be reported in detail at a later date. Other substitution reactions which might proceed by similar mechanisms will warrant investigation.

Acknowledgments.—The author is greatly indebted to Professor R. E. Rundle and members of his research group for many helpful discussions during the course of this work. The facilities of the Institute for Atomic Research of Iowa State College were used during this investigation.

AMES, IOWA

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Kinetics of 1,10-Phenanthroline Chelation. II. Effect of Hydroxide Ion on the Dissociation Rate of Tris-(1,10-phenanthroline)-iron(II)[1,2]

BY D. W. MARGERUM

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Hydroxide ion greatly increases the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) despite the fact that there are no acidic protons in the complex. The value of k_0, first-order dissociation rate constant with respect to the complex, is dependent on the hydroxide ion concentration: $k_0 = k_d + k_1[OH^-] + k_2[OH^-]^2 + k_3[OH^-]^3$. The kinetics may be explained by an SN2 mechanism with nucleophilic attack by water or hydroxide ion to form reaction intermediates, which are in turn attacked by water or hydroxide ion, or by an SN1 mechanism with similar intermediates.

Introduction

It is known that the brightly colored complex, tris - (1,10 - phenanthroline) - iron(II), is stable in aqueous solution in the pH range 2–9.[3] Outside this pH range there is noticeable dissociation of the complex. Although the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) (hereafter abbreviated $FePh_3^{++}$) has been studied by a number of workers,[4-6] all of these studies have been performed in acidic solutions. Under the conditions of these studies, the rate of dissociation of the complex is first order with respect to the concentration of $FePh_3^{++}$ and independent of acidity. The acidities examined were from 0.005 to 0.50 M H_2SO_4. The kinetics of the over-all iron(II)-1,10-phenanthroline system are summarized as follows,[4] omitting the coördinated water molecules

$$\left.\begin{array}{l} Fe^{++} + Ph \rightleftharpoons FePh^{++} \\ FePh^{++} + Ph \rightleftharpoons FePh_2^{++} \end{array}\right\} \text{Fast}$$

$$FePh_2^{++} + Ph \underset{k_d}{\rightleftharpoons} FePh_3^{++} \quad \text{Slow}$$

where k_d = 0.0045 min.$^{-1}$. Only the addition or removal of the third 1,10-phenanthroline molecule to iron(II) proceeds at a measurable rate. Because of the stability of the mono and tris complexes, the bis-(1,10-phenanthroline)-iron(II) ion, $FePh_2^{++}$, does not exist in any appreciable concentration in solutions of varying iron(II) and 1,10-phenanthroline concentration.[7]

Tris-(1,10-phenanthroline)-iron(II) has been resolved into its optical isomers and the rate of its racemization has been studied.[6] The racemization rate is also independent of acidity (from 0.1 to 1.0 M HCl), but is greater than the dissociation rate. It has been suggested that racemization of $FePh_3^{++}$ proceeds both by a dissociation mechanism and by an intramolecular racemization mechanism.

Much more work has been done on the mechanism of substitution reactions with cobalt(III) complexes than with other coördination compounds. When weak nucleophilic groups react with cobalt(III) complexes, the reactions proceed by SN1 kinetics. More powerful nucleophilic substitutions may be interpreted as SN2[8] or SN-1CB[9,10] reactions. The SN1CB reaction is one where the conjugate base of the complex is formed prior to a slow first-order step in the reaction mechanism. In support of the SN1CB kinetics it has been pointed out that "complexes containing no acidic protons release their replaceable ligands at a rate independent of the pH of the solution."[10] This generalization may be applicable to the cobalt(III) complexes but it does not fit all complexes. Tris - (1,10 - phenanthroline) - iron(II) contains no acidic protons but its dissociation rate in basic solution is highly dependent upon the pH of the solution. This paper is concerned with the nature and significance of the hydroxide ion effect on the rate of dissociation of $FePh_3^{++}$.

Experimental

A stock solution of $FePh_3^{++}$ was prepared using a slight excess of 1,10-phenanthroline so that the concentration of $FePh_3^{++}$ was 4.87 × 10^{-4} M and the excess 1,10-phenanthroline was 2.55 × 10^{-4} M. Ten-ml. aliquots of this solution were diluted to 100 ml. volumes in solutions containing KCl, NaOH and slight amounts of ethylenediaminetetraacetic acid. The latter was added to help displace the equilibrium by reacting with Fe(II) and to prevent the precipitation of iron hydroxides. The KCl was used to maintain constant ionic strength. The dissociation rates were followed at 510 mμ with a thermostated (25.0°) Beckman DU spectrophotometer. All measurements were started 1 to 3 minutes after mixing the reagents and readings were taken every 30 or 60 seconds for 10 to 20 minutes.

