Multistep Oxidation Kinetics of [Fe^{II}(cdta)] [cdta = N,N',N'',N'''-(1,2-Cyclohexanediamine)tetraacetate] with Molecular Oxygen

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The complicated oxidation kinetics of the reaction of [Fe^{II}(cdta)] [cdta = 1,2-(N,N'- cyclohexanediamine)tetraacetate] with molecular oxygen was investigated as a function of [Fe^{II}], [O_2], pH, temperature and pressure. In the presence of an excess of [Fe^{II}(cdta)] three steps could be observed, for which the following rate constants were found at 25°C; $k_1 = 1080 \pm 16$ M^{-1} s^{-1}, $k_2 = 103 \pm 4$ M^{-1} s^{-1} and $k_3 = 59 \pm 5$ M^{-1} s^{-1}. These reaction steps can be accounted for in terms of the following mechanism: (1) [Fe^{II}(cdta)H_2O]$^{2-}$ reacts with O_2 by a substitution process to form [Fe^{II}(cdta)O_2]$^{2-}$; (2) electron-transfer to form an Fe^{III}-superoxo species; (3) subsequent bridge formation followed by electron-transfer to give [(cdta)Fe^{III}-$O_2$$^{2-}$-Fe^{III}(cdta)]$^{4-}$; and (4) a fast decomposition of the peroxide intermediate yielding the monomeric [Fe^{III}(cdta)] and H_2O_2. Rate and activation parameters for these steps are reported and discussed in terms of the postulated mechanism and in reference to available literature data.

Introduction

During the past decades there has been a continued interest in the study of oxidation reactions of [Fe^{II}(aminopolycarboxylato)] complexes, especially with dioxygen or hydrogen peroxide.[1−12] Of particular interest in the present context was their importance in several biochemical processes, for example the cleavage of DNA, the decomposition of H_2O_2 or the dismutation of superoxide.[13−20] Many investigators have tried to solve these complicated reactions before, but in most cases they could only observe a single reaction step spectroscopically, even when more than one step was postulated in the mechanism.[1−12,21]

We recently reported a detailed kinetic study of the oxidation kinetics of [Fe^{II}(edta)] with molecular oxygen.[22] For the first time we could observe three steps spectroscopically and could investigate two of them in detail. The first step was so fast that we were not able to analyse it systematically on the stopped-flow time scale. We have therefore searched for a ligand, which would tune the reactivity of the complex in such a way, that this first step would become slower. Since the cdta ligand (cdta = N,N'-(1,2-cyclohexanediamine)tetraacetate) is known to stabilize its metal complexes, we thought that it would also affect their reactivity.[23−27] Moreover, it is known from several kinetic investigations that the cdta complex always reacts slower than the corresponding edta complex.[28−30] We, therefore, performed detailed kinetic measurements on the rather complicated oxidation reactions of [Fe^{II}(cdta)] with dioxygen.

The present work describes how the selected chelate can tune the reactivity of the complex. We were now able to investigate three reaction steps in detail. A mechanism is presented that accounts for all spectroscopic and kinetic observations, and is discussed in reference to our earlier work on the [Fe^{II}(edta)] system[22] and work reported in the literature.[4,6,7,10,12,21]

Results and Discussion

Spectral Observations

A number of test experiments on the [Fe^{II}(cdta)] system showed that its spectroscopic behavior is very similar to the [Fe^{II}(edta)] system, which we investigated recently.[22] Typical spectra indicate that both [Fe^{II}(cdta)] and [Fe^{III}(cdta)] exhibit an absorbance maximum at 260 nm and that the molar extinction coefficient for [Fe^{III}(cdta)] is significantly higher than for the [Fe^{II}(cdta)] complex. Since the overall oxidation reaction is accompanied by a significant decrease in [H^+], it was necessary to use buffers for pH $\geq$ 3 throughout the study.[31] The reaction of [Fe^{II}(cdta)] with molecular oxygen can best be followed at 370 nm in the presence of an excess of [Fe^{II}(cdta)] and at 260 nm in the presence of an excess of O_2 using a 1 cm cuvette. All kinetic traces were measured over more than 5 half-lives.

Kinetic Measurements

Kinetic traces measured in the presence of an excess of [Fe^{II}(cdta)] showed a complicated multistep process. In contrast to the [Fe^{II}(edta)] system, we could now fit the kinetic traces in most cases to three exponential functions (see Figure 1). This means we were able to confirm our earlier observations, where we only had limited evidence for the first

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fast step.[22] For the present system the fast step was only about a factor of ten faster than the subsequent steps. According to the data analysis this step is accompanied by a small decrease in absorbance which results in the non-linear increase in absorbance seen in Figure 1b. The two subsequent steps differ by a factor of ca. two, which is in good agreement with the data we obtained for the [Fe^{II}(edta)] system. However, in comparison, the rate constants for the [Fe^{II}(edta)] system are two times faster than for the [Fe^{II}(cdta)] system. The values of k_{obs} for all three reaction steps vary linearly with [Fe^{II}(cdta)] over the investigated concentration range (see Figure 2). The dependence for the first step shows a significant intercept, whereas the two other lines go through the origin. At pH = 6.0, the three reaction steps have the following second-order rate constants, $k_1 = 1080 \pm 16\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_2 = 103 \pm 4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_3 = 59 \pm 5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 25°C, which are assigned to the reaction steps outlined in (2), (4), and (6), respectively (see further Discussion).

