

Kinetics of the Dimerisation Reaction of the Iron(III)-  
Ethylenediaminetetra-acetate Complex

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The dimerisation reaction of the iron(III)-ethylenediaminetetra-acetate complex ( $\text{FeEDTA}^-$ ), has been studied at an ionic strength of 0.2 M in sodium perchlorate at 25° using a temperature jump relaxation technique. One relaxation is observed at high complex ion concentrations and the data are consistent with a two-step mechanism. Rate constants for the reaction:



are  $k_{34} = 1.1 \pm 0.3 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$  and  $k_{43} = 1.7 \pm 0.3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  respectively. The forward rate constant is consistent with an  $S_N 1$  mechanism.

## Introduction

The nature and reactivity of iron(III) complexes in solution is the subject of recent interest. Dimeric species in aqueous solution are well established<sup>1-3</sup> and the associated thermodynamic<sup>4,6</sup> and structural<sup>1,2,7,8</sup> aspects investigated. Two possible structures have been suggested for dimeric species, those involving an oxo bridge and those where two hydroxy groups bridge the iron atoms. In the case of the iron-ethylenediamine-tetraacetate dimer, the oxo bridge has been assigned by analogy with the known structure of the corresponding N-hydroxyethylene-diaminetetra-acetate species<sup>7</sup> with which it has similar spectral and magnetic properties.<sup>2</sup> In a recent study<sup>9</sup> Wilkins has applied the temperature-jump technique to the reaction involving the iron(III) EDTA dimers. At the same time in these laboratories, we have examined this system using the same method under slightly different conditions.

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In the present study, a large excess of complexing agent was added in order to buffer the reactions, the total EDTA concentration being varied over a 2.5 fold range. Any variation of relaxation time was within experimental error.

## Experimental Section

Solutions of iron(III)-perchlorate were made by dissolving freshly precipitated and washed iron(III) hydroxide in excess perchloric acid. Iron(III) contents of stock solutions were determined as described previously.<sup>10</sup> Analar grade disodium ethylenediaminetetraacetate was used without further purification. The pH's of reactant solutions were adjusted to the required values by dropwise addition of sodium hydroxide or perchloric acid and measured (to  $\pm 0.002$  pH units) using a Beckman Research pH meter. Using excess ethylenediaminetetraacetate as a buffering agent it was possible to prepare stable solutions at high pH. The ionic strength of the solutions was adjusted in each case to 0.2 M using sodium perchlorate.

Temperature-jump measurements were made using a single beam model (Messanlagen Studiengesellschaft, Göttingen, Germany). A jump of 5°C was obtained by discharging 30 KV through the solution, the final solution temperature being 25°. Amplified signals were monitored using a Tektronix type 564 storage oscilloscope. The relaxation of the dimer was observed at 480-500 n.m. All relaxation times represent the mean of at least four separate determinations, the mean deviation for  $\tau$  values listed in Table I being  $\pm 5\%$ .

## Results and Discussion

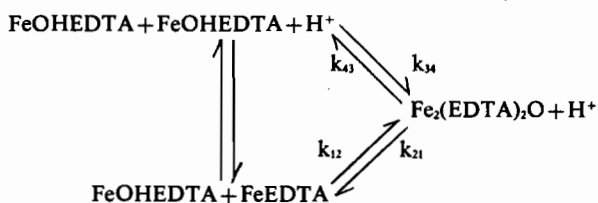
In common with the previous study made on this system, only 1 relaxation was observed in the wavelength range used. The relaxation time was found to be a function of both the  $(\text{FeOHEDTA})^{2-}$  concentration and hydrogen ion concentration. In Table I the relaxation times are reported at various  $(\text{FeOHEDTA})^{2-}$  concentrations, pH, and EDTA concen-

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Table I.

