iodine bands seems to be worthwhile for a better understanding of the nature of these upper states.

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The Acid Decomposition of Tris-(2-pyridinalalkylimine)-iron(II) Compounds[1]

By R. Kent Murmann[2] and Edward A. Healy

The rate of acid dissociation of tris-(2-pyridinalalkylimine)-iron(II) compounds is first order in complex over at least 95% of the reaction. No intermediates were observed indicating that the rate of dissociation of the first ligand $k_1 \gg k_2$ or k_3. The acid dependence parallels that of [Fe(bipy)$_3$]$^{+2}$ and may be explained on the basis of either "half-bonded" or "protonated" intermediates. With either intermediate, complete ligand dissociation apparently precedes hydrolysis of the Schiff base. Evidence is presented for the existence of paramagnetic "protonated" species in concentrated acid solutions. The rate of decomposition is dependent on the alkyl group and increases in this order: (MePI), (EtPI), (BuPI), (PrPI). Thus the rate is inversely proportional to the base strength of the amine. Evidence for isomerization is presented with (QEtPI) and a large difference in rate of dissociation is noted between the isomers.

Introduction

In recent years there has been considerable interest in the mechanism of the formation and decomposition of [Fe(o-phen)$_3$]$^{+2}$ and [Fe(bipy)$_3$]$^{+2}$.[3-7] Although the decomposition of the former is essentially acid independent, there is an important H$^+$ dependence in the latter. This has been explained on the basis of the greater flexibility of the ligand allowing one coördinating nitrogen to dissociate while leaving the other intact ("half-bonded" structures).[5,6] Another postulated intermediate is the "protonated" species.[3,4] Mechanisms based on either intermediate will satisfy the H$^+$ dependence of the dissociation of [Fe(bipy)$_3$]$^{+2}$, but it is necessary to assume the presence of a large fraction of the total complex in the "protonated" form using the latter concept. The inability of several investigators to demonstrate the presence of "protonated" species lends credence to the alternate mechanism. It has been shown[8] that 2-pyridinalalkylimines form compounds with Fe(II) which are structurally similar to [Fe(bipy)$_3$]$^{+2}$. It was thought that kinetic studies of the decomposition of a series of these compounds might distinguish between the "half-bonded" and "protonated" intermediates. Since the mechanism presented by Basolo, et al.,[6] and supported by Krumholz[5] postulates the partial regeneration of the original complex from the "half-bonded" intermediate and since Schiff bases are known to hydrolyze rapidly in acid solution,[9]

the rate of dissociation might be expected to include a contribution from the hydrolysis of the "half-bonded" intermediate and thus have a modified H$^+$ dependence.

Since the ligands are unsymmetrical, two isomers of the tris-complexes are possible. It was of interest to determine whether both isomers are formed and to what extent their rates of dissociation differ. For this purpose, the n-propyl derivative was selected as having sufficient size to give isomers with measurable solubility differences while steric effects would not unduly affect the stability. While the major emphasis was on (PrPI),[10] various other alkyl-2-pyridinalimines were studied for a comparison.

Experimental

[Fe(o-phen)$_3$]$^{-2}$ and $^{+3}$ and [Fe(bipy)$_3$]$^{+2}$ and $^{+3}$ perchlorates were prepared by methods in the literature.[11]

The alkyl-2-pyridinalimine complexes of the type [Fe(RPI)$_3$](ClO$_4$)$_2$ were all prepared by the same general method. To 0.1 mole of pyridine-2-aldehyde dissolved in 50.00 ml. of acetone was added 0.09 mole of the amine (with the lower boiling amines the equivalent amount of a concentrated water solution of the amine was used). After standing at room temperature for 15 minutes, 0.10 mole of FeCl$_2 \cdot 6$H$_2$O dissolved in 50 ml. of water was added. The deeply colored solution was stirred for 15 minutes, filtered to remove suspended particles and slowly treated with a slight excess of 20% aqueous NaClO$_4$ to precipitate the product. Recrystallization from water (occasionally containing NaClO$_4$), followed by drying under vacuum at room temperature gave dark purple micro-crystals. The yields varied from 20–90% of theoretical depending on the solubility characteristics.

[Fe(PrPI)$_3$](ClO$_4$)$_3$: a mixture of 0.29 g. of n-propyl amine and 0.60 g. of pyridine-2-aldehyde was added to 0.50 g. of Fe(SO$_4$)$\cdot 7$H$_2$O dissolved in 100 ml. of water. After filtration and cooling to 0°, an excess of chlorine was added. Four ml. of a 30% aqueous NaClO$_4$ solution was slowly

(1) Taken in part from the Ph.D. thesis of Edward A. Healy, University of Connecticut, 1958.

(2) University of Missouri, Columbia, Missouri.

(3) J. H. Baxendale and P. George, *Nature*, **162**, 777 (1948); **163**, 725 (1949); *Trans. Faraday Soc.*, **46**, 736 (1950).

(4) P. Krumholz, *Nature*, **163**, 724 (1949); *Anais. acad. brasil. cienc.*, **22**, 263 (1950).

(5) P. Krumholz, *J. Phys. Chem.*, **60**, 87 (1956).

(6) F. Basolo, J. C. Hayes and H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 3807 (1954).

