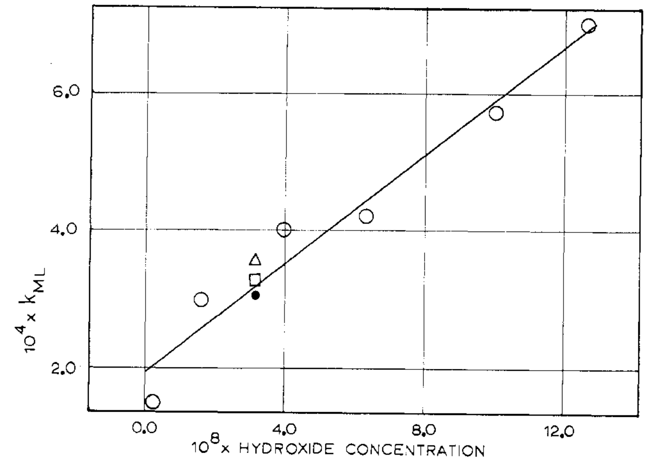

Figure 4.—Plot of pseudo-first-order rate constants with respect to the 1:1 nickel(II):ethyl glycinate complex as a function of hydroxide ion concentration (hydroxide calculated from pH and K_w for water). Initial concentrations of ester and nickel are, respectively: ○, 0.00796, 0.00901 *M;* △, 0.0384, 0.00870 *M;* ●, 0.0402, 0.00455 *M;* and □, 0.00796, 0.0901 *M.*

Table III

Specific Rate Constants for the Nickel(II)-, Cobalt(II)-, and Zinc(II)-Catalyzed Hydrolysis of Ethyl Glycinate at 30° (Ionic Strength = 1.0)

Metal	$10^{-4}k_{OH}$, M^{-1} sec^{-1}	10^6k_{HOH}, M^{-1} sec^{-1}
Ni(II)	0.398 ± 0.013	3.5 ± 1.6
Co(II)	0.99 ± 0.11	8.3 ± 1.4
Zn(II)	2.33 ± 0.18	7.07 ± 0.83

The results obtained here are in agreement with the mechanism of Conley and Martin in that the 1:1 metal:ester complex is the principal species undergoing hydrolysis. No complex of the type $[Me(OH)L]_x$ is required to explain the data. Following a suggestion from Martin, the copper(II) data obtained previously in this laboratory was reevaluated and found to be consistent with the mechanism of Conley and Martin. The data obtained under most conditions, especially at low pH, may be explained more readily with this mechanism.

The kinetic constants reported by Conley and Martin[2] ($k_{OH} = 7.64 \times 10^4\ M^{-1}$ sec^{-1} and $k_{HOH} = 0.77 \times 10^{-6}\ M^{-1}$ sec^{-1} using $K_1 = 7400$ for CuE) are of the same order of magnitude as those found for the ions examined in the present work. The rate constants for metal–ester complex attack by hydroxide are of the order Cu(II) ≫ Zn(II) > Co(II) > Ni(II), which is the same order as that found for the stability constants of the 1:1 metal:hydroxide complexes.[7] The order indicates that the same basic factors may be implicated in the determination of both orders. The rate constants for attack by water (Co(II) > Zn(II) > Ni(II) ≫ Cu(II)) vary inversely with the stabilities of the 1:1 metal:ester complexes as determined in the present work.[10]

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(10) Material supplementary to this article has been deposited as Document No. 9045 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540 A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Contribution from the Chemistry Department,
Brookhaven National Laboratory, Upton, New York 11973

Rate and Equilibrium Constants for the Formation of the Monooxalate Complex of Iron(III) (1)

By ELIZABETH G. MOORHEAD and NORMAN SUTIN

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The rate of formation of the monooxalate complex of iron(III) has been studied by the use of flow techniques. The first and second dissociation constants of oxalic acid determined by pH measurements are $8.4 \times 10^{-2}\ M$ and $2.79 \times 10^{-4}\ M$, respectively, at ionic strength 1.0 *M* and 25.0°; and $5.5 \times 10^{-2}\ M$ and $1.58 \times 10^{-4}\ M$, respectively, at ionic strength 3.0 *M* and 25.0°. From spectrophotometric measurements, the stability constant K_1 for the reaction $Fe^{3+} + Ox^{2-} \rightleftharpoons FeOx^+$ is $3.9 \times 10^7\ M^{-1}$ at ionic strength 1.0 *M* and 25.0°; and $5.5 \times 10^7\ M^{-1}$ at ionic strength 3.0 *M* and 25.0°. The results of the kinetic studies are interpreted in terms of the reactions $FeOH^{2+} + HOx^- \underset{k_{2d}}{\overset{k_{2f}}{\rightleftharpoons}} FeOx^+$ and $Fe^{3+} + HOx^- \underset{k_{3d}}{\overset{k_{3f}}{\rightleftharpoons}} FeOx^+ + H^+$. At 25.0° and ionic strength 1.0 *M*, $k_{2f} = 2.0 \times 10^4\ M^{-1}$ sec^{-1}, $k_{3f} = 8.6 \times 10^2\ M^{-1}$ sec^{-1}, $k_{2d} = 3.0 \times 10^{-3}$ sec^{-1}, and $k_{3d} = 7.8 \times 10^{-2}\ M^{-1}$ sec^{-1}. The results are discussed in terms of a model in which loss of the first water molecule coordinated to the iron(III) is the rate-determining step.