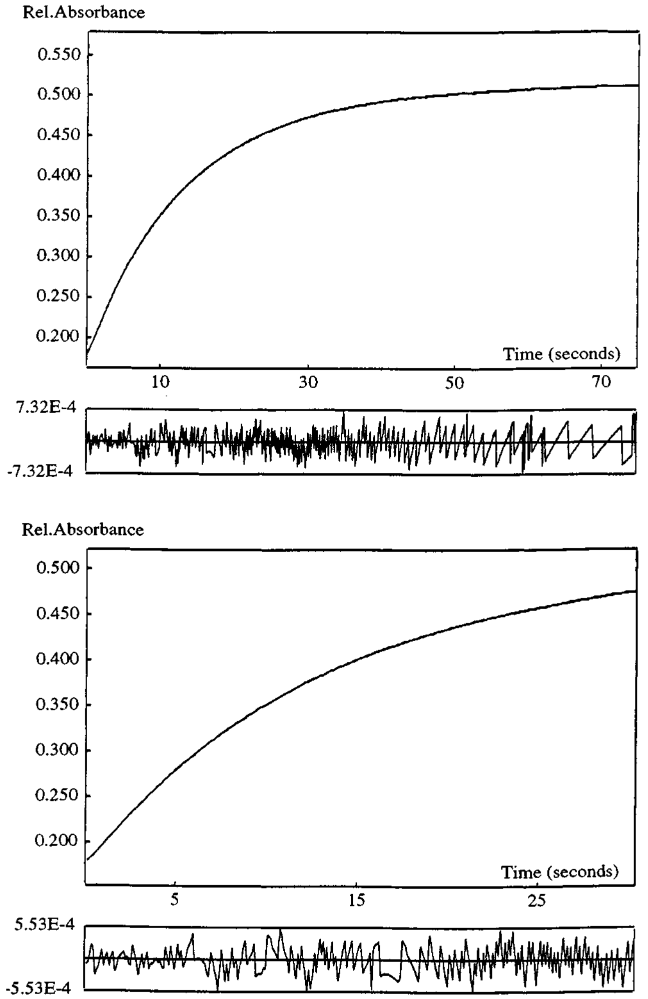


Figure 1. Typical absorbance time trace obtained in an excess of [Fe^{II}(cdta)] fitted with three exponential functions. – Experimental conditions: [Fe^{II}(cdta)] = $2.5 \cdot 10^{-3}$ M, [O$_2$] = $1.25 \cdot 10^{-4}$ M, ionic strength = 0.5 M, [acetate buffer] = 0.1 M, pH = 6, T = 25°C, λ = 370 nm

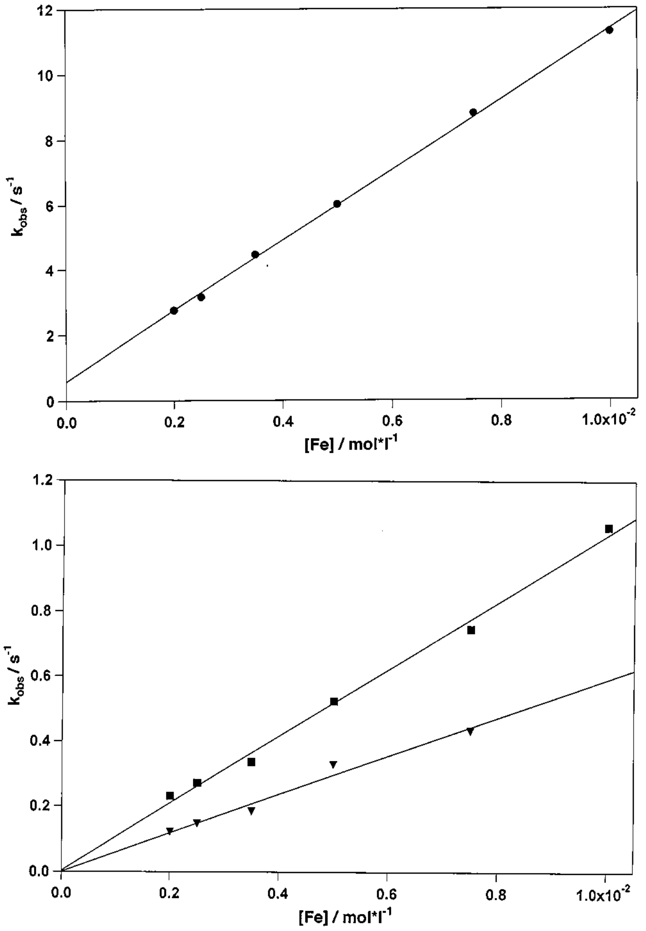


Figure 2. a: k_{obs1} (●) as a function of [Fe^{II}(cdta)] for the oxidation of [Fe^{II}(cdta)]. – b: k_{obs2} (■) as a function of [Fe^{II}(cdta)] for the oxidation of [Fe^{II}(cdta)]. – c: k_{obs3} (▼) as a function of [Fe^{II}(cdta)] for the oxidation of [Fe^{II}(cdta)]
Experimental conditions: [O$_2$] = $1.25 \cdot 10^{-4}$ M, ionic strength = 0.5 M, [acetate buffer] = 0.1 M, pH = 6, T = 25°C, λ = 370 nm.

The pH dependence of the reaction in the presence of an excess [Fe^{II}(cdta)] was studied in the range pH = 2 to 7 (see Figure 3). The resolution of the time traces at a pH > 4 showed a more complicated kinetic behavior, but we were able to analyze the three main steps. All three steps show a bell-shaped pH dependence with a maximum around pH = 2.5. The maximum rate of all three observed steps corresponds quite well to the distribution of species in solution (see Figure 4). The kinetic pH dependence indicates that the monoprotonated species in solution is the most reactive one. This behavior was also observed for different [Fe^{II}(edta)] reactions before. For example, the oxidation kinetics of [Fe^{II}(edta)] with molecular oxygen showed the same pH dependence.[21,22] But, moreover, kinetic studies of the reaction of [Fe^{II}(edta)] with HONO or NO$_2^-$ also showed the same pH dependence,[35,36] which supports our suggestion that the observed bell-shaped curves are due to the distribution of species in solution and not due to an acid-catalyzed process, as suggested in an earlier study.[21]

