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New Reaction Path in the Dissociation of the $Fe_2(\mu\text{-}OH)_2(H_2O)_8^{4+}$ Complex

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Introduction

Iron(III) has a strong tendency to hydrolyze in aqueous solution. Under mildly acidic conditions the hydrolysis is slow, and the time required to reach true equilibrium can be as long as several years.[1] Sluggish formation of colloidal oligonuclear hydroxo species may lead to fallacious interpretation of the equilibrium and kinetic properties of this system. In more acidic solutions the hydrolysis is faster and the speciation is far more simple. Equilibrium studies related to the hydrolysis of iron(III) have been reviewed several times since the early 1970s.[2−4] It was confirmed that under pH 3.0 the dominant species are $Fe(H_2O)_6^{3+}$, $Fe(OH)(H_2O)_5^{2+}$, $Fe(OH)_2(H_2O)_4^{+}$, and a dimeric form of the monohydroxo complex. There is some discrepancy regarding the exact composition of the dimer hydroxo species, which may exist either as an oxo-bridged, $Fe_2(\mu\text{-}O)(H_2O)_{10}^{4+}$, or as a dihydroxo-bridged, $Fe_2(\mu\text{-}OH)_2(H_2O)_{10}^{4+}$, complex.[5] Overwhelming indirect evidence from previous studies strongly supports the dihydroxo form.[6−14] (For simplicity, the coordinated water molecules in the complexes are not shown in the rest of the paper.)

The kinetics of the dimerization of $FeOH^{2+}$ has been extensively studied by several sets of authors.[9−13] The results obtained from the pH < 2.0 region were always interpreted by considering a spontaneous and an acid-catalyzed path for the formation and dissociation of the dimer hydroxo species. Our recent studies on the iron(III)−sulfite ion system have indicated that an additional path may be required for proper interpretation of the data under less acidic conditions.[14] Now we report new kinetic data from an extended pH region and propose an improved kinetic model for the dissociation of the $Fe_2(OH)_2^{4+}$ complex.

Experimental Section

Reagents. Iron(III) perchlorate (Aldrich, low chloride) of reagent grade quality was used without further purification. The iron(III) and free acid concentrations of the stock solutions were determined as described earlier.[15,16] No aging effects were observed in the iron(III) solutions during the entire study, i.e., the same results were obtained with freshly prepared and several month old stock solutions. The polymerization of iron(III) hydroxo complexes and the formation of polynuclear species could not be observed. Experiments were carried out at 25.0 ± 0.1 °C and 1.0 M ionic strength adjusted with $NaClO_4$. Sodium perchlorate stock solutions were prepared from perchloric acid (Carlo Erba) and Na_2CO_3 (Reanal, Hungary).[17] All solutions were made with doubly deionized and ultrafiltered water obtained from a MILLI-Q RG (Millipore) water purification system.

Instrumentation and Computation. In the equilibrium studies the spectra were recorded on a HP-8543 diode array spectrophotometer using a 2 mm cell. Data were evaluated with the software PSEQUAD.[18]

In the kinetic runs pH (= −log [H$^+$]) never exceeded 3.0. The speciation in the samples was calculated from the total concentrations of the components by using the appropriate stability constants. Kinetic measurements were made under pseudo-first-order conditions with an Applied Photophysics DX-17 MV sequential stopped-flow apparatus at the 340 nm absorbance maximum of the $Fe_2(\mu\text{-}OH)_2^{4+}$ complex. Control experiments at 430 nm were fully consistent with the results obtained at 340 nm.

The kinetic traces were evaluated by using the software package provided with the stopped-flow instrument. Each experimental rate constant, k_{obs}, was obtained as the average of at least five values determined from replicate kinetic runs and was reproducible within 5%. The kinetic data were fitted with the software package SCIENTIST.[19]

Results and Discussion

Equilibria. In dilute, moderately acidic solutions of iron(III) the relevant hydrolytic reactions are as follows:

$$Fe^{3+} \rightleftharpoons FeOH^{2+} + H^+ \qquad \beta_{11} = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]} \tag{1}$$

$$Fe^{3+} \rightleftharpoons Fe(OH)_2^{\ +} + 2H^+ \qquad \beta_{12} = \frac{[Fe(OH)_2^{\ +}][H^+]^2}{[Fe^{3+}]} \tag{2}$$

$$2Fe^{3+} \rightleftharpoons Fe_2(OH)_2^{\ 4+} + 2H^+ \qquad \beta_{22} = \frac{[Fe_2(OH)_2^{\ 4+}][H^+]^2}{[Fe^{3+}]^2} \tag{3}$$

The existence of a trimer with the formula $Fe_3(OH)_4^{5+}$ has also been suggested.[20] However, this species is formed only at very high total iron(III) concentrations and could be neglected throughout this study.