The kinetics of formation of complexes of iron(III) with monodentate ligands have been extensively studied.[2-4] These studies have shown that the rate of complex formation is primarily determined by the rate of loss of a water molecule coordinated to the iron(III).

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

(3) J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958).

(4) R. E. Connick and C. P. Coppel, *ibid.*, **81**, 6389 (1959).

The purpose of the present work was to study the kinetics of the formation of the iron(III) monooxalate complex and to compare the kinetic properties of bidentate oxalate with those of the monodentate ligands previously studied.

The evaluation of the kinetic data required a knowledge of the formation constant of $FeC_2O_4^+$ and of the dissociation constants of oxalic acid. Since the available data[5] did not include values of these constants at ionic strength 1.0 M and 25.0° (the experimental conditions used in this work), it was necessary to determine these values under our experimental conditions. While this study was in progress, the work of Bauer and Smith[6,7] on the iron(III) monooxalate complex was published. Their equilibrium and kinetic studies were made at ionic strength 0.5 M and 25.0° and, while their work had much the same aim as ours, their results were different, largely because they concluded that significant amounts of the protonated complex $FeC_2O_4H^{2+}$ were present under their experimental conditions. We therefore undertook additional studies of the formation constant of the monooxalate complex of iron(III) in the hope of resolving these differences.

Experimental Section

Materials.—A stock solution of iron(III) perchlorate in perchloric acid was prepared from iron(III) perchlorate which had been recrystallized from perchloric acid. The iron(III) perchlorate was obtained from the G. F. Smith Chemical Co. and the perchloric acid (70%) from the J. T. Baker Chemical Co. The concentration of iron in the stock solution was determined by reduction of the iron(III) with a Jones reductor and titration of the resulting iron(II) with standard cerium(IV) using ferroin as the indicator.

Sodium perchlorate stock solution was made from sodium carbonate and perchloric acid (both from the J. T. Baker Chemical Co.) as described previously.[2] The potassium oxalate stock solution was prepared from Fisher reagent potassium oxalate, and the sodium oxalate solution for the pH measurements was made up from Mallinckrodt primary standard sodium oxalate. The oxalate concentrations were determined by permanganate titrations.

The Dissociation Constants of Oxalic Acid.—The dissociation constants of oxalic acid were determined at 25.0° and ionic strengths 1.0 and 3.0 M by measuring the pH of oxalate solutions containing varying amounts of perchloric acid.[8] A Beckman Research pH meter with glass and calomel electrodes was used for the pH measurements. To avoid precipitation of potassium perchlorate at ionic strengths 1.0 and 3.0 M, supporting electrolytes of 1 M NaCl and saturated NaCl, respectively, were used in the calomel electrode. A calibration curve of perchloric acid added *vs.* measured (H^+) was constructed by measuring the pH of solutions containing known amounts of perchloric acid and sodium perchlorate. The solutions contained either 1×10^{-2} or 2×10^{-2} M total oxalate and from 8×10^{-3} to 1.1×10^{-1} M perchloric acid.

The Formation Constant of Iron(III) Monooxalate.—The formation constant of iron(III) monooxalate was determined at 25.0° and at ionic strengths 1.0 and 3.0 M by using a spectrophotometric method. The concentration of iron(III) in the solutions varied from 2×10^{-3} to 2×10^{-2} M and the perchloric acid concentration from 0.5 M to the maximum allowed by the ionic strength. The total oxalate concentration in the solutions was 5×10^{-4} M, and sodium perchlorate was used to maintain the desired ionic strength. The solutions were kept in dark flasks to avoid photodecomposition of the oxalate complex[9] and the measurements were made within 1 hr after the solutions were prepared. The oxalate concentration was kept low to avoid the formation of higher oxalate complexes and the acidity was high enough to suppress the hydrolysis of iron(III). The absorbance of each solution was measured at 310 mμ using a thermostated Beckman DU and 1-cm quartz cells. The spectrum of iron(III) monooxalate shows a peak in the region of 300 mμ;[10] oxalate absorbs very little at 310 mμ, and the absorbance due to the uncomplexed iron(III) was corrected for by using an iron(III) perchlorate blank. The amount of iron(III) complexed by oxalate was not negligible so the correction for uncomplexed iron(III) was made by a method of successive approximations.

Kinetic Measurements.—The kinetic studies were carried out at 25.0° and ionic strength 1.0 M, using the flow techniques and apparatus previously described.[11] The formation of the iron(III) monooxalate complex was observed through the change of absorbance at 300 mμ when solutions of iron(III) and potassium oxalate, each adjusted to the same acidity and ionic strength with perchloric acid and sodium perchlorate, were mixed. The concentration ranges used in the kinetic measurements were $[Fe(III)] = 5 \times 10^{-4}$ to 1×10^{-2} M, $(Ox)_T = 1 \times 10^{-5}$ to 1×10^{-4} M, and $(HClO_4) = 5 \times 10^{-2}$ to 1.0 M and were chosen to avoid problems due to higher oxalates and to iron hydrolysis and dimerization. The dissociation of the monooxalate complex was also studied, although not as extensively, by mixing a solution containing iron(III) and oxalate of a particular acid concentration with a solution of perchloric acid and of a different concentration but the same ionic strength. The iron(III) and oxalate were mixed just before use in order to avoid photodecomposition of the oxalate, and the disappearance of the monooxalate was then followed by observing the change in absorbance at 300 mμ. The concentration ranges covered in the dissociation runs were $[Fe(III)] = 2 \times 10^{-5}$ to 2.5×10^{-4} M, $(Ox)_T = 5 \times 10^{-5}$ M, and $(HClO_4) = 0.1$ to 0.75 M.

