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Kinetic Study of the Hydroxoiron(III) Dimer

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Received January 13, 1970

The rate of acid decomposition of $Fe_2(OH)_2^{4+}$ is measured in $HClO_4$ (0.05–3.5 *M*) and equals $(k_1 + k_2[H^+])[Fe_2(OH)_2^{4+}]$ where k_1 is 0.4 (±0.2) sec^{-1} and k_2 is 3.1 (±0.1) M^{-1} sec^{-1} at 25.0° and 3 *M* (Na)ClO_4. The $\Delta H^{\ddagger}$ values are 16 and 6 kcal/mol and the $\Delta S^{\ddagger}$ values are −6 and −36 cal deg^{-1} mol^{-1} for k_1 and k_2, respectively. The HCl decomposition has two additional terms, $k_3[Cl^-]$ and $k_4[H^+][Cl^-]$, where k_3 is 16 (±2) M^{-1} sec^{-1} and k_4 is 199 (±17) M^{-2} sec^{-1}. Relaxation studies of the dimerization reaction (3 *M* $NaClO_4$) at low acidity and low Fe(III) concentrations agree with the two-term rate law observed in the perchloric acid decomposition. However, at high Fe(III) concentrations the relaxation data deviate from this behavior. At the same conditions there is spectral evidence for other hydrolytic species which could account for the deviations. Nevertheless, the kinetics of acid decomposition of these solutions are identical with the kinetics observed for the dimer.

Introduction

Di-μ-hydroxo-octaaquodiiron(III) (or more simply the hydroxoiron(III) dimer, $Fe_2(OH)_2^{4+}$) is well characterized in solution from thermodynamic,[2-4] spectral,[5,6] and magnetic[6,7] studies. Wendt[8] reported the kinetics of the hydroxoiron(III) monomer–dimer equilibrium using pressure-jump relaxation techniques. The rate constants he reported for the dimerization

$$2FeOH^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Fe_2(OH)_2^{4+} \qquad (1)$$

and dissociation reactions are 450 (±50) M^{-1} sec^{-1} and 1 (±0.5) sec^{-1}, respectively, at 25° (ionic strength 0.6). Recently he proposed[9] a water-loss mechanism for the acid-independent formation of $Fe_2(OH)_2^{4+}$.

Conocchioli, Hamilton, and Sutin[10] measured the acid decomposition of $Fe_2(OH)_2^{4+}$ from 0.15 to 1.5 *M* $HClO_4$ and found a two-term rate law

$$[Fe(H_2O)_4OH]_2^{4+} + 2H_3O^+ \longrightarrow 2Fe(H_2O)_6^{3+} \qquad (2)$$

$$\text{rate} = (k_1 + k_2[H^+])[Fe(H_2O)_4(OH)_2] \qquad (3)$$

with an acid-independent constant, k_1 (0.35 sec^{-1}), and an acid-dependent constant, k_2 (3.5 M^{-1} sec^{-1}), in 3 *M* $NaClO_4$ at 25°. In the present work an extended range of $HClO_4$ concentration (0.05–3.5 *M*) is used. There is no evidence of a limiting rate at high acidities such as that observed with $Ni_4(OH)_4^{4+}$.[11] Our rate constants at 25° agree with the earlier acid decomposition studies,[10] and we have measured the activation parameters for k_1 and k_2. The acid decomposition data indicate that an acid-dependent term also should be present under the conditions of the relaxation kinetic studies of Wendt. Attempts to resolve his data in this way do not give the correct ratios for the two reaction paths. Therefore, the relaxation experiments were repeated using concentration-jump relaxation techniques. At the same conditions the same relaxation times as those reported by Wendt are observed. However, lower Fe(III) concentrations give data consistent with the acid dissociation studies.

Experimental Section

Iron(III) perchlorate was prepared[6] by heating $Fe(NO_3)_3 \cdot 9H_2O$ with 60–70% $HClO_4$ and lavender crystals of $Fe(ClO_4)_3 \cdot nH_2O \cdot nHClO_4$ were recrystallized from $HClO_4$ solution. Solutions of $Fe(ClO_4)_3$ were freshly prepared before use by dissolving the salt in sufficient $NaClO_4$ to give an ionic strength of 3 *M*. The exact molarity of the iron was determined iodometrically.[12]

When fine pH adjustments were necessary, an NaCl–calomel reference electrode (in contact with the solution by means of a capillary) and a glass electrode were used. The pH readings were calibrated to give −log [H+] by using $HClO_4$ solutions in 3 *M* $NaClO_4$.

