution for which $2 < pH < 9$. A close examination of the published data shows that this is not the case, and that there is in fact a decrease in k_d with increasing $[H^+]$, and a sharp increase [12,15-17] with increasing $[OH^-]$. The rate of dissociation is also enhanced [18,19] by the addition of other nucleophiles.

TABLE 1

Kinetic results for racemization and dissociation at 25 °C

Complex	Solvent (c/mol dm^{-3})	k_r/s^{-1}	k_d/s^{-1}
$[Fe(phen)_3]^{2+}$	Water	5.95×10^{-4}	
	HCl (1.00)	4.78×10^{-4}	
	(2.00)	4.38×10^{-4}	
	(2.84)	3.77×10^{-4}	
	(5.00)	3.57×10^{-4}	
	(11.36)	3.37×10^{-4}	
$[Fe(phen)_3]^{3+}$	H_2SO_4 (1.00)	3.77×10^{-2}	2.15×10^{-5}
	(2.00)	2.68×10^{-2}	1.45×10^{-5}
	(2.50)	2.05×10^{-2}	
	(3.00)	1.22×10^{-2}	1.32×10^{-5}
	(4.00)	5.67×10^{-3}	7.17×10^{-6}
	(5.00)	2.00×10^{-3}	4.67×10^{-6}
	(7.00)	2.33×10^{-4}	1.33×10^{-6}
	conc.	0	0
	HNO_3 (0.623)		2.63×10^{-5}
	(1.246)		2.13×10^{-5}
$[Fe(bipy)_3]^{3+}$	H_2SO_4 (0.50)		4.58×10^{-4}
	(2.00)	7.55×10^{-3}	6.82×10^{-4}
	(2.50)	7.52×10^{-3}	
	(3.00)		7.32×10^{-4}
	(4.00)	2.48×10^{-3}	6.53×10^{-4}
	(5.00)	1.17×10^{-3}	4.60×10^{-4}
	(7.00)	2.80×10^{-4}	8.33×10^{-5}
	conc.	0	0
	Water		8.17×10^{-5}

The racemization rate constant for $[Fe(phen)_3]^{2+}$ also shows similar effects.[14,16,20] The results of our study of the rate of racemization of this ion in HCl solutions are summarized in Table 1 and Figure 1. While the magnitude of k_r decreases slowly with increasing [HCl], it appears that a limiting value is reached at a_{H_2O} *ca.* 0.5. There is little variation in k_r from a_{H_2O} *ca.* 0.2 (11 mol dm^{-3} HCl) to 0.7. Unfortunately, it is not possible to measure k_r in concentrated solutions of HNO_3 or H_2SO_4 with a_{H_2O} <0.2 because of oxidation of the complex to Fe^{III}.

We have previously shown [2] that similar curves for the racemization and dissociation of $[Ni(phen)_3]^{2+}$ reflect the presence of an equilibrium between that molecule and a covalent hydrate (1) and pseudo-base (2) in aqueous solution as shown in Scheme 1. We now propose a similar mechanism for the racemization and dissociation of $[Fe(phen)_3]^{2+}$.

Dickens *et al.*[20] suggested that the decrease in k_r for $[Fe(phen)_3]^{2+}$ with added acids was most probably due to the decrease in a_{H_2O} (and hence the increased amount of unsolvated complex) but emphasized that this was not the sole effect. However, our proposed mechanism couples the increase of a_{H_2O} with the concentration of hydrogen ions. As $[H^+]$ increases, the equilibrium (K_2) must be shifted in favour of the protonated covalent hydrate, and as a_{H_2O} decreases with increasing acid the equilibrium (K_1) must be shifted towards the unsolvated species.

An explanation for the plots of k_r and k_d against pH and a_{H_2O} is readily available if one assumes that the pseudo-base is much more reactive than the covalent hydrate or the unsolvated parent ion as is the case [2] with $[Ni(phen)_3]^{2+}$. Buffering between pH 2 and 10 arises from the presence of the covalent hydrate, which does of course have a titratable proton at the N α to the substituted carbon atom. The mechanism therefore not only explains the variation of rate with pH but also the unusual shape of the curve found.