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[1] Presented at the Atlantic City Meeting of the American Chemical Society, September, 1956.

[2] For paper I in this series see THIS JOURNAL, **78**, 4211 (1956).

[3] W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

[4] T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 3596 (1948).

[5] W. W. Brandt and D. K. Gullstrom, *ibid.*, **74**, 3532 (1952).

[6] F. Basolo, J. C. Hayes and H. M. Neuman, *ibid.*, **76**, 3807 (1954).

[7] I. M. Kolthoff, D. L. Leussing and T. S. Lee, *ibid.*, **72**, 2173 (1950).

[8] D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953).

[9] J. S. Anderson, H. V. A. Briscoe and N. F. Spoor, *ibid.*, 361 (1943).

[10] R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).

Hydroxide ion concentrations were calculated either from the amount of NaOH added or from the *p*H of the solution using a Beckman Model G *p*H meter equipped with an E-2 (high alkalinity) electrode. Since some NaOH will react with the added ethylenediaminetetraacetic acid (abbreviated H_4Y), the following calculation was used. It is possible to assume that all the H_4Y added, Y_T, will be present as either HY^{-3} or Y^{-4}. Then from the charge balance in the solution

$$[OH^-] = [NaOH\ added] + [Na^+]_0 - 3[Y_T] - [Y^{-4}]$$

where $[Na^+]_0$ is the original concentration of Na^+ resulting from the use of the disodium salt of ethylenediaminetetraacetic acid. The $[Y^{-4}]$ can be estimated from titration curves and the approximate *p*H of the solution. Since the $[Y_T]$ was maintained between 0.002 and 0.010 *M*, these corrections were not significant at the higher hydroxide ion concentrations. At low hydroxide ion concentrations *p*H was also used to calculate the $[OH^-]$ from

$$\log m_{OH} = pH + \log \frac{K_w}{f_{NaOH}}$$

where $K_w = 1.008 \times 10^{-14}$ and f_{NaOH} was taken from the ionic strength of the solution.[11]

Results

When $FePh_3{}^{++}$ is placed in basic solutions, its rate of dissociation is much faster than when it is in acidic solutions. The half-life of the bright red complex in sulfuric acid solutions is 2.5 hours while in strong base the colored complex may completely disappear in only ten minutes. Spectrophotometric evidence indicates none of the blue, oxidized state of the complex $FePh_3{}^{+++}$ is formed during the disappearance of $FePh_3{}^{++}$. Two additional tests show that oxidation is not responsible for the rapid disappearance of the red complex in strong base. First, the reaction is just as fast in the presence of a reducing agent such as sodium hydrosulfite ($Na_2S_2O_4$). Second, when the solid blue iron(III) complex, $FePh_3(ClO_4)_3$, is dissolved in water and strong base is added, the blue solution immediately turns red due to the formation of the iron(II) complex. Although the 1,10-phenanthroline molecule does not decompose readily, it is also conceivable that hydroxide ion could attack the 1,10-phenanthroline molecule in the iron(II) complex. In order to test for decomposition of 1,10-phenanthroline, a solution of $FePh_3{}^{++}$ was allowed to dissociate completely in 0.72 *M* NaOH in the absence of ethylenediaminetetraacetic acid. On neutralization of the solution, the bright red complex, identical with the original solution, re-formed. (It was necessary to add more Fe(II) or else hydroxylamine to re-form all the complex, as the original Fe(II) released from the $FePh_3{}^{++}$ rapidly formed iron(III) hydroxide in the strong base.) From these tests it is apparent that the 1,10-phenanthroline itself is not decomposed and it can be assumed that the disappearance of the red color is, in fact, due only to the dissociation of the original complex.

The hydroxide ion concentration is either in large excess of the $[FePh_3{}^{++}]$ or else it is well buffered by the ethylenediaminetetraacetic acid. Hence, during any given kinetic run the $[OH^-]$ is a constant. The presence of excess hydroxide ion and of ethylenediaminetetraacetic acid also displaces the equilibrium so far that the reverse reaction, *i.e.*, the formation of $FePh_3{}^{++}$, is in all cases negligible over the time the reaction was followed kinetically. Therefore, the dissociation of $FePh_3{}^{++}$ appears to be first order

$$\frac{-\,d[FePh_3{}^{++}]}{dt} = k_0[FePh_3{}^{++}] \qquad (1)$$

where k_0 is a function of $[OH^-]$, ionic strength and temperature. A variation in the $[Y^{-4}]$ from 0.001 to 0.010 *M* at constant $[OH^-]$ and constant ionic strength indicated that for the concentration range used in these experiments Y^{-4} had no appreciable effect on the dissociation rate.

