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The Kinetics of the Formation and Dissociation of Mono-(1,10-phenanthroline)-iron(II)[1]

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The kinetics of formation and dissociation of mono-(1,10-phenanthroline)-iron(II) have been studied in $HClO_4$ solutions. The rates increase with (H^+). E_a and ΔS^* for the dissociation are 12.8 kcal. mole^{-1} and -16 cal. deg.$^{-1}$ mole^{-1}, respectively. The results are discussed in terms of crystal-field theory.

Introduction

These equilibria exist in solutions containing aquo iron(II) ions and 1,10-phenanthroline (phen)

$$\text{Fephen}^{2+} \underset{k_{1f}}{\overset{k_{1d}}{\rightleftarrows}} \text{Fe}^{2+} + \text{phen} \qquad K_1$$

$$\text{Fe(phen)}_2{}^{2+} \underset{k_{2f}}{\overset{k_{2d}}{\rightleftarrows}} \text{Fephen}^{2+} + \text{phen} \qquad K_2$$

$$\text{Fe(phen)}_3{}^{2+} \underset{k_{3f}}{\overset{k_{3d}}{\rightleftarrows}} \text{Fe(phen)}_2{}^{2+} + \text{phen} \qquad K_3$$

$$\text{Hphen}^{+} \rightleftarrows \text{H}^{+} + \text{phen} \qquad K_a$$

where the coördinated water molecules are not shown and the (H^+) is less than 1.0. Systematic studies of the above equilibria have been made by Lee, Kolthoff, and Leussing[3,4] and by Irving and Mellor.[5] They obtained values of 1.1×10^{-5}, 1.3×10^{-6}, 5.0×10^{-6}, and 1.0×10^{-10} for the dissociation constants K_a, K_1, K_2, and K_3, respectively, at 25.0°. The kinetics of formation and dissociation of tris(1,10-phenanthroline)-iron(II) have been studied by several investigators and shown to have a complex acid dependence.[3,6–11] Relatively little has been reported about the kinetics of formation or dissociation of the mono complex. It generally is assumed that the rate of dissociation of the mono complex proceeds much more rapidly than that of the tris complex.

We have investigated the rate of formation and dissociation of mono-(1,10-phenanthroline)-iron-(II) as a function of iron(II), phenanthroline, and perchloric acid concentrations, ionic strength, and temperature. The dissociation kinetics are compared with those of the tris-(1,10-phenanthroline)-iron(II) complex and of the mono- and tris-(1,10-phenanthroline)-cobalt(II) and -nickel(II) complexes.[12–15]

Experimental

Chemicals.—Iron(II) perchlorate was obtained from the G. Frederick Smith Chemical Company. A stock solution (about 0.5 *F* in $Fe(ClO_4)_2$ and 0.1 *F* in $HClO_4$) was electrolyzed to reduce any iron(III) present. The iron(II) was estimated by titration with ceric sulfate using erioglaucine as indicator (ferroin is precipitated in perchlorate medium). The stock solution was kept under nitrogen and stored in a refrigerator. A stock solution of sodium perchlorate was prepared by dissolving sodium carbonate in water and neutralizing to *p*H 5.0 with perchloric acid. The sodium perchlorate concentration was determined gravimetrically after evaporation. A 0.01 *F* solution of 1,10-phenanthroline (G. Frederick Smith Chemical Co.) was prepared by dissolving the appropriate weight of the compound in dilute sulfuric acid.

Apparatus.—The kinetics were studied using the rapid-mixing and flow apparatus which has been described previously.[16] The distance from the mixing chamber to the point of observation was decreased to 2 cm. Absorption spectra were measured with a Beckman DU spectrophotometer.