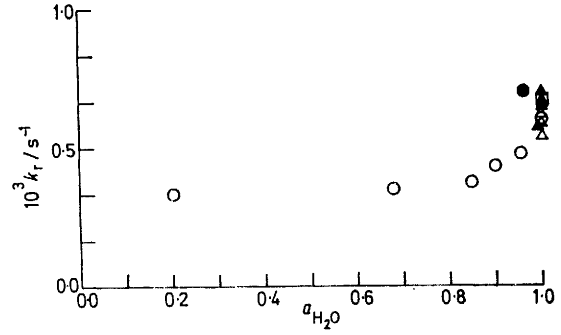

FIGURE 1 Racemization of $[Fe(phen)_3]^{2+}$ in HCl: (○) this work; (●) ref. 13; (□) A. Jensen, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1958, **80**, 2354; (△) ref. 16; (▲) ref. 17

Of some interest is the fact that k_r does not appear to decrease to zero with increasing acid concentration as is the case with $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ below. There are two possible explanations for this phenomenon. The first is that the reaction *may* reach a zero point at $a_{H_2O} = 0$, but that K_1 is large, and at $a_{H_2O} = 0.2$ there is still a considerable concentration of covalent hydrate.*

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* The value [21] of K is 8 at 25 °C for the association of a water molecule with $[Ni(phen)_3]^{2+}$. Other workers have commented [22] on the fact that water is intimately associated with reactions of tris(phenanthroline) complexes, and that even trace amounts of water appear to be highly significant.

[11] T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596.

[12] D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728.

[13] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807.

[14] W. B. Fortune and M. G. Mellon, *Ind. and Eng. Chem. Analyt. Edn.*, 1938, **10**, 60.

[15] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

[16] G. Nord, *Acta Chem. Scand.*, 1973, **27**, 743.

[17] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, 1953, **49**, 180.

[18] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

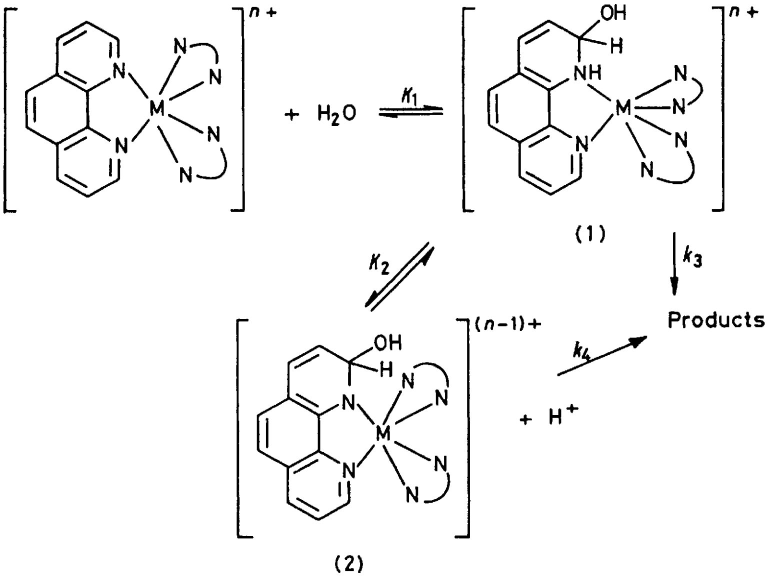
[19] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[20] J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1957, **79**, 1286.

[21] T. Fujiwara and Y. Yamamoto, *Abs. 17th Conf. Co-ordination Chem.*, Hamburg, 1976, p. 166.

[22] R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 1957, 1963.