The rates of dissociation are highly dependent on the $[OH^-]$ as shown in Fig. 1, where three typical first-order plots are given. As the hydroxide ion concentration is increased, the value of k_0 becomes larger and larger. Figures 2 and 3 illustrate the effect of $[OH^-]$ on k_0 with three different series of constant ionic strength runs. Increased ionic strength decreases the effect of $[OH^-]$ on k_0, but k_0 still increases rapidly with $[OH^-]$ even at $\mu = 4.5$. The experimental data are summarized in Table I.

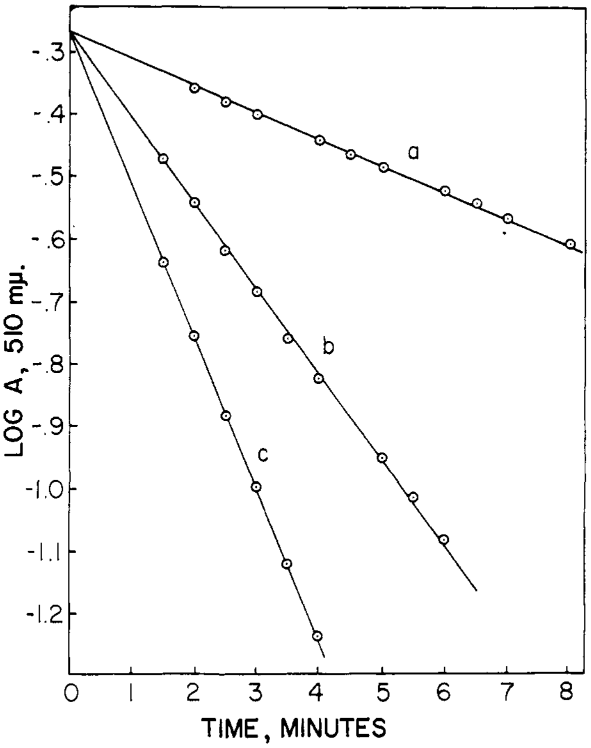

Fig. 1.—First-order plot of dissociation of $FePh_3{}^{++}$ at various $[OH^-]$: a is 0.098 *M* $[OH^-]$; b is 0.496 *M* $[OH^-]$; and c is 0.997 *M* $[OH^-]$.

At low $[OH^-]$, k_0 can be expressed as $k_d + k_1[OH^-]$, where k_d is the intercept in Figs. 2 and 3 and k_1 is the slope of the straight line near the intercept. The constant, k_d, is merely k_0 in neutral (or acid) solutions and experimental values for k_d at various ionic strengths are summarized in Table II. These values are in agreement with the previously determined values in acidic solutions except that previously the effect of ionic strength was not taken into account.

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[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 560.

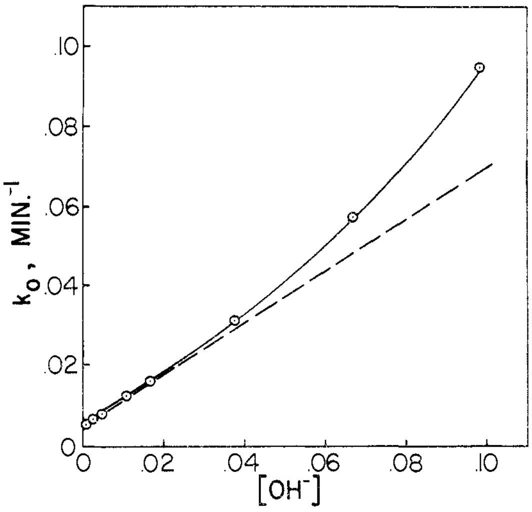

Fig. 2.—Effect of $[OH^-]$ on the observed first-order constant with $\mu = 0.15$.

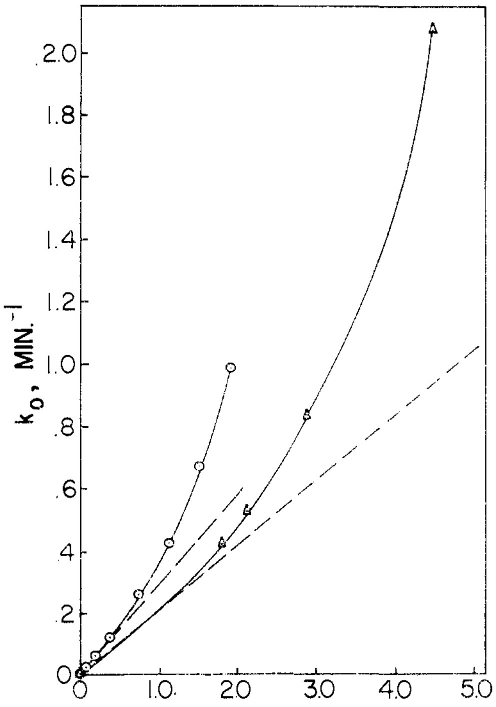

Fig. 3.—Effect of $[OH^-]$ on the observed first-order constant: ○, for $\mu = 2.01$; △, for $\mu = 4.55$.