(7) E. A. Healy and R. K. Murmann, *ibid.*, **79**, 5827 (1957).

(8) J. C. Bailar, Jr., and D. H. Busch, *ibid.*, **78**, 1137 (1956).

(9) This was substantiated by measurements in our Laboratories.

(10) (MePI), (EtPI), (PrPI), (BuPI), (i-PrPI), (QEtPI) and (AQPI) refer to 2-pyridinalalkylimines in which the alkyl group is methyl, ethyl, n-propyl, n-butyl, i-propyl, α-phenylethyl and 8-aminoquinoline, respectively; (o-phen) = 1,10-phenanthroline, (bipy) = 2,2'-bipyridine.

(11) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1950); F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

added and after 2 hr. the blue-green crystals were collected, washed with water and dried in vacuum; yield, 60%.

The infrared absorption spectra were obtained on KBr-complex compressed disks with a Perkin–Elmer, model 21 instrument and a sodium chloride prism. Visible spectra were obtained at constant temperature with a Beckman Model DU spectrophotometer using matched 1 cm. silica absorption cells.

Magnetic moment measurements were carried out in nitrogen on a Gouy type apparatus having a field strength of 4000–8000 oersteds and a micro-balance ($\pm$ 0.05 mg.). Ferromagnetic impurities were not observed in either the liquid or solid samples. Diamagnetic corrections for the organic portion of the molecule were estimated from the values given in Selwood.[12]

All the rate studies were carried out spectrophotometrically using a Beckman DU spectrophotometer equipped with thermospacers through which water from a constant temperature bath was circulated. The temperature of the cell compartment was constant to $\pm 0.05°$. With soluble compounds the solid complex was added to the prethermostated spectrophotometric cell, shaken and readings begun in less than $^1/_2$ minute. With the slightly soluble complexes, a large excess of the compound was added to about 50 ml. of the (constant temperature) solvent, shaken vigorously and then filtered directly into the pre-thermostated spectrophotometric cell. Measurements were begun within 1 minute of addition of the complex. The absorption change at the wave length of maximum absorption was followed for several half-times and corrections made for the small absorption at T_∞. Since the initial concentrations of the coördination compounds were in the range of 10^{-3} to 10^{-4} M, it was assumed that the absorption followed Beers law. A graph of log I_0/I (corr.) vs. time gave straight lines (except where noted) over 95% of the decomposition. From the slope of these lines $T^1/_2$ was obtained which was converted to the pseudo first order rate constant by the expression $k_{obsd.} = 0.693/T^1/_2$.

The solubility of [Fe(bipy)$_3$](ClO$_4$)$_2$·2H$_2$O was determined by adding an excess of the solid complex to a well stirred, prethermostated solvent and sampling the resulting solution at intervals until equilibrium was established. Samples were withdrawn by applying suction to the end of a thermostated sintered-glass filtering tube submerged in the main flask. Upon inverting the filtering tube, the solution was placed directly in a spectrophotometer cell. Absorption measurements were begun within 1 minute of the start of filtration. The temperature, pH, and ionic strength as well as the purity of the complex were controlled carefully. Medium-small crystals of the complex had to be used to prevent a colloidal suspension of solid from passing through the filter. Under these conditions nearly 2 hr. were necessary for equilibrium to be established. The pH of the final solutions were reported since a small portion of the complex decomposes during the equilibration period.

Results

The decrease in absorbance of acidic solutions of [Fe(PrPI)$_3$]$^{+2}$ approximately 5 $\times$ 10^{-5} M at the wave length of $\epsilon_{max.}$ gives a straight line in the graph of log [Fe(PrPI)$_3$]$^{+2}$ vs. time providing the [H$^+$] is greater than 1 $\times$ 10^{-3} M. Below this value the [H$^+$] changes during the reaction due to release of PrPI and a slight curvature is obtained. The first 1–2% of reaction cannot be accurately measured because of the time of mixing and slight temperature differences from the bath, while the last 2–3% of the reaction are outside the precision of the spectrophotometer. Thus the reaction is first order in complex through the approximately 95% which can be measured. This is also true of the tris- complexes formed with o-phen, bipy, AQPI, MePI, EtPI, i-PrPI and n-BuPI. The ammonia analog decomposes by rather complex kinetics which are neither first nor second order in

complex when carried out in excess acid. Intermediates of moderate kinetic stability appear to be produced which complicate spectral measurements.

Since the dissociation ultimately involves three molecules of PrPI per complex ion, there is the possibility that mono or bis intermediates may be present in quantities sufficient to be demonstrated spectrophotometrically. Table IF shows that the pseudo first order rate constant does not change with wave length on either side of $\epsilon_{max.}$ in the visible range. In the ultraviolet region the apparent rate was considerably slower due to absorption of PrPI and its hydrolysis products. Changes in [H$^+$] did not alter the conclusion that the rate was independent of the wave length in the visible region. The constant rate at various wave lengths indicates that either the intermediates are present in only minute amounts or that their extinction coefficients are rather small. On the basis of the extinction coefficients of the mono and bis complexes of o-phen[13] and on the basis of the exchange data,[14] it is probable that the former postulate is correct.