Alternatively, it might be that there is a 'residual' intramolecular racemization rate of $[Fe(phen)_3]^{2+}$ which does not involve the covalent hydrate–pseudo-base mechanism. While we believe that this is most probably correct, $[Fe(phen)_3]^{2+}$ is the only complex we have studied which displays this phenomenon. Coupled with this problem is the fact [23a] that this ion racemizes faster in MeOH than in water. While this might not be initially expected, we have shown [4] that it is quite easy to form methoxide and ethoxide pseudo-bases with tris(5-nitro-1,10-phenanthroline)ruthenium(II), and there is some evidence [23b] that $[Ni(phen)_3]^{2+}$ forms a methanol adduct in alcoholic solution.



Scheme 1

(*b*) $[Fe(phen)_3]^{3+}$.—Table 1 summarizes k_d and k_r values obtained in this work for $[Fe(phen)_3]^{3+}$ in various aqueous sulphuric acid solutions. Plots of k_d and k_r against a_{H_2O} are shown in Figures 2 and 3 respectively, which also include earlier data on these reactions.

Our results for k_r agree well with those of Dickens *et al.*[20] but differ significantly from those of Davies and Dwyer.[24] These latter workers however used an oxidation-reduction technique to measure the rate of racemization, and this apparently leads to low values of k_r. Our results for the dissociation of $[Fe(phen)_3]^{3+}$ also agree well with those of Dickens *et al.* in H_2SO_4.

There are some noticeable differences between reported k_d values measured in H_2SO_4 and HNO_3. We have, however, measured k_d in 0.623 and 1.264 mol dm^{-3} HNO_3 (Table 1) and the values of k lie within experimental error on the curve described by the plot of k_d against a_{H_2O}. We offer no explanation for these differences in the most concentrated solutions of HNO_3 that other workers have studied. It is clear that in dilute HNO_3, previous results agree well with ours.

The most notable feature of the variations of k_r and k_d with a_{H_2O} is that they decrease to zero in concentrated acid. Unlike the racemization of $[Fe(phen)_3]^{2+}$ in (*a*) above, no limiting rate is reached in aqueous acid. One previous study [25] had found that k_d was lower by a factor of up to 10^6 in 82.9—98.1 wt.% H_2SO_4 compared to that in water alone. While solvent effects might be expected to play some part in the rate processes,* it is *not* expected that the rates of reaction would decrease to zero. What *is* clear is the fact that *no* reaction takes place in the absence of water! We attribute these remarkable findings to the same pre-equilibria shown in Scheme 1 between (1), (2), and the unhydrated molecule. The reactive hydrated species (1) and (2) then react to yield the products. In the absence of water (*i.e.* in concentrated H_2SO_4) all the iron is present as the parent $[Fe(phen)_3]^{3+}$ which is apparently inert to dissociation and racemization. The shapes of the curves in Figures 2 and 3 are consistent with our proposed reaction scheme. Assuming that K_1 and K_2 are genuine pre-equilibrium constants, $k_{obs.}$ is given by expression (1). At low acid concentration, a_{H_2O} remains nearly constant causing $[H^+]^{-1}$ to dominate the variation in $k_{obs.}$, resulting in the sharp decrease

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* Burgess [1,26–28] found variations in k_d with changing solvent composition for many iron(II) complexes of phen and bipy.

[23] (*a*) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, 1954, **50**, 1325; (*b*) R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, unpublished work.

[24] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, 1954, **50**, 820.

[25] A. F. Richards, J. H. Ridd, and M. L. Tobe, *Chem. and Ind.*, 1963, 1726.

[26] J. Burgess, F. M. Mekhail, and E. R. Gardner, *J.C.S. Dalton*, 1973, 1335.

[27] M. J. Blandamer, J. Burgess, and M. Dupree, *J.C.S. Dalton*, 1976, 1298.

[28] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.

found. However, at higher acid concentrations, the variation in a_{H_2O} is the most significant term, resulting in nearly linear behaviour over the range $0 < a_{H_2O} < 0.5$.

In the above simplified treatment reaction at only one ligand is considered. Inclusion of all the possibilities

$$k_{obs.} = (k_3K_1[H_2O] + k_4K_1K_2[H_2O][H^+]^{-1})/(1 + K_1[H_2O] + K_1K_2[H_2O][H^+]^{-1}) \quad (1)$$

of multiple-ligand attack and differences between geometric isomers thus formed would lead to an unwieldy expression for $k_{obs.}$, which would nevertheless retain the overall features of equation (1).