The increase in rate at pH > 6 (see Figure 3a) is not expected on the basis of the distribution of species in solution. This may be an effect of the selected buffer and we therefore selected other buffers. This, however, did not solve the problem. It was noticed that a precipitate occurred at

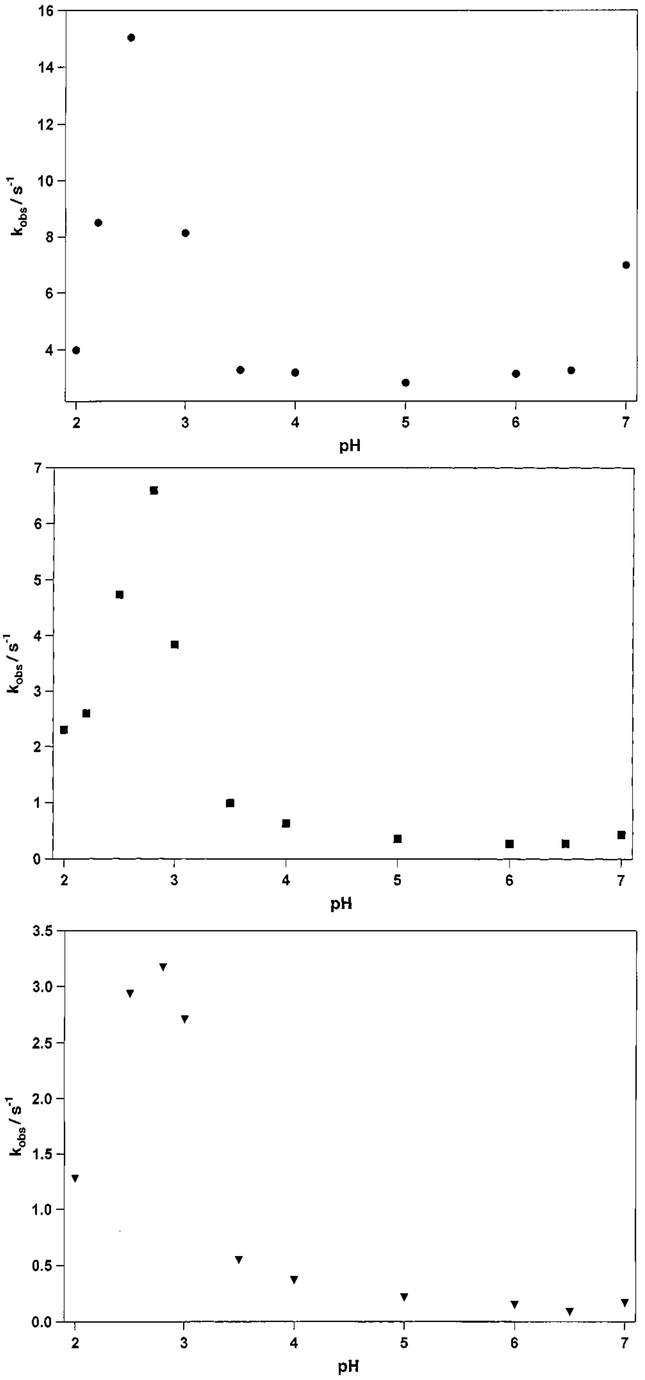


Figure 3. a: pH dependence of k_{obs1} (●) for the oxidation of [Fe^{II}(cdta)] in the presence of an excess of [Fe^{II}(cdta)]. – b: pH dependence of k_{obs2} (■)for the oxidation of [Fe^{II}(cdta)] in the presence of an excess of [Fe^{II}(edta)]. – c: pH dependence of k_{obs3} (▼) for the oxidation of [Fe^{II}(cdta)] in the presence of an excess of [Fe^{II}(cdta)]
Experimental conditions: [Fe^{II}(cdta)] = $2.5 \cdot 10^{-3}$ M, [O$_2$] = $1.25 \cdot 10^{-4}$ M, ionic strength = 0.5 M, [acetate buffer] = 0.1 M for pH > 3, [Tris buffer] = 0.1 M or [MOPS buffer] = 0.1 M for pH > 6 , T = 25°C, λ = 370 nm.

pH = 7.5, which prevented measurements in a higher pH range. The precipitate suggested that the investigated [Fe^{II}(cdta)] complex is not as stable as reported in the literature[38] and that some free Fe^{II} may be present in solution. The addition of FeSO$_4 \cdot 7$ H$_2$0 to the test solution accelerated the observed reactions with dioxygen, and the presence of free Fe^{II} can therefore account for the unexpected increase in rate at pH > 6.