Kinetic data were obtained from a manual-push stopped-flow[13] and a Durrum–Gibson stopped-flow apparatus. The per cent transmittance changes during the reactions were stored on an oscilloscope and recorded on Polaroid film.

Spectral scan data were measured on a Cary 14 recording spectrophotometer. Both $Fe_2(OH)_2^{4+}$ and $FeCl^{2+}$ show maxima at 335 mμ with molar absorptivities of 3.4 (±0.7) × 10^3 and 1.7 × 10^3 M^{-1} cm^{-1},[10] respectively. In studies of the decomposition of $Fe_2(OH)_2^{4+}$ with HCl at 335 mμ the decrease in $Fe_2(OH)_2^{4+}$ absorbance is preceded by an increase in absorbance due to the reaction of monomeric iron to give $FeCl^{2+}$. Figure 1 gives the per cent transmittance–time scan observed on the oscilloscope under these conditions.

Relaxation studies were carried out using stopped-flow concentration-jump techniques. The perturbation from equilibrium was accomplished by dilution of the iron(III) solution with an equal volume of $NaClO_4$ solution or dilute $HClO_4$ solution.

Species distributions were calculated using the computer program outlined by Perrin and Sayce[14] and the equilibrium constants compiled[2-5,15] in Table I.

Results and Discussion

Perchloric Acid Decomposition Kinetics.—A plot of

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TABLE I
COMPILATION OF EQUILIBRIUM CONSTANTS AT 25° AND AT SEVERAL IONIC STRENGTHS

Constant	μ = 0.6 ref 5	μ = 1.0 ref 5	μ = 2.0 ref 15	μ = 3.0 ref 2
$K_{OH} = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]}$	1.7×10^{-3}	1.6×10^{-3}	...	9×10^{-4}
$\beta_{2,1} = \frac{[Fe(OH)_2^+][H^+]^2}{[Fe^{3+}]}$	...	...	...	4.7×10^{-7}
$\beta_{2,2} = \frac{[Fe_2(OH)_2^{4+}][H^+]^2}{[Fe^{3+}]^2}$	1.5×10^{-3} [a]	1.9×10^{-3}	...	1.2×10^{-3}
$K_D = \frac{[Fe_2(OH)_2^{4+}]}{[FeOH^{2+}]^2}$	500	700	...	1510[b]
$\beta_{4,3} = \frac{[Fe_3(OH)_4^{5+}][H^+]^4}{[Fe^{3+}]^3}$	...	...	...	1.7×10^{-6} [d]
$K_1^{Cl} = \frac{[FeCl^{2+}]}{[Fe^{3+}][Cl^-]}$	...	...	5.7[c]	...
$\beta_{2,1}^{Cl} = \frac{[FeCl_2^+]}{[Fe^{3+}][Cl^-]^2}$	...	...	11.4[c]	...
$\beta_{3,1}^{Cl} = \frac{[FeCl_3]}{[Fe^{3+}][Cl^-]^3}$	...	...	10.0[c]	...

[a] Calculated from K_{OH} and K_D determined at μ = 0.6. [b] Calculated from $\beta_{2,2}$ and K_{OH} determined at μ = 3.0. [c] 20°. [d] Reference 4.

TABLE II
OBSERVED RATE CONSTANTS FOR THE $HClO_4$ DECOMPOSITION OF $Fe_2(OH)_2^{4+}$ [λ 335 NM AND μ 3.0 M ($NaClO_4$)]