Our mechanism indicates that the pseudo-base is more reactive than the covalent hydrate, in accord with our previous findings. It should be pointed out that the magnitude of the equilibrium constants K_1 and K_2 need not necessarily be large to be significant. The only requirement is that the equilibria be rapidly established. This is indeed the case with other pseudo-base formation with $[OH]^-$,[29] $[CN]^-$,[30] and alkoxide ions.[4]

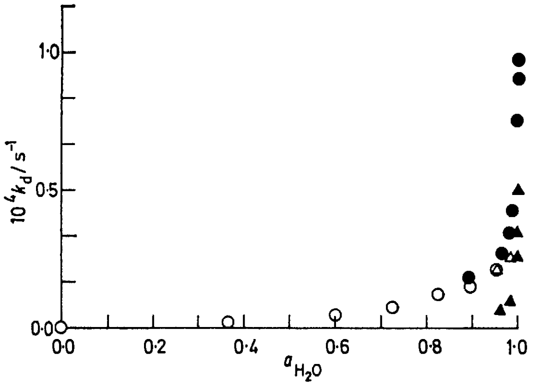

FIGURE 2 Dissociation of $[Fe(phen)_3]^{3+}$ in H_2SO_4 and HNO_3: (○) this work, H_2SO_4; (△) this work, HNO_3; (●) ref. 20, H_2SO_4; (▲) ref. 20, HNO_3

The nature of the complexes $[FeL_3]^{3+}$ (L = phen or bipy) in concentrated acids has been disputed by a number of workers. Healy and Murmann[31] proposed that $[Fe(bipy)_3]^{2+}$ is protonated under such conditions, and Murmann[32] has indicated that he believes that $[Fe(phen)_3]^{3+}$ behaves in a similar manner. On the other hand, Briscoe *et al.*[33] showed that the blue species formed from $[Fe(phen)_3]^{2+}$ in concentrated H_2SO_4 is identical with an isolable iron(III) species in HNO_3. Dickens *et al.*[20] noticed some ion-pairing effects with $[Fe(phen)_3]^{3+}$, and other workers[25] showed that there is no observable difference between the electronic spectra of this ion in water and in 98% H_2SO_4. It therefore seems most likely that the species in H_2SO_4 is unprotonated (and indeed unsolvated), and indeed we observe no change in the visible region of the electronic spectrum of $[Fe(phen)_3]^{3+}$ in concentrated H_2SO_4 whether in the presence of Ce^{IV} or not. While parts of the spectrum of $[Fe(phen)_3]^{3+}$ in aqueous H_2SO_4 are masked by the presence of Ce^{III} and Ce^{IV}, we do however have some c.d. evidence for the equilibria we have proposed.

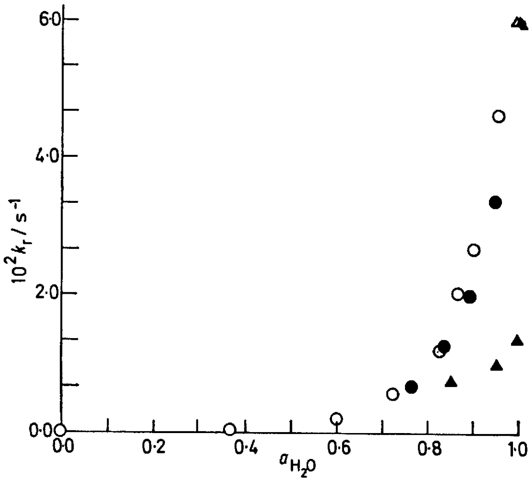

FIGURE 3 Racemization of $[Fe(phen)_3]^{3+}$ in acid solution: (○) this work, H_2SO_4; (△) ref. 11, H_2SO_4; (●) ref. 20, HNO_3; (▲) ref. 24, HCl