Results

The dissociation constants of oxalic acid

$$H_2Ox \rightleftharpoons H^+ + HOx^- \qquad K_{1a}$$

$$HOx^- \rightleftharpoons H^+ + Ox^{2-} \qquad K_{2a}$$

were calculated as follows. K_{2a} was calculated from the pH data using the equation[8]

$$K_{2a} = \frac{(H^+)[(Ox)_T - (H^+)_T + (H^+)]}{[(H^+)_T - (H^+)]} \tag{1}$$

where (H^+) is the measured concentration of free acid, $(H^+)_T$ is the total hydrogen ion concentration, and $(Ox)_T$ is the total oxalate concentration. In deriving eq 1, (H_2Ox) is assumed to be negligible and consequently only data obtained at low acid concentrations were used in the calculations. The first dissociation constant was calculated using the exact expression involving K_{2a}

$$K_{1a} = \frac{(H^+)^2[2(Ox)_T - (H^+)_T + (H^+)]}{K_{2a}[(H^+)_T - (H^+)] + (H^+)[(H^+)_T - (H^+) - (Ox)_T]} \tag{2}$$

The following values of the dissociation constants were obtained from the data presented in Table I: $K_{1a} = (8.4 \pm 0.2) \times 10^{-2}$ M and $K_{2a} = (2.79 \pm 0.01) \times 10^{-4}$ M at ionic strength 1.0 M and 25.0°; $K_{1a} =$

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(5) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(6) R. F. Bauer and W. M. Smith, *Can. J. Chem.*, **43**, 2755 (1965).

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(8) N. K. Dutt and B. Sur, *Z. Anorg. Allgem. Chem.*, **293**, 195 (1957).

(9) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953).

(10) A. K. Babko and L. I. Dubovenko, *J. Gen. Chem. USSR*, **26**, 757 (1956) [*Zh. Obshch. Khim.*, **26**, 660 (1956)].

(11) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

TABLE I

DISSOCIATION CONSTANTS OF OXALIC ACID AT 25.0°

$(H^+)_T \times 10^2$, M	$(Ox)_T \times 10^2$, M	pH_{measd}	$(H^+) \times 10^3$, M	$K_{1a} \times 10^2$, M	$K_{2a} \times 10^4$, M
Ionic Strength = 0.10 M					
9.252	1.000	1.180	76.5	5.1	...
9.252	1.000	1.182	76.4	5.0	...
8.224	1.000	1.238	66.6	4.7	...
7.196	1.000	1.300	57.2	4.7	...
Ionic Strength = 1.0 M					
10.12	2.000	0.972	71.9	8.4	...
9.108	2.000	1.024	62.5	8.2	...
8.096	2.000	1.088	53.3	8.5	...
0.8120	2.000	3.453	0.184	...	2.80
0.9129	2.000	3.368	0.224	...	2.79
1.014	2.000	3.284	0.272	...	2.79
Ionic Strength = 3.0 M					
10.12	1.000	1.076	8.54	6.1	...
11.13	1.000	1.028	9.48	5.1	...
10.12	1.100	1.085	8.37	5.7	...
11.13	1.100	1.036	9.31	5.0	...
0.8194	2.000	3.201	0.108	...	1.59
0.9211	2.000	3.116	0.131	...	1.58
1.022	2.000	3.031	0.159	...	1.57

(5.5 ± 0.4) × 10^{-2} M and K_{2a} = (1.58 ± 0.01) × 10^{-4} M at ionic strength 3.0 M and 25.0°. K_{1a} was also measured at ionic strength 0.1 M and the resulting value (4.8 ± 0.2) × 10^{-2} M at 25.0° is in good agreement with the value 4.3 × 10^{-2} M determined under the same experimental conditions by McAuley and Nancollas.[12] The errors given for the dissociation constants are the average deviations of the measurements. The dissociation constants for oxalic acid found here are consistent with those determined by Bauer and Smith[6] at ionic strength 0.5 M and 25.0° as well as with the results of Dutt and Sur[8] at ionic strength about 1.1 M and 32°.[13]

The following equilibria were considered in determining the formation constant of iron(III) monooxalate

$$Fe^{3+} + Ox^{2-} \rightleftharpoons FeOx^{+} \qquad K_1$$

$$Fe^{3+} + HOx^{-} \rightleftharpoons FeOxH^{2+} \qquad K_4$$

K_1 and K_4 denote bidentate attachment of oxalate and monodentate attachment of binoxalate, respectively. The absorbance A of an iron oxalate solution after corrections for the absorbance of uncomplexed iron(III) is, under our conditions,

$$A = \epsilon_1(FeOx^+) + \epsilon_4(FeOxH^{2+}) \tag{3}$$

where ϵ_1 and ϵ_4 are the molar absorptivities of $FeOx^+$ and $FeOxH^{2+}$, respectively, at the wavelength used. Since the total oxalate concentration is

$$(Ox)_T = (Ox^{2-}) + (HOx^-) + (H_2Ox) + (FeOx^+) + (FeOxH^{2+}) \tag{4}$$

we can substitute this and the various equilibrium expressions into eq 3 to give

$$\frac{A}{(Fe^{3+})} = (Ox^{2-})[\epsilon_1K_1 + \epsilon_4K_4(H^+)/K_{2a}] \tag{5}$$

and therefore

$$\frac{A}{(Fe^{3+})} = (Ox)_T \frac{[\epsilon_1K_1 + \epsilon_4(H^+)/K_{2a})]}{[1 + (H^+)/K_{2a} + (H^+)^2/(K_{1a}K_{2a})]} - A\frac{[K_1 + K_4(H^+)/K_{2a}]}{[1 + (H^+)/K_{2a} + (H^+)^2/(K_{1a}K_{2a})]} \tag{6}$$