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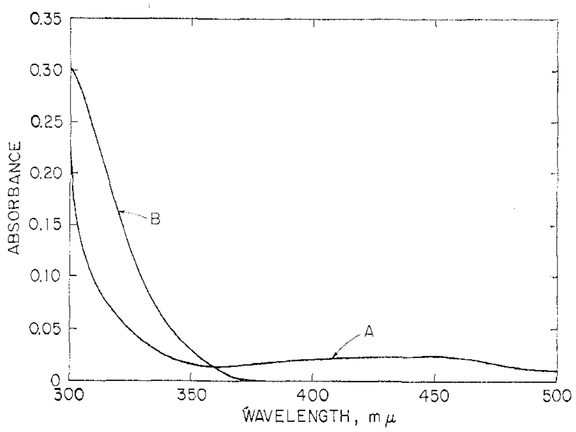

Fig. 1.—Absorption spectra of the mono-(1,10-phenanthroline)-iron(II) and 1,10-phenanthrolium ions at 25.0°: A, 5.0 × 10^{-5} F phenanthroline, 5.0 × 10^{-2} F $Fe(ClO_4)_2$, $pH = 5.0$ *vs.* 5.0 × 10^{-2} F $Fe(ClO_4)_2$, $pH = 5.0$; B, 5.0 × 10^{-5} F phenanthroline, 0.10 F $HClO_4$ *vs.* 0.10 F $HClO_4$.

Procedure.—The absorption spectra between 300 and 500 mμ of the mono-(1,10-phenanthroline)-iron(II) complex and of the 1,10-phenanthrolium ion are shown in Fig. 1 (under the conditions used in these measurements the concentration of free phenanthroline was negligible compared to that of the phenanthrolium ion and of the mono-(1,10-phenanthroline)-iron(II) complex). It is apparent from Fig. 1 that there is a large difference in the extinction coefficients of $Hphen^+$ and $Fephen^{2+}$ at 310 mμ. For this reason the change in absorbance as the reaction proceeds was followed at 310 mμ. In a few runs the reaction also was followed at 420 mμ, where $Hphen^+$ does not absorb, with the same results (420 mμ was preferred to 450 mμ since the extinction coefficient of the mono complex is only slightly smaller at 420 mμ than at 450 mμ, while the extinction coefficient of the tris complex is considerably smaller at 420 mμ than at 450 mμ[4]).

Both the formation and the dissociation of the mono complex were followed. In the first case a solution of iron(II) with a given acid concentration, and ionic strength of 1.00, was mixed with a phenanthroline solution of equal acidity and ionic strength, and the disappearance of the 1,10-phenanthrolium ion followed spectrophotometrically. The dissociation of the mono complex was studied by mixing a solution of mono-(1,10-phenanthroline)-iron(II) in 0.01 F perchloric acid with a stronger solution of perchloric acid and sufficient sodium perchlorate to give the required ionic strength. The formation of the 1,10-phenanthrolium ion in the reaction mixture was followed spectrophotometrically. In addition, a phenanthroline solution was mixed with a 10^{-3} F perchloric acid solution and the formation of the phenanthrolium ion found to be too fast to follow with our technique. A solution of aquo iron(II) ion in 10^{-3} F perchloric acid also was mixed with a 2.0 F perchloric acid solution and no spectrophotometric evidence of a reaction was found at 310 mμ.

The range of concentrations which could be used in these studies was restricted by these considerations:

(a) From the values of K_1, K_2, and K_3 it can be shown that $(Fe^{2+})/(phen)_T$ should be greater than 400 in order for the concentration of the bis and tris complexes to be less than 1% of the concentration of the mono complex.

(b) From the values of K_a and K_1, it can be shown that the $(Fe^{2+})/(H^+)$ ratio should be greater than ~0.1 to ensure the formation of a relatively high concentration of the mono complex. Conversely, the $(Fe^{2+})/(H^+)$ ratio should be less than ~1.0 in dissociation measurements to produce a relatively large extent of dissociation.