Table 2 shows the c.d. of $[Fe(phen)_3]^{3+}$ in 100% H_2SO_4 and in 7.00 mol dm^{-3} H_2SO_4. The results for 7.00 mol dm^{-3} H_2SO_4 have been corrected for racemization. There is a slight decrease in c.d. associated with the π→π* long-axis-polarized transition, and it is obvious that these are not simply concentration effects. This is amply demonstrated by the ratios of Δε from one solvent to the next. We have also found that the visible c.d. transitions are slightly enhanced on changing solvent from concentrated H_2SO_4 to 7.00 mol dm^{-3} H_2SO_4 to 5.00 mol dm^{-3} H_2SO_4, but the changes are not more than three times the experimental error in determination. However, all of these changes are remarkably similar to those observed[2,34,35] when pseudo-bases are formed with optically active tris(di-imine) complexes of phen and 5-nitro-1,10-phenanthroline. We conclude that the change

TABLE 2

Circular dichroism of Δ $[Fe(phen)_3]^{3+}$ in acid solution

	Δε	
λ/nm	concentrated H_2SO_4	7.00 mol dm^{-3} H_2SO_4
283	+285.6	+261.7
268	−237.9	−208.2
240	+65.4	+59.5
237	−5.9	−11.8

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[29] R. D. Gillard, C. T. Hughes, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 51.

[30] R. D. Gillard, C. T. Hughes, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 226.

[31] E. A. Healy and R. K. Murmann, *J. Amer. Chem. Soc.*, 1957, **79**, 5827.

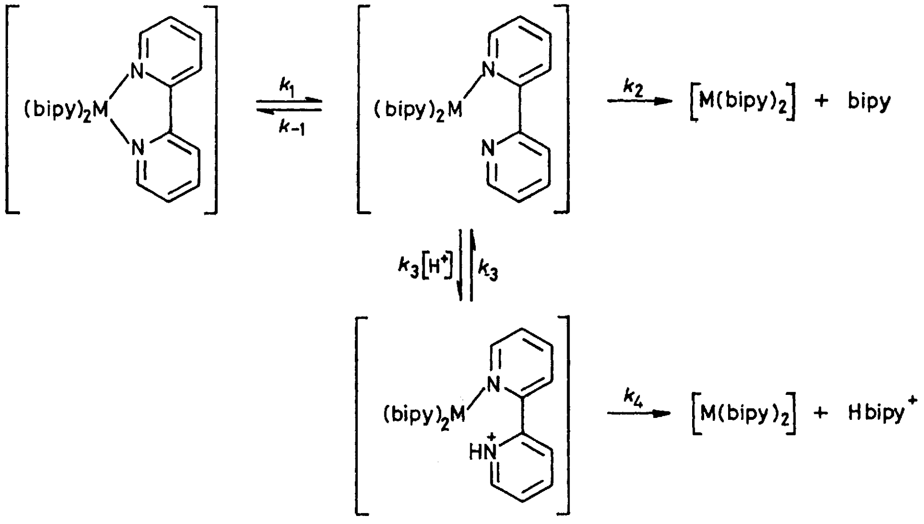
[32] R. K. Murmann, personal communication.

[33] G. B. Briscoe, M. E. Fernandopulle, and W. R. McWhinnie, *Inorg. Chim. Acta*, 1972, **6**, 598.

[34] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, **2**, 12.

[35] R. D. Gillard and R. E. E. Hill, *J.C.S. Dalton*, 1974, 1217.

in the c.d. spectrum from concentrated to 7.00 mol dm^{-3} H_2SO_4 reflects the formation of the covalently hydrated species.



SCHEME 2

(c) $[Fe(bipy)_3]^{3+}$.—Some of the most striking effects of covalent hydration and pseudo-base formation are found in the study of the racemization and dissociation [3] of $[Fe(bipy)_3]^{3+}$ in aqueous acid. Table 1 summarizes our results for the racemization and dissociation of this molecule in aqueous H_2SO_4. A plot of k_r against a_{H_2O} shows the same general features as that for $[Fe(phen)_3]^{3+}$ above, decreasing to zero at the concentrated-acid end and $k_r > k_d$ at all acid strengths. Because of this latter finding, the curve for the intramolecular racemization rate is closely analogous.