The stability constants β_{11} and β_{22} were determined spectrophotometrically in this work. The agreement of the data with previous spectrophotometric results[21,22] is excellent (Table 1). The value of β_{11} also agrees well with the stability constants obtained by pH-potentiometric methods.[20,23] However, there is a significant difference between the spectrophotometric and pH-metric values for β_{22}. A possible reason for this is that the formation of the dimer complex is associated with a small pH

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(1) Feitknecht, W.; Michaelis, W. *Helv. Chim. Acta* **1962**, *45*, 212.
(2) Sylva, R. N. *Rev. Pure Appl. Chem.* **1972**, *22*, 115.
(3) Flynn, C. M. *Chem. Rev.* **1984**, *84*, 31.
(4) Cornell, R. M.; Giovanoli, R.; Schneider, W. *J. Chem. Technol. Biotechnol.* **1989**, *46*, 115.
(5) Richens, D. T. In *The Chemistry of Aqua Ions*; John Wiley & Sons: Chichester, England, 1997; p 372.
(6) Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1991**, *30*, 2190.
(7) Chatlas, J.; Jordan, R. B. *Inorg. Chem.* **1994**, *33*, 3817.
(8) Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1995**, *34*, 6015.
(9) Sommer, B. A.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 2517.
(10) Wendt, H. *Z. Elektrochem.* **1962**, *66*, 235.
(11) Conocchioli, T. J.; Hamilton, E. J., Jr.; Sutin, N. *J. Am. Chem. Soc.* **1965**, *87*, 926.
(12) Po, H. N.; Sutin, N. *Inorg. Chem.* **1970**, *10*, 428.
(13) Lutz, B.; Wendt, H. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 372.
(14) Lente, G.; Fábián, I. *Inorg. Chem.* **1998**, *37*, 4204.
(15) Fábián, I.; Gordon, G. *Inorg. Chem.* **1991**, *30*, 3994.
(16) Fábián, I.; Gordon, G. *Inorg. Chem.* **1991**, *30*, 3785.
(17) Gordon, G.; Tewari, P. *J. Phys. Chem.* **1966**, *70*, 200.
(18) Zékány, L.; Nagypál, I. In *Computational Methods for the Determination of Formation Constants*; Legett, D. J., Ed.; Plenum Press: New York, 1985; p 291.
(19) SCIENTIST 2.0: Micromath Software, 1995.
(20) Khoe, G. H.; Brown, P. L.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1986**, 1901.
(21) Milburn, R. M.; Vosbourgh, W. C. *J. Am. Chem. Soc.* **1955**, *77*, 1352.
(22) Milburn, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 537.
(23) Hedström, B. O. A. *Ark. Kemi* **1953**, *6*, 1.

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Table 1. Formation Constants for the Hydroxo Complexes of Iron(III) in Aqueous Solution at 25.0 °C

$-\log \beta_{11}$	$-\log \beta_{12}$	$-\log \beta_{22}$	μ (M)[a]	method[b]	ref
2.72 ± 0.04		2.86 ± 0.03	1.0	sp	*c*
2.73	6.29	3.20	1.0	pH	20
2.78		2.72	1.0	sp	22
2.80		2.72	1.0	sp	21
2.77		2.82	0.6	sp	21
3.05	6.33	2.92	3.0	pH	23

[a] Ionic strength was set with $NaClO_4$. [b] sp, spectrophotometry; pH, pH-potentiometry. [c] This work.

effect, and the potentiometric method is bound to be less accurate for the determination of the corresponding stability constant. Under the conditions applied in our measurements, $Fe(OH)_2^+$ formed at very low concentration levels and for β_{12} we used the value reported by Khoe et al.[20]