Consequently, a plot of $A/(Fe^{3+})$ *vs.* A for constant $(Ox)_T$ and (H^+) should give a straight line with negative slope S defined by

$$S = \frac{[K_1 + K_4(H^+)/K_{2a}]}{[1 + (H^+)/K_{2a} + (H^+)^2/(K_{1a}K_{2a})]} \tag{7}$$

Rearranging eq 7 gives

$$\beta S = K_4 + \frac{K_1K_{2a}}{(H^+)} \tag{8}$$

where

$$\beta = 1 + \frac{(H^+)}{K_{1a}} + \frac{K_{2a}}{(H^+)} \tag{9}$$

Therefore, a straight line should result with slope K_1 and intercept K_4 when the values of βS obtained at different acidities are plotted *vs.* $K_{2a}/(H^+)$. This derivation follows that of Bauer and Smith,[6] and their method of presenting the data was used here so that their results could be more readily compared with ours.

In Figure 1, the results obtained at ionic strengths 1.0 and 3.0 M are shown along with those of Bauer and Smith at ionic strength 0.5 M. These authors reported a value of K_4 = 2.22 × 10^4 M^{-1}. From our data, where higher acidities were possible because the ionic strengths were larger, the intercept in Figure 1 is not significantly different from zero, and consequently we estimate that K_4 is very probably not larger than 2 × 10^3 M^{-1}.

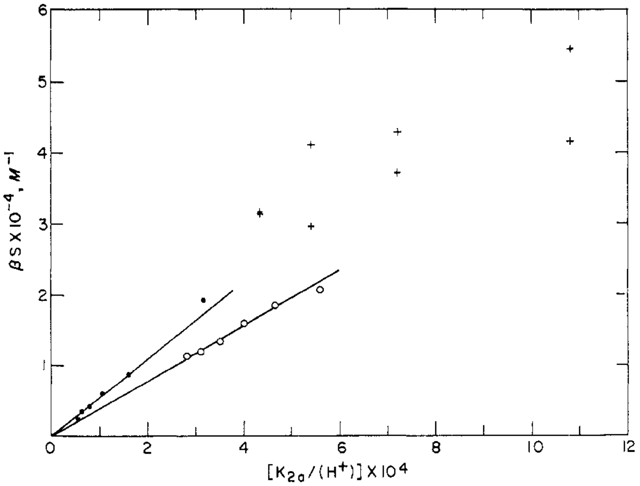

Figure 1.—Plot of βS *vs.* $K_{2a}/(H^+)$ at 25.0° for which a straight line should result with slope K_1 and intercept K_4. The crosses represent the data of Bauer and Smith[6] at ionic strength 0.5 M, the open circles and the solid circles are data obtained in this work at ionic strengths 1.0 and 3.0 M, respectively.

Values of K_1 determined by this method are K_1 = (3.9 ± 0.1) × 10^7 M^{-1} at ionic strength 1.0 M and K_1 = (5.5 ± 0.3) × 10^7 M^{-1} at ionic strength 3.0 M

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[12] A. McAuley and G. H. Nancollas, *Trans. Faraday Soc.*, **56**, 1165 (1960).

[13] K_{1a} can be estimated from the values of K_a for HOAc given by H. S. Harned and F. C. Hickey, *J. Am. Chem. Soc.*, **59**, 1284 (1937). This calculation, performed by C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1089 (1966), gives K_{1a} = 8.3 × 10^{-2} M at ionic strength 1.0 M and 25.0°, which is in very good agreement with our experimental value.

and 25.0°. The molar absorptivities of $FeOx^+$ at 310 mμ were found to be $(1.30 \pm 0.01) \times 10^3$ cm^{-1} M^{-1} and $(1.33 \pm 0.01) \times 10^3$ cm^{-1} M^{-1} at ionic strengths 1.0 and 3.0 M, respectively. The data leading to these results are presented in Table II. According to Bauer and Smith, $K_1 = 2.45 \times 10^7$ M^{-1}. However, a recalculation of K_1, using their data and assuming $K_4 = 0$, gives $K_1 = (6 \pm 1) \times 10^7$ M^{-1} at ionic strength 0.5 M and 25.0°.

TABLE II

FORMATION CONSTANT OF IRON(III) MONOOXALATE AT 25.0°; $(Ox)_T = 4.96 \times 10^{-4}$ M, $[Fe(III)] = 2 \times 10^{-3}$–$2 \times 10^{-2}$ M

(H^+), M	$S \times 10^{-2}$, M^{-1}	$K_1 \times 10^{-7}$, M^{-1}	(H^+), M	$S \times 10^{-2}$, M^{-1}	$K_1 \times 10^{-7}$, M^{-1}
Ionic Strength = 1.0 M			Ionic Strength = 3.0 M		
0.500	29.9	3.73	0.500	19.1	6.11
0.600	22.9	4.00	1.00	4.54	5.52
0.700	17.1	4.01	1.50	2.14	5.77
0.800	12.7	3.84	2.00	1.14	5.39
0.900	10.6	4.00	2.50	0.782	5.76
1.00	8.82	4.09	3.00	0.442	4.65

