Inorg. Chem. **1990**, *29*, 1705–1711 **1705**

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Kinetics and Mechanism of the Autoxidation of Iron(II) Induced through Chelation by Ethylenediaminetetraacetate and Related Ligands

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Received October 16, 1989

The oxidation of $Fe^{II}(L)$ complexes by molecular oxygen is significantly enhanced by the presence of a chelating ligand L. The kinetics of this reaction was studied for L = ethylenediaminetetraacetate, *N*-(hydroxyethyl)ethylenediaminetriacetate, and diethylenetriaminepentaacetate as a function of $[Fe^{II}(L)]$, $[O_2]$, pH, temperature, and pressure. All the observed kinetic relationships can be accounted for in terms of a mechanism in which O_2 rapidly reacts with $Fe^{II}(L)$ to produce $Fe^{II}(L)O_2$, followed by three parallel reaction steps. These include spontaneous and acid-catalyzed electron transfer, as well as a reaction with $Fe^{II}(L)$ to produce $(L)Fe^{III}-O_2^{2-}-Fe^{III}(L)$. The results are discussed in reference to the available literature data for these and related oxidation processes.

Introduction

The substitution and redox reactions of edta (ethylenediaminetetraacetate) and related polyamino carboxylate complexes of Fe(II) and Fe(III) have increasingly received attention from researchers in a variety of areas in recent years. Our own interest lies in the kinetic and mechanistic behavior of such complexes, especially in terms of their possible catalytic role in the simultaneous removal of SO_2 and NO_x (i.e. NO and its oxidation products) from flue gases of coal-fired power plants.[1-8] The oxidation of polyamino carboxylate complexes of Fe(II) by O_2 is a complication in the catalytic cycle of such processes, since it produces nonreactive Fe(III) complexes.

The autoxidation of Fe(II) to Fe(III) is, in general, significantly enhanced by the presence of edta and related chelating ligands. The kinetic behavior of this process is also of fundamental importance in biochemical reactions. In this respect, it is appropriate to note that Dervan et al.[9-11] have accomplished sequence-specific recognition as well as cleavage of DNA with modified edta complexes of Fe(II), viz. bis(Fe^{II}–edta–distamycin)fumaramide and methidiumpropyl–edta–Fe^{II}, respectively. It was found that the latter complex cleaves DNA in the presence of O_2, presumably via the formation of hydroxy radicals. In addition, a number of mechanistic studies have been reported on the $Fe^{II/III}$(edta)/H_2O_2/HO_2^- system and for related polyamino carboxylate complexes.[12-18] These studies describe the catalytic effect of these complexes on the decomposition of H_2O_2 and dismutation of superoxide, some of them in view of model systems for nonheme-iron-containing oxygenases.[14]

The enhanced autoxidation of such Fe(II) complexes can be ascribed to a thermodynamic driving force as reflected by a more favorable redox potential and/or a kinetic labilization of one or more coordination sites on the metal center. In this respect it is important to note that the exact nature of the coordination geometry of, for instance, $Fe^{II/III}$(edta) in aqueous solution remains uncertain, notwithstanding a good number of indirect observations.[1,13,19-22] It is generally assumed that the coordination sphere includes at least one labile water molecule independent of whether the edta ligand occupies five or six coordination sites.[13,15,20,23,24] In this way, it is possible to account for the very rapid binding of NO to Fe^{II}(edta) to produce Fe^{II}(edta)NO.[1,25] It is especially this kinetic labilization effect that has interested us in recent years and encouraged us to perform a parallel investigation of the substitution reactions of the corresponding Ru(II/III) complexes.[26-28] Our earlier studies have, in general, demonstrated the usefulness of systematically varying the nature of the chelate ligand in order to influence the coordination geometry and the kinetic labilization of the coordinated water molecule(s).

