at pH ~2, persisted through pH ~6, at which point it dissolved. However, the pH of the system kept drifting, presumably because of a slow hydrolytic reaction of the thorium(IV) chelate, and no equilibrium calculations could be carried out.

Aminophosphonic acids are becoming increasingly important for biological systems as well as in the design of new synthetic ligands as sequestering agents for metal ions.[13] This note provides new evidence for the effectiveness of aminophosphonate donor groups in the binding of metal ions, and provides more precise data for the phosphonate analogue of EDTA.

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Kinetics and Mechanism of μ-Oxo Dimer Formation by Ethylenediaminetetraacetatoiron(III), [FeEDTA]⁻

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The reactions of the FeEDTA system have attracted considerable attention for their importance in inorganic chemistry,[2-4] in biochemistry,[4-6] as catalysts,[7-9] and in industrial chemistry.[10] Martell and Gustafson[2] carried out early investigations of the thermodynamics of the interaction of Fe^{3+} and $EDTA^{4-}$ and identified several major species, including [FeEDTA]⁻, its hydrolyzed form $[FeEDTAOH]^{2-}$, and a hydrolyzed dimer, and defined the equilibria between these species. The later investigations of Schugar and Gray,[3a,4] Walling,[9] and others coupled with the crystallographic determination of the structure of the analogous FeHEDTA dimer[11] showed the binuclear species to be an oxo bridged complex $[(FeL)_2O]^{(2n-4)-}$ (H_nL = EDTA, HEDTA (N-hydroxyethylethylenediaminetriacetic acid, NTA (nitrilotriacetic acid), . . .), characterized by strong exchange interaction of the iron centers through the nearly linear oxo bridge. (Such linearity is consistent with maximum spin pairing.[12])

This extensive delocalization through an oxo bridge is reflected in the strongly reduced magnetic susceptibility of the dimer (and its antiferromagnetic behavior), as well as in the spectral properties of the dimer, which exhibits a characteristic Fe–O–Fe stretch at approximately 840 cm⁻¹, and a series of uv–visible bands of enhanced intensity,[4] with molar absorptivities (for $[(FeEDTA)_2O]^{4-}$ ϵ_{475} = 180 M⁻¹ cm⁻¹) two orders of magnitude larger than the corresponding mononuclear complexes, resulting in the dark red-orange color of solutions in which dimer is present. Gray has reviewed the spectral and magnetic properties of oxo bridged iron complexes, with special emphasis on the biochemical significance of such complexation.[4]

Thus, the identity of the major species in solution and the thermodynamics governing their interconversions have been established. The pathway for this interconversion, however, has remained unclear. In the present work, we have determined the kinetics of dimer formation and decomposition, and thereby established the probable pathway for the dimerization reaction.

Materials and Methods

Ferric solutions were prepared by dissolving reagent grade $Fe(NO_3)_3$ in acidic distilled water, and standardized by EDTA titration. All spectra were obtained on a Cary 14 spectrophotometer using matched 1.00 cm cells. For the determination of the dimerization constant under present experimental conditions, absorbance at 475 nm was monitored as a function of pH and metal ion concentration. With the value of ϵ_{dimer} = 180 M⁻¹ cm⁻¹ and the application of the appropriate hydrolysis and formation constants,[2] together with the appropriate mass balance equations, a value of K_{dimer} was obtained. It should be noted that this value is quite sensitive to the extinction coefficient, so that the errors inherent in the method are rather high. The method of limiting spectra cannot be used, since dimer never reaches >70% of the possible total.

Kinetic runs were monitored on a Durrum Gibson D150 stopped flow spectrophotometer by following dimer concentration at 475 nm. For the dimerization reaction, a low pH solution of [FeEDTA]⁻ was mixed with a high pH buffer solution (ammonia and borate were both used with essentially identical results). Dimerization data were analyzed by calculating the concentration of dimer at time t, using ϵ_{dimer} = 180 M⁻¹ cm⁻¹, and the known path length of the flow cell. Concentration of the mononuclear species was then obtained from the mass balance equations. Analogously, in the monomerization reaction, a high pH solution of FeEDTA, in which dimer formation was maximal, was reacted with a low pH buffer solution (potassium acid phthalate or phosphate, pH 5.5–7.0).