[$HClO_4$], M	Rate constants,[a] sec^{-1} 14.3 (±0.1)°	25.0 (±0.1)°	34.8 (±0.4)°
0.05	0.33 (±0.03)	0.54 (±0.04)	1.2 (±0.1)
0.15		0.96 (±0.04)	
		1.0 (±0.1)	
		1.1 (±0.1)	
0.25	0.72 (±0.04)	1.0 (±0.1)	1.7 (±0.1)
0.35		1.7 (±0.2)	
		1.7 (±0.1)	
0.45		1.8 (±0.1)	
0.50	1.3 (±0.1)	2.0 (±0.2)	3.9 (±0.1)
		2.1 (±0.1)	
		2.3 (±0.1)[b]	
1.0	2.7 (±0.1)	3.8 (±0.4)	6.2 (±0.5)
		4.1 (±0.1)	
		3.7 (±0.1)	
1.5		4.9 (±0.6)	
		5.3 (±0.1)	
2.0	4.9 (±0.2)	6.3 (±0.4)	12.9 (±0.5)
2.5		7.8 (±0.1)	
3.0	7.6 (±0.5)	8.6 (±0.1)	16.2 (±0.6)
		8.6 (±0.2)[b]	
3.5		12.4 (±0.4)	

[a] Standard deviations of a minimum of three kinetic runs are indicated. [b] Solutions for which there is spectral evidence of the presence of another species in addition to the dimer. Reactions followed at 360 and at 400 nm.

the observed rate constants (k_o at 25.0°, Table II) against $HClO_4$ concentration gives a linear plot in which the weighted least-squares intercept (k_1) and slope (k_2) have values of 0.4 (±0.2) sec^{-1} and 3.1 (±0.1) M^{-1} sec^{-1}, respectively. The resolved rate constants are in excellent agreement with those previously determined.[10] The mode of preparation of the iron-hydroxo dimer was tested by varying the initial concentrations of iron(III), the pH, and the age of the hydrolyzed solution. (Hydroxo polymers are known to form[16] in nitrate solutions at 0.3 M Fe(III).) The rate constants for the reaction with $HClO_4$ are independent of the methods of preparation tested. The initial conditions used in 3 M $NaClO_4$ were [Fe(III)] = 0.040 M, $-\log [H^+]$ = 1.6; [Fe(III)] = 0.038 M, $-\log [H^+]$ = 1.2; [Fe(III)] = 0.040 M, $-\log [H^+]$ = 1.7, aged 8 days; [Fe(III)] = 0.22 M, $-\log [H^+]$ = 1.8. The latter set of conditions gave spectrophotometric evidence that some hydrolytic species is present in addition to the dimer, but the kinetic behavior was the same as the other solutions.

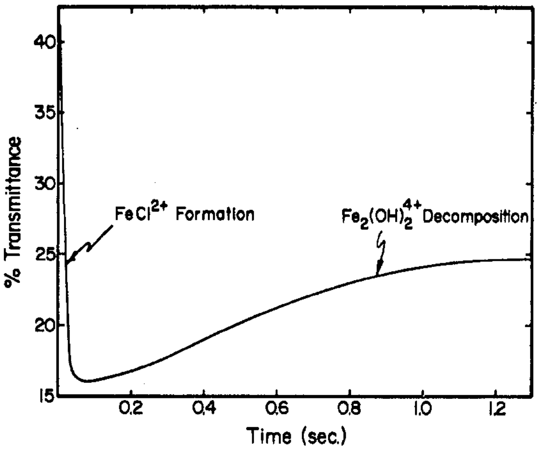

Figure 1.—Per cent transmittance–time plot for the $FeCl^{2+}$ formation (k_{Cl} = 47.4 sec^{-1}) and the $Fe_2(OH)_2^{4+}$ decomposition (k_o' = 2.0 sec^{-1}). Conditions: [Fe(III)] = 0.015 M, [H^+] = 0.1 M, [Cl^-] = 0.05 M; $-\log [H^+]$ = 1.65; λ 335 mμ; cell path 0.2 cm.

Reactions run in 0.5 M $NaClO_4$ at 25.0° gave the resolved rate constants: k_1 = 0.63 (±0.04) sec^{-1} and k_2 = 1.95 (±0.3) M^{-1} sec^{-1}.

The observed rate constants at 14.3 and 34.8° (Table II) show the same dependence with $HClO_4$ concentration as those at 25.0°. The resolved rate constants for the acid-independent and the acid-dependent paths and the activation parameters are given in Table III.