The unusual shape of the plot of k_d against $[H^+]$ or a_{H_2O} has been discussed previously.[3] The generally accepted mechanism [1] (Scheme 2) for the dissociation of complexes of bipy in aqueous acid predicts that k_d will increase with increasing $[H^+]$ and reach a limiting rate as shown in equation (2). By including k_{-3} (*i.e.* $k_3/k_{-3} = K_3$), Twigg [36] pointed out that equation (3) is obtained

$$k_{obs.} = k_1(k_2 + k_3[H^+])/(k_{-1} + k_2 + k_3[H^+]) \quad (2)$$

which also gives rise to a limiting rate with increasing $[H^+]$. Evidence [36,37] from the rate of dissociation of

$$k_{obs.} = k_1(k_2 + K_3k_4[H^+])/(k_{-1} + k_2 + K_3k_4[H^+]) \quad (3)$$

$[Fe(bipy)_3]^{2+}$ has been used to support this mechanism. Similarly, in the present study of $[Fe(bipy)_3]^{3+}$, equations (2) and (3) accurately predict the increase in k_d as $[H^+]$ is increased *in dilute acid.* However, a maximum rate is reached at *ca.* 3 mol dm^{-3} H_2SO_4 and at higher acid concentrations the rate decreases, finally reaching *zero*! Such behaviour is *not* anticipated from Scheme 2.

However, the covalent hydrate-pseudo-base mechanism we propose (Scheme 1 with bipy for phen) fits the data well for *all* the acid concentrations and for all the various complexes of phen and bipy we have studied. The present results strongly suggest that the dissociation and racemization of $[Fe(bipy)_3]^{3+}$ is preceded by the equilibria shown in (4) and (5) with the species $[Fe(bipy)_2(bipy{\cdot}H_2O)]^{3+}$ and $[Fe(bipy)_2(bipy{\cdot}OH)]^{2+}$ similar to those shown in Scheme 1. Interestingly, the formation of pseudo-bases has been suggested in the oxidation [38] of

$$[Fe(bipy)_3]^{3+} + H_2O \rightleftharpoons [Fe(bipy)_2(bipy{\cdot}H_2O)]^{3+} \quad (4)$$

$$[Fe(bipy)_2(bipy{\cdot}H_2O)]^{3+} \rightleftharpoons [Fe(bipy)_2(bipy{\cdot}OH)]^{2+} + H^+ \quad (5)$$

$[Os(phen)_3]^{2+}$, the reduction [39] of $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$, and the reduction [40] of $[Ru(bipy)_3]^{3+}$.

Conclusions.—Various mechanisms have been proposed for the racemizations and dissociation we have studied. We suggest that the preliminary step in all of the reactions studied above is the formation of a covalent hydrate in equilibrium with the pseudo-base, and that these species are the reactive ones. These pre-equilibria have several attractive features. First they explain the bimolecular rate laws found for attack at these complexes by hydroxide (and indeed attack by other nucleophiles [1,18,19]). Secondly, they elegantly explain the intimacy of association of water molecules

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[36] M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 17.

[37] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, 1950, **46**, 736.

[38] G. Nord, *Inorg. Chem.*, 1976, **15**, 1921.

[39] G. Nord and O. Wernberg, *J.C.S. Dalton*, 1972, 866.

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with the complexes. Thirdly, the mechanism fits all of the observations. Furthermore, the new reaction path provides a qualitative rationalization for the racemization and dissociation. The ligands phen and bipy are known to form very stable complexes with many transition-metal ions. When the aromaticity of the ligand is disrupted on formation of these novel species, it might be expected that the ligand flexibility is enhanced. This must in turn influence any ' twist ' mechanisms of racemization. Also, since the strength of the metal–ligand bond should be reduced, dissociation may be facilitated.

Finally, it does indeed seem that the phenomena of covalent hydration and pseudo-base formation are rather widespread in complexes of phen and bipy in spite of a comment by Nord[41] to the contrary.

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