| Fe <sup>III</sup> × 10 <sup>3</sup> M | EDTA | [Fe(OH)EDTA] × 10 <sup>3</sup> M | pH   | τ <sup>-1</sup> sec <sup>-1</sup> | 10 <sup>3</sup> k <sub>a</sub> M <sup>-1</sup> sec <sup>-1</sup> | k <sub>b</sub> M <sup>-1</sup> sec <sup>-1</sup> |
|---------------------------------------|------|----------------------------------|------|-----------------------------------|--|--|
| 2.0                                   | 0.02 | 0.745                            | 8.26 | 13.2                              |  |  |
| 2.5                                   | 0.02 | 0.86                             | 8.26 | 13.6                              | 10.0 ± 0.5   |  |
| 3.0                                   | 0.02 | 0.96                             | 8.26 | 15.4                              |  | 5.6 ± 0.4  |
| 5.0                                   | 0.02 | 1.31                             | 8.26 | 19.0                              |  |  |
| 2.0                                   | 0.02 | 0.75                             | 8.38 | 10.8                              |  |  |
| 3.0                                   | 0.02 | 0.97                             | 8.38 | 12.0                              |  |  |
| 4.0                                   | 0.02 | 1.155                            | 8.38 | 12.5                              | 5.5 ± 0.3  | 10.5 ± 1.0                                       |
| 2.0                                   | 0.02 | 0.78                             | 8.97 | 2.7                               |  |  |
| 2.5                                   | 0.02 | 0.895                            | 8.97 | 3.3                               | 1.78 ± 0.5   | 1.8 ± 0.3  |
| 3.0                                   | 0.02 | 1.00                             | 8.97 | 3.5                               |  |  |
| 5.0                                   | 0.02 | 1.35                             | 8.26 | 3.7                               |  |  |
| 2.0                                   | 0.03 | 0.745                            | 8.26 | 17.0                              |  |  |
| 3.0                                   | 0.03 | 0.96                             | 8.26 | 17.2                              |  |  |
| 4.0                                   | 0.03 | 1.15                             | 8.26 | 18.2                              | 10.4 ± 0.8   | 8.7 ± 0.5  |
| 5.0                                   | 0.03 | 1.31                             | 8.26 | 22.8                              |  |  |
| 6.0                                   | 0.03 | 1.45                             | 8.26 | 24.8                              |  |  |
| 2.0                                   | 0.03 | 0.75                             | 8.38 | 12.5                              |  |  |
| 3.0                                   | 0.03 | 0.97                             | 8.38 | 13.5                              | 5.9 ± 0.4  | 8.0 ± 0.6  |
| 4.0                                   | 0.03 | 1.155                            | 8.38 | 14.4                              |  |  |
| 5.0                                   | 0.03 | 1.32                             | 8.38 | 16.0                              |  |  |
| 6.0                                   | 0.03 | 1.457                            | 8.38 | 16.2                              |  |  |
| 2.0                                   | 0.03 | 0.75                             | 8.48 | 10.4                              |  |  |
| 3.0                                   | 0.03 | 0.97                             | 8.48 | 11.5                              |  |  |
| 4.0                                   | 0.03 | 1.165                            | 8.48 | 12.1                              | 4.5 ± 0.2  | 6.7 ± 0.3  |
| 5.0                                   | 0.03 | 1.32                             | 8.48 | 12.8                              |  |  |
| 6.0                                   | 0.03 | 1.47                             | 8.48 | 13.8                              |  |  |
| 2.0                                   | 0.03 | 0.78                             | 8.74 | 5.5                               |  |  |
| 3.0                                   | 0.03 | 1.00                             | 8.74 | 5.75                              |  | 3.7 ± 0.4  |
| 4.0                                   | 0.03 | 1.18                             | 8.74 | 6.4                               | 2.3 ± 0.4  |  |
| 5.0                                   | 0.03 | 1.35                             | 8.74 | 6.8                               |  |  |
| 6.0                                   | 0.03 | 1.50                             | 8.74 | 8.1                               |  |  |
| 2.0                                   | 0.03 | 0.78                             | 9.1  | 2.0                               |  |  |
| 3.0                                   | 0.03 | 1.00                             | 9.1  | 2.4                               | 2.15 ± 0.1   | 0.4 ± 0.1  |
| 4.0                                   | 0.03 | 1.18                             | 9.1  | 3.0                               |  |  |
| 5.0                                   | 0.03 | 1.35                             | 9.1  | 3.3                               |  |  |
| 6.0                                   | 0.03 | 1.50                             | 9.1  | 3.7                               |  |  |
| 2.0                                   | 0.05 | 0.74                             | 8.20 | 18.5                              |  |  |
| 4.0                                   | 0.05 | 1.14                             | 8.20 | 24.0                              |  |  |
| 6.0                                   | 0.05 | 1.445                            | 8.20 | 25.0                              | 10.2 ± 0.8   | 11.0 ± 1.2                                       |
| 8.0                                   | 0.05 | 1.72                             | 8.20 | 28.7                              |  |  |
| 3.0                                   | 0.05 | 0.97                             | 8.48 | 10.7                              |  |  |
| 5.0                                   | 0.05 | 1.32                             | 8.48 | 12.5                              |  |  |
| 8.0                                   | 0.05 | 1.72                             | 8.48 | 14.2                              |  | 5.7 ± 0.3  |
| 10.0                                  | 0.05 | 1.95                             | 8.48 | 16.0                              | 5.0 ± 0.2  | 5.7 ± 0.3  |
| 3.0                                   | 0.05 | 1.00                             | 8.62 | 8.0                               |  |  |
| 5.0                                   | 0.05 | 1.35                             | 8.62 | 10.3                              |  |  |
| 8.0                                   | 0.05 | 1.77                             | 8.62 | 12.2                              |  |  |
| 10.0                                  | 0.05 | 2.0                              | 8.62 | 14.0                              | 4.1 ± 0.3  | 5.0 ± 0.3  |
| 20.0                                  | 0.05 | 2.92                             | 8.62 | 15.7                              |  |  |
| 3.0                                   | 0.05 | 1.0                              | 8.8  | 5.6                               |  | 3.8 ± 0.5  |
| 8.0                                   | 0.05 | 1.71                             | 8.8  | 8.5                               | 2.9 ± 0.4  | 3.8 ± 0.5  |
| 10.0                                  | 0.05 | 2.0                              | 8.8  | 10.0                              |  |  |
| 20.0                                  | 0.05 | 2.92                             | 8.8  | 11.3                              |  |  |
| 2.0                                   | 0.05 | 0.78                             | 9.0  | 2.65                              |  |  |
| 3.0                                   | 0.05 | 1.00                             | 9.0  | 2.85                              | 2.0 ± 0.5  | 1.5 ± 0.6  |
| 5.0                                   | 0.05 | 1.35                             | 9.0  | 3.90                              |  |  |
| 6.0                                   | 0.05 | 1.50                             | 9.0  | 4.7                               |  |  |