TABLE III
RESOLVED RATE CONSTANTS FOR THE ACID DECOMPOSITION OF $Fe_2(OH)_2^{4+}$ AT VARIOUS TEMPERATURES

Temp, °C	k_1, sec^{-1}	k_2, M^{-1} sec^{-1}
14.3 (±0.1)	0.1 (±0.1)	2.4 (±0.1)
25.0 (±0.1)	0.4 (±0.2)	3.1 (±0.1)
34.8 (±0.4)	1.0 (±0.5)	5.4 (±0.3)
Activation Parameters		
$\Delta H^{\ddagger}$, kcal mol^{-1}	16 (±2)	6 (±2)
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	−6 (±1)	−36 (±4)

Hydrochloric Acid Decomposition Kinetics.—The addition of HCl to solutions of Fe^{3+}, $FeOH^{2+}$, and $Fe_2(OH)_2^{4+}$ results in the formation of $FeCl^{2+}$ as well as the decomposition of $Fe_2(OH)_2^{4+}$. These reactions can be separated under certain conditions because the $FeCl^{2+}$ formation from the monomeric iron has a 1/[H^+] dependence[17] and the $Fe_2(OH)_2^{4+}$ decomposition is dependent upon [H^+]. The observed rate constants, k_o', for the HCl decomposition are compiled in Table IV. In order to resolve these data at least the four terms in eq 4 are needed, where k_1 and k_2 are the con-

$$k_o' = k_1 + k_2[H^+] + k_3[Cl^-] + k_4[H^+][Cl^-] \qquad (4)$$

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TABLE IV
OBSERVED RATE CONSTANTS, k_o' (SEC^{-1}), FOR THE HCl DECOMPOSITION OF $Fe_2(OH)_2^{4+}$ [a]

$[H^+]$, *M* (after mixing)	$[Cl^-]$, *M* (after mixing) 0.05	0.07	0.10	0.20
	Rate constants, sec^{-1}			
0.025	1.4 (±0.02)[b]	1.7 (±0.03)	2.4 (±0.01)	...
0.05	1.8 (±0.2)	1.9 (±0.03)	3.5[c]	5.6[c]
0.10	2.0 (±0.1)	2.7 (±0.1)	4.0 (±0.2)	7.0[c]
0.20	3.9 (±0.1)	4.9 (±0.1)	...	...

[a] 25.0°, $\mu = 3.0$ *M* ($NaClO_4$), $[Fe(III)]_{total} = 0.010$–$0.020$ *M*, after mixing, $-\log [H^+]_{initial} = 1.5$ (±0.1); λ 300–335 mμ region; cell path 0.2 cm. [b] Standard deviations of a minimum of three kinetic runs. [c] Two kinetic runs.

stants determined for the decomposition of $Fe_2(OH)_2^{4+}$ with H_3O^+ (*i.e.*, $HClO_4$ studies). Equation 4, then, can be written as

$$k_{cor} = k_3[Cl^-] + k_4[H^+][Cl^-]$$

where

$$k_{cor} = k_o' - (k_1 + k_2[H^+])$$

Figure 2 is a plot of k_{cor} against Cl^- concentration with the least-squares slopes and intercepts for each H^+ concentration. Within one standard deviation the intercepts are zero. The slopes ($k_3 + k_4[H^+]$) are plotted in Figure 3 and give a nonzero intercept, indicating the necessity of an acid-independent chloride term, $k_3 = 16$ (±2) M^{-1} sec^{-1}. The value of k_4 is 199 (±17) M^{-2} sec^{-1}.

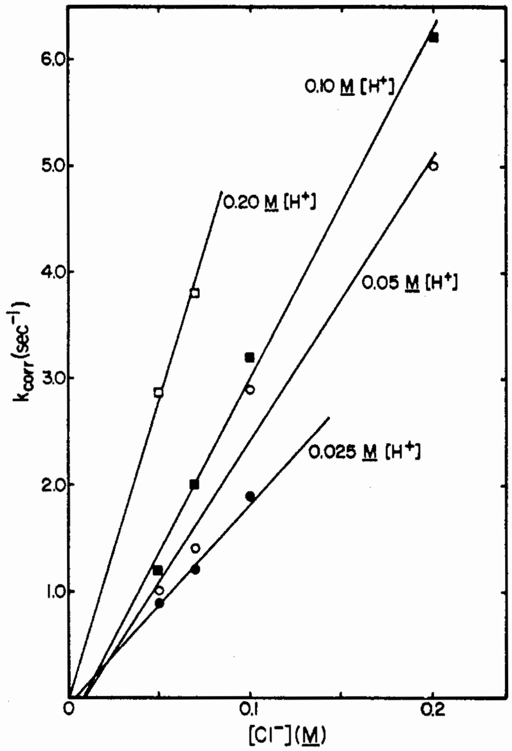


Figure 2.—Plots of k_{cor} against Cl^- concentration for various H^+ concentrations.