The kinetic results are consistent with the following reaction scheme

$$Fe^{3+} + Ox^{2-} \underset{k_{1d}}{\overset{k_{1f}}{\rightleftharpoons}} FeOx^+ \qquad K_1$$

$$FeOH^{2+} + HOx^- \underset{k_{2d}}{\overset{k_{2f}}{\rightleftharpoons}} FeOx^+ \qquad K_2$$

$$Fe^{3+} + HOx^- \underset{k_{3d}}{\overset{k_{3f}}{\rightleftharpoons}} FeOx^+ + H^+ \qquad K_3$$

where $K_1 = 3.9 \times 10^7$ M^{-1}, $K_2 = K_1K_{2a}/K_h = 6.7 \times 10^6$ M^{-1}, $K_3 = K_1K_{2a} = 1.1 \times 10^4$, and K_h, the equilibrium constant for the reaction

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_h$$

is equal to 1.65×10^{-3} M at ionic strength 1.0 M and 25.0°.[2] The rate of formation of $FeOx^+$ is given by

$$\begin{aligned}\frac{d(FeOx^+)}{dt} &= k_{1f}(Fe^{3+})(Ox^{2-}) - k_{1d}(FeOx^+) + k_{2f}(FeOH^{2+}) \times \\ &\quad (HOx^-) - k_{2d}(FeOx^+) + k_{3f}(Fe^{3+})(HOx^-) - \\ &\quad k_{3d}(FeOx^+)(H^+) \\ &= [k_{1f} + k_{2f}K_h/K_{2a} + k_{3f}(H^+)/K_{2a}](Fe^{3+})(Ox^{2-}) - \\ &\quad [k_{1d} + k_{2d} + k_{3d}(H^+)](FeOx^+) \qquad (10)\end{aligned}$$

The observed first-order rate constant derived from this expression (see Nancollas and Sutin[14]) is

$$k_{obsd} = \frac{0.693}{t_{1/2}} = [k_{1d} + k_{2d} + k_{3d}(H^+)]\left\{1 + \frac{K_1K_{2a}(Fe^{3+})}{\beta(H^+)}\right\} \qquad (11)$$

where $t_{1/2}$ is the half-time for the reaction and β is defined in eq 9. The assumptions made in deriving eq 11 are that the oxalic acid equilibria are much faster than the metal complex reactions, that $(Fe^{3+}) \gg (Ox)_T$, and that $(H^+)_T \cong (H^+)$.

In the experimental studies at ionic strength 1.0 M and 25.0°, oxalate, iron(III), and perchloric acid were varied in turn to confirm the rate law. The results are summarized in Table III. The rate constants $(k_{1d} + k_{2d})$ and k_{3d} were determined from the formation data by plotting βk_{obsd} *vs.* $1/(H^+)$ at $(Fe^{3+}) = 4.16 \times 10^{-3}$ M. For $K_1K_{2a}(Fe^{3+}) \gg \beta(H^+)$, this plot gives a straight line with slope equal to $(k_{1d} + k_{2d})K_1K_{2a}(Fe^{3+})$ and intercept $k_{3d}K_1K_{2a}(Fe^{3+})$. The rate constants determined from this plot are $(k_{1d} + k_{2d}) = (3.0 \pm 0.4) \times 10^{-3}$ sec^{-1} and $k_{3d} = (7.8 \pm 0.4) \times 10^{-2}$ M^{-1} sec^{-1}. The values of $(k_{1f} + k_{2f}K_h/K_{2a})$ and k_{3f}, calculated from $(k_{1f} + k_{2f}K_h/K_{2a}) = (k_{1d} + k_{2d})K_1$ and $k_{3f} = k_{3d}K_3$, are 1.2×10^5 M^{-1} sec^{-1} and 8.6×10^2 M^{-1} sec^{-1}, respectively.

TABLE III

OBSERVED RATE CONSTANTS FOR FORMATION AND DISSOCIATION OF IRON(III) MONOOXALATE AT IONIC STRENGTH 1.0 M AND 25.0°

Formation Reaction

Acid Dependence. $(Ox)_T = 4.96 \times 10^{-5}$ M

(H^+), M	$t_{1/2}$, sec	k_{obsd}, sec^{-1}	(H^+), M	$t_{1/2}$, sec	k_{obsd}, sec^{-1}
$[Fe(III)] = 4.16 \times 10^{-3}$ M					
0.0700	0.23	3.0	0.100	0.32	2.2
0.0800	0.26	2.7	0.125	0.36	1.9
0.0900	0.29	2.4			
$[Fe(III)] = 1.07 \times 10^{-3}$ M					
0.100	1.1	0.63	0.600	4.1	0.17
0.200	2.0	0.35	0.700	4.4	0.16
0.300	2.7	0.26	0.800	4.5	0.15
0.400	3.4	0.20	0.900	4.6	0.15
0.500	4.0	0.17	1.00	4.6	0.15

Iron(III) Dependence.
$(Ox)_T = 4.96 \times 10^{-5}$ M, $(H^+) = 0.500$ M

$[Fe(III)] \times 10^3$, M	$t_{1/2}$, sec	k_{obsd}, sec^{-1}	$[Fe(III)] \times 10^3$, M	$t_{1/2}$, sec	k_{obsd}, sec^{-1}
0.534	5.2	0.13	5.34	1.0	0.69
1.07	4.0	0.17	6.40	0.70	0.99
2.14	2.2	0.31	8.56	0.61	1.1
4.28	1.1	0.63	10.7	0.50	1.4