Kinetics. When iron(III) solutions were diluted in the stopped-flow experiments, single first-order kinetic traces were observed over a wide range of [Fe(III)] and pH. For the interpretation of the results two opposite effects need to be considered. When the sample is diluted with sodium perchlorate solution, the concentration of iron(III) drops to the half of its original value and simultaneously the pH increases by an 0.3 unit. The concentration change favors the dissociation of $Fe_2(OH)_2^{4+}$ while the pH change alone would lead to the formation of more dimer. When the experiments are made with perchloric acid, both the concentration and pH jumps favor the dissociation of the dimer. Thus, the absorbance may either decrease or increase depending on how reaction 3 is shifted.

Very similar results were reported for this system by Sommer and Margerum. They proposed the following two-step mechanism for the dissociation of the dimer:[9]

$$Fe_2(OH)_2^{4+} \rightleftharpoons 2FeOH^{2+} \tag{4}$$

$$v_1 = k_1[Fe_2(OH)_2^{4+}] - k_{-1}[FeOH^{2+}]^2$$

$$Fe_2(OH)_2^{4+} + H^+ \rightleftharpoons FeOH^{2+} + Fe^{3+} \tag{5}$$

$$v_2 = k_2[Fe_2(OH)_2^{4+}][H^+] - k_{-2}[FeOH^{2+}][Fe^{3+}]$$

Since reactions 1 and 2 can be treated as fast pre-equilibria[24] and the monomeric iron(III) species are always in large excess over the dimer, this scheme predicts pseudo-first-order kinetic behavior. The corresponding rate constant is given as

$$k_{obs} = k_1 + k_2[H^+] + \frac{4[Fe_{mon}]\beta_{11}}{(\beta_{11} + [H^+])^2}(k_{-1}\beta_{11} + k_{-2}[H^+]) \tag{6}$$

where

$$[Fe_{mon}] = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^{+}]$$

Below pH 2.0, eq 6 predicted the experimental results reasonably well, and the model was also supported by others.[10−13]

In acidic solutions our measurements were consistent with eq 6 as k_{obs} was independent of the total iron(III) concentration and was a linear function of $[H^+]$. Significant deviations from the model were observed above pH 2.0. Under such conditions the third term of eq 6 becomes significant, and at constant pH k_{obs} is expected to be a linear function of $[Fe_{mon}]$ (Figure 1). According to eq 6, the intercepts should decrease linearly with decreasing $[H^+]$, int $= k_1 + k_2[H^+]$. In fact, the opposite trend was observed in the 1.97−2.83 pH region, as the intercepts increased by about a factor of 4.

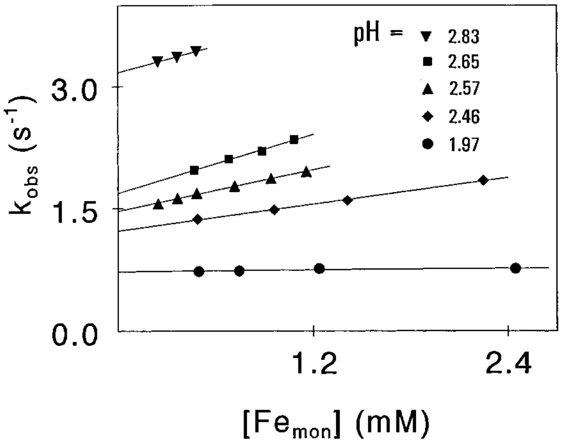

Figure 1. Experimental rate constants as a function of monomeric iron(III) concentration: $T = 25.0$ °C; $\mu = 1.0$ M ($NaClO_4$).