(c) In order to prevent the formation of appreciable quantities of the doubly-protonated 1,10-phenanthrolium ion, the (H^+) should be less than about 1.0. (The K_a of H_2phen^{2+} has been estimated to be about 5 at 25.0°.[13])

Results and Discussion

The rate of formation of $Fephen^{2+}$ is given by the expression

$$\frac{d(Fephen^{2+})}{dt} = k_{1f}(Fe^{2+})(phen) - k_{1d}(Fephen^{2+})$$

If equilibrium between phenanthroline and $Hphen^+$ exists throughout the course of the reactions then

$$(phen) = \frac{K_a(Hphen^+)}{(H^+)}$$

and

$$\frac{d(Fephen^{2+})}{dt} = \frac{k_{1f}K_a(Fe^{2+})(Hphen^+)}{(H^+)} - k_{1d}(Fephen^{2+})$$

At equilibrium $d(Fephen^{2+})/dt = 0$, and provided (Fe^{2+}) and (H^+) are much larger than $(phen)_T$, it follows that

$$k_{1f} = \frac{k_{1d}(H^+)(Fephen^{2+})_{eq}}{K_a(Fe^{2+})(Hphen^+)_{eq}}$$

$$\therefore \frac{d(Fephen^{2+})}{dt} = \frac{k_{1d}K_a(Fe^{2+})}{K_1(H^+)} \times \left[\frac{(Hphen^+)(Fephen^{2+})_{eq} - (Fephen^{2+})(Hphen^+)_{eq}}{(Fephen^{2+})_{eq}}\right]$$

Since $(phen)_T \simeq [(Fephen^{2+}) + (Hphen^+)]$, it can be shown that

$$\frac{d(Fephen^{2+})}{dt} = k_{1d}\left[1 + \frac{K_a(Fe^{2+})}{K_1(H^+)}\right][(Hphen^+) - (Hphen^+)_{eq}]$$

$$\therefore \frac{0.693}{t_{1/2}} = k_{1d}\left[1 + \frac{K_a(Fe^{2+})}{K_1(H^+)}\right] \qquad (1)$$

where $t_{1/2}$ is the half-time for the disappearance of $Hphen^+$. Equation 1 also applies to the dissociation of $Fephen^{2+}$ provided the half-time for the formation of $Hphen^+$ is substituted for $t_{1/2}$.

The assumption of rapid equilibrium between phenanthroline and $Hphen^+$ is supported by the results of the experiments in which phenanthroline solutions were mixed with 10^{-3} F perchloric acid solutions. These experiments established a lower limit of 10^6 M^{-1} sec.$^{-1}$ for the second order rate constant for the formation of Hphen$^+$ from H$^+$ and phenanthroline at 25.0°.

The half-times for the disappearance and formation of the 1,10-phenanthrolium ion in solutions of varying composition are presented in Tables I and II. Each of the half-times is the mean of at least six determinations; the individual determinations differed from the mean by $<10\%$. No correction was applied for the contribution of Fephen^{2+} to the absorbance at 310 mμ in calculating the half-times from the absorbances at this wave length. Such corrections are unnecessary under the conditions used in these studies since the Fephen^{2+} and Hphen$^+$ concentrations are much larger than the free phenanthroline concentrations of the solutions.

It is apparent from Tables I and II that the half-times are independent of the total phenanthroline concentration provided $(\text{Fe}^{2+})/(\text{phen})_T > 400$. This suggests that the bis- and tris-phenanthroline complexes do not interfere in the kinetic measurements provided $(\text{Fe}^{2+})/(\text{phen})_T > 400$. This is in agreement with the calculations based on the relative stabilities of the mono-, bis-, and tris-phenanthroline complexes.

TABLE I

RATE OF FORMATION OF Fephen^{2+} AT 25.0°

Ionic strength = 1.00

10^2(Fe^{2+}), *F*	10^5(phen)$_T$, *F*	(HClO$_4$), *F*	(NaClO$_4$), *F*	$t_{1/2}$, sec. obsd.	$t_{1/2}$, sec. calcd.
2.00	1.00	0.040	0.90	0.24	0.27
2.00	2.50	.040	.90	.25	.27
2.00	5.00	.040	.90	.25	.27
2.00	7.50	.040	.90	.25	.27
2.00	10.00	.040	.90	.25	.27
1.00	5.00	.10	.87	.49	.49
2.00	5.00	.10	.84	.41	.40
4.00	5.00	.10	.78	.28	.29
10.0	5.00	.10	.60	.15	.16
15.0	5.00	.10	.45	.11	.12
2.00	5.00	.005	.94	.07	.06
2.00	5.00	.020	.92	.19	.18
2.00	5.00	.070	.87	.36	.35
2.00	5.00	.100	.84	.41	.40
2.00	5.00	.200	.74	.47	.44