We have now completed a detailed kinetic study of the oxidation of $Fe^{II}(L)$ by molecular oxygen for a series of polyamino carboxylate ligands, viz. L = edta, hedtra (*N*-(hydroxyethyl)ethylenediaminetriacetate), and dtpa (diethylenetriaminepentaacetate). These selected ligands enable a systematic variation of the coordination geometry around the Fe(II) center. The results of our study are presented in this report and discussed in reference to earlier work performed on the autoxidation of Fe^{II}(edta)[29-31] and related Fe(II) complexes.[32-36]

Experimental Section

Materials. Chemicals of analytical reagent grade and deionized water (Millipore) were used throughout this study. The various Fe(II) complexes were prepared in solution from $FeSO_4$ and $Na_2(H_2edta)$, Na_4(edta), Na_3(hedtra), and H_5dtpa. NaOH, H_2SO_4, acetic acid/sodium acetate, and Tris buffers[37] were used to control the pH of the test solu-

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tions. The ionic strength of the medium was adjusted with the aid of $NaClO_4$.

Preparation of Solutions. All the Fe(II) complexes investigated in this study are extremely oxygen-sensitive and are rapidly oxidized to the corresponding Fe(III) complexes. The Fe(II) complexes were therefore prepared under the exclusion of oxygen in the following way: a stock solution of the ligand at the appropriate acidity and ionic strength was degassed on a vacuum line and washed a few times with O_2-free argon, before a degassed solution of the Fe(II) salt was added. Such complex solutions remained stable for up to 6 h before a noticeable color change (monitored spectrophotometrically) indicated the partial formation of the corresponding Fe(III) complex. O_2-saturated solutions were prepared by bubbling O_2 or air through a thermostated (25 °C) solution for at least 15 min. This solution was diluted to the required O_2 concentration level, after which the actual concentration was measured with a WTW OXI 91 O_2 detector. All solutions were prepared freshly before the measurements. The ionic strength was adjusted to 0.5 M, and buffers were employed for pH > 3. Test measurements demonstrated that neither the acetate nor the Tris buffer had any significant effect on the observed kinetics. Test solutions were transferred with the aid of gastight syringes to the stopped-flow unit or spectrophotometer cells.

A slightly different procedure was adopted in the experiments where the O_2 concentration was varied in the case of significantly lower complex concentrations. Here both the Fe(II) and ligand solutions were saturated with O_2 or air by bubbling for 30 min at 25 °C. When the solutions were mixed in the stopped-flow instrument, complex formation occurred significantly faster than the subsequent oxidation reaction. In these cases the O_2 concentration was calculated from the Ostwald coefficients, temperature, and pressure.

Kinetic Measurements. The fast oxidation reactions were studied on a Durrum D 110 stopped-flow spectrophotometer connected to a Tektronix 5111A oscilloscope and an Apple II data acquisition and analysis system.[38] The pH of the reaction mixture was measured directly behind the stop-syringe with the aid of a Metrohm 632 pH meter equipped with a Sigma glass electrode. Kinetic measurement at pressures up to 100 MPa were performed on a homemade high-pressure stopped-flow unit.[39]

UV–vis spectra and slow kinetic measurements were performed in gastight cuvettes in the thermostated (±0.1 °C) cell compartment of a Shimadzu UV 250 spectrophotometer. Rapid-scan spectra were recorded with the aid of a Durrum D110 stopped-flow unit coupled to an OSMA (Spectroscopy Instruments GmbH, Gilsching, FRG) detector. This system can simultaneously record a signal and reference intensity scan from 250 to 550 nm in 16-ms intervals. These data can be directly converted into absorbance/wavelength and absorbance/time plots.