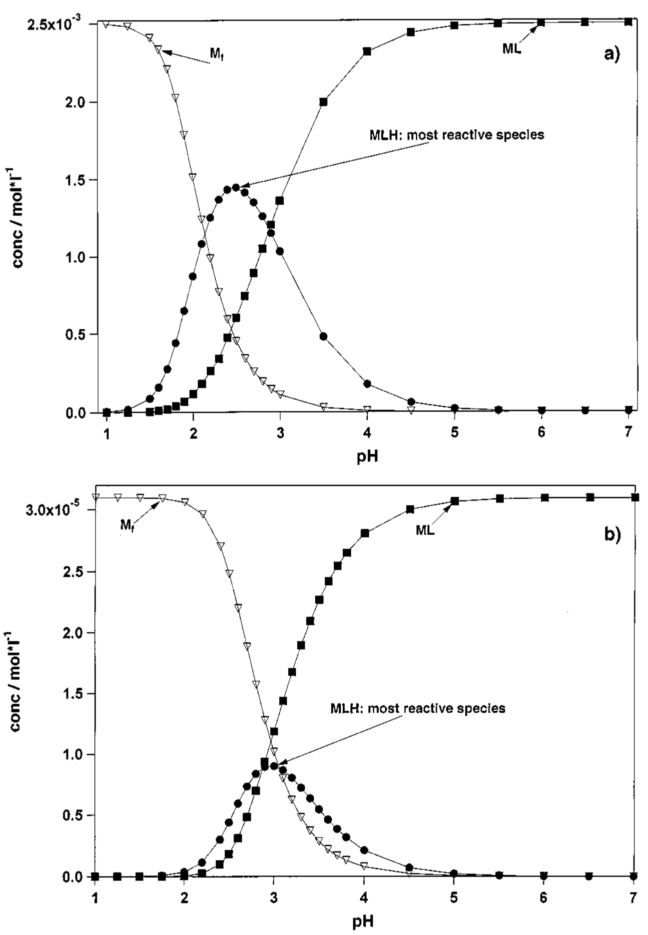


Figure 4. a: Distribution of [Fe^{II}(cdta)] species in solution, [Fe^{II}(cdta)] = 2.5×10^{-3} M. – b: Distribution of [Fe^{II}(cdta)] species in solution, [Fe^{II}(cdta)] = 3.0×10^{-5} M; M$_f$ = free Fe$_2$+, ML = [Fe^{II}(cdta)(H$_2$O)]$^{2-}$, MLH = [Fe^{II}(cdtaH)(H$_2$O]$^-$

Reactions in the presence of an excess of oxygen could in most cases be fitted to two exponential functions between pH = 6.0 and pH = 2.0. However, near the maximum reactivity, the kinetic behavior was even more complicated, so that it was sometimes necessary to fit the kinetic traces to three exponential functions. In these cases we only report rate constants for the two main reaction steps for reason of comparison with the other pH data. The complicated kinetic behavior in more acidic medium is also reflected by the difficulties encountered to fit our data in the presence of an excess of [Fe^{II}(edta)] in that pH region (vide supra). The studied pH dependence exhibits a maximum at pH = 3 (see Figure 5), which is in good agreement with the data obtained for the pH dependence in an excess of [Fe^{II}(cdta)] (see Figure 3) and corresponds also quite well to the distribution of species in solution at the appropriate concentration of [Fe^{II}(cdta)] (see Figure 4b).

Various efforts were made to study the oxygen concentration dependence under these conditions, especially to

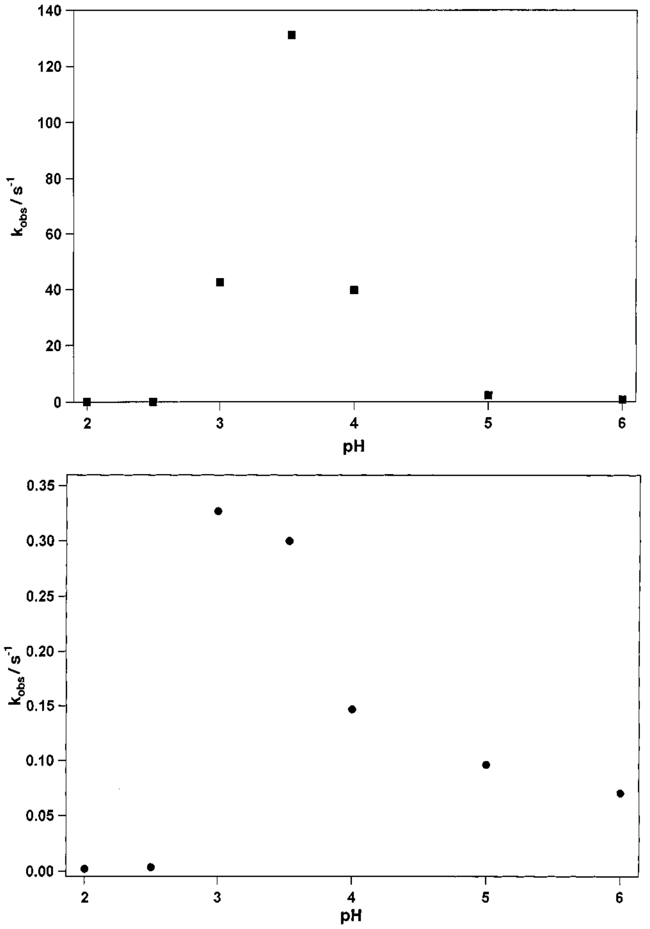


Figure 5. a: pH dependence of k_{obs1} (■) for the oxidation of [Fe^{II}(cdta)] in the presence of an excess of O_2. – b: pH dependence of k_{obs2} (●) for the oxidation of [Fe^{II}(cdta)] in the presence of an excess of O_2
Experimental conditions: [O_2] = $6.25 \cdot 10^{-4}$ M, [Fe^{II}(cdta)] = $3.0 \cdot 10^{-5}$ M, ionic strength = 0.5 M, [acetate buffer] = 0.1 M for pH > 3, T = 25°C, λ = 260 nm

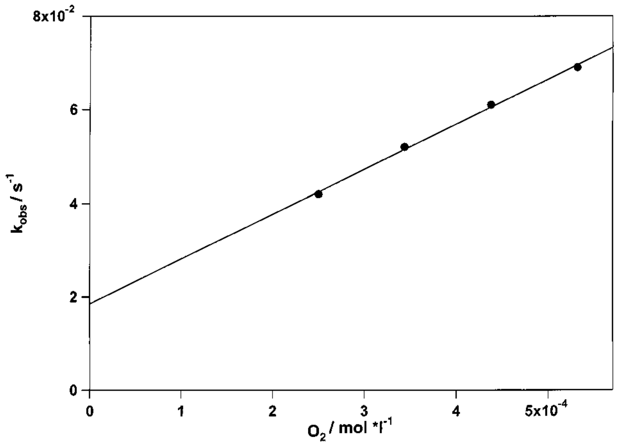


Figure 6. k_{obs2} (●) as a function of [O_2] for the oxidation of [Fe^{II}(cdta)]
Experimental conditions: [Fe^{II}(cdta)] = $3.0 \cdot 10^{-5}$ M, ionic strength = 0.5 M, [acetate buffer] = 0.1 M, pH = 6, T = 25°C, λ = 260 nm

analyse the mentioned additional faster reaction step, which could also be observed in the case of the [Fe^{II}(edta)] system.[22] First we used a concentration range where we worked in a 10- to 20-fold excess of oxygen. We could fit the obtained traces quite well to two exponential functions. The k_{obs} values for the second step observed under these conditions varied linearly with the O_2 concentration at pH = 6.0 (see Figure 6). The slope of the line, viz. 96 ± 3 M^{-1} s^{-1}, is in very close agreement with that observed for the second reaction step in the presence of an excess of [Fe^{II}(cdta)], viz. k_2 = 103 ± 4 M^{-1} s^{-1} under similar conditions.