Figure 2 shows that $0.693/t_{1/2}$ is linearly related to the iron(II) ion concentration at constant (H$^+$), as required by eq. 1. However the intercepts of the plots depend on the hydrogen ion concentrations of the solutions. This suggests that the dissociation and formation reactions proceed *via* two paths, one acid-independent and the other acid-dependent. If a linear dependence on the hydrogen ion concentration is assumed eq. 1 may be written

$$\frac{0.693}{t_{1/2}} = [k_{1d}' + k_{1d}''(\text{H}^+)]\left[1 + \frac{K_a(\text{Fe}^{2+})}{K_1(\text{H}^+)}\right] \quad (2)$$

where k_{1d}' and k_{1d}'' represent the acid-independent and acid-dependent dissociation paths, respectively. Values of k_{1d}' and k_{1d}'' equal to 0.99 sec.$^{-1}$ and 1.13 F^{-1} sec.$^{-1}$, respectively, and $K_a/K_1 = 2.9$ were calculated from the intercepts and the slopes of the plots in Fig. 1. The value of K_a/K_1 is in satisfactory agreement with the value determined under different conditions by

TABLE II

RATE OF DISSOCIATION OF Fephen^{2+} AT 25.0°

10^2(Fe^{2+}), *F*	10^5(phen)$_T$, *F*	(HClO$_4$), *F*	(NaClO$_4$), *F*	Ionic strength	$t_{1/2}$, sec. obsd.	$t_{1/2}$, sec. calcd.
5.00	10.0	0.050	...	0.20	0.12	...
5.00	10.0	.100	...	.25	.16	...
5.00	10.0	.250	...	.40	.27	...
5.00	10.0	.500	...	.65	.31	...
5.00	10.0	1.00	...	1.15	.26	...
10.0	5.00	0.700	...	1.00	.28	0.28
10.0	7.00	.700	...	1.00	.28	.28
10.0	10.0	.700	...	1.00	.28	.28
10.0	25.0	.700	...	1.00	.26	.28
10.0	50.0	.700	...	1.00	.25	.28
1.00	5.00	.700	0.270	1.00	.37	.37
1.50	5.00	.700	.255	1.00	.36	.36
3.00	5.00	.700	.210	1.00	.34	.35
5.00	5.00	.700	.150	1.00	.33	.32
5.00	10.0	.050	.800	1.00	.16	.17
5.00	10.0	.100	.750	1.00	.25	.26
5.00	10.0	.250	.600	1.00	.34	.34
5.00	10.0	.500	.350	1.00	.32	.34
5.00	10.0	.850	...	1.00	.27	.30

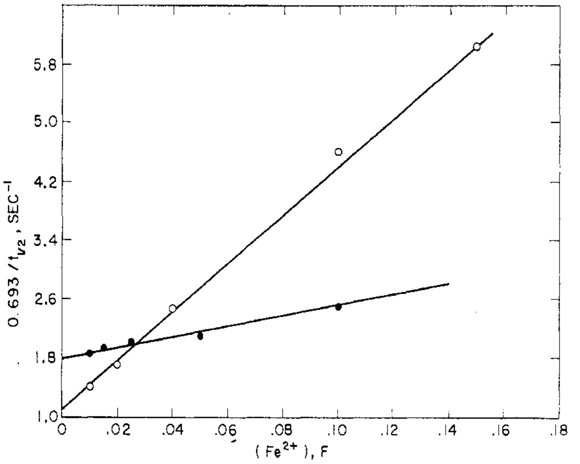

Fig. 2.—Plot of $0.693/t_{1/2}$ *vs.* iron(II) ion concentration at 25.0° and $\mu = 1.0$: ○, formation reaction, $(H^+) = 0.10$; ●, dissociation reaction, $(H^+) = 0.70$.

other workers.[3,5,17] The above values of k_{1d}', k_{1d}'', and K_a/K_1 were used to calculate the values of $t_{1/2}$ presented in Tables I and II. The agreement between the observed and calculated values of $t_{1/2}$ is satisfactory.