Results and Discussion

Preliminary Observations. A number of preliminary experiments were performed in order to check the feasibility of the kinetic procedures. All three investigated systems exhibit a maximum absorbance at 260 nm for $Fe^{II}(L)$ as well as for $Fe^{III}(L)$. The molar extinction coefficients of the $Fe^{III}(L)$ complexes are substantially higher than those of the corresponding Fe(II) complexes.[29] It follows that the oxidation of $Fe^{II}(L)$ to $Fe^{III}(L)$ is accompanied by a significant increase in absorbance in the range 260–420 nm, depending on the $Fe^{II}(L)$ concentration employed. Spectra recorded immediately after mixing in the stopped-flow instrument (using the described rapid-scan technique) exhibited no evidence for the formation of a possible intermediate or adduct species; i.e. the spectra observed immediately after mixing $Fe^{II}(L)$ and O_2 are similar to those of $Fe^{II}(L)$. Under pseudo-first-order conditions, i.e. at least a 10-fold excess of one of the components, the kinetic traces resulted in linear first-order plots over at least 3 half-lives of the reaction. The oxidation reactions are accompanied by a decrease in $[H^+]$, such that buffers had to be employed for kinetic measurements at pH > 3.0. These had no significant effect on the observed kinetics and showed no meaningful interference with the system.

Kinetic Measurements. The autoxidation reactions were first studied in the presence of an excess of $Fe^{II}(L)$ to ensure pseudo-first-order conditions. The reactions exhibit very characteristic pH dependences, as indicated for the three investigated systems in Figure 1. Both the edta and dtpa complexes exhibit a maximum rate constant at pH ≤ 3, although the observed acceleration is significantly enhanced in the case of the edta complex. In contrast, the hedtra complex exhibits no maximum and k_{obs} decreases with increasing $[H^+]$ at pH < 4.5. In all three cases a pH-independent region is reached at pH ≥ 5, where the reactivity order is Fe(hedtra) > Fe(edta) ≫ Fe(dtpa). This order changes to Fe(edta) ≫ Fe(hedtra) ≫ Fe(dtpa) at pH ≈ 3. The observed acceleration is even markedly stronger in the presence of an excess

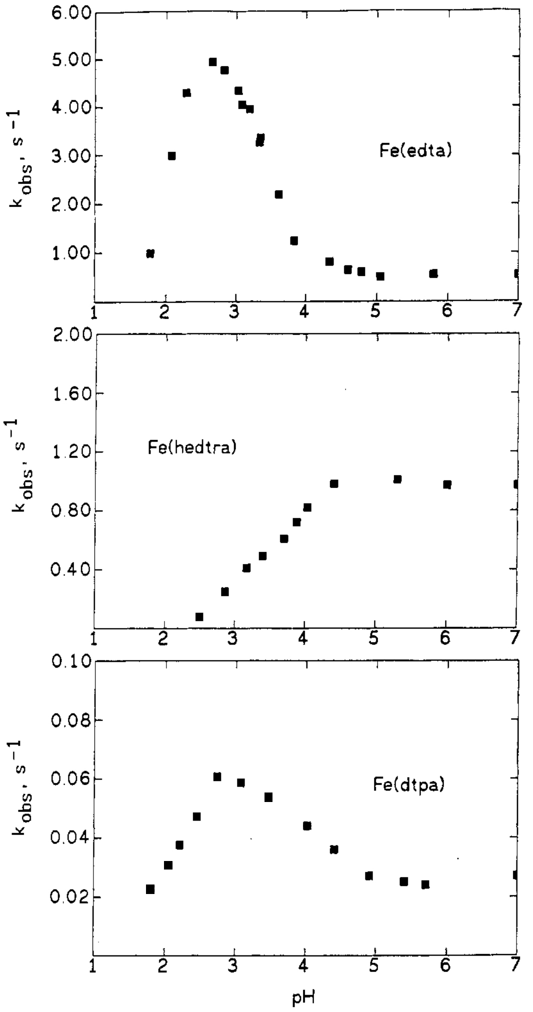

Figure 1. pH dependence of k_{obs} for the autoxidation of $Fe^{II}(L)$ in the presence of excess $Fe^{II}(L)$. $[Fe^{II}(L)] = 2.5 \times 10^{-3}$ M; $[O_2] = 1.25 \times 10^{-4}$ M; ionic strength = 0.5 M; temperature = 25 °C; [acetic acid/acetate buffer] = 0.05 M for 3 < pH < 6; [Tris buffer] = 0.05 M for pH = 7.