In general the obtained kinetic traces were of a too poor quality to allow analysis of the fast step, due to the relatively low [Fe^{II}(cdta)] concentration that had to be selected in order to have the oxygen in a large enough excess. We, therefore, tried to increase the concentration of [Fe^{II}(cdta)] and measured in a 6- to 10-fold excess of oxygen. Under these conditions the data could best be fitted to three exponential functions. The initial fast rate constant showed, within experimental error limits, no meaningful dependence on the oxygen concentration. In principle such a reaction step could involve ring-opening of the cdta ligand prior to or following the binding of dioxygen. Unfortunately, it was not possible to determine within reasonable accuracy the thermal activation parameters for this reaction. The second subsequent step exhibited a decrease in absorbance comparable to the first fast step observed in the presence of an excess of [Fe^{II}(cdta)]. The determined second order rate constant for this step is k_1 = 611 ± 234 M^{-1} s^{-1} , which is of the same order as k_1 = 1080 ± 16 M^{-1} s^{-1} determined in the presence of an excess of [Fe^{II}(cdta)]. It follows that the data obtained in the presence of an excess of oxygen, despite their relatively poor quality, do support the overall trends observed in the presence of an excess of [Fe^{II}(cdta)].

Mechanistic Interpretation

pH titrations for the [Fe^{II}(cdta)] complex[37] show a similar behavior as reported for the [Fe^{II}(edta)] complex.[38] As these complexes are very similar, it is reasonable that [Fe^{II}(cdta)] shows a similar behavior like [Fe^{II}(edta)] in solution and in the solid state. It is known from X-ray data for the [Fe^{II}(edta)] complex, which was crystallized from neutral solution, that it exists as a seven coordinate [Fe^{II}(edta)H_2O]$^{2-}$ species with a mono-capped trigonal-prismatic geometry (MCP).[39] The edta chelate can be protonated when the solution is acidified.[4,40,41] This results in a monoprotonated species [Fe^{II}(edtaH)(H_2O)]$^-$, which has a pentagonal bipyramidal geometry (PB) in the solid state.[41] Although such X-ray data are not available for the [Fe^{II}(cdta)] complex, it is quite realistic to expect that [Fe^{II}(cdta)] behaves in a similar way, and that the structure in solution is comparable to the structure in the solid state. For example, from NMR and Raman studies,[42–46] it is known for the [Fe^{III}(edta)] complex, that the structure in solution is the same as in the crystalline state.[47–49]

The increase in k_{obs} with increasing [H^+] at pH < 5 could result from the protonation of the cdta ligand which is accompanied by a change in geometry from MCP to PB. The PB geometry has a higher reactivity due to the greater bite angle in the PB form such that the incoming oxygen molecule has more space to enter the coordination sphere and to substitute the coordinated water. On further acidification, another changeover in geometry occurs which is associated with the diprotonation of the complex as shown in (1). This diprotonated form of the complex results again in a mono-capped trigonal-bipyramidal geometry.[41] Here the Fe$-$OH$_2$ bond of the [Fe^{II}(edta)(H$_2$O]$^{2-}$ complex is shortened as a result of protonation of two acetate arms. The decrease in reactivity can therefore also be due to a shortening of the Fe$-$OH$_2$ bond of the corresponding [Fe^{II}(cdtaH$_2$)(H$_2$O)] complex at pH < 2.5.

For the deprotonation of the monoprotonated complex a pK_a of 2.88 was reported in the literature.[37] The resulting distribution diagramms (see Figure 4) correlate very well with the found kinetic pH dependencies, such that these titration data strongly support our assumption that the monoprotonated form of the complex is the reactive one.

$$\begin{aligned}
&\underset{\text{MCP}}{[\mathrm{Fe^{II}(cdta)(H_2O)}]^{2-}} + \mathrm{H^+} \overset{K_{a1}}{\rightleftharpoons} \underset{\text{PB}}{[\mathrm{Fe^{II}(cdtaH)(H_2O)}]^{-}} \\
&\underset{\text{PB}}{[\mathrm{Fe^{II}(cdtaH)(H_2O)}]^{-}} + \mathrm{H^+} \overset{K_{a2}}{\rightleftharpoons} \underset{\text{MCP}}{[\mathrm{Fe^{II}(cdtaH_2)(H_2O)}]}
\end{aligned} \tag{1}$$

All three complexes can react with O$_2$ to produce [Fe^{II}(cdta)(O$_2$)]$^{2-}$, [Fe^{II}(cdtaH)(O$_2$)]$^-$, and [Fe^{II}(cdtaH$_2$)(O$_2$)], respectively, as shown in (2). We believe that these reactions account for the first fast step, especially because they correlate with the pH-dependent profile (see Figure 3a). Moreover, the substitution of coordinated H$_2$O by O$_2$ on the [Fe^{II}(cdta)] complexes is not expected to cause a significant UV-Vis spectral change. The concentration dependence in Figure 2a suggests that the process is reversible. From the slope and the intercept an apparent equilibrium constant was calculated to be K_1 = 1862 M^{-1}. However, this is based on the assumption that the intercept in Figure 2a is entirely due to the back reaction, which does not have to be the case.