One mechanism consistent with the acid dependences of the rate constants involves the participation of intermediates in which the iron(II) is attached to only one nitrogen atom. Such intermediates have been invoked to explain the acid dependence of the dissociation of the mono-(1,10-phenanthroline)-nickel(II), tris-(1,10-phenanthroline)-iron(II), and tris-(2,2′-dipyridine)-iron(II) ions.[7,13,18]

Plots of log $(0.693/t_{1/2})$ against $1/T$ in the range 5–30° give values of E_a for the over-all dissociation process of 10.6 ± 0.6 kcal. mole^{-1} at $(Fe^{2+}) = 0.100\ F$ and $(HClO_4) = 0.70\ F$ and 11.6 ± 0.5 kcal. mole^{-1} at $(Fe^{2+}) = 0.050\ F$ and $(HClO_4) = 0.85\ F$. From eq. 2 it is apparent that E_a (over-all) is equal to the sum of E_a (dissociation) and $\Delta H\ [1 + K_a(Fe^{2+})/K_1(H^+)]$. Since the value of $K_a(Fe^{2+})/K_1(H^+)$ at $(Fe^{2+}) = 0.050\ F$ and $(H^+) = 0.85\ F$ is only 0.17 at 25.0°, $\Delta H[1 + K_a(Fe^{2+})/K_1(H^+)] \sim$ 1–2 kcal. at this $(Fe^{2+})/(H^+)$ ratio. If it is assumed that the difference in the above values of E_a (over-all) is due entirely to differences in $\Delta H[1 + K_a \cdot (Fe^{2+})/K_1(H^+)]$ arising from the different $(Fe^{2+})/(H^+)$ ratios used in the two measurements, a value for $\Delta H[1 + K_a(Fe^{2+})/K_1(H^+)]$ of -1.2 kcal. mole^{-1} at $(Fe^{2+}) = 0.050\ F$ and $(HClO_4) = 0.85\ F$ is obtained. These considerations lead to a value of $E_a = 12.8 \pm 1.2$ kcal. mole^{-1} for the dissociation in 0.85 F $HClO_4$.

TABLE III

KINETIC DATA FOR THE DISSOCIATION OF $M(phen)_3^{2+}$ AND $Mphen^{2+}$ COMPLEXES

Complex ion	ΔS^*, cal. deg.$^{-1}$ mole^{-1}	E_a, kcal. mole^{-1}	Ref.
$Fephen^{2+}$	-16^a	12.8^a	^{c}
$Fe(phen)_3^{2+}$	$+28^b$	32.1^b	4
$Cophen^{2+}$	+5	20.6	6
$Co(phen)_3^{2+}$	−4	19.4	6
$Niphen^{2+}$	+1	25.2	12
$Ni(phen)_3^{2+}$	+5	26.2	12

[a] In 0.85 F $HClO_4$. [b] In 1.0 F HCl. [c] This work.

Kinetic data for the dissociation of $M(phen)_3^{2+}$ and $Mphen^{2+}$ complexes where M = Fe(II), Co(II), and Ni(II) are presented in Table III. The entropies of activation, referred to a standard state of one mole per liter, were calculated from the equation[19]