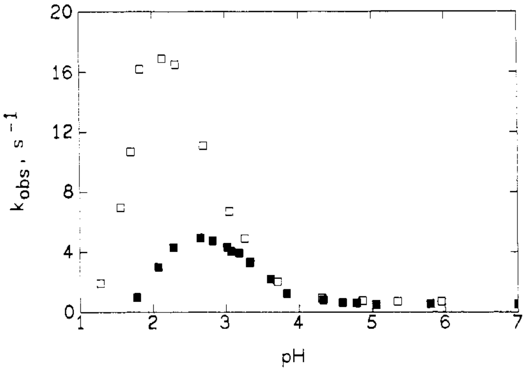

Figure 2. pH dependence of k_{obs} for the autoxidation of Fe^{II}(edta) as a function of excess edta concentration: (□) [Fe(II)]:[edta] = 1:1; (■) [Fe(II)]:[edta] = 1:20. [Fe(II)] = 2.5×10^{-3} M; $[O_2] = 1.25 \times 10^{-4}$ M; [edta] = 2.5×10^{-3} and 5×10^{-2} M; ionic strength = 0.5 M; temperature = 25 °C; [acetic acid/acetate buffer] = 0.05 M for 3 < pH < 6; [Tris buffer] = 0.05 M for pH = 7.

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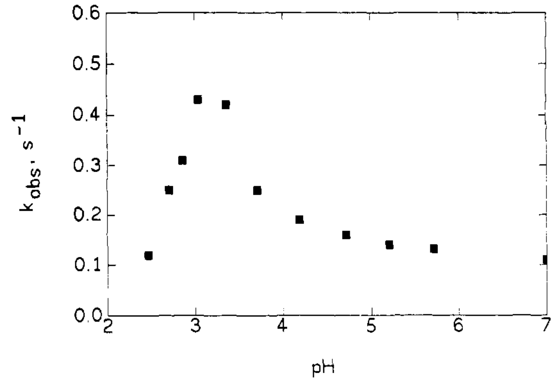

Figure 3. pH dependence of k_{obs} for the oxidation of Fe^{II}(edta) in the presence of excess O_2. [Fe(II)] = 2.5×10^{-5} M; [edta] = 5×10^{-5} M; $[O_2]$ = 2.5×10^{-4} M; ionic strength = 0.5 M; temperature = 25 °C; [acetic acid/acetate buffer] = 1×10^{-4} M for 4.5 < pH < 5.8; [Tris buffer] = 1×10^{-4} M for pH = 7.

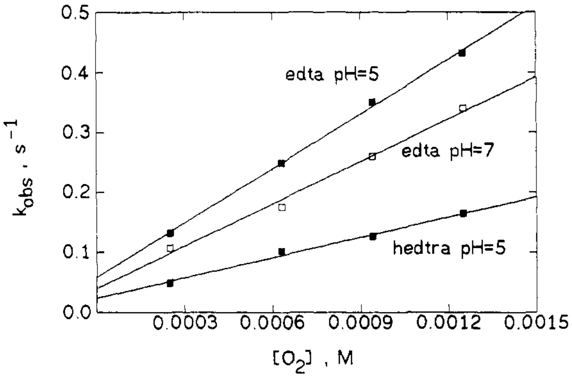

Figure 4. k_{obs} as a function of $[O_2]$ for the oxidation of Fe^{II}(L). [Fe(II)] = 2.5×10^{-5} M; [edta] = 5×10^{-5} M; ionic strength = 0.5 M; temperature = 25 °C; [acetic acid/acetate buffer] = 1×10^{-4} M for pH = 5; [Tris buffer] = 1×10^{-4} M for pH = 7.