Results and Discussion

Spectra of the $Fe^{III}EDTA$ system as a function of pH are given in Figure 1. The band at 475 nm, which is characteristic of dimer formation,[4] increases with increasing pH, as required by eq 1. As the pK for hydrolysis of the [FeEDTA]⁻ species

$$2[FeEDTA]^- \rightleftharpoons [(FeEDTA)_2O]^{4-} + 2H^+ \qquad (1)$$
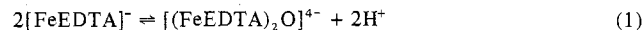
to $[FeEDTAOH]^{2-}$ is approximately 7.4, above pH 9.4 essentially all monomeric FeEDTA will be converted to the hydrolyzed forms. The dimerization reaction of [FeEDTAOH]²⁻ is pH independent as shown in eq 3 and dependent only on concentration.

$$[FeEDTA]^- \xrightarrow{K_{OH}} [FeEDTAOH]^{2-} + [H^+] \qquad (2)$$

$$2[FeEDTAOH]^{2-} \xrightarrow{K_d} [(FeEDTA)_2O]^{4-} \qquad (3)$$
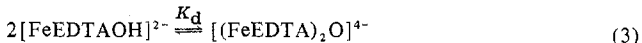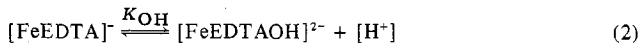
The study of the 475-nm peak as a measure of dimer formation yields a dimerization constant which depends only on temperature and ionic strength. At 25.0 °C and μ = 1.00 M, log K_d = 2.8 ± 0.2[2] and at $\mu \cong$ 0.50 M (the ionic strength de-
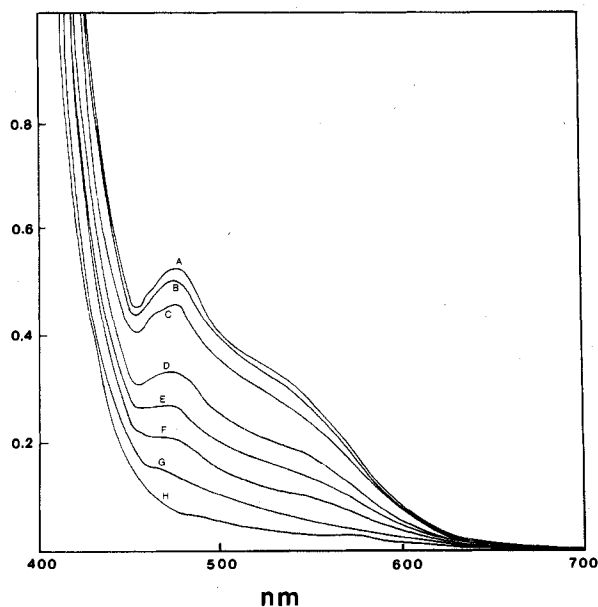
Figure 1. Spectra of FeEDTA as a function of [H$^+$]. [Fe] = [EDTA] = 8 × 10^{-3} M; μ = 1.0 M (KNO$_3$); T = 25 °C; pH (A) 9.51, (B) 8.41, (C) 7.87, (D) 7.34, (E) 7.16, (F) 6.97, (G) 6.76, (H) 6.46.
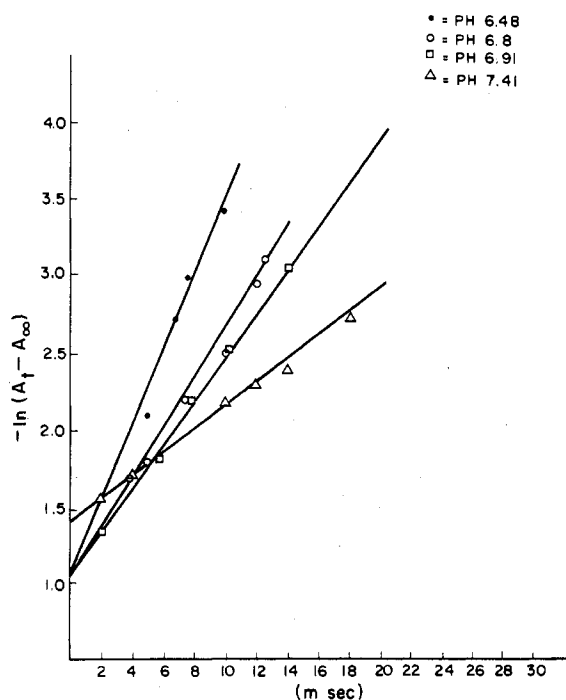

Figure 2. Pseudo-first-order plot of the observed kinetics for the monomerization reaction, T = 25.0 ± 0.1 °C, $\mu \cong$ 0.5 M.

Figure 3. Pseudo-second-order plot of the observed kinetics for the dimerization reaction, T = 25.0 ± 0.10 °C, $\mu \cong$ 0.5 M.

termined by the ammonia buffer system used in this study), log K_d = 2.5 ± 0.2.

While the stoichiometry and thermodynamics of the reaction were thus established, the mechanism for the conversion of monomer to dimer remained unclear. This has now been established by the study of the kinetics of the monomerization and dimerization reactions as a function of pH and concentration. Using buffers to hold the pH constant (and thus reduce the kinetics to first order), the results obtained for the monomerization and dimerization reactions are given in Figures 2 and 3.