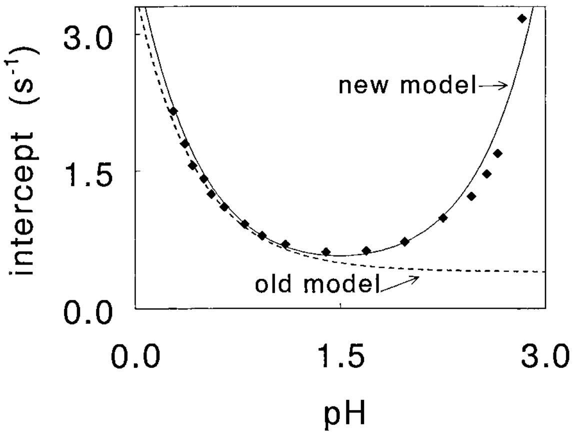

Figure 2. Plots of the intercepts for k_{obs} vs $[Fe_{mon}]$ (eq 9) as a function of pH: $T = 25.0$ °C; $\mu = 1.0$ M ($NaClO_4$).

The results clearly indicate that an additional pathway needs to be operative at higher pH. The extension of the model with the following reaction sequence may account for the observed effect:

$$Fe_2(OH)_2^{4+} \rightleftharpoons H^+ + Fe_2(OH)_3^{3+} \tag{7}$$

$$Fe_2(OH)_3^{3+} \rightleftharpoons FeOH^{2+} + Fe(OH)_2^{+} \tag{8}$$

$$v_3 = k_3[Fe_2(OH)_2^{4+}]\frac{1}{[H^+]} - k_{-3}[FeOH^{2+}][Fe(OH)_2^{+}]$$

Provided that the deprotonation step is fast, and $Fe_2(OH)_3^{3+}$ is present at a low concentration level, the following equation applies for k_{obs}:

$$k_{obs} = k_1 + k_2[H^+] + \frac{k_3}{[H^+]} + \frac{4[Fe_{mon}]\beta_{11}}{(\beta_{11} + [H^+] + \beta_{12}/[H^+])^2}\left(k_{-1}\beta_{11} + k_{-2}[H^+] + \frac{k_{-3}\beta_{12}}{[H^+]}\right) \tag{9}$$

This equation implies that the concentrations of the monomeric iron(III) complexes and the pH do not change significantly during the measurements. This was confirmed by calculating and comparing the initial and final speciations for each kinetic

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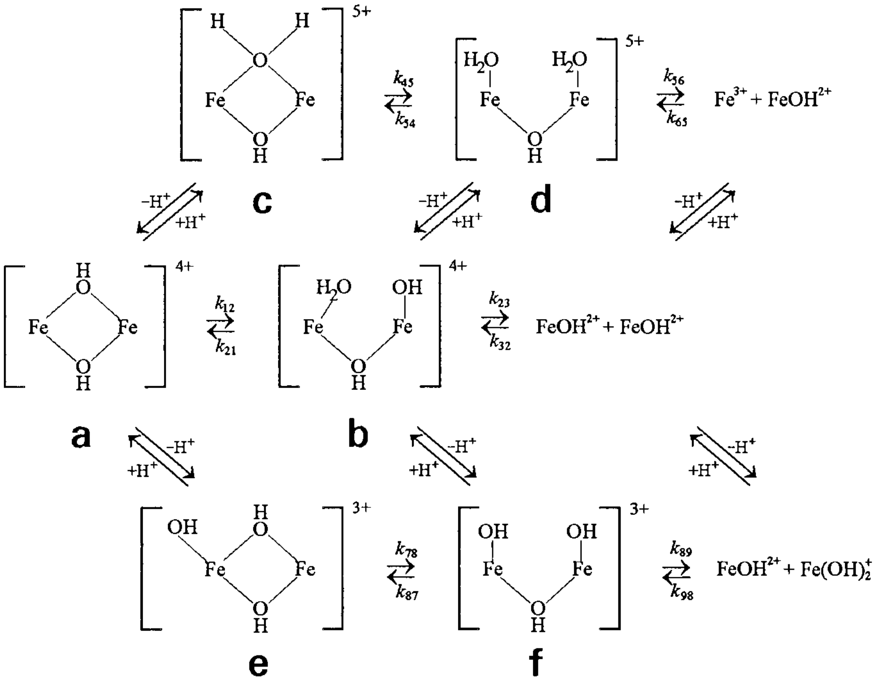
(24) Hemmes, P.; Rich, L. D.; Cole, D. L.; Eyring, E. M. *J. Phys. Chem.* **1971**, *75*, 929.