$$\begin{aligned}
&[\mathrm{Fe^{II}(cdta)(H_2O)}]^{2-} + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe^{II}(cdta)(O_2)}]^{2-} + \mathrm{H_2O} \\
&[\mathrm{Fe^{II}(cdtaH)(H_2O)}]^{-} + \mathrm{O_2} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} [\mathrm{Fe^{II}(cdtaH)(O_2)}]^{-} + \mathrm{H_2O} \\
&[\mathrm{Fe^{II}(cdtaH_2)(H_2O)}] + \mathrm{O_2} \underset{k''_{-1}}{\overset{k''_1}{\rightleftharpoons}} [\mathrm{Fe^{II}(cdtaH_2)(O_2)}] + \mathrm{H_2O}
\end{aligned} \tag{2}$$

The reactions in (2) are reversible substitution processes in which the protonated pentagonal bipyramidal species can bind O$_2$ more rapidly than the nonprotonated and diprotonated mono-capped trigonal-prismatic species.

The following rate law for the forward reactions can account for the bell shaped pH dependence at pH = 2.0:

$$k_{\text{obs1}} = \left\{ \frac{k_1 + k'_1 K_{a1}[\mathrm{H^+}] + k''_1 K_{a1}K_{a2}[\mathrm{H^+}]^2}{1 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}[\mathrm{H^+}]^2} \right\} [\mathrm{Fe^{II}(cdta)}] \tag{3}$$

The subsequent redox reactions (4) to produce superoxo complexes of [Fe^{III}(cdta)] will induce a significant spectral change and are suggested to account for the first slower reaction step. Thus electron transfer is the rate-determining step following the rapid coordination of O$_2$ in (2). The observed rate constants, k_{obs2}, are expected to depend on pH since the different species produced in (2) are expected to undergo oxidation at different rates.

$$\begin{aligned}
&[\mathrm{Fe^{II}(cdta)(O_2)}]^{2-} \xrightarrow{k_2} [\mathrm{Fe^{III}(cdta)(O_2^-)}]^{2-} \\
&[\mathrm{Fe^{II}(cdtaH)(O_2)}]^{-} \xrightarrow{k'_2} [\mathrm{Fe^{III}(cdtaH)(O_2^-)}]^{-} \\
&[\mathrm{Fe^{II}(cdtaH_2)(O_2)}] \xrightarrow{k''_2} [\mathrm{Fe^{III}(cdtaH_2)(O_2^-)}]
\end{aligned} \tag{4}$$

The given rate law (5), derived under conditions that [Fe^{II}(cdta)] >>[O$_2$], can account for the bell shaped pH dependence observed at pH = 2.0 in Figure 3b. Furthermore, this rate law is also in agreement with the linear dependence on the concentration of [Fe^{II}(cdta)] as found in Figure 2b.

$$k_{\text{obs2}} = \left\{ \frac{k_2K_1 + k'_2 K'_1 K_{a1}[\mathrm{H^+}] + k''_2 K''_1 K_{a1}K_{a2}[\mathrm{H^+}]^2}{1 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}[\mathrm{H^+}]^2} \right\} [\mathrm{Fe^{II}(cdta)}] \tag{5}$$

The subsequent reaction step, k_{obs3}, exhibits a similar pH profile (Figure 3c) and is on the average ca. two times slower than k_{obs2}. Since these experiments are performed in the presence of an excess of [Fe^{II}(cdta)], we suggest that equilibrium (1) must also account for the pH dependence found for this reaction step. Thus the superoxo species produced in (4) may react further as shown in (6). The rate law for these reactions will be similar to that in (5), as summarized in (7).

$$\begin{aligned}
&[\mathrm{Fe^{III}(cdta)(O_2^-)}]^{2-} + [\mathrm{Fe^{II}(cdta)(H_2O)}]^{2-} \xrightarrow{k_3} [\mathrm{(cdta)Fe^{III}(O_2^{2-})Fe^{III}(cdta)}]^{4-} + \mathrm{H_2O} \\
&[\mathrm{Fe^{III}(cdtaH)(O_2^-)}]^{-} + [\mathrm{Fe^{II}(cdtaH)(H_2O)}]^{-} \xrightarrow{k'_3} [\mathrm{(cdtaH)Fe^{III}(O_2^{2-})Fe^{III}(cdtaH)}]^{2-} + \mathrm{H_2O} \\
&[\mathrm{Fe^{III}(cdtaH_2)(O_2^-)}] + [\mathrm{Fe^{II}(cdtaH_2)(H_2O)}] \xrightarrow{k''_3} [\mathrm{(cdtaH_2)Fe^{III}(O_2^{2-})Fe^{III}(cdtaH_2)}] + \mathrm{H_2O}
\end{aligned} \tag{6}$$

$$k_{\text{obs3}} = \left\{ \frac{k_3 + k'_3 K_{a1}[\mathrm{H^+}] + k''_3 K_{a1}K_{a2}[\mathrm{H^+}]^2}{1 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}[\mathrm{H^+}]^2} \right\} [\mathrm{Fe^{II}(cdta)}] \tag{7}$$

The temperature and pressure dependence of the reactions were also studied in the presence of an excess of [Fe^{II}(cdta)]. As the concentration dependence of the first fast step exhibits a significant intercept, it was neccessary to measure the temperature dependence as a function of concentration in order to separate the contribution of the intercept from the slope (see Supplementary Table S1). The volumes of activation could only be obtained for the second and the third step (see Supplementary Figure S1). Since the first fast step exhibits only very small absorbance changes and is ca. ten times faster in comparison to the subsequent steps, our instrumentation did not allow a determination of the associated volume of activation. All obtained rate and activation parameters are summarized in Table 1.