It can been seen that the monomerization reaction follows good pseudo-first-order kinetics in [(FeEDTA)$_2$O]$^{4-}$ and is first order in [H$^+$], thus second order overall. This dependence
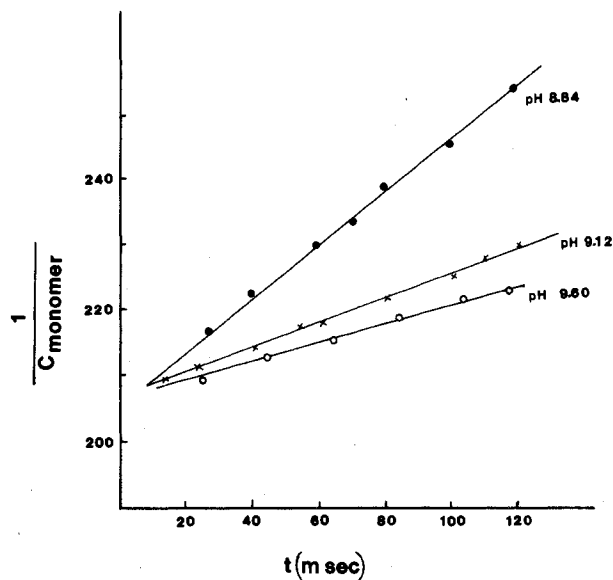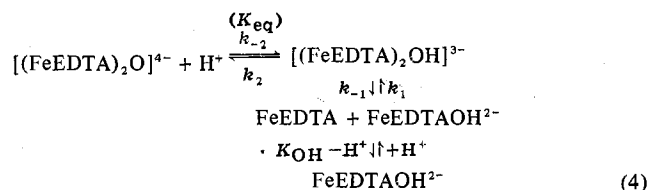
suggests the possibility of a preequilibrium involving a hydroxo bridged intermediate in the dimerization pathway, as shown in eq 4. This is certainly a realistic and chemically probable

$$[(FeEDTA)_2O]^{4-} + H^+ \underset{k_2}{\overset{(K_{eq})}{\underset{\rule{0pt}{1.5ex}}{\rightleftharpoons}}} [(FeEDTA)_2OH]^{3-}$$
$$k_{-1} \updownarrow k_1$$
$$FeEDTA + FeEDTAOH^{2-}$$
$$\cdot K_{OH} \underset{-H^+ \updownarrow +H^+}{}$$
$$FeEDTAOH^{2-} \tag{4}$$

intermediate, as hydroxo bridged complexes are well known, both for Co^{3+} and Fe^{3+}.

Such a preequilibrium would account for the observed rate dependences of both the monomerization and dimerization reactions. For the monomerization reaction, the observed second-order rate would be described by

$$-d(\text{dimer})/dt = K_{eq}k_{-1}[(FeEDTA)_2O^{4-}] = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

For the dimerization reaction, the above scheme predicts a decrease in rate with increasing pH, since the amount of active FeEDTA is decreased by the hydrolytic equilibrium (K_{OH}), in accord with experimental observation. Assuming a steady state in [(FeEDTA)$_2$OH]$^{3-}$, and $k_2 \gg k_{-1}$, the formation rate is:

$$\frac{d(\text{dimer})}{dt} = K_{OH}k_1[\text{FeLOH}^{2-}]^2 [\text{H}^+] = 3.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$$

Thus the reaction is second order in monomer FeLOH^{2-} and first order in hydrogen ion, as observed (Figure 3).

Treating the data as a steady state in [(FeEDTA)$_2$OH]$^{3-}$ for the dimerization reaction and assuming preequilibrium between [(FeEDTA)$_2$OH]$^{3-}$ and [(FeEDTA)$_2$O]$^{4-}$ for the monomerization implies the basic energy diagram for the reaction pathway shown in Figure 4 ($E^a k_2$, $E^a k_{-2} \ll E^a k_1$, $E^a k_{-1}$). These relative magnitudes are reasonable, since k_2 and k_{-2}, which involve only protonation reactions, would be expected to be fast, whereas bond breaking or forming processes occur in steps k_1 and k_{-1}. Under limiting conditions, a competitive reaction 5 might be expected. That such a