TABLE I

EFFECT OF HYDROXIDE ION AND IONIC STRENGTH ON THE OBSERVED DISSOCIATION RATE CONSTANT OF $FePh_3^{++}$

Ionic strength μ	$[OH^-]$	k_0 (min.$^{-1}$)	Ionic strength μ	$[OH^-]$	k_0 (min.$^{-1}$)
0.150	0.000470	0.00524	1.047	0.0653	0.0286
.150	.00210	.00656	1.047	.137	.0571
.154	.00460	.00800	1.047	.352	.151
.149	.0103	.0125	1.049	.495	.226
.151	.0163	.0157	1.049	.710	.349
.151	.0374	.0311	1.048	.854	.450
.152	.0665	.0571	1.050	.997	.559
.153	.0982	.0946	2.01	.0635	.0237
.556	.000421	.00478	2.01	.178	.0596
.551	.00595	.00672	2.01	.369	.1203
.556	.0143	.0113	2.02	.752	.260
.552	.0453	.0244	2.01	1.134	.427
.553	.0608	.0336	2.00	1.517	.670
.551	.1373	.0743	2.00	1.897	.990
.549	.281	.161	4.56	1.79	.425
.549	.353	.206	4.55	2.15	.526
.550	.496	.310	4.56	2.87	.838
1.045	.00790	.00832	4.56	4.46	2.07

TABLE II

EFFECT OF IONIC STRENGTH ON THE INDIVIDUAL DISSOCIATION RATE CONSTANTS OF $FePh_3^{++}$

Ionic strength μ	Dissociation constants, min.$^{-1}$ k_d	k_1	k_2	k_3
0.15	4.96×10^{-3}	0.64	2.5	0.3
.55	4.54×10^{-3}	.45	0.33	.06
1.05	4.27×10^{-3}	.36	.17	.03
2.01	3.86×10^{-3}	.29	.06	.02
4.56	3.25×10^{-3}	.21	.014	.006

As the $[OH^-]$ increases, k_0 becomes more dependent on $[OH^-]$ and can be expressed as

$$k_0 = k_d + k_1[OH^-] + k_2[OH^-]^2 \qquad (2)$$

so that

$$\frac{k_0 - k_d}{[OH^-]} = k_1 + k_2[OH^-] \qquad (3)$$

From eq. 3, a plot of $(k_0 - k_2)/[OH^-]$ against $[OH^-]$ should give a straight line of intercept k_1 and slope k_2. Figure 4 indicates that eq. 2 adequately fits the behavior of k_0 up to about 1 *M* hydroxide ion. Despite the inherent errors from small differences between k_0 and k_d at low $[OH^-]$, the intercepts correspond to k_1 and straight line plots are obtained. However, Fig. 5 indicates that at still higher $[OH^-]$ k_0 increases even more rapidly with $[OH^-]$ than by eq. 2. It is possible to fit all the values of k_0 up to 4.5 *M* NaOH by assuming the expression

$$k_0 = k_d + k_1[OH^-] + k_2[OH^-]^2 + k_3[OH^-]^3 \qquad (4)$$

The values of k_d, k_1, k_2 and k_3, which become increasingly dependent on the ionic strength of the solution, are given in Table II for various ionic strengths. In the evaluation of all these constants,

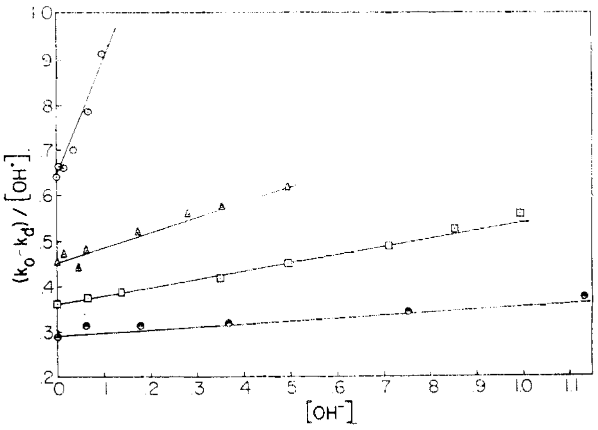

Fig. 4.—Dependence of k_0 on eq. 3: ○, for $\mu = 0.15$; △, for $\mu = 0.55$; □, for $\mu = 1.05$; ●, for $\mu = 2.01$.