Oxalate Dependence. $[Fe(III)] = 1.07 \times 10^{-3}$ M,
$(H^+) = 0.500$ M

$(Ox)_T \times 10^5$, M	$t_{1/2}$, sec	k_{obsd}, sec^{-1}	$(Ox)_T \times 10^5$, M	$t_{1/2}$, sec	k_{obsd}, sec^{-1}
0.990	2.6	0.27	5.94	3.9	0.18
1.98	3.5	0.20	6.94	3.2	0.22
2.97	3.9	0.18	7.93	3.8	0.18
3.97	3.8	0.18	8.92	3.8	0.18
4.96	4.0	0.17	9.90	3.9	0.18

Dissociation Reaction

Acid Dependence. $(Ox)_T = 4.96 \times 10^{-5}$ M,
$[Fe(III)] = 5.34 \times 10^{-5}$ M

(H^+), M	$t_{1/2}$, sec	$k_{obsd} \times 10^2$, sec^{-1}	(H^+), M	$t_{1/2}$, sec	$k_{obsd} \times 10^2$, sec^{-1}
0.150	26	2.7	0.550	12	5.8
0.300	18	3.8	0.750	9.6	7.2
0.450	14	5.0			

Discussion

By analogy with other complex-formation reactions[15,16] the individual steps in the acid-independent paths may be represented as follows

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(14) G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964).

(15) R. G. Wilkins and M. Eigen in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

(16) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

$$\mathrm{Fe(H_2O)_6^{3+} + Ox^{2-} \rightleftharpoons (H_2O)_5Fe(H_2O)^{3+}\cdot Ox^{2-}} \qquad K_0$$

$$\mathrm{(H_2O)_5Fe(H_2O)^{3+}\cdot Ox^{2-}} \underset{k_{01}}{\overset{k_{10}}{\rightleftharpoons}} \mathrm{(H_2O)_5FeOx^+ + H_2O} \qquad K_{10}$$

$$\mathrm{(H_2O)_5FeOx^+} \underset{k_{02}}{\overset{k_{20}}{\rightleftharpoons}} \mathrm{(H_2O)_4FeOx^+ + H_2O} \qquad K_{20}$$

and

$$\mathrm{(H_2O)_5FeOH^{2+} + HOx^- \rightleftharpoons (H_2O)_4(OH)Fe(H_2O)^{2+}\cdot OxH^-} \qquad K_0'$$

$$\mathrm{(H_2O)_4(OH)Fe(H_2O)^{2+}\cdot OxH^-} \underset{k_{01}'}{\overset{k_{10}'}{\rightleftharpoons}} \mathrm{(H_2O)_5FeOx^+ + H_2O} \qquad K_{10}'$$

Similarly, the acid-dependent path to be considered is

$$\mathrm{Fe(H_2O)_6^{3+} + HOx^- \rightleftharpoons (H_2O)_5Fe(H_2O)^{3+}\cdot OxH^-} \qquad K_0''$$

$$\mathrm{(H_2O)_5Fe(H_2O)^{3+}\cdot OxH^-} \underset{k_{01}''}{\overset{k_{10}''}{\rightleftharpoons}} \mathrm{(H_2O)_5FeOxH^{2+} + H_2O} \qquad K_{10}''$$

$$\mathrm{(H_2O)_5FeOxH^{2+} \rightleftharpoons (H_2O)_5FeOx^+ + H^+} \qquad K_{\mathrm{H}}$$

The kinetic data do not exclude a dissociation mechanism involving attack of a hydrogen ion on a coordinated carboxylate group (that is, the hydrogen ion attacks the complex before one end of the oxalate has dissociated).

$$\mathrm{(H_2O)_5FeOxH^{2+} \rightleftharpoons (H_2O)_4FeOxH^{2+} + H_2O}$$

$$\mathrm{(H_2O)_4FeOxH^{2+} \rightleftharpoons (H_2O)_4FeOx^+ + H^+}$$

This mechanism is undoubtedly of importance in the dissociation of complexes such as $\mathrm{(NH_3)_5MOOCR}$ which contain monodentate carboxylate ligands.[17] However, it is unlikely that this type of mechanism competes successfully with the acid-dependent path for the bidentate ligands considered above and it will therefore not be considered further.

In terms of the above reactions, $k_{1\mathrm{f}} = k_{10}k_{20}K_0/\alpha$, $k_{2\mathrm{f}} = k_{10}'k_{20}K_0'/\alpha$, $k_{3\mathrm{f}} = k_{10}''k_{20}K_0''/\alpha$, $k_{1\mathrm{d}} = k_{01}k_{02}/\alpha$, $k_{2\mathrm{d}} = k_{01}'k_{02}/\alpha$, and $k_{3\mathrm{d}} = k_{01}''k_{02}/(K_{\mathrm{H}}\alpha)$, where $\alpha = [k_{01} + k_{01}' + k_{20} + k_{01}''(\mathrm{H}^+)/K_{\mathrm{H}}]$. In deriving the above expressions, it has been assumed that the concentrations of the intermediates $\mathrm{(H_2O)_5FeOxH^{2+}}$ and $\mathrm{(H_2O)_5FeOx^+}$ are in a steady state and that the dissociation rate constant of the acid intermediate is greater than k_{01}''.[18,19] Moreover, if $k_{20} \gg [k_{01} + k_{01}' + k_{01}''(\mathrm{H}^+)/K_{\mathrm{H}}]$; then $k_{1\mathrm{f}} = k_{10}K_0$, $k_{2\mathrm{f}} = k_{10}'K_0'$, $k_{3\mathrm{f}} = k_{10}''K_0''$, $k_{1\mathrm{d}} = k_{01}/K_{20}$, $k_{2\mathrm{d}} = k_{01}'/K_{20}$, and $k_{3\mathrm{d}} = k_{01}''/(K_{20}K_{\mathrm{H}})$. The acid dependence of the observed rate constant is consistent with this assumption. In order to evaluate the rate constants for the individual steps, it is necessary to estimate some of the appropriate equilibrium constants, and this will therefore be considered next.