Table I. Rate Data for the Autoxidation of Fe^{II}(L) in Aqueous Solution

Fe(L)[a]	pH	k_b, M^{-1} s^{-1}	k_a, s^{-1}
Fe(hedtra)[c]	5	112 ± 7	0.024 ± 0.006
Fe(edta)[c]	5	302 ± 8	0.058 ± 0.007
Fe(edta)[d]	7	231 ± 4	0.045 ± 0.011
Fe(L)[b]	**pH**	**k_c, M^{-1} s^{-1}**	**k_d, M^{-2} s^{-1}**
Fe(hedtra)[e]	5–7		(9.77 ± 0.06) × 10^4
Fe(edta)[e]	5	187 ± 3	(1.87 ± 0.03) × 10^4
Fe(edta)[f]	7		(1.51 ± 0.04) × 10^4
Fe(dtpa)[e]	5.5	8.6 ± 0.4	(1.55 ± 0.09) × 10^3

[a] Conditions: $[Fe^{II}(L)]$ = 2.5×10^{-5} M; ionic strength = 0.5 M; T = 25 °C; variation of the oxygen concentration. [b] Conditions: $[O_2]$ = 1.25×10^{-4} M; ionic strength = 0.5 M; T = 25 °C; variation of the complex concentration. [c] [Acetic acid/acetate buffer] = 1×10^{-4} M. [d] [Tris buffer] = 1×10^{-4} M. [e] [Acetic acid/acetate buffer] = 0.05 M. [f] [Tris buffer] = 0.05 M.

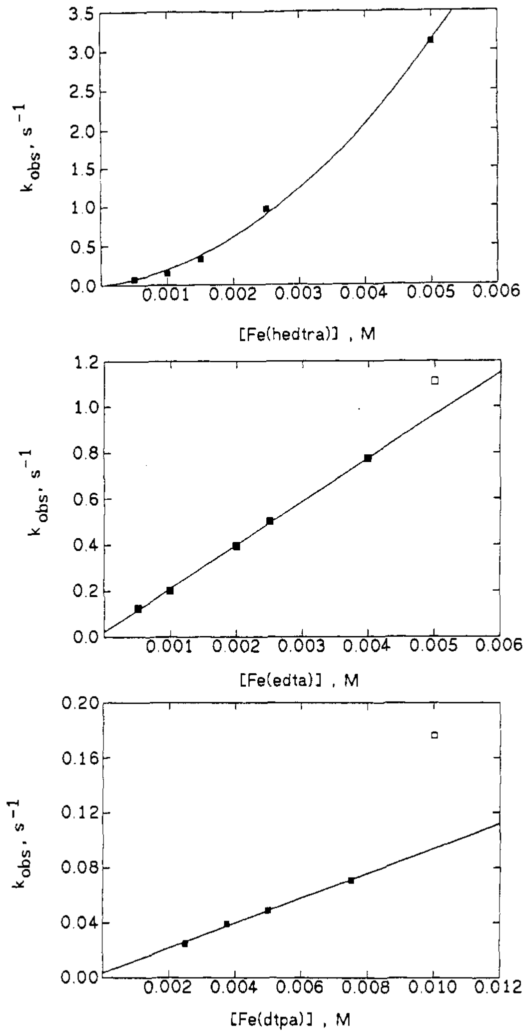

Figure 5. k_{obs} as function of $[Fe^{II}(L)]$ for the autoxidation of Fe^{II}(L) at low $[Fe^{II}(L)]$. $[O_2]$ = 1.25×10^{-4} M; ionic strength = 0.5 M; temperature = 25 °C; [acetic acid/acetate buffer] = 0.05 M for pH = 5.

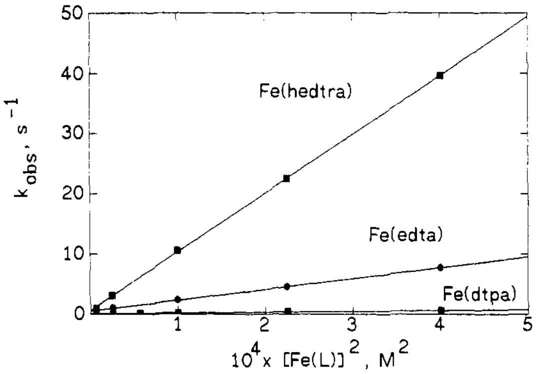

Figure 6. k_{obs} as function of $[Fe^{II}(L)]^2$ for the autoxidation of Fe^{II}(L) at high $[Fe^{II}(L)]$. $[O_2]$ = 1.25×10^{-4} M; ionic strength = 0.5 M; temperature = 25 °C; [acetic acid/acetate buffer] = 0.05 M for pH = 5.