$$k = \frac{eRT}{Nh} e^{-E_a/RT} e^{\Delta S^*/R}$$

It is apparent from Table III that the values of the energy and entropy of activation for the $Fe(phen)_3^{2+}$ dissociation are considerably more positive than the values for the $Co(phen)_3^{2+}$ and $Ni(phen)_3^{2+}$ dissociations. This has been interpreted in terms of crystal-field effects.[12,20,21] The $Fe(phen)_3^{2+}$ ion is diamagnetic while the $Fe(phen)_2^{2+}$ ion is paramagnetic.[22,23] The diamagnetism of $Fe(phen)_3^{2+}$ indicates that the complex possesses considerable crystal-field stabilization. The relatively high activation energy for the $Fe(phen)_3^{2+}$ dissociation can be ascribed to the loss of a large amount of this crystal-field stabilization energy in going from the diamagnetic $Fe(phen)_3^{2+}$ to the paramagnetic $Fe(phen)_2^{2+}$ ion.[12,20,21] In a similar manner, the high positive value of ΔS^* for the $Fe(phen)_3^{2+}$ dissociation can be attributed to the increase in the mobility of the ligands in forming the activated complex.[12,20] Similar spin changes do not occur in the $Co(phen)_3^{2+}$ and $Ni(phen)_3^{2+}$ dissociations.[12,23,24]

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The above interpretations are supported by the results of the present study. As is apparent from Table III, the energy of activation for the Fephen^{2+} dissociation is considerably lower and the entropy of activation considerably more negative than the corresponding values for the Fe(phen)$_3^{2+}$ dissociation. In contrast to the Fe(phen)$_3^{2+}$ dissociation, the dissociation of Fephen^{2+} is not accompanied by a change in the spin state of the iron(II).[23] In both the cobalt(II) and nickel(II) systems, on the other hand, the activation energies and entropies for the dissociation of the mono complexes are similar to those for the dissociation of the tris complexes. These dissociations are not accompanied by changes in the spin states of the central metal ions.[12, 23, 24]

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The Electronic Structures and Spectra of Chromyl and Molybdenyl Ions

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The reflectance spectra of $(NH_4)_2[CrOCl_5]$ and $(NH_4)_2[MoOCl_5]$ are measured and interpreted in terms of a molecular orbital energy level scheme. As in VO^{2+}, substantial π-bonding between metal and oxygen in the oxycations CrO^{3+} and MoO^{3+} is assumed. The charge transfer transitions involve the excitation of an electron from the metal–oxygen π-bonding orbital into orbitals located mainly on the metal atom. The solution spectrum of $(NH_4)_2[MoOCl_5]$ in 10 *M* HCl is examined, and a comparison is made between the calculated and observed band intensities.

Introduction

Metal ions at the beginning of the transition series have a remarkable capacity to form oxycations with the general formula MO^{n+}. The vanadyl ion, VO^{2+}, is one of the simplest and most stable ions of this type. An electrostatic model of the vanadyl ion consists of V^{4+}, with the electronic structure [argon]$3d^1$, and an oxide ion. However, the spectral and magnetic properties of the vanadyl ion are understood best in terms of the molecular orbital theory; in particular, the most significant feature of the electronic structure of VO^{2+} seems to be the existence of considerable oxygen to metal π-bonding.[3]

The chromyl and molybdenyl ions, CrO^{3+} and MoO^{3+}, are electronically equivalent to VO^{2+}, since they can be formulated as containing $Cr^{5+}(3d^1)$ and $Mo^{5+}(4d^1)$. These ions are rather rare, and the only well characterized complexes containing CrO^{3+} and MoO^{3+} are of the types $M_2[CrOCl_5]$, prepared by Weinland and Fiederer,[4] and $M_2[MoOCl_5]$, prepared by James and Wardlaw[5] (M can be NH_4^+, Na^+, K^+, Rb^+, or Cs^+). In the present paper the molecular orbital level scheme derived for the vanadyl ion[3] will be used to interpret the electronic spectra of $(NH_4)_2[CrOCl_5]$ and $(NH_4)_2[MoOCl_5]$. The structure of solutions of Mo(V) also will be discussed.

Molecular Orbitals for Chromyl and Molybdenyl Ions.—The $[MOCl_5]^{2-}$ (M = Cr(V), Mo(V)) ions are assumed to have a tetragonal structure, with a notably short M–O bond, analogous to the known structure of $VOSO_4 \cdot 5H_2O$[6] (see Fig. 1). Thus the molecular field is dominated by the axial MO^{3+} interaction.

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