Since the +2 and +3 complexes are in equilibrium, there is the possibility that the dissociation proceeds partially through the minute quantities of the +3 complex. In order to check this, Fe-(II) and Sn(II) were added to the reaction and were shown to have the same small effect on the rate as non-reductive +2 ions (Table IIB). Thus the rate is not affected by the small amount of [Fe(PrPI)$_3$]$^{+3}$ present.

Changes in ionic strength in both the Cl$^-$ and ClO$_4^-$ systems effect a large change in the rate (Table ID). In the NaCl system at 0.10 M HCl the rate decreases by more than a factor of 2 upon adding NaCl to 3.9 M. The change in the ClO$_4^-$ system is not as great. Table IE shows the differences in the rate for several negative ions. At the same concentration, positive ion and ionic strength, the rate increases in the order: ClO$_4^-$, Br$^-$, HSO$_4^-$, Cl$^-$, NO$_3^-$. A small effect also is noted with several positive ions whose rates increase in the order: Ba^{+2} < Li$^+$ < Rb$^+$ = Na$^+$.

At constant ionic strength, the decomposition of [Fe(PrPI)$_3$]$^{+2}$ is acid dependent as shown by Table I(A, B, C). The graph of log $k_{obsd.}$ vs. log [H$^+$] is nearly linear, but small deviations are evident which are outside of experimental error. These are present in the Br$^-$, Cl$^-$ and ClO$_4^-$ systems. The apparent order with respect to [H$^+$] is about 0.15 and identical for different anions. At high acidities the rate does not reach a limiting value.

The increase in rate with increasing [H$^+$] appears to be a general phenomenon. Neglecting [Fe(o-phen)$_3$]$^{+2}$ whose decomposition has been shown[15] to be essentially acid independent, the tris complexes of bipy, QEtPI, MePI, EtPI, n-BuPI and the bis complex of AQPI are all acid dependent as shown by Table I(G, H, I) and IIA.

(12) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 51–53.

(13) P. Krumholz, J. Am. Chem. Soc., 71, 3654 (1949).

(14) I. B. Whitney, G. K. Schweitzer and C. L. Comer, ibid., 77, 1390 (1955).

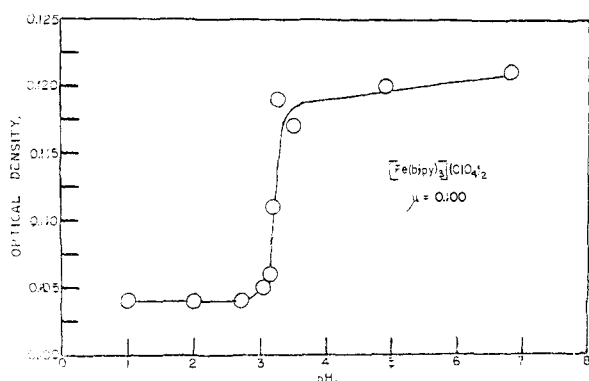(15) J. C. Dickens, Fred Basolo and H. M. Neumann, ibid., 79, 1286 (1957).

Fig. 1.—Equilibrium solubility of $[Fe(bipy)_3]^{+2}(ClO_4)_2 \cdot 2\text{-}H_2O$ as a function of acidity: μ, 0.10; T, 24.2° C.

From previous work on the o-phen and bipy systems, it appears that there are two possible mechanisms through which this $[H^+]$ dependence could originate: the "half-bonded" structures proposed by Basolo, et al.,[6] or the "protonated" intermediate originally proposed by Baxendale

TABLE I

RATES OF DISSOCIATION OF $[Fe(AB)_3]^{+2}$ TYPE COMPOUNDS

A. $[Fe(PrPI)_3]^{+2}$, (HCl-NaCl), $\mu = 1.00$, $T = 24.2°$

[HCl]	$k_{obsd} \times 10^3$ min.$^{-1}$	[HCl]	$k \times 10^3$ min.$^{-1}$
1.000	9.12	0.100	6.30
0.750	8.56	.050	5.95
.600	8.16	.025	5.35
.500	7.86	.010	4.68
.400	7.66	.005	4.22
.250	7.01	.001	3.50

B. $[Fe(PrPI)_3]^{+2}$, (HBr-NaBr), $\mu = 1.00$, $T = 24.2°$

[HBr]	$k \times 10^3$ min.$^{-1}$	[HBr]	$k \times 10^3$ min.$^{-1}$
0.000	7.62	0.050	4.90
.750	7.01	.025	4.51
.500	6.53	.016	4.10
.380	6.21	.010	3.76
.250	5.80	.005	3.42
.160	5.50	.0025	3.28
.100	5.29	.0012	3.11

C. $[Fe(PrPI)_3]^{+2}$, (HClO_4-NaClO_4), $\mu = 1.00$, $T = 24.2°$

[HClO_4]	$k \times 10^3$ min.$^{-1}$	[HClO_4]	$k \times 10^3$ min.$^{-1}$
1.000	6.11	0.050	3.66
0.500	5.23	.010	3.20
.250	4.44	.005	2.90
.100	4.16	.001	2.28

D. $[Fe(PrPI)_3]^{+2}$, (HClO_4-NaClO_4), HClO_4 = 1.000 M, $T = 24.2°$

[NaClO_4]	$k \times 10^3$ min.$^{-1}$	[NaClO_4]	$k \times 10^3$ min.$^{-1}$
0.000	6.11	3.000	5.87