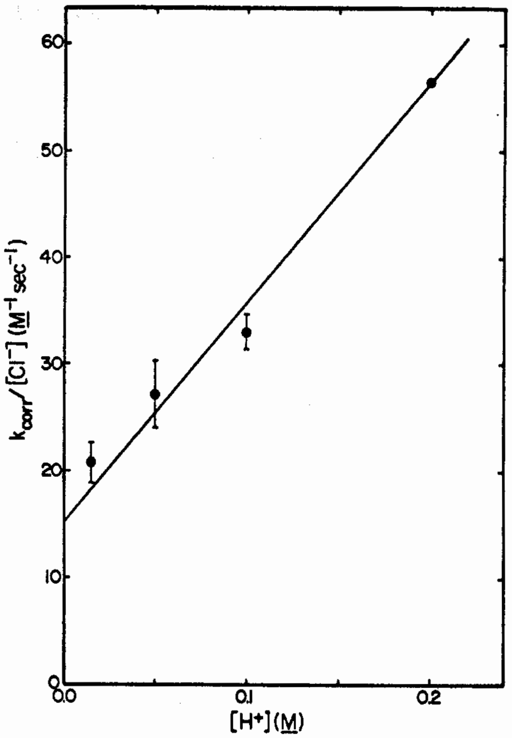
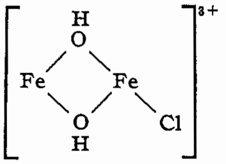
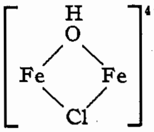


Figure 3.—Slopes of Figure 2 ($k_3 + k_4[H^+]$) plotted against hydrogen ion concentration.

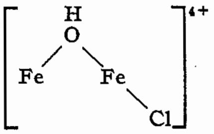
The addition of chloride to $Fe_2(OH)_2^{4+}$ is assumed to be fast, based on the fact that the addition of Cl^- to $FeOH^{2+}$ is known to be 1.1×10^4 M^{-1} sec^{-1}.[17] However, appreciable concentrations of an intermediate species of the type



could not be detected. Such a species is assumed to be a steady-state intermediate in which the coordinated chloride ion makes the hydroxide–iron bond rupture more facile. There is also no evidence for any significant amounts of intermediate species such as



or



At 0.1 *M* chloride the nonacid dissociation of the dimer is enhanced by approximately a factor of 4 and the acid attack by about a factor of 6.

When 0.5 *M* or greater concentrations of acid containing 0.05–0.2 *M* Cl^- are added to solutions of the dimer, the rates of $FeCl^{2+}$ formation and of $Fe_2(OH)_2^{4+}$ decomposition (which give opposite absorbance changes) overlap. The kinetics were not resolved but the observed absorbance–time curves were nearly the same as the sum of the calculated absorbance–time curves for the two reactions. When no $Fe_2(OH)_2^{4+}$ was present initially, the rate constants for the formation of $FeCl^{2+}$ from Fe^{3+} and from $FeOH^{2+}$ were 8.1 and 2.0×10^4 M^{-1} sec^{-1}, respectively. These constants are in agreement with those previously determined, 9.4 (±1.0) and 1.1×10^4 M^{-1} sec^{-1}, respectively.[17]

Relaxation Studies.—Under relaxation conditions

(5×10^{-3}–4×10^{-2} M H^+), the contribution of the acid-dependent term to the decomposition of $Fe_2(OH)_2^{4+}$ should be appreciable. By microscopic reversibility, the formation of $Fe_2(OH)_2^{4+}$ should also involve an acid-dependent path in addition to the acid-independent path previously postulated[8] and both must have the same relative contribution as in the dissociation reaction. If the $Fe_2(OH)_2^{4+}$ equilibrium is expressed in terms of $Fe_{monomer}$ (where $[Fe_{monomer}] = [Fe^{3+}{}_{free}] + [FeOH^{2+}]$), eq 5, then the relaxation expression in eq 6[18] holds for any given acidity.