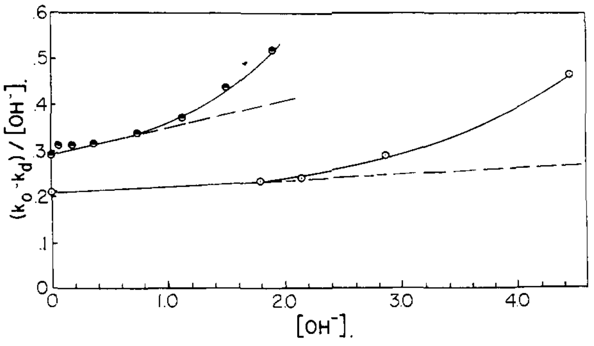

Fig. 5.—Dependence of k_0 on eq. 3: ●, for μ = 2.01; O, for μ = 4.56.

it was useful to assume that their logarithms *versus* $\sqrt{\mu}$ would appear as smooth curves. The values of k_3 are only estimates, especially at low ionic strengths. Increased ionic strength consistently suppresses the size of the rate constants even at very high ionic strengths. There is no apparent inversion of the k_1 or k_2 values above one molar KCl that can account for the rapid increase in k_1 at high $[OH^-]$. Equation 4 and the k values in Table II can be used to accurately predict the dissociation rate of $FePh_3^{++}$ at any concentration of hydroxide ion.

Discussion

It has previously been shown that only the loss of the first Ph molecule from $FePh_3^{++}$ is a kinetically important step in the dissociation of the complex. The present study has borne this out as in all cases the kinetics appear first order with respect to $FePh_3^{++}$ and independent of Ph concentration. Therefore, any mechanism involving the formation of kinetically significant bis-(1,10-phenanthroline)-iron(II) complexes, such as that below, would be ruled out,

$$FePh_3^{++} \rightleftarrows \left\{\begin{matrix} FePh_2(H_2O)_2^{++} + Ph \\ FePh_2(OH)(H_2O)^{+} + Ph \\ FePh_2(OH)_2 + Ph \end{matrix}\right\} \longrightarrow \text{Products}$$

This mechanism is not possible because the varying concentration of Ph during a reaction would alter the kinetics from those observed.

If the $FePh_3^{++}$ complex is compared to the cobalt(III) complexes, the question arises whether or not the iron(II) complex is subject to nucleophilic attack by water or hydroxide ion. Two sets of mechanisms can be considered, one assuming water and hydroxide ion attack and the other assuming hydroxide ion catalysis. The nucleophilic mechanism is discussed first.

1. Nucleophilic Attack.—If it is assumed that hydroxide ion is capable of nucleophilic attack on $FePh_3^{++}$, it would be consistent to assume that the water molecule behaves similarly so that in neutral solutions the dissociation of $FePh_3^{++}$ proceeds by attack of water. The observed kinetics show that k_0 has greater than a first-order dependence on hydroxide ion. Since a combination of attack by water and hydroxide ions to give bi-, tri- and tetramolecular reactions is unreasonable, it is necessary to assume some type of unstable reaction intermediate where H_2O or OH^- is associated with $FePh_3^{++}$. Although this intermediate might be pictured as some type of complex with a coördination number of seven, it is more convenient to represent it as having one singly-bonded 1,10-phenanthroline molecule. The latter is assumed in Fig. 6. Since two nitrogen–iron bonds must be broken in the dissociation of a Ph molecule, it would be reasonable to expect that under nucleophilic attack both bonds would not react and break simultaneously. In other words, a four centered reaction would not be expected. If the bonds do not break simultaneously then there must be an intermediate species such as A or C in Fig. 6. The species A is formed by the attack of H_2O and the species C by the attack of OH^-. Once A is formed it would be expected to come to rapid equilibrium with C because only a proton transfer is involved in going from one intermediate to the other. The intermediates, A or C, may revert back to $FePh_3^{++}$ by unimolecular reactions or they may lose the activated Ph molecule by subsequent nucleophilic attack by another H_2O or OH^-.