$[Fe(PrPI)_3]^{+2}$, (HCl-NaCl), HCl = 0.100, $T = 24.2°$

[NaCl]	$k \times 10^3$ min.$^{-1}$	[NaCl]	$k \times 10^3$ min.$^{-1}$
0.000	7.66	0.900	6.30
.150	7.12	1.900	5.10
.400	6.76	3.900	3.22

E. $[Fe(PrPI)_3]^{+2}$, $[HA] = 0.100$ M. $\mu = 1.00$, $T = 24.2°$

[Salt]	$k \times 10^3$ min.$^{-1}$	[Salt]	$k \times 10^3$ min.$^{-1}$
NaNO_3	6.68	LiCl	5.98
NaCl	6.30	NaCl	6.30
NaHSO_4	6.30	RbCl	6.23
NaBr	5.29	BaCl_2	5.78
NaClO_4	4.17		

F. $[Fe(PrPI)_3]^{+2}$, (HCl-NaCl), $\mu = 1.00$, $T = 24.2°$

Wave length, mμ	$[H^+] = 0.1$	$[H^+] = 0.01$	$[H^+] = 0.001$
580	6.29	4.70	3.50
563 (ϵ max.)	6.30	4.68	3.49
540	6.29	4.67	3.50
514	6.30	4.67	3.50
500	6.30	4.68	3.50
362	5.52	3.89	2.38
350	4.50	3.52	2.22

G. $[Fe(bipy)_3]^{+2}$, (HCl-NaCl), $\mu = 4.00$ M, $T = 24.2°$

[HCl]	$k \times 10^2$ min.$^{-1}$	[HCl]	$k \times 10^2$ min.$^{-1}$
4.00	4.10	0.200	2.08
2.00	3.79	.100	1.48
1.000	3.31	.050	1.03
0.500	2.70	.010	0.649
0.250	2.30	.005	0.502

H. $[Fe(AQPI)_3]^{+2}$, (HCl-NaCl), $\mu = 4.00$ M, $T = 24.2°$

[HCl]	$k \times 10^2$ min.$^{-1}$	[HCl]	$k \times 10^2$ min.$^{-1}$
1.600	13.4	0.300	9.12
0.960	13.4	.160	7.06
.750	12.6	.080	4.50
.480	11.7	.010	0.69

I. $[Fe(QEtPI)_3]^{+2}$, (HBr-NaBr), $\mu = 1.00 M$, $T = 24.2°$

[HBr]	$k \times 10^3$ min.$^{-1}$	[HBr]	$k \times 10^3$ min.$^{-1}$
1.000	1.22	0.160	1.01
0.750	1.21	.100	0.903
.500	1.19	.050	.758
.380	1.14	.010	.437
.250	1.07	.001	.298

TABLE II

$[Fe(RPI)_3]$ $(ClO_4)_2$, $\mu = 1.00$, (NaCl-HCl), $T = 24.2°$, $k \times 10^3$ min.$^{-1}$

A. Rates of dissociation, alkyl effect

R	$[H^+] = 0.10$	0.25	0.50	pKa (amine (RNH_2))
CH_3-	0.498	0.70	0.89	10.64[a]
C_2H_5-	3.70	4.19	4.51	10.44[b]
n-C_3H_7-	6.30	7.01	7.86	10.35[b]
n-C_4H_9-	5.78	6.54	7.36	10.61
i-C_3H_7-	119	119	119	10.72

B. Rate of dissociation of $[Fe(PrPI)_3]^{+2}$, $\mu = 1.00$, 24.2°, $[HCl] = 0.25$ M

SnCl_2	0.01 M	$k = 7.04 \times 10^{-3}$ min.$^{-1}$
FeCl_2	.01 M	7.11×10^{-3} min.$^{-1}$
BaCl_2	.01 M	6.97×10^{-3} min.$^{-1}$
AlCl_3	.01 M	7.11×10^{-3} min.$^{-1}$
FeCl_3	.01 M	7.04×10^{-3} min.$^{-1}$

[a] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955. [b] Corrected from 18 to 25° assuming $\Delta H = 10$ kcal.

and George.[3] The latter concept demands the formation of appreciable quantities of a protonated species which would be expected to exhibit a different adsorption from the original and would
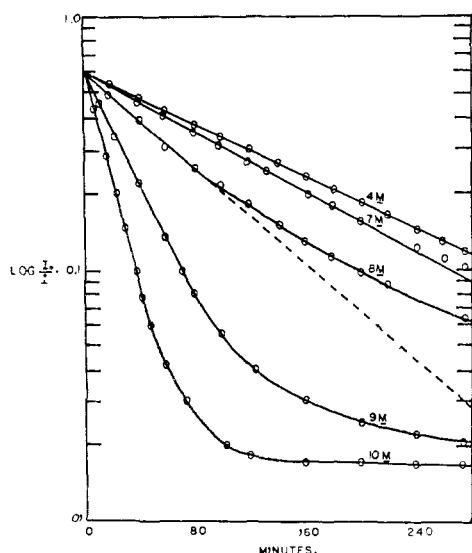
Fig. 2.—Absorbance changes of solutions of [Fe(PPI)₃]⁺² in 4, 7, 8, 9, 10 M HClO₄.