$$2Fe_{monomer} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Fe_{dimer} \qquad (5)$$

$$\frac{1}{\tau} = 4k_f[Fe_{monomer}] + k_r \qquad (6)$$

The two reaction paths are

$$Fe_2(OH)_2^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2FeOH^{2+} \qquad (7)$$

$$Fe_2(OH)_2^{4+} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe^{3+} + FeOH^{2+} \qquad (8)$$

and assuming a rapid equilibrium between Fe^{3+} and $FeOH^{2+}$, then eq 9 results. The value for k_r at any

$$k_f = \left(\frac{K_{OH}}{(K_{OH} + [H^+])^2}\right)(k_{-1}K_{OH} + k_{-2}[H^+]) \qquad (9)$$

given acidity is known from the dissociation data and eq 9 can be substituted into eq 6 and rearranged to give eq 10. Wendt's data,[8] treated according to eq

$$\frac{\left(\frac{1}{\tau} - k_r\right)(K_{OH} + [H^+])^2}{[Fe_{monomer}](4K_{OH})} = k_{-1}K_{OH} + k_{-2}[H^+] \qquad (10)$$

10, give a slope $k_{-2} = 35\ (\pm 8)\ M^{-1}\ sec^{-1}$ and an intercept $k_{-1}K_{OH} = 2.3\ (\pm 0.1)\ sec^{-1}$. The ratio of $k_{-1}K_{OH}/k_{-2}$ is 0.06 instead of 0.11 (as calculated from k_1/k_2), indicating the relative contribution of the acid-dependent path is too high.

Our relaxation studies were carried out to determine the reason for this discrepancy in the ratios. The data obtained can be separated into two somewhat distinct groups, based on the amount of monomeric iron ($Fe_{monomer}$) in solution. When most of the iron (about 80% or higher) is in monomeric forms (Fe^{3+}, $FeOH^{2+}$), the $1/\tau$ values (Table V) are lower than Wendt's and a plot of these data (eq 10) gives a slope $k_{-2} = 6.6\ (\pm 5.3)\ M^{-1}\ sec^{-1}$ and an intercept $k_{-1} = 0.6\ (\pm 0.2)\ sec^{-1}$. Although the precision is poor, the mean values give a relative contribution of the two paths, $k_{-1}K_{OH}/k_{-2}$, of 0.09, which is close to the expected value of 0.11. However, when appreciable amounts of the iron (about 40%) are not monomeric, the $1/\tau$ values are about the same as those determined by Wendt. A plot of these data (the lower set in Table V) according to eq 10 yields a slope (k_{-2}) and an intercept ($k_{-1}K_{OH}$) equal to 41 (±17) M^{-1} sec^{-1} and 1.2 (±0.1) sec^{-1}, respectively. The ratio of $k_{-1}K_{OH}/k_{-2} = 0.03$, which indicates, as Wendt's data did, that the relative contribution of the acid-dependent rate constant is too large.

TABLE V

RELAXATION DATA AT 25.0° AND μ 3.0 M ($NaClO_4$)

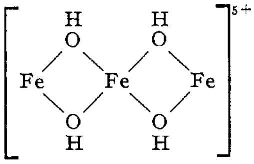
R^a	$[H^+]_{final}$, M	$1/\tau$, sec^{-1}	R^a	$[H^+]_{final}$, M	$1/\tau$, sec^{-1}
0.81	0.013	0.53 (±0.04)[b]	0.48	0.0055	1.5 (±0.1)
0.84	0.014	0.60 (±0.04)	0.40	0.0069	2.8 (±0.3)
0.89	0.015	0.66 (±0.05)	0.60	0.0076	1.4 (±0.1)
0.91	0.025	0.52 (±0.05)	0.64	0.0093	1.7 (±0.1)
0.99	0.028	0.56	0.72	0.010	0.95 (±0.02)
0.92	0.029	0.67 (±0.03)	0.60	0.011	1.2 (±0.1)
0.93	0.035	0.52 (±0.01)	0.53	0.014	2.8 (±0.3)
0.88	0.040	0.75 (±0.03)	0.54	0.015	1.5 (±0.1)
0.93	0.042	0.66 (±0.03)	0.75	0.024	1.4 (±0.1)
0.91	0.048	0.66 (±0.01)			

[a] $R = [Fe_{monomer}]/[Fe(III)]_{total}$. $[Fe_{monomer}] = [Fe^{3+}] + [FeOH^{2+}]$. The ratios are calculated from K_{OH}, $\beta_{2,2}$, and $\beta_{4,3}$.
[b] Standard deviations of a minimum of three values.