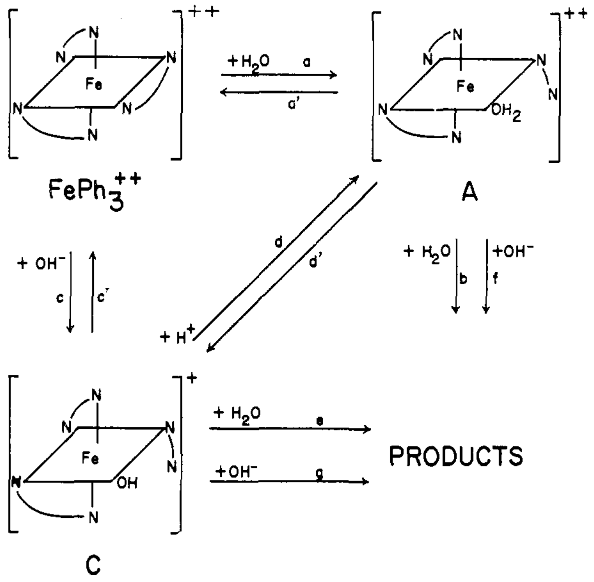

Fig. 6.—Mechanism for the dissociation of $FePh_3^{++}$ by nucleophilic attack of H_2O and OH^-: N–N represents 1,10-phenanthroline; A and C are unstable intermediates.

Let

$$K_d = \frac{d'}{dK_w} = \frac{[C]}{[OH^-][A]}$$

and use the steady-state approximations to assume that $d[A]/dt + d[C]dt = 0$. From Fig. 6

$$\frac{-d[FePh_3^{++}]}{dt} = k_0[FePh_3^{++}] = (a + c[OH^-])\,[FePh_3^{++}] - a'[A] - c'[C]$$

and assuming no reversible reaction from the products

$$[A] = \frac{a + c[OH^-]}{a' + b + f[OH^-] + K_d[OH^-](c' + e + g[OH^-])}\,[FePh_3^{++}]$$

and

$$[C] = K_d[OH^-][A]$$

Therefore, the rate constant[12] is

$$k_0 = (a + c[\mathrm{OH}^-])\frac{b + f[\mathrm{OH}^-] + K_\mathrm{d}[\mathrm{OH}^-](e + g[\mathrm{OH}^-])}{a' + b + f[\mathrm{OH}^-] + K_\mathrm{d}[\mathrm{OH}^-](c' + e + g[\mathrm{OH}^-])} \quad (5)$$

In eq. 5, the numerator and denominator of the part in the brackets are identical except for a' and $K_\mathrm{d}[\mathrm{OH}^-]c'$ in the denominator. In order for this mechanism to agree with the observed high order of dependence of hydroxide ion concentration, $a' + K_\mathrm{d}[\mathrm{OH}^-]c'$ must be larger than the other terms in the denominator. In other words, b, f, e and g are the rate-controlling steps and the intermediates A and C are in equilibrium with $\mathrm{FePh_3}^{++}$. Then $a' + K_\mathrm{d}[\mathrm{OH}^-]c'$ equals $a'/a(a + c[\mathrm{OH}^-])$, because $K_\mathrm{d} = a'c/ac'$, if these species are in equilibrium with each other. Equation 5 then becomes

$$k_0 = \frac{a}{a'}\{b + f[\mathrm{OH}^-] + K_\mathrm{d}[\mathrm{OH}^-](e + g[\mathrm{OH}^-])\}$$

or

$$k_0 = \frac{ab}{a'} + \frac{af + aeK_\mathrm{d}}{a'}[\mathrm{OH}^-] + \frac{agK_\mathrm{d}}{a'}[\mathrm{OH}^-]^2 \quad (6)$$

In agreement with previous definition, k_d equals ab/a', because ab/a' represents the value of k_0 in the absence of hydroxide ion. Equation 6 corresponds to the zero-order, first-order and second-order dependence of k_0 on hydroxide ion concentration and fits the observed kinetics up to one molar $[\mathrm{OH}^-]$. The introduction of a $[\mathrm{OH}^-]^3$ term above one molar hydroxide ion concentration may be due to several factors. At such high ionic strengths it is possible that specific salt effects, characteristic of NaOH as opposed to KCl, might change the activity coefficients. This would be equivalent to having a high concentration of NaOH cause an increase in the values of k_d, k_1 and k_2, something which is not observed with KCl. Another explanation of the $[\mathrm{OH}^-]^3$ term can be derived by extending the kinetic picture of Fig. 6. A second Ph molecule in intermediate C can be activated to form another intermediate, D, with two singly bonded phenanthroline molecules. If D then goes to product by OH^- attack, the system would have a $[\mathrm{OH}^-]^3$ term.