Table 1. Rate constants and activation parameters determined in the presence of an excess of [Fe^{II}(cdta)] for the oxidation by dioxygen

	1. Reaction	2. Reaction	3. Reaction
rate constant (M^{-1} s^{-1})	1080 ± 16	103 ± 4	59 ± 5
$\Delta H^{\#}$ (kJ mol^{-1})	44.1 ± 2.3	66.5 ± 0.9	67.1 ± 0.8
$\Delta S^{\#}$ (J mol^{-1} K^{-1})	−236 ± 8	18.7 ± 2.4	18.0 ± 2.7
$\Delta V^{\#}$ (cm^3 mol^{-1})	not determined	−20.2 ± 2.3	−23.0 ± 3.9

Experimental conditions: [Fe^{II}(cdta)] = $2.5 \cdot 10^{-3}$ M, [O$_2$] = $1.25 \cdot 10^{-4}$ M, ionic strength = 0.5 M, [acetate buffer] = 0.10 M, pH = 6.0, λ = 370 nm.

Overall Suggested Mechanism

All three reaction steps could be resolved during the interaction of dioxygen with an excess of [Fe^{II}(cdta)]. These include at first substitution of a coordinated water molecule by dioxygen, where this process probably follows an associative mechanism as a result of the strongly negative entropy of activation (see Table 1). This step is then followed by an intramolecular electron-transfer reaction to produce an Fe^{III}-superoxo complex, which in the third step reacts with another [Fe^{II}(cdta)] species to produce a dimeric [Fe^{III}−O$_2$$^{2-}$−Fe^{III}] complex, which is postulated to dissociate rapidly to form the monomeric [Fe^{III}(cdta)] complex and H$_2$O$_2$. The latter species was shown to react considerably faster with [Fe^{II}(cdta)] than dioxygen (typical rate constants of $k_1 = 1.9 \cdot 10^4$ M^{-1}s^{-1} and $k_2 = 1.6 \cdot 10^3$ M^{-1}s^{-1} were found at T = 25°C and pH = 6). In principle, it should be possible to observe four reaction steps of which two are associated with substitution and electron-transfer of the first [Fe^{II}(cdta)] complex, and two associated with similar reactions of the second [Fe^{II}(cdta)] complex. With the aid of a Global Analysis Program it could be shown that the fit with a three-step mechanism is not perfect. But due to the similarity of the two postulated substitution processes, we were not successful to separate it into four rate constants. The fact that all three observed concentration dependences are linear means that the substitution equilibria for the first and third steps must be unfavorable in order to result in a linear concentration dependence of the second and fourth reaction steps.

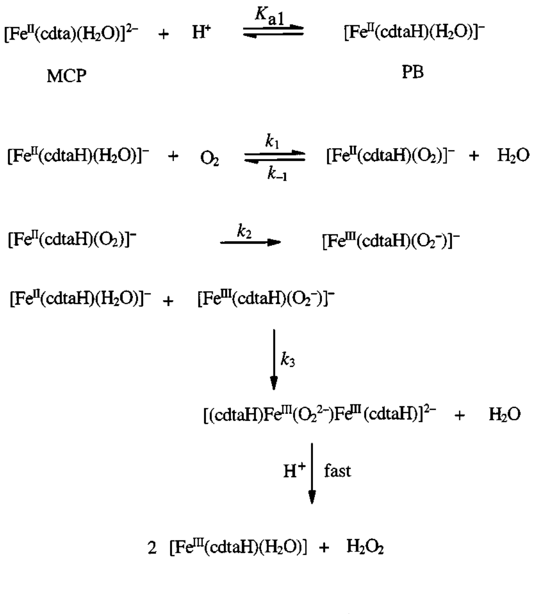
The extinction coefficient of [Fe^{II}(cdta)] at pH = 6 was found to be 743 M^{-1} cm^{-1} at 261 nm, which is much lower than for the corresponding [Fe^{II}(edta)] complex.[22] The extinction coefficient of [Fe^{III}(cdta) H$_2$O]$^-$ under similar conditions was found to be 7817 M^{-1} cm^{-1} and for [Fe^{III}(cdta) OH]$^{2-}$ to be 7644 M^{-1} cm^{-1}. From this data a final spectrum could be calculated. Due to our assumption that only the monomeric [Fe^{III}(cdta)] species is formed, the stoichiometry of the reaction is only between 2:1 and 3:1 (Fe/O$_2$). That leads to the result that the applied model could be too simple and that a small amount of free Fe^{II} (vide supra) or bridged species affect the final absorbance.

The rate constants clearly show that the substitution processes are very fast and are followed by the rate-determining electron-transfer processes. This is one of the reasons, why we were unable to detect the postulated intermediates as the superoxo or peroxo species, since they immediately react once they are formed. Furthermore, for the related [Fe(edta)] complex it was reported that the characteristic bands for the [Fe^{III}(edta)O$_2$]$^{2-}$ complex at 287 nm (ε = 6100 M^{-1} cm^{-1}) and 520 nm (ε = 530 M^{-1} cm^{-1}) show, in comparison to [Fe^{III}(edta)H$_2$O]$^-$ with ε = 9290 M^{-1} cm^{-1} (256 nm),[15,16,50] low extinction coefficients, such that the spectra of the intermediates would be hidden by the product spectrum. Such data are presently not available for the corresponding [Fe(cdta)] complexes.

The reaction with dioxygen proceeds via a fast substitution process on the [Fe^{II}(cdta)H$_2$O]$^{2-}$ complex. For this process only $\Delta H^{\#}$ and $\Delta S^{\#}$ could be determined, where $\Delta S^{\#}$ is strongly negative (see Table 1). Our assumption that this first fasty step is a substitution process is strongly supported by these activation parameters. They are rather similar to related substitution processes on corresponding Ru complexes.[51−53] The subsequent slower intramolecular electron-transfer process must be controlled by a reorganization barrier in order to convert [Fe^{II}−O$_2$] to [Fe^{III}−O$_2$$^-$]. This reaction is characterized by a significantly negative $\Delta V^{\#}$ value (Table 1), which must be related to the oxidation of Fe^{II} to Fe^{III} and the reduction of O$_2$ to O$_2$$^-$. The corresponding value for $\Delta S^{\#}$, however, is small and positive; this apparent discrepancy can be explained by the large experimental error of $\Delta S^{\#}$. Both these processes are expected to involve a significant decrease in partial molar volume and an increase in electrostriction.[54−56] The efficiency of the ligand substitution process is controlled by the nature of the [Fe^{II}(cdta)H$_2$O]$^{2-}$ complex, which on protonation produces a more labile [Fe^{II}(cdtaH)H$_2$O]$^-$ species. The latter accounts for the drastic increase in observed rate constant on decreasing the pH in the range from 5 to 3.