The Acid Dissociation Constant of $\mathrm{(H_2O)_5FeOxH^{2+}}$.—It follows from the definitions of the equilibrium constants that

$$K_{\mathrm{H}} = \frac{K_0K_{10}'K_{2\mathrm{a}}}{K_0''K_{10}''} \tag{12}$$

The value of K_{H} is, of course, independent of the detailed mechanism of the reaction. It is readily seen that

$$K_{\mathrm{H}} = \frac{K_0K_{2\mathrm{a}}}{K_0''} \tag{13}$$

provided $K_{10} \approx K_{10}''$. This is likely to be the case since k_{10} and k_{10}'', the water exchange rates of the ion pairs, are probably very similar; and k_{01} and k_{01}'', the rate constants for the rupture of the iron–oxalate and iron–binoxalate bonds, respectively, are probably not too different. Approximate values of the equilibrium constants for the formation of the outer-sphere complexes may be estimated from a simple electrostatic model.[20] According to this model

$$K_0 = \frac{4\pi Na^3}{3000}\, e^{-U(a)/kT} \tag{14}$$

$$K_0/K_0'' = e^{-[U(a) - U''(a)]/kT} \tag{15}$$

where $U(a)$, the Debye–Hückel interaction potential, is given by

$$U(a) = \frac{z_1z_2e^2}{aD(1 + \kappa a)} \tag{16}$$

and a, the distance of closest approach of the ion partners, is assumed equal to 5 A. The other symbols have their usual significance. The values of K_0, K_0', and K_0'' calculated from eq 14 are 7.7 M^{-1}, 0.91 M^{-1}, and 1.6 M^{-1}, respectively. Substitution in eq 13 gives $K_{\mathrm{H}} = 1.5 \times 10^{-3}\ M$ at ionic strength 1.0 M and 25.0°. The value of K_4, the stability constant of $\mathrm{FeOxH^{2+}}$, is given by

$$K_4 = \frac{K_1K_{2\mathrm{a}}}{K_{20}K_{\mathrm{H}}} \tag{17}$$

We can therefore calculate K_4 provided K_{20} is known. K_{20} can be estimated by introducing the formation constant of iron(III) formate[21]

$$\mathrm{Fe^{3+} + HCOO^- \rightleftharpoons FeOOCH^{2+}} \qquad K_5$$

According to Perrin,[22] $K_5 = 1.3 \times 10^3\ M^{-1}$ at ionic strength 1.0 M and 20°. The formation of $\mathrm{(H_2O)_5FeOOCH^{2+}}$ very probably parallels the formation of $\mathrm{(H_2O)_5FeOxH^{2+}}$ and consequently K_5 may be set equal to $K_0''K_{10}''$. Since $K_3 = K_0''K_{10}''K_{\mathrm{H}}K_{20}$, $K_3/K_5 = K_{\mathrm{H}}K_{20}$. This approximation gives $K_{20} \approx 5.6 \times 10^3$ and therefore $K_4 \approx 1.3 \times 10^3\ M^{-1}$. This value of K_4 is consistent with the upper limit of $2 \times 10^3\ M^{-1}$ estimated from the equilibrium measurements.

The Rate Constants for the Individual Steps.—The values of the rate constants for the individual steps can now be calculated. The results are summarized in Table IV. The kinetic measurements give $(k_{1\mathrm{f}} + k_{2\mathrm{f}}K_{\mathrm{h}}/K_{2\mathrm{a}}) = 1.2 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$. By analogy with the reactions of $\mathrm{Fe(H_2O)_6^{3+}}$ and $\mathrm{Fe(H_2O)_5OH^{2+}}$ with

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[17] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

[18] F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).

[19] The above expressions for the rate constants are more general than those derived by Cavasino[18] for the reactions of nickel with malonate. His derivation treated the reactions with bimalonate and malonate separately and, consequently, the equations do not contain all the cross terms; *i.e.*, the final equations for $k_{1\mathrm{f}}$ and $k_{1\mathrm{d}}$ derived by Cavasino do not contain terms involving (H^+), and his equations for $k_{3\mathrm{f}}$ and $k_{3\mathrm{d}}$ do not contain k_{01} in the denominator. The rate constant $k_{2\mathrm{d}}$ is not present in his derivation as he considered only one acid-independent path.

[20] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[21] The equilibrium constants for the formation of iron(III) formate and iron(III) acetate[22] are very similar.

[22] D. D. Perrin, *J. Chem. Soc.*, 1710 (1959).