Fig. 3.—Regeneration of [Fe(PPI)₃]⁺² from protonated species.

be expected to form at a rapid rate. To test this possibility the extinction coefficient (at 580, 563, 540, 514, 500, 362, 350, 340 mμ) was carefully measured by following the initial rate and extrapolating to t_0. In the range $[\text{H}^+] = 10^{-1}$ to 10^{-3} the extinction coefficients did not change within the experimental limit of the method (0.5%). Since the spectra of the protonated species could be nearly identical with the initial complex, potentiometric titrations of the complex in anhydrous acetic with HClO₄ were carried out, but there was no indication that $[\text{Fe}(\text{PrPI})_3]^{+2}$ was behaving as a base. Since later work indicated that protonation in high concentrations of strong acids occurred and was not instantaneous, the possibility that in dilute acids protonation also was slow prompted equilibrium solubility studies. For this purpose $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ had the most satisfactory solubility characteristics and possessed the symmetry necessary to alleviate the possibility of geometric isomer fractionation. Figure 1 shows the change in absorption of saturated solutions, at constant ionic strength, which is directly proportional to the solubility of the complex. The remarkable decrease in solubility with increasing acid is extremely sharp and cannot be due to the increasing rate of decomposition with acidity. Two possibilities present themselves: (a) There is a change in the composition of the solid phase perhaps involving a change in the hydration number, or (b) the slow formation of a protonated species which, at equilibrium, partially covers the surface of the particles, and in the acid range behaves as if it were entirely the protonated complex. A distinction between these alternatives has not been made.

In HClO₄ solutions above 4 M, the solubility of these complexes increases rapidly. Furthermore, a slow color change occurs which is not due to total decomposition. In more concentrated acid (8–12 M) this color change is more rapid, and the product is quite stable in this medium.
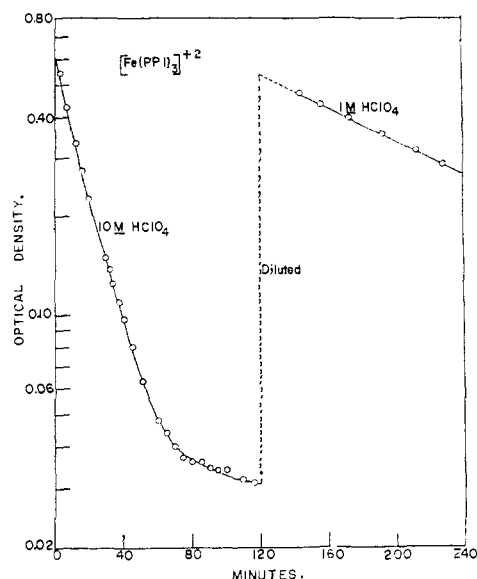
Figure 2 contains the changes in absorption occurring in strong HClO₄ solutions. As one proceeds from 4 to 10 M a gradual curvature of the first order graph is apparent, and above 10 M the final absorption reaches a constant value significantly above 0. This value is not appreciably altered after one day. It appears that a new species is formed in strong acid which is relatively stable to dissociation. Assuming that dissociation does not take place above 9 M HClO₄, the conversion of $[\text{Fe}(\text{PrPI})_3]^{+2}$ to the new species is first order in $[\text{Fe}(\text{PrPI})_3]^{+2}$. This is not exactly true in 6–8 M HClO₄ because hydrolysis is simultaneously taking place. The formation of this species is accompanied by changes in spectra and magnetic susceptibility and is almost completely reversible upon dilution. A shift in the wave length of maximum absorption from 563 to 540 mμ and ε from 8,790 to 40.5 accompanies this reaction. The magnetic susceptibility measurements are shown in Table III and are in agreement with a change from a diamagnetic to a paramagnetic complex with four unpaired electrons. This moment corresponds to hexacoördinated iron-(II) in a weak ligand field. The rate of change of magnetic moment as a function of time was followed in 10 M H₂SO₄ and paralleled the rate of change of color. This reaction which governs the color change is the same one in which the magnetic moment changes.

Dilution with 1 M HClO₄ results in the rapid, but not instantaneous, regeneration of [Fe(PrPI)₃]⁺² in yields as high as 95% of theory. Figure 3 contains a spectrophotometric demonstration of the reaction of $[\text{Fe}(\text{PrPI})_3]^{+2}$ with 10 M HClO₄ and its regeneration upon dilution with 0.2 M HClO₄. After the initial reaction was nearly complete, 0.2 M HClO₄ was added to give a final [HClO₄] of 1 M. The spectrum of the regenerated complex was identical with $[\text{Fe}(\text{PrPI})_3]^{+2}$, and the rate of decomposition in 1 M HClO₄ was the same as that observed for the unregenerated complex.
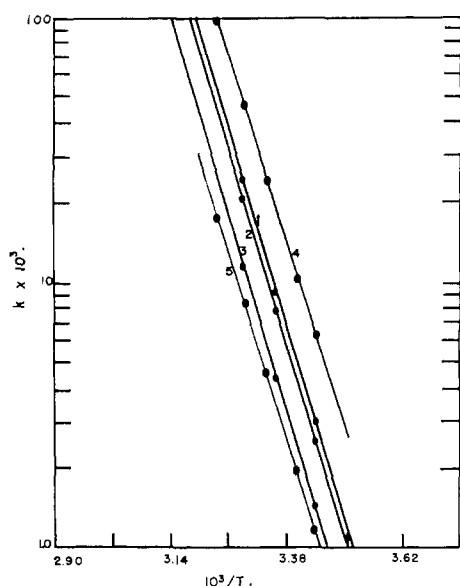
Fig. 4.—Rates of change of $[Fe(PPI)_3]^{+2}$ as a function of absolute temperature: (1) 1 M HCl, (2) 1 M HBr, (3) 0.01 M HCl–0.99 M NaCl, (4) 9 M HClO$_4$, (5) 10 M HClO$_4$ (1–3 dissociation, 4–5 protonation.)