of free L. This is demonstrated in Figure 2 for L = edta, where the maximum rate constant increases from 5 to 17 s^{-1} on going from a 1:1 to a 1:20 [Fe(II)]:[edta] mixture. A series of bell-shaped curves were obtained by gradually increasing the [edta], and only the extreme cases are reported in Figure 2. All the available experimental data are summarized in Table A of the supplementary material. Noteworthy is the fact that the same limiting rate constant is reached at pH ≥ 5 independent of the [edta]. Similar pH dependences were reported by other investigators for the edta complex.[13,29-31] In addition, a very similar dependence is found for the Fe^{II}(edta) system in the presence of an excess of O_2.[29] Our results under such conditions are summarized in Figure 3, from which it follows that the oxidation process is independent of pH at pH ≥ 5.

Concentration dependence studies were performed in the pH-independent range. The observed rate constant increases linearly with increasing $[O_2]$ (see Figure 4), which can be described by eq 1. The values of k_a and k_b are summarized in Table I. The

$$k_{obs} = k_a + k_b[O_2] \tag{1}$$

$[Fe^{II}(L)]$ dependence of k_{obs} is more complicated, as can be seen from the plots in Figure 5. k_{obs} increases linearly with increasing $[Fe^{II}(L)]$ at low $[Fe^{II}(L)]$ but increases exponentially at higher $[Fe^{II}(L)]$. All the kinetic data (Table B of the supplementary material) can be fitted by a quadratic function, eq 2, as demon-

$$\begin{aligned} k_{obs} &= k_c[Fe^{II}(L)] + k_d[Fe^{II}(L)]^2 \\ &= k_c[Fe^{II}(L)] \text{ at low } [Fe^{II}(L)] \end{aligned} \tag{2}$$

Table II. Rate Data and Activation Parameters for the Autoxidation of Fe^{II}(L)[a]

L	[Fe(L)], M	T, °C	P, MPa	k_{obsd},[b] s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}
edta	0.0025	13.5	0.1	0.225 ± 0.005			
		17.0		0.292 ± 0.006			
		22.0		0.428 ± 0.008			
		31.0		0.78 ± 0.01			
		38.0		1.17 ± 0.04			
		44.0		1.66 ± 0.05			
		49.0		2.37 ± 0.04	47.6 ± 0.6	-91 ± 2	
		25.0	5	0.550 ± 0.006			
			20	0.646 ± 0.007			
			25	0.668 ± 0.004			
			50	0.803 ± 0.011			
			75	0.96 ± 0.02			
			100	1.05 ± 0.02			-16.9 ± 1.2
	0.02	15.8	0.1	4.09 ± 0.05			
		20.0		5.39 ± 0.09			
		24.5		7.2 ± 0.5			
		32.0		9.4 ± 0.2			
		40.0		14.0 ± 0.2			
		46.0		17.6 ± 0.5	33.9 ± 1.4	-115 ± 4	
		25.0	5	6.76 ± 0.16			
			25	7.59 ± 0.33			
			50	8.15 ± 0.18			
			75	9.57 ± 0.14			
			95	10.9 ± 0.5			-12.7 ± 0.9
hedtra	0.0025	16.0	0.1	0.59 ± 0.02			
		21.5		0.69 ± 0.01			
		29.0		1.13 ± 0.02			
		33.0		1.27 ± 0.02			
		39.0		1.66 ± 0.03			
		43.0		2.09 ± 0.04			
		50.0		2.61 ± 0.04	33.1 ± 1.3	-135 ± 4	
		25.0	5	0.86 ± 0.01			
			25	0.95 ± 0.03			
			50	1.05 ± 0.01			
			75	1.18 ± 0.02			
			95	1.32 ± 0.05			-11.6 ± 1.2
dtpa	0.02	21.0	0.1	0.45 ± 0.01			
		25.0		0.62 ± 0.01			
		29.0		0.73 ± 0.01			
		37.5		1.22 ± 0.01			
		48.0		1.93 ± 0.05	39.4 ± 1.8	-117 ± 6	
		25.0	5	0.62 ± 0.005			
			25	0.67 ± 0.01			
			50	0.72 ± 0.01			
			75	0.76 ± 0.01			
			100	0.82 ± 0.01			-7.1 ± 0.4