The reaction of the second [Fe^{II}(cdta)H$_2$O]$^{2-}$ species results in very similar concentration, pH, temperature and pressure dependencies, which are once again interpreted in terms of a rapid complex-formation reaction followed by a rate-determining electron-transfer process. This reaction is once again characterized by a significantly negative $\Delta V^{\#}$ value for the same reasons as outlined above. A comparison with the data reported in our last study,[22] indicates that the determined $\Delta V^{\#}$ values are very similar for both complexes, which confirms our assumption that they are due to electron-transfer processes. The very similar activation parameters observed for both oxidation processes indicate that a similar reorganization barrier must exist. When oxygen is used in excess, only one electron transfer reaction is observed since a peroxo-bridged complex cannot be formed under these conditions. This is in good agreement with the second reaction step observed in the presence of an excess of [Fe^{II}(cdta)]. Again the reaction is controlled by electron-transfer and the associated reorganization barrier. The additional fast process which was observed in an excess of [O_2] may be related to ring-opening of the cdta ligand when dioxygen enters the coordination sphere as mentioned above.

The results of this study have shown that a change in the chelate ligand has decelerated the fast substitution process, which could not be studied in detail in our recent paper.[22] The change in reactivity can be due to the different geometry of the here employed ligand,[23−30] which has its acetate arms in the trans position. This seems to lead to a less reactive binding of O_2. We are now able to suggest a detailed multistep mechanism for the reaction in the presence of an excess of [Fe^{II}(cdta)] as shown in Scheme 1. At high pH (pH = 6), mostly the nonprotonated form will react, whereas at low pH (pH = 4) the more reactive monoprotonated form will react. The mechanism in Scheme 1 is given for the more reactive protonated species



$$[Fe^{II}(cdta)(H_2O)]^{2-} + H^+ \xrightleftharpoons{K_{a1}} [Fe^{II}(cdtaH)(H_2O)]^-$$

$$[Fe^{II}(cdtaH)(H_2O)]^- + O_2 \xrightleftharpoons[k_{-1}]{k_1} [Fe^{II}(cdtaH)(O_2)]^- + H_2O$$

$$[Fe^{II}(cdtaH)(O_2)]^- \xrightarrow{k_2} [Fe^{III}(cdtaH)(O_2^-)]^-$$

$$[Fe^{II}(cdtaH)(H_2O)]^- + [Fe^{III}(cdtaH)(O_2^-)]^- \xrightarrow{k_3} [(cdtaH)Fe^{III}(O_2^{2-})Fe^{III}(cdtaH)]^{2-} + H_2O \xrightarrow[fast]{H^+} 2\ [Fe^{III}(cdtaH)(H_2O)] + H_2O_2$$

$$2\ [Fe^{II}(cdtaH)(H_2O)]^- + H_2O_2 \xrightarrow[fast]{H^+} 2\ [Fe^{III}(cdtaH)(H_2O)] + 2\ H_2O$$

Scheme 1. Multistep mechanism for the reaction of [Fe^{II}(cdta)] with molecular oxygen

Experimental Section

Materials: Chemicals of analytical reagent grade and ultrapure water were used throughout this study. [Fe^{II}(cdta)] was prepared in solution from $FeSO_4 \cdot 7\ H_2O$ and H_4(cdta). NaOH, $HClO_4$, and NaOAc were used to adjust the pH of the test solutions.[31] The ionic strength of the medium was adjusted with $NaClO_4$.

Preparation of Solutions: [Fe^{II}(cdta)] is extremely oxygen sensitive and is rapidly oxidized to [Fe^{III}(cdta)].[32] Test solutions were therefore prepared under the exclusion of oxygen as described in our earlier report.[22] The ionic strength was adjusted with $NaClO_4$ to 0.50 M for all solutions. Acetate buffer was employed for 3 < pH < 6 and Tris or MOPS buffer was used for 6 < pH < 7. Test measurements showed that the employed buffers had no significant effect on the observed kinetics. Test solutions were transferred to the stopped-flow unit by using gastight syringes.

Instrumentation: The kinetic experiments were performed on a Applied Photophysics SX.18MV stopped-flow unit, to which an on-line data acquisition system was connected. Rapid scan spectra were obtained with the Applied Photophysics Instrument by addition of obtained absorbance-time traces over the investigated wavelength range. Kinetic measurements at pressures up to 120 MPa were performed on a homemade high-pressure stopped-flow unit.[3,34] UV-Vis spectra were recorded on a Hewlett-Packard HP 8452A diode array spectrophotometer. The pH of the stock solutions was measured with the aid of a Mettler Delta 340 pH meter. The reference electrode was filled with NaCl instead of KCl in order to prevent precipitation of $KClO_4$. All kinetic traces were analyzed by using OLIS KINFIT (OLIS, Bogart, Georgia, USA) and Applied Photophysics Kinfit (Applied Photophysics Limited, Leatherhead, UK) software. For Global Analysis, spectra were recorded on the Applied Photophysics Instrument and fitted with the aid of the Applied Photophysics Software Package.

Supporting Information

Figure S1 reports pressure dependences obtained in the presence of an excess of [Fe^{II}(cdta)]. Table S1 reports second-order rate constants as a function of temperature. This material is available on the WWW under http://www.wiley-vch.de/home/eurjic or from the authors.

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