A change in oxidation state cannot be the cause of these changes because the reaction and regeneration will take place in the presence of a large excess of Sn^{+2}, H_3PO_2 or As^{+3}. After regeneration, the amount of Sn^{+2} is equal to that present initially as shown by Ce^{+4} titration. With As^{+3}, the regenerated complex was titrated with Ce^{+4} without interference by As^{+3}, and this was followed by the titration of As^{+3} with Ce^{+4} after the addition of catalytic amounts of OsO_4. These results show that Sn^{+2} and As^{+3} are not oxidized by the strong

TABLE III

MAGNETIC MOMENTS[a]
in 10 M HClO$_4$, μ_{eff}.

Complex	μ effect
$[Fe(bipy)_3]^{+2}Br_2$	5.32, 5.11, 5.22
$[Fe(o\text{-phen})_3]^{+2}Cl_2$	4.67, 4.91, 4.72
$[Fe(PrPI)_3]^{+2}(ClO_4)_2$	4.67, 4.58, 4.99
$[Fe(PrPI)_3]^{+3}(ClO_4)_3$	1.69 (in H_2O, 1.69)

[a] Diamagnetic corrections after Selwood.[12]

acid media, which would not be expected if the complex were oxidized. The wave length of maximum absorption of the +2 complex in strong acid is very similar to that of the +3 complex, but the molar absorptivity is somewhat greater than that of the former. These spectral changes and similarity to the +3 ion are anticipated on the basis of acid interaction and lowered ligand field.

In order to test the possibility that the new species formed in strong acid solution was the mono or bis complex, these were prepared in the o-phen and bipy series by method of Dwyer and Basolo.[16] $Fe(o\text{-phen})_2Cl_2$ reacted instantaneously with 10 M HClO$_4$ to form Fe(II) and a white precipitate of o-

(16) F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, **76**, 1454 (1954).

phen·HClO$_4$. $Fe(bipy)_2Cl_2$ and $Fe(bipy)Cl_2$ with 10 M HClO$_4$ produced initially a light pink color which gradually disappeared, apparently behaving as if they contained a small percentage of $[Fe(bipy)_3]^{+2}$. The infrared spectra in KBr-compressed pellets were carried out on $Fe(bipy)_2Cl_2$, $Fe(bipy)Cl_2$ and $Fe(o\text{-phen})_2Cl_2$, and the first two compounds had essentially the identical absorption spectra as $[Fe(bipy)_3]^{+2}$, neglecting concentration. The spectrum of $Fe(o\text{-phen})_2Cl_2$ on the other hand differed from that of $[Fe(o\text{-phen})_3]Cl_2$ in several regions. Thus it appears that the compounds having the empirical formula $Fe(bipy)_2Cl_2$ and $Fe(bipy)Cl_2$ contain appreciable amounts of the tris complex. On the basis of the reaction of $Fe(o\text{-phen})_2Cl_2$, it appears that bis complexes are very unstable with respect to strong HClO$_4$.

Treatment of $d\text{-}[Fe(o\text{-phen})_3]^{+2}$ with concd. $H_2SO_4(0°)$ until the reaction was complete, then regeneration with 0.1 M H_2SO_4, resulted in solutions which retained a portion of the original optical activity. In two such runs 30% and 50% (after correcting for dilution) of the original activity remained. This rules out all lower species except the bis complex having the two o-phen coordination positions cis to each other.

In the Fe(III) methine system definite absorption shifts are observed, but no changes in magnetic susceptibility occur. Lowering the acid concentration regenerates the starting material. The stability toward dissociation of the +2 and +3 complexes is enhanced in concentrated acids.

$[Fe(PrPI)_3]^{+2}$ is only one of a large series of compounds which exhibit this reaction with strong acids. $[Fe(o\text{-phen})_3]^{+2}$ on treatment with strong acid changes from red (ϵ max. at 510 mμ = 11,500) to blue (ϵ max. at 605 mμ = 175). Although some dissociation to Fe(II) takes place, the solution will partially revert to the initial complex on dilution with 1 M acid in about 45% yield. The action of concentrated HClO$_4$ on $[Fe(bipy)_3]$-$(ClO_4)_2$ results in a slow reaction. Initial (ϵ max. at 522 mμ = 8,700; $\mu_{eff.}$ = 0), final (ϵ max. at 620 mμ = 15; $\mu_{eff.}$ = 5.2). Considerable dissociation takes place, but the solution will partially revert to $[Fe(bipy)_3]^{+2}$ on dilution with 1 M HClO$_4$. The Fe(II) tris complexes containing MePI, EtPI, n-BuPI, AQPI, 2,2',2''-terpyridine and glyoxal-(di)-n-butylimine all give characteristic changes in absorption spectra when treated with 10 M HClO$_4$ and are capable of being regenerated.