$$2[\text{FeEDTAOH}]^{2-} \rightarrow [(FeEDTA)_2OH]^- + OH^- \tag{5}$$
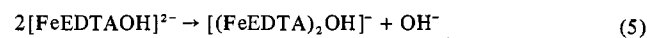
reaction need not be invoked to explain the present data implies the reaction in eq 5 must proceed at a rate much slower than
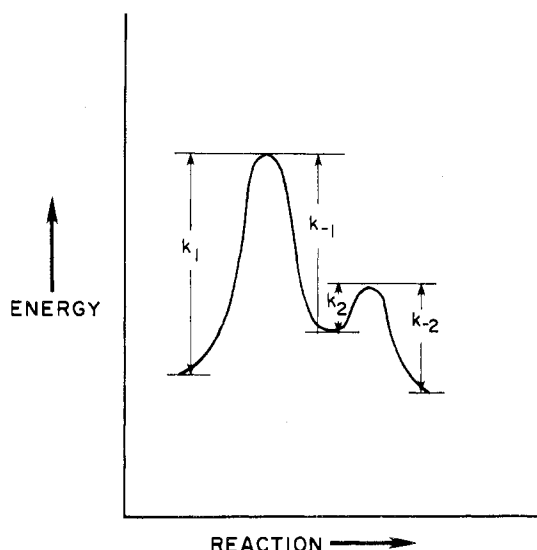
Figure 4. Diagramatic representation of the relative activation energies implied by the mechanism in eq 4.

that in eq 4 and makes an insignificant contribution to the total rate under the conditions studied. This is not unreasonable, as OH^- would be a poor leaving group relative to H_2O.

While the observed kinetics cannot rule out the formation of a ternary $H^+-(FeEDTAOH)_2$ complex, such a reaction is obviously unlikely on statistical grounds.

A final check of the validity of the proposed scheme is provided by the ratio of the rate of dimerization to monomerization, $\log k_D/k_M = \log K_{kinetic}$ which should equal log K_d. The equilibrium constant thus determined ($\log K_{kinetic} = 2.4$) is in good agreement with the thermodynamic value (2.5 $\pm$ 0.2).

Thus, the mechanism for oxo bridging appears to involve dimerization of a hydrolyzed and nonhydrolyzed chelate to yield a hydroxo bridged intermediate. The stabilization of oxo bridged complexes, however, must depend on balancing the energy required for deprotonation of hydroxide against that gained by superexchange mediated delocalization. Delocalization will be maximal through a linear bridge[12] and minimal for a hydroxo bridged complex (with a bond angle of approximately 120°), in accord with experiment.[13,14] On formation of the

$$\underset{M-O-M}{\overset{H}{|}}$$

species, linearity of the bridge may be obtained simply by a molecular vibration, resulting in a configuration favorable for superexchange and concomitant deprotonation to yield the linear oxo bridge.

Thus, energy for the deprotonation of the hydroxo bridged intermediate is supplied by delocalization, and the inherent hydrolytic tendencies of iron(III), which is a strong Lewis acid. By contrast to the ferric complexes, cobalt(III) complexes, which are even stronger Lewis acids, cannot gain delocalization energy by superexchange since Co(III) complexes are generally spin paired. Thus Co(III) complexes do not form oxo bridges, but dimerize through two cis hydroxo bridges, as favored by a statistical (chelate) effect. Similarly, weaker Lewis acids which might be expected to exhibit superexchange such as nickel(II) cannot labilize the hydroxide proton and thus also do not undergo oxo bridging. For such ions, the energy of superexchange might overcome the energy required for deprotonation if the bridging group was less basic. Such appears to be the case with sulfide ($pK \cong 7$ for the first deprotonation $H_2S \rightarrow HS^-$ vs. $pK \cong 14$ for $H_2O \rightarrow OH^-$). Thus, linear sulfide bridges resulting in superexchange are well established

for nickel(II)[15] and iron(II)[16] complexes.

Note Added in Proof. A kinetic study by Wilkins[17] of analogous $(FeL_2)O$ systems has come to our attention. The results are in substantial agreement with our own, but differ with respect to the $(FeLOH)_2$ dependent pathway. Temperature dependence studies are being performed to clarify the reason for the discrepancy.

Registry No. $[FeEDTA]^-$, 15275-07-7; $[(FeEDTA)_2O]^{4-}$, 22992-05-8.

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Conditions of Formation of α and β Phases of Germanic Nitride

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Germanic nitride is usually prepared by interaction of ammonia with elementary germanium or germanium dioxide between 700 and 750 °C. Popper and Ruddlesden[1] showed that the proportions of α and β crystalline phases varied depending upon the preparative conditions: heating germanium in ammonia at 750 °C gave a product which was almost entirely α phase, whereas heating germanium dioxide under the same conditions gave β phase with traces of α. Later, Lyutaya and co-workers[2] and other authors[3-6] observed the same phenomena. Labbe and co-workers[7] thought the β phase stabilized when oxide, oxygen, or steam were present, because this phase can be obtained in its pure form by having ammonia react with germanium dioxide and because the proportion of α phase is increased when purer ammonia is used. This assumption was at variance with the results of Wild and co-workers[8] who claimed the α phase of silicon and germanium nitrides to be, actually, oxynitrides $Si_{11.5}N_{15}O_{0.5}$ and