2. **Hydroxide Ion Catalysis.**—An alternative explanation to nucleophilic attack may be postulated by assuming that $\mathrm{FePh_3}^{++}$ spontaneously forms an intermediate, $(\mathrm{FePh_3}^{++})^*$, where one Ph molecule is only partially bonded to Fe(III). This intermediate might rapidly accept a water molecule or hydroxide ion prior to the complete dissociation of the Ph molecule from the Fe(II). The intermediate with a hydroxide ion, $(\mathrm{FePh_3OH}^+)^*$, would lose the partially bonded Ph molecule more readily than the intermediate formed with water, $(\mathrm{FePh_3H_2O}^{++})^*$.

$$\begin{tikzcd}
\mathrm{FePh_3}^{++} \arrow[r, shift left, "k"] & (\mathrm{FePh_3}^{++})^* \arrow[l, shift left] \arrow[r, shift left, "\mathrm{H_2O}"] \arrow[d, shift right, "\mathrm{OH}^-"'] & (\mathrm{FePh_3H_2O}^{++})^* \arrow[l, shift left] \arrow[dl, shift left] \arrow[d] \\
& (\mathrm{FePh_3OH}^+)^* \arrow[u, shift right, "\mathrm{H}^+"'] \arrow[ur, shift left] \arrow[r] & \text{Products}
\end{tikzcd}$$

With such a mechanism it might be expected that as $[\mathrm{OH}^-]$ greatly increased, the rate-determining step would become the first activation step with rate constant k. This, of course, is not the case as k_0 increases more rapidly at high $[\mathrm{OH}^-]$ rather than leveling off. Therefore, to apply this mechanism it must be assumed that regardless of the $[\mathrm{OH}^-]$, the rate-determining steps are those involving the loss of the partially bonded Ph molecule. To fit this mechanism to the observed data it is necessary to assume the formation of additional intermediates, $(\mathrm{FePh_3(OH)_2}^0)^*$ and $(\mathrm{FePh_3(OH)_3}^-)^*$, with two and three one-bonded phenanthroline molecules, respectively. If nucleophilic attack is not allowed, then each of these intermediates must be preceded by their corresponding activated species with which OH^- equilibrates.

Another mechanism should be mentioned in addition to the two already considered, both of which change the bonding to Fe(II). Ion pair formation between $\mathrm{FePh_3}^{++}$ and OH^- could conceivably lead to intermediates with one or more OH^-, which would dissociate at different rates. However, other ions such as Cl^-, F^-, $\mathrm{NO_3}^-$ and $\mathrm{ClO_4}^-$ might be expected to form ion pairs as readily as OH^-, but none of these ions increase the dissociation rate. In fact, as noted earlier, increased ionic strength decreases the dissociation rate rather than increasing it. Hence, an ion pair type mechanism is not possible unless OH^- forms some unique species with $\mathrm{FePh_3}^{++}$, in which case it would essentially be bonded to Fe(II) and no longer a mere ion pair.

The dissociation of $\mathrm{FePh_3}^{++}$ is not the only phenanthroline reaction where it has been necessary to postulate reaction intermediates to explain the kinetics. The dissociation and formation rates of mono-(1,10-phenanthroline)-nickel(II) are affected by acidity in such a way as to necessitate the assumption of a partially bonded intermediate.[2] Other studies on the racemization of $\mathrm{FePh_3}^{++}$ have shown an intramolecular racemization in addition to the dissociation racemization.[6] The intramolecular racemization can be explained readily from the point of view of a partially bonded intermediate. It is possible to predict that the racemization reaction should proceed faster in basic solutions.

The exact nature of the reaction intermediates with 1,10-phenanthroline complexes is not clear. The intermediate might be considered as having opened a chelate ring and coördinated another nucleophilic group to the central ion shown in Fig. 6. However, the fact that the nitrogen atoms in 1,10-phenanthroline are only 2.5 Å. apart and that the 1,10-phenanthroline molecule is a fixed planar structure has been used as steric arguments against any tendency for 1,10-phenanthroline to behave as a monodentate group.[6] On the other hand, optical isomers of 4,5-disubstituted phenanthrenes have been obtained.[13] These compounds have a structure similar to 1,10-phenanthroline and optical isomers can exist only by steric repulsion causing nonplanarity of the molecule. Hence, it is not impos-

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[12] Equation 5 may also be derived by first assuming only that $d[A]/dt = 0$, and $d[C]/dt = 0$ and then simplifying the resulting expression by assuming that d' and d are very large.

[13] M. S. Newman and A. S. Hussey, THIS JOURNAL, **69**, 3023 (1947).

sible to have a reaction intermediate with a broken chelate ring. The alternative explanation is a reaction intermediate with a seven coördinated iron(II) ion. Such a coördination intermediate would presumably necessitate changes in electron configuration of the complex, which would account for the slowness of its formation. Somewhere in the dissociation reaction the electronic configuration for iron(II) changes from $d^2d^2d^2D^2SP^3$ to $d^2d^1d^1d^1d^1SP^3D^2$.