trations. The data are consistent with the following mechanism (charges are omitted for simplicity):



The interconversion of FeEDTA<sup>-</sup> and FeOHEDTA<sup>2-</sup> is fast compared to the dimerisation reactions and

since only one relaxation time was observed, we may write

$$\frac{d(\text{Fe}_2(\text{EDTA})_2\text{O})}{dt} = k_{34}(\text{FeOHEDTA})(\text{FeEDTA}) - k_{33}(\text{Fe}_2(\text{EDTA})_2\text{O})(\text{H}^+) + k_{12}(\text{FeCHEDTA})^2 - k_{21}(\text{Fe}_2(\text{EDTA})_2\text{O})$$

Using the conditions:

$$\Delta[\text{FeOHEDTA}] + [\text{FeOHEDTA}] = (\text{FeOHEDTA}) \text{ etc.,}$$

and also



and

$$K_a \cdot \Delta[\text{FeEDTA}] = [\text{H}^+] \cdot \Delta[\text{FeOHEDTA}]$$

where

$$K_a = \frac{[\text{FeOHEDTA}][\text{H}^+]}{[\text{FeEDTA}]}$$

then

$$\frac{d\Delta[\text{Fe}_2(\text{EDTA})_2\text{O}]}{dt} = -\frac{1}{\tau} \cdot \Delta[\text{Fe}_2(\text{EDTA})_2\text{O}]$$

where

$$\tau^{-1} = 4[\text{Fe}(\text{OH})\text{EDTA}] \frac{k_{12}K_a + k_{34}(\text{H}^+)}{K_a + [\text{H}^+]} + k_{43}[\text{H}^+] + k_{21}$$

i.e.

$$\tau^{-1} = k_a[\text{Fe}(\text{OH})\text{EDTA}] + k_b$$

where

$$k_a[K_a + [\text{H}^+]] = 4(k_{12}K_a + k_{34}[\text{H}^+])$$

and

$$k_b = k_{21} + k_{43}[\text{H}^+]$$

Using the value of the complex hydrolysis constant,  $K_a = 2.63 \times 10^{-8} \text{ l.mole}^{-1}$ ,<sup>11</sup> the constants  $k_a$  and  $k_b$  were derived from plots of  $\tau^{-1}$  against  $[\text{Fe}(\text{OH})\text{EDTA}]^{2-}$  and are reported in Table I.