Identical changes with all of the complexes described occur in concentrated H_2SO_4 and to a lesser extent in HClO$_4$–HAc. The spectra of the species in HClO$_4$ and H_2SO_4 are identical.

The activation energy, E_a, in the $[Fe(PrPI)_3]^{+2}$ system was determined from the temperature dependence of the rates in both strong and weak acid (Fig. 4). Over the limited temperature range (17–36°) the Arrhenius expression was followed. Since the slope of the lines in Fig. 4 is directly related to E_a, it is apparent that the activation energy of decomposition is independent of the negative ion and the acidity. Furthermore, it is the same for the association with acid (9–10 M)

as that observed for decomposition in dilute acid. Rate changes with acid concentration, ionic strength, type of negative ion and nature of reaction are primarily due to a change in the value of ΔS.

E_a, ΔH, ΔF and ΔS for $[Fe(PrPI)_3]^{+2}$ in acid solution with $\mu = 1.0$ have the values 28.5, 27.9, 22.6 kcal./mole and 17.8 eu., respectively. These values are very similar to those obtained by Basolo, Hayes and Neumann[6] on $[Fe(bipy)_3]^{+2}$.

Discussion

The kinetics of the acid dissociation of the tris-(2-pyridinalalkylimine)-iron(II) compounds are very similar to that observed for tris-(bipyridine)-iron(II). Size and geometry of the alkyl group play an important part in the magnitude of the rate without modifying the general characteristics of the rate law.[17] There is a correlation between the base strength of the amine and the rate of acid dissociation which is valid for at least three acid strengths and which is independent of the negative ion (Table IIA). That geometrical factors are also important can be seen by comparing the methyl and n-butyl derivatives whose basicities are about equal. The rate for the latter is faster by about a factor of ten probably due to steric hindrance between neighboring groups. It is interesting to note that the isopropyl complex decomposes about twenty times faster than the normal derivative and that the rate is independent of the acid concentration. The increased rate is expected on the basis of steric interaction between adjacent alkyl groups with a resulting decrease in the thermodynamic and kinetic stability. The acid independence may result from dissociation without utilizing the protonated or protonated-half-bonded structure. This might be expected of complexes having low thermodynamic stability. Preliminary data on aromatic substituents show that the rates of decomposition are p-CH$_3$OC$_6$H$_4$- < p-CH$_3$C$_6$H$_4$- < C$_6$H$_5$- < p-NO$_2$C$_6$H$_4$-, which is the order of decreasing base strength. Since the thermodynamic stability of the complex will, in this case, be closely related to the base strength of the ligand (which is related to the base strength of the amine), an inverse relationship between base strength of amine and kinetic stability is expected if the rate determining step is a rupture of the ligand to metal bonds.

The mechanism of the acid dissociation of $[Fe(PrPI)_3]^{+2}$ appears to be of the same general type as that previously observed with $[Fe(bipy)_3]^{+2}$. The rate expression, acid dependence, salt effects and temperature dependence are about the same. If the mechanism of $[Fe(PrPI)_3]^{+2}$ included as a rate determining step the hydrolysis of the chelated ligand, the kinetics would not be similar to those in the bipy system where hydrolysis of the ligand cannot occur. It seems clear then that dissociation of the complex precedes ligand hydrolysis.

The half-bonded intermediate suggested in the mechanism for the dissociation of $[Fe(bipy)_3]^{+2}$ is somewhat less plausible with the iron(II) complexes

of Schiff bases. With one end of the ligand unattached, there would be a strong tendency for hydrolysis of the —C=N— linkage in the ligand with a resultant modification in the acid dependence of the kinetics. Many Schiff base complexes were studied, but in no case could a modified acid behavior be found to demonstrate this effect.

The evidence for the interaction of dilute acids with these complexes in a non-dissociative manner has not been completely established. There are, however, several experimental results which strongly suggest such behavior.

In more concentrated acids the presence of an acid adduct has been shown to be important and may completely overshadow the dissociation reaction in the more concentrated regions.

In concentrated HClO$_4$ or H$_2$SO$_4$, the dissociation path becomes slow compared to a reaction producing a new species. This new substance is formed at a measurable rate only in concentrated solutions of strong acids and has a visible spectrum differing from that observed in H$_2$O or that of $[Fe(PrPI)_3]^{+3}$ in the same acid. Reaction is accompanied by a magnetic moment change corresponding to a change in the number of unpaired electrons from 0 to 4. This corresponds to a change from spin-paired to spin-free iron(II). The results in concentrated solutions of strong acids cannot be explained on the basis of dissociation, oxidation to the +3 state, half-bonded structures or mono or bis complexes. Since no non-acidic solvent could be found which would cause this change to occur, it appears likely that association of the complex with either H$^+$ or the acid (HClO$_4$, H$_2$SO$_4$) is responsible for these changes. A distinction between these possibilities is not possible on the basis of the identical spectra in the two acids because the modification of the 3d electron energy levels would be expected to be nearly the same. Furthermore in solvents of this type, the distinction between H$^+$ and HClO$_4$ or H$_2$SO$_4$ association has little meaning due to the high degree of ion-pair association certainly present.