[a] Conditions: [O$_2$] = 1.25 × 10^{-4} M; ionic strength = 0.5 M; pH = 5, acetic acid/acetate buffer. [b] Mean value of at least five kinetic runs.

strated in Figure 6. The values of k_c and k_d are also included in Table I.

Temperature- and pressure-dependence studies were also performed in the pH-independent range, in the presence of an excess of Fe^{II}(L). The latter concentration was selected such that either the linear or the quadratic [Fe^{II}(L)] dependence of k_{obs} was valid. The observed rate constants and corresponding activation paramaters are summarized in Table II. These parameters enable us to gain insight into the intimate nature of the autoxidation process, as will be seen in the following section.

Suggested Mechanism. No direct structural information is available for the studied Fe^{II}(L) complexes. Most of the indirect information has been reported for the edta complex. A pH titration of Fe^{II}(edta) in the range 3-11[1,13] reveals no evidence for any acid-base equilibrium. Thus, if Fe^{II}(edta) binds a water molecule, this does not hydrolyze in the mentioned pH range. Some evidence does exist for the partial protonation of the edta ligand at pH < 3, presumably in terms of a ring-opened species, and the following pK values have been reported: 3,0,[20] 2.8,[29] ≈2.5,[22] 2.06.[24] It is generally assumed that Fe^{II}(edta) binds a single rapidly exchanging H$_2$O molecule over the pH range 3-11.[1,13] This means that edta can occupy either five or six coordination sites for a coordination number of 6 or 7, respectively. It is quite possible that Fe^{II}(edta) has a structure similar to that of Fe^{III}(edta), which has a coordination number of 7 in the crystalline state,[40] one site being occupied by a water molecule. Recent NMR studies on aqueous solutions of Fe^{III}(edta) indicate that the structure in solution is the same as that in the crystalline state.[21,41-43] In the case of the Fe^{II}(hedtra) complex, the ligand is pentadentate and at least one water molecule will be present in the coordination sphere. The dtpa ligand is octadentate, such that the Fe^{II}(dtpa) complex is not expected to have a coordinated water molecule on the basis of the available structural data for Fe^{III}(dtpa).[20,43]

The pH dependences reported in Figures 1-3 can be interpreted in terms of a protonation of the ligand accompanied by dechelation and an acid-catalyzed oxidation process. The significant decrease in k_{obs} with increase [H$^+$] in the lower pH range observed in all cases can be assigned to ligand protonation and dechelation,[20,29] resulting in a less reactive metal center. The significant increase in k_{obs} with increasing [H$^+$] observed for the edta and dtpa complexes in the higher pH range can only be interpreted in terms of an acid-catalyzed autoxidation process. Our earlier work on the oxidation of Fe^{II}(edta) by HONO/NO$_2^-$ revealed a very

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similar effect.[1] Other investigators[13,29-31] also observed the significant increase in oxidation rate constant with increasing [H$^+$] for the Fe^{II}(edta) complex. This catalytic effect is most probably not due to the protonation of the edta or hedtra ligands, since it occurs in a too high pH range and, in addition, protonation of a ring-opened edta ligand results in a drastic decrease in substitution lability, as demonstrated for the corresponding Ru(III) complexes.[26-28] We therefore suggest that the oxidant binds directly to Fe^{II}(L), probably more rapidly for L = edta and hedtra, since both these complexes are expected to bind a labile water molecule.[13,30,31,44] This step is then followed by a spontaneous and/or an acid-catalyzed oxidation reaction as indicated in (3).[30,31]

$$\mathrm{Fe^{II}(L) + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{II}(L)O_2}$$