TABLE IV

SUMMARY OF THE EQUILIBRIUM CONSTANTS AND RATE CONSTANTS AT IONIC STRENGTH 1.0 M AND 25.0°[a]

K_{1a}	$8.4 \times 10^{-2}\ M$
K_{2a}	$2.79 \times 10^{-4}\ M$
K_1	$3.9 \times 10^{7}\ M^{-1}$
$K_2 = K_1K_{2a}/K_h$	$6.7 \times 10^{6}\ M^{-1}$
$K_3 = K_1K_{2a}$	1.1×10^{4}
$*K_0$	$7.7\ M^{-1}$
$*K_0'$	$0.91\ M^{-1}$
$*K_0''$	$1.6\ M^{-1}$
$*K_{10} = K_1/(K_0K_{20})$	9.0×10^{2}
$*K_{20} = K_3/(K_5K_H)$	5.6×10^{3}
$*K_{10}' = K_2/(K_0'K_{20})$	1.3×10^{3}
$*K_{10}'' = K_3/(K_0''K_HK_{20})$	8.2×10^{2}
$*K_H$	$1.5 \times 10^{-3}\ M$
k_{2f}	$2.0 \times 10^{4}\ M^{-1}\ \text{sec}^{-1}$
k_{3f}	$8.6 \times 10^{2}\ M^{-1}\ \text{sec}^{-1}$
k_{2d}	$3.0 \times 10^{-3}\ \text{sec}^{-1}$
k_{3d}	$7.8 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$
$*k_{10}' = k_{2f}/K_0'$	$2.2 \times 10^{4}\ \text{sec}^{-1}$
$*k_{01}' = k_{2d}K_{20}$	$1.7 \times 10^{1}\ \text{sec}^{-1}$
$*k_{10}'' = k_{3f}/K_0''$	$5.4 \times 10^{2}\ \text{sec}^{-1}$
$*k_{01}'' = k_{3d}K_{20}K_H$	$6.6 \times 10^{-1}\ \text{sec}^{-1}$

[a] The quantities indicated with asterisks were not determined directly, but were calculated using a theoretical expression for the ion-pair association constants.

monodentate ligands,[2] it is likely that $k_{2f} \gg k_{1f}$. Consequently, $k_{2f}K_h/K_{2a} \gg k_{1f}$, and therefore $k_{2f} = 2.0 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ at ionic strength 1.0 M and 25.0°. Similarly, $k_{2d} = 3.0 \times 10^{-3}\ \text{sec}^{-1}$ under the same conditions. The rate constants presented in Table IV were calculated from the values of k_{2f}, k_{3f}, k_{2d}, and k_{3d}, together with the appropriate equilibrium constants.

The values of the rate constants obtained in this work are consistent with the assumed mechanism. The rate constants for the reaction of $Fe(H_2O)_5OH^{2+}$ with a variety of monodentate ligands vary from 3×10^3 to $3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ at 25.0°.[2] The value of k_{2f} falls within this range, while the value of k_{3f} is not very different from the rate constant for the reaction of $Fe(H_2O)_6^{3+}$ with SCN^-. These studies thus provide further support for the view that a second water molecule coordinated to the iron(III) is lost much more rapidly than the first and that the loss of the first water molecule is the rate-determining step in the reaction of iron(III) with oxalate. This in turn suggests that monodentate attachment of oxalate labilizes the complex so that a second water molecule is lost more rapidly than the first. This effect has been noted in the case of some monodentate ligands where the monosubstituted complex frequently undergoes substitution much faster than does the unsubstituted complex.[3,16]

Values of K_H for $(H_2O)_5NiOxH^+$ and $(NH_3)_5CoOxH^{2+}$ can also be estimated from the above model. Thus, additional support for the mechanism is provided by the prediction that[18]

$$\frac{k_{1d}}{k_{3d}} = \frac{k_{01}K_H}{k_{01}''} \tag{18}$$

If it is assumed that $k_{01} \approx k_{01}''$, then k_{1d}/k_{3d} gives $K_H = 2.4 \times 10^{-3}\ M$ for $(H_2O)_5NiOxH^+$ at ionic strength 0.1 M and 25.0°. This estimate of K_H is in good agreement with the value of $1.0 \times 10^{-3}\ M$ calculated for ionic strength 0.1 M from eq 13. Ting, Kelm, and Harris[23] have recently determined K_H for $(NH_3)_5CoOxH^{2+}$ at zero ionic strength and 25° by conductivity methods. They found $K_H = 6.3 \times 10^{-3}\ M$, which is also in good agreement with the value of $3.7 \times 10^{-3}\ M$ calculated for zero ionic strength from eq 13.

A further check on the above mechanism is provided by comparing the rate constants for the formation and dissociation of the iron(III) monoformate complex with the estimates of k_{10}' and k_{01}' given in Table IV. Recent measurements indicate that, provided $k_{2f} \gg k_{1f}$, the rate constant k_{2f} for the formation of $(H_2O)_5FeOOCH^{2+}$ is approximately $2.5 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ and $k_{2d} = 1.0 \times 10^1\ \text{sec}^{-1}$ at ionic strength 1.0 M and 25.0°. These rate constants were calculated using $K_5 = 1.3 \times 10^3\ M^{-1}$ and $K_a = 3.2 \times 10^{-4}\ M$ at ionic strength 1.0 M and 20°.[22] For the reaction of HCOOH with $(H_2O)_5FeOH^{2+}$, we estimate that $k_{10}' = k_{2f}/K_0' = 7.9 \times 10^3\ \text{sec}^{-1}$ and $k_{01}' = k_{2d} = 1.0 \times 10^1\ \text{sec}^{-1}$. The agreement of k_{10}' and k_{01}' for the formate system with the corresponding quantities for the oxalate system is encouraging and provides additional evidence that the loss of the first water molecule coordinated to iron(III) is the rate-determining step in the formation of the iron(III) monooxalate complex.

Acknowledgment.—It is a pleasure to acknowledge helpful discussions with Dr. J. K. Rowley.

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[23] S. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966).