In dilute acid solutions (below 4 M), the evidence for an interaction between the complex and acid is less conclusive. Three lines of evidence suggest such an interaction, however. These are: (a) the solubility decrease of $[Fe(bipy)_3](ClO_4)_2$ in the pH range 2–3 and the great solubility increase of $[Fe(PrPI)_3](ClO_4)_2$ above 0.5 M acid, (b) the demonstration by Schilt[18] of relatively stable and acid associated $[Fe(o\text{-}phen)_2(CN)_2]^0$ and $[Fe(bipy)_2(CN)_2]^0$ species and (c) titration of $[Fe(PrPI)_3](ClO_4)_2$ with HClO$_4$ in acetic acid. The first of these, (a), may be explained equally as well by several other phenomena. The fact that the association of acid with the compounds used by Schilt does not modify the C–N stretching frequency suggests that the interaction is in some way associated with the organic ligands or the d-orbitals of the metal ion. The lower tendency of $[Fe(PrPI)_3]^{+2}$ to associate with acids, compared to the neutral complexes of Schilt, is partially due to the decreased negative charge on the ligands as a result of the net positive charge on the ion.

(17) Thein Aung, E. A. Healy and R. Kent Murmann, *Analyst*, **49**, 73 (1960).

(18) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

Recently, using a Ag–AgCl electrode and a glass electrode, potentiometric titrations of $[Fe(PrPI)_3]$-$(ClO_4)_2$ in acetic acid were possible.[19] The basicity of this complex is somewhat less than the neutral complexes of Schilt and the ratio of complex to acid is about 1.

Since the half-bonded intermediate is expected to hydrolyze rapidly giving the rate a hydrogen ion dependence quite different from that observed, several mechanisms involving protonated species were tried. The most successful of these involves an equilibrium between the complex and its protonated species followed by a first order dissociation of these intermediates which rapidly convert to the hydrolyzed ligand and iron(II) ions. With the assumptions: (a) $[Fe(PrPI)_3]^{+2}$ and $[Fe-(PrPI)\cdot H]^{+3}$ are in rapid equilibrium and have essentially the same molar absorbancy at the wave length used, (b) that the steady state approximation can be applied to $[Fe(PrPI)_3\cdot2H]^{+4}$ and (c) in the acid range 10^{-3} to 1 M the spin-free complex is not kinetically important, the following expression for the hydrogen ion dependence of the first order rate constant can be derived. Within 1%

$$k_{\text{obsd.}} = \frac{k_1 + k_2[H^+]k_3[H^+]^2}{k_4 + [H^+]}$$

this expression is in agreement with experiment in 10^{-3} to 1 M acid at $25°$, 1.0 with NaBr–HBr mixtures. Use of the activity of H^+ from the known activity coefficients of the NaBr–HBr system modified the form of the acid dependence very slightly. These values for the constants in the above equation were obtained: $k_1 = 3.0 \times 10^{-3}$ min.$^{-1}$, $k_2 = 6.3 \times 10^{-3}$ min.$^{-1}$, $k_3 = 1.45 \times 10^{-3}$ min.$^{-1}$ and $k_4 = 5.2 \times 10^{-2}$ min.$^{-1}$. The value of k_4 is the acid dissociation constant for the first protonation and is likely to be in error because of the tendency of the formation reaction to increase in importance at low H^+. An error due to the backward reaction would increase the apparent value of k_4.

There are many mechanisms which give an equation of the above form using the half-bonded, the protonated or other intermediates. We wish to indicate that in the 2-pyridinalimine complexes

the kinetics can be justified on the basis of the protonated concept. This approach satisfies equally well the hydrolysis kinetics of $[Fe(bipy)_3]^{+2}$ and many related systems.

A comparison of the rates of dissociation in weak acid with the rates of acid-association in strong acid cannot be very useful. A factor contributing to this is the unknown but major changes in ionic atmosphere with concentrated acids compared to water solutions. It is interesting to note however, that the activation energies are nearly identical, suggesting similar or identical activated states for the processes. Apparently the solvent has an important role in the dissociation either by replacing the ligands or by displacement because in favorable circumstances little or no dissociation takes place in anhydrous acids (concd. H_2SO_4).

The type of bonding and the positions of attachment (if in fact definite positions are taken) between acid and these complexes cannot be discerned at present. On the basis of increased stability in strong acid and steric considerations, it is doubtful that the interaction is localized around the individual nitrogen atoms. Interaction with the aromatic portion of the ligand seems to be indicated. With either approach, the change in magnetic susceptibility and, thus, the spectral changes may be explained.

Although two geometrical forms of these complexes $[M(ab)_3]^{+2}$ are possible, all indications pointed to only one isomer being generated. An exception to this was noted in the species containing the Schiff base formed from α-phenylethylamine and 2-pyridinealdehyde. In this case, even after careful purification of the starting materials, a mixture of two different substances was obtained which differed radically in their reaction rates; $k_1 = 2.05 \times 10^{-3}$ and 3.42×10^{-2} min.$^{-1}$ at $28°$, $\mu = 1.0$ (0.1 HCl). Work is continuing on these observations in view of its potential value in clarifying the general mechanism of acid hydrolysis.

(19) Thein Aung and R. Kent Murmann, to be published.