Table 2. Rate Constants for the Dissociation of $Fe_2(\mu\text{-}OH)_2(H_2O)_8^{4+}$ in Aqueous Solution at 25.0 °C

k_1 (s^{-1})	k_2 ($M^{-1}\ s^{-1}$)	k_3 ($M\ s^{-1}$)	k_{-1} ($M^{-1}\ s^{-1}$)	k_{-2} ($M^{-1}\ s^{-1}$)	k_{-3} ($M^{-1}\ s^{-1}$)	μ^a (M)	ref
0.35 ± 0.02	3.5 ± 0.1	$(3.6 \pm 0.2) \times 10^{-3}$	$1.3 \times 10^{2\ b}$	2.5^b	$(6.7 \pm 1.8) \times 10^3$	1.0	*c*
0.4	3.1		6.7×10^2	6.6		3.0	9
0.63	1.95					0.5	9
0.4	3.1					3.0	13
0.8	1.0					0.5	13
0.42	3.33					3.0	12
0.35	3.5					3.0	11
1.0			450			0.5	10
1.0			1.4×10^3	35		0.5	*d*

[a] Ionic strength was set with $NaClO_4$. [b] $k_{-1} = k_1\beta_{22}/(\beta_{11})^2$ and $k_{-2} = \beta_2\beta_{22}/\beta_{11}$. [c] This work. [d] Data from ref 10 reinterpreted in ref 9.

Scheme 1



run. As expected, the only significant change occurred in the concentration of the dimeric species. The rate constants were calculated on the basis of eq 9. Since the contribution of the k_{-1} and k_{-2} terms to k_{obs} was marginal, in the final calculations these rate constants were replaced by $k_1\beta_{22}/(\beta_{11})^2$ and $k_2\beta_{22}/\beta_{11}$, respectively. The results and the relevant literature data are listed in Table 2. The intercepts of the k_{obs} vs $[Fe_{mon}]$ plots are shown as a function of pH in Figure 2. This figure clearly demonstrates the improvement of the model by the inclusion of the third reaction path.

The results obtained here may also explain some of the unclear points in earlier studies. Sommer and Margerum[9] noticed that their kinetic data were not fully consistent with the equilibrium constants. Apparently, their estimated values for k_{-1} and k_{-2} are rather uncertain. This is not surprising, because at low pH the back reactions are negligible. When the pH is increased, reactions 7 and 8 become significant, and the variation of k_{obs} is mainly due to the hydrolytic path. Consequently, very limited information is available for k_{-1} and k_{-2} from the pH dependence of k_{obs}, and they cannot be fitted with any acceptable precision. Since in earlier studies the effect of the third path was assigned to the first two back reactions, k_{-1} and k_{-2} were overestimated.

The validity of the results presented here can be tested by comparing the $\beta_{22}/(\beta_{11}\beta_{12})$ term calculated from the stability constants and from the kinetic results as k_{-3}/k_3. The excellent agreement of the corresponding values, 1.4×10^6 M^2 and 1.8×10^6 M^2, confirms that the three pathways are sufficient for the interpretation of the dissociation kinetics of $Fe_2(OH)_2^{4+}$. On the basis of the new results, the mechanism postulated earlier can be extended as shown in Scheme 1. Formally, various sets of rate-determining steps are consistent with the experimentally confirmed rate law. However, it is very likely that whenever one of the two hydroxide ion bridges is broken in the dimer, the two iron(III) moieties dissociate very quickly. Protonation and hydrolysis can break the symmetry of the dimeric structure and accelerate the dissociation of $Fe_2(OH)_2^{4+}$. The exact structure of the $Fe_2(OH)_3^{3+}$ complex proposed here is not known. However, the formation of a third hydroxo bridge would probably stabilize the dimer structure. Thus, we assume that the third hydroxide ion is coordinated to one iron center only. These considerations imply that the rate-determining steps are **a** $\rightleftharpoons$ **b**, **c** $\rightleftharpoons$ **d**, and **e** $\rightleftharpoons$ **f**.

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Supporting Information Available: Table of observed rate constants with standard devations as a function of total iron(III) and H^+ concentrations, plot of observed rate constants as a function of $[H^+]$, and time-dependent spectra during a particular kinetic run (3 pages). Ordering information is given on any current masthead page.

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