It is not possible from this work to definitely establish whether the hydroxide ion effect on $FePh_3^{++}$ is due to an S_N1 or an S_N2 mechanism. Both mechanisms involve partially dissociated species and neither mechanism accounts for the observed $[OH^-]^3$ term without the introduction of several intermediates. However, the S_N2 mechanism is the simpler of the two. It has fewer intermediates and gives a $[OH^-]^2$ dependence at low hydroxide ion concentrations without the necessity of assuming an intermediate with two activated Ph molecules. The hydroxide ion is not the only nucleophilic ion which can accelerate the dissociation of $FePh_3^{++}$. Cyanide ion and thiocyanate ion both cause faster dissociation of $FePh_3^{++}$.[14] The cyanide ion kinetics with $FePh_3^{++}$ resemble the hydroxide ion kinetics, with a reaction intermediate likely. The aqueous cyanide ion causes faster dissociation than the hydroxide ion. All of these factors contribute to the feasibility of an S_N2 mechanism with reaction intermediates containing nucleophilic groups.

The fact that it is possible to bring about the rapid dissociation of $FePh_3^{++}$ should prove of value in analytical separations involving the use of 1,10-phenanthroline kinetics.[15]

It is naturally of considerable interest to know whether hydroxide ion will affect the dissociation kinetics of other 1,10-phenanthroline complexes such as nickel(II) and cobalt(III). These systems, as well as a comparison of the effect of other nucleophilic groups besides hydroxide ion, are now under investigation.

(14) P. Grimes, "Reactions of Anions with 2,2′-Bipyridine, 1,10-Phenanthroline and the Iron(II) Complexes of These Reagents," M.S. Thesis, Ames, Iowa, Iowa State College, 1956.

(15) D. W. Margerum and Charles V. Banks, *Anal. Chem.*, **26**, 200 (1954).

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Tridentate Chelate Compounds. I

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New tridentate chelate compounds containing three donor nitrogen atoms and possessing structural features resembling those of terpyridine have been prepared and shown to form coördination compounds readily. Some polymers possessing recurring tridentate chelate groups also have been prepared and their capacity to combine with metal salts demonstrated. Some of the iron containing polymers have unusual magnetic properties.

2,6-Bis-(α-pyridyl)-pyridine (I), better known by its trivial name "terpyridine," is a most important tridentate chelate compound which has been extensively studied. However, it is relatively inaccessible. In 1953 one of the authors and his coworkers[2] reported briefly on the preparation and use of 8-(α-pyridylmethyleneamino)-quinoline (II) as a tridentate chelate compound with constitutional features similar to those of I and showed that it coördinated with iron(II) salts similarly to I. The present paper describes a number of new tridentate chelate compounds, each containing three donor nitrogen atoms and some possessing details of molecular structure similar to I.

2-Aminomethylpyridine (III) is available from the reduction with zinc dust and acetic acid of pyridine-2-aldoxime.[3] We have also found that it can be synthesized from the 2-chloromethylpyridine of Matsumura[4] by condensation with potassium phthalimide using Bolhofer and Sheahan's[5] modification of the Gabriel reaction, and hydrolysis of the 2-phthalimidomethylpyridine so obtained. However, the over-all yield is small and the method of Craig and Hixon is preferable.

III reacts readily with pyridine-2-aldehyde to give the Schiff base 2-(α-pyridylmethyleneaminomethyl)-pyridine (IV) as a pale yellow oil. IV might well be expected to function as a tridentate chelate compound with all three nitrogen atoms acting as donors and attaching the tridentate residue to a metal atom in two coplanar 5-membered ring "chelate loops."[6] The molecules of both I and IV possess the same sequence of atoms and bonds, *viz.*, –N=C–C=N–C–C=N–, in the donor chain, so that at least some of the possibilities which exist for double bonding and resonance must be similar for the molecules of both substances.

Addition of iron(II) sulfate to an aqueous suspension of II results in formation of an intensely red-colored solution from which bis-(2-(α-pyridylmethyleneaminomethyl) - pyridine) - iron(II) perchlorate (V) can be precipitated. This salt is diamagnetic and must apparently be an octahedral iron(II) complex salt with lower level ($3d^24s4p^3$) covalent bonds. Its complex cation must be very similar structurally to that of the bis-terpyridine iron(II) salts, each tridentate residue lying in one

(1) University Research Fund Student of the University of Sydney.

(2) F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **75**, 3834 (1953).

(3) L. C. Craig and R. M. Hixon, *ibid.*, **53**, 4367 (1931).

(4) E. Matsumura, *J. Chem. Soc. Japan*, **74**, 363 (1953); *cf. C.A.* **48**, 6442b (1954).

(5) J. C. Bolhofer and W. A. Sheban, THIS JOURNAL, **72**, 2786 (1950).

(6) *Cf.* F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **74**, 4188 (1952).