The acid-independent and acid-dependent rate constants can be calculated for the formation of $Fe_2(OH)_2^{4+}$, using the equilibrium constants for eq 7 and 8 and the decomposition rate constants previously determined. The calculated k_{-1} and k_{-2} values are 530 and 4.2 M^{-1} sec^{-1}, respectively, at 3 M $NaClO_4$. (Values were measured in 0.5 M $NaClO_4$ and gave $k_{-1} = 315\ M^{-1}\ sec^{-1}$ and $k_{-2} = 1.8\ M^{-1}\ sec^{-1}$.) When the amount of monomeric iron in the solution is ≥ 80%, the experimentally determined values of k_{-1} (670 M^{-1} sec^{-1}) and k_{-2} (6.6 M^{-1} sec^{-1}) from eq 10 are in fair agreement with these calculated values. However, Wendt's data[8] (when corrected), as well as ours for the condition where only a relatively small amount of monomeric iron is present, give substantially larger values of k_{-1} (approximately 1350 M^{-1} sec^{-1}) and k_{-2} (approximately 40 M^{-1} sec^{-1}) than expected. It should be pointed out that Wendt first reported a k_{-1} value of only 450 M^{-1} sec^{-1} in 0.6 M $NaClO_4$ but he was not aware of the acid path which was found later, and at his higher acidity the acid path cannot be neglected.[18a]

A trimer with the suggested formula $Fe_3(OH)_4^{5+}$ has been reported[4] to exist in solutions of high Fe_{total} and low acidity such as those used for the relaxation studies. However, the actual data for the calculation of $\beta_{4,3}$ have not been given. Our experimental data show that under conditions where the trimer is reportedly present, Beers' law plots (based on the dimer concentrations) are nonlinear and the $1/\tau$ values are quite large (those in the lower half of Table V). These $1/\tau$ values, then, are probably due to the contribution of another hydrolytic species (such as a trimer) to the relaxation.

A trimer having the structure



would be expected to have decomposition kinetics different from that of the dimer because the environ-

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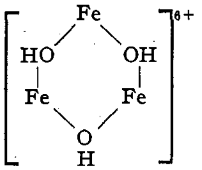
[18] M. Eigen and L. De Maeyer in "Technique of Organic Chemistry," Vol. III, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Wiley, New York, N. Y., 1963, part 2, p 903.

[18a] NOTE ADDED IN PROOF.—A recent paper by B. Lutz and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **74**, 372 (1970), reports an acid-dependent path in a stopped-flow study of the dissociation of the dimer. The data are in general agreement with the present work, but the initial discrepancies in the relaxation work are not considered.

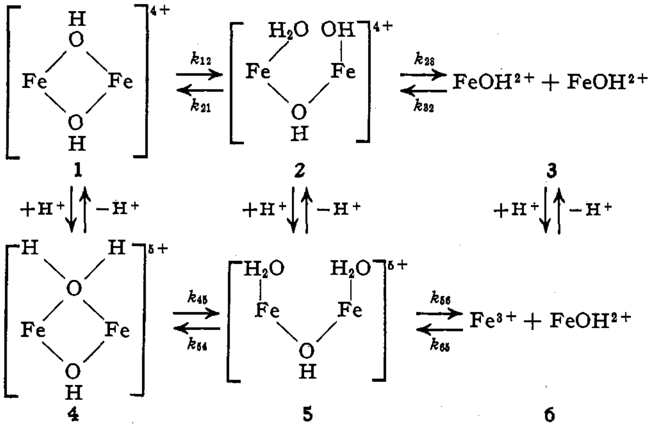
ment of the central Fe(III) is different from the terminal ones. However, the same rate constants as determined for the dimer decomposition in acid were observed (Table II) for solutions known to contain another hydrolytic species (presumably, the trimer). There was no evidence for an immediate decrease in absorbance on the addition of acid, ruling out a fast trimer to dimer conversion. The reaction mixtures gave excellent first-order plots for at least 4 half-lives. There was no evidence of a residual absorbance ruling out any polymeric species remaining after the $Fe_2(OH)_2^{4+}$ decomposition. No aging effects were observed. Evidence that the hydrolytic species present, in addition to the dimer, has a low molecular weight is given by the fact that ultracentrifugation of these solutions showed no schlieren pattern (20 min at 56,100 rpm).