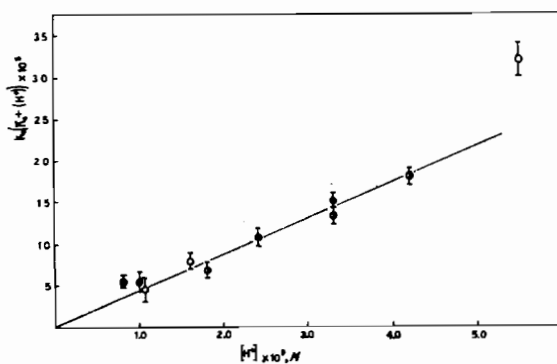


Figure 1. Plots of  $k_a(K_a + [\text{H}^+])$  against  $[\text{H}^+]$  at various EDTA concentrations.  $\circ = 2 \times 10^{-2} M$ ;  $\bullet = 3 \times 10^{-2} M$ ;  $\bullet = 5 \times 10^{-2} M$ .

From plots of  $k_a(K_a + [\text{H}^+])$  against  $[\text{H}^+]$  the rate constant  $k_{34}$  was derived from the slope, (Figure 1) the value being  $1.1 \pm 0.3 \times 10^4 M^{-1} \text{ sec}^{-1}$ . No determination could be made of the other formation constant  $k_{12}$  since the intercept ( $k_{12}K_a/4$ ) was considered to be insignificant. From plots of  $k_b$  against  $(\text{H}^+)$ , however, values of  $k_{21}$  and  $k_{43}$  were derived, being  $\sim 0.25 \text{ sec}^{-1}$  and  $1.7 \pm 0.3 \times 10^9 M^{-1} \text{ sec}^{-1}$  respectively. These values may be compared with those of  $k_{34} = 2 \times 10^4 M^{-1} \text{ sec}^{-1}$  and  $k_{43} = 5 \times 10^8 M^{-1} \text{ sec}^{-1}$  obtained previously<sup>9</sup> at an ionic strength of 1.0 M.

It is known that EDTA may act as a pentadentate ligand in solution and recent studies using X-ray<sup>12</sup> and n.m.r.<sup>13</sup> techniques have shown that the sixth equatorial coordination position is occupied by a water molecule. Wilkins has postulated that the rate determining step in the iron(III)-dimer formation is the loss of such a water molecule in a  $S_N1$  type of mechanism.<sup>14,15</sup>

In the decomposition reaction of dimeric iron species, the rate equation is of the form.<sup>9,14</sup>

$$k_b = k_{21} + k_{43}[\text{H}^+],$$

the value for the hydrogen ion dependent pathway in the case of the aquo dimer  $(\text{H}_2\text{O})_4\text{Fe}(\text{OH})_2^{4+}$  being  $\sim 0.35 \text{ sec}^{-1}$ .<sup>16</sup> Under the present conditions, an approximate  $k_{21}$  value is  $0.25 \text{ sec}^{-1}$  which compares reasonably with that of  $\sim 0.5 \text{ sec}^{-1}$  obtained previously.<sup>8,9</sup> A mechanism postulated to account for this fairly large value is considered to involve the assistance of a water molecule to form the symmetrical dihydroxy bridged species an an unstable intermediate.<sup>8</sup> In the case of the decomposition path involving hydrogen ions, the rate constants are larger and it has been suggested that the reaction takes place with the attack of a proton on the oxo bridge. The reaction rate for the aquo dimer is  $\sim 3.5 M^{-1} \text{ sec}^{-1}$  whereas it has been found that when the iron is complexed with either EDTA (or CDTA) the rate is increased by a factor of  $\sim 10^8$  the process being almost diffusion controlled.

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