There is the possibility that the trimer can be formulated as $Fe_3(OH)_3^{6+}$ where the structure would be



A cerium(IV) trimer, $Ce_3O_3(HOAc)^{6+}$, has been reported[19] and a cyclic structure has been proposed. The decomposition of such an iron(III) trimer could give the same rate constants as the dimer if the first iron–hydroxide bond cleavage were the rate-determining step. Whatever the form of the higher hydrolytic iron species, the relaxation data will be complex in its presence due to coupled relaxations.

Mechanism of Dimer Formation and Dissociation.—A combination of the reaction paths gives the following mechanism for the dimer formation and dissociation where species **2**, **4**, and **5** are reaction intermediates not



present in appreciable concentrations. The acid-dependent dissociation reaction could follow the **1–4–5–6** path with **4–5** as the rate-determining step or it could follow the **1–2–5–6** path with **5–6** as the rate-determining step. Similarly the nonacid dissociation could have either **1–2** or **2–3** as the rate-determining step. The choice is not clear-cut but the data appear to be more consistent if the rate-determining steps involve the breakage of the first Fe–OH–Fe bridge in the dimer, namely, the **1–2** step or the **4–5** step. Facts supporting this are that (a) the rate of acid decomposition remains first order in hydrogen ion at high acidities which suggests a direct H^+ attack on the dimer [path **1–4–5**] rather than H^+ addition after step **1–2**, (b) the presence of single-bridged species has not been detected, and (c) the sizable contribution of the acid-independent dissociation path at high acidities indicates that there are no free FeOH groups before the rate-determining step.

The acid decomposition of $(FeEDTA)_2O^{4-}$ has been studied[20] and there is no evidence for a single hydroxo-bridged intermediate, even though the acid-independent path is postulated to occur *via* a dihydroxo-bridged species. Mechanisms for the acid decomposition of hydrolytic dimers in which the second M–OH–M bond-breaking is slower than the first postulate appreciable concentrations of single-bridged intermediates.[21–24]

If steps **4–5** and **1–2** are rate determining, then it follows that in the formation reaction it is the ring closure which controls the rate; that is, it is the loss of H_2O from intermediate species **2** or **5** rather than the loss of H_2O from $FeOH^{2+}$ which governs the rate. The water substitution of $FeOH^{2+}$ is 3×10^4 sec^{-1} [25] which is sufficiently large to keep steps **3–2** and **6–5** from limiting the rate at this high ionic strength. It also means that $k_{23} > k_{21}$ and that $k_{56} > k_{54}$, or the loss of FeOH in intermediates **2** and **5** is faster than their loss of H_2O, which seems reasonable.

The difference between the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the acid-independent and acid-dependent dissociation rate constants are -10 kcal/mol and -30 cal deg^{-1} mol^{-1}, respectively. These are comparable to the values[8] of ΔH and ΔS determined for the addition of a proton to $FeOH^{2+}$, -11 (± 1.8) kcal/mol and -22 (± 6) cal deg^{-1} mol, respectively. This suggests that the proton transfer is essentially complete before the rate-determining step and is consistent with the intermediate species **4** in the mechanisms.

The $Fe_2(OH)_2^{4+}$ species appears to be subject to direct proton attack, whereas the $Ni_4(OH)_4^{4+}$ species must be distorted before it can be protonated.[11] HCl enhances the decomposition rate of $Fe_2(OH)_2^{4+}$ by a factor of about 3; however, HCl has no effect on the $Ni_4(OH)_4^{4+}$ acid decomposition rate. Both decomposition reactions are similar in that the rate-determining step occurs after the addition of only one proton.

Acknowledgment.—This investigation was supported by National Science Foundation Grant GP6725X.

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