$$\mathrm{Fe^{II}(L)O_2 \xrightarrow{k_2} Fe^{III}(L) + O_2^-}$$

$$\mathrm{Fe^{II}(L)O_2 + H^+ \xrightarrow{k_3} Fe^{III}(L) + HO_2} \tag{3}$$

The spontaneous reaction must account for the limiting rate constants reached at pH ≥ 5. The formation of Fe^{II}(L)O$_2$ is expected to be fast when compared to the reaction with NO,[25] and k_1 could be as high as 10^7 M^{-1} s^{-1} for L = edta. Purmal et al.[30] reported values of $k_1 = 2.3 \times 10^3$ M^{-1} s^{-1} and $k_{-1} = 10^6$ s^{-1}, such that K_1 ($=k_1/k_{-1}$) = 2×10^{-3} M^{-1} for L = edta. This means that a relatively small fraction of the Fe^{II}(L) complex exists as the dioxygen complex. They[30] report a value of 10^{10} M^{-1} s^{-1} for k_3, such that K_1k_3 has a value of 2×10^7 M^{-2} s^{-1}. Rate constants reported in the literature for the uncatalyzed path, i.e. K_1k_2, are 6×10^2 and 2.7×10^2 M^{-1} s^{-1} for L = edta,[13,29] 1×10^2 M^{-1} s^{-1} for L = hedtra,[29] and 7 M^{-1} s^{-1} for L = dtpa.[29]

The rate law for the reaction sequence in (3), under conditions where [O$_2$] ≫ [Fe^{II}(L)], is given in (4). This equation reduces to (5) in the absence of the acid-catalyzed reaction path, i.e. at

$$k_{\mathrm{obs}} = \{k_2 + k_3[\mathrm{H^+}]\}K_1[\mathrm{O_2}] \tag{4}$$

$$k_{\mathrm{obs}} = k_2K_1[\mathrm{O_2}] \tag{5}$$

higher pH. Comparison with (1) reveals that $k_b = k_2K_1$, from which it follows that our values (Table I) are in good agreement with the literature values mentioned above.[13,29] The sequence of k_b (and k_c; see later) clearly reflects the influence of the coordination geometry on the ability to bind O$_2$, the lowest reactivity therefore being observed for the dtpa complex. The k_a term in (1) does not appear in either (4) or (5), and we will return to this aspect later. A plot of k_{obs} versus [H$^+$] at constant [O$_2$] for the data in Figure 3 over the range 3 < pH < 5 results in an intercept of 0.16 ± 0.02 s^{-1} and a slope of 628 ± 94 M^{-1} s^{-1}. With the aid of the data in Table I, we can predict an intercept of 0.13 s^{-1} for [O$_2$] = 2.5×10^{-4} M, which is in good agreement with the quoted value as well as the limiting rate constant observed in Figure 3 at high pH. The slope can be used to calculate k_3K_1 according to (4), which has a value of $(2.5 \pm 0.4) \times 10^6$ M^{-2} s^{-1}.

The corresponding rate laws under conditions where [Fe^{II}(L)] ≫ [O$_2$] are given in (6) and (7) for the presence and absence of

$$k_{\mathrm{obs}} = \{k_2 + k_3[\mathrm{H^+}]\}K_1[\mathrm{Fe^{II}(L)}] \tag{6}$$

$$k_{\mathrm{obs}} = k_2K_1[\mathrm{Fe^{II}(L)}] \tag{7}$$

an acid-catalyzed reaction path, respectively. Plots of k_{obs} versus [Fe^{II}(L)] are linear for L = edta and dtpa over a limited concentration range, and k_d in Table I represents the value of k_2K_1. The value obtained for the edta complex is in fair agreement with those reported above, whereas the value for the dtpa complex is in excellent agreement with the literature value.[29] Plots of k_{obs} versus [H$^+$] for L = edta and dtpa at constant [Fe^{II}(L)] are linear (Figure 7) over the range 3 ≤ pH < 5. From the slope and intercept it follows that k_2K_1 = 216 ± 22 M^{-1} s^{-1}, k_3K_1 = (2.4 ± 0.1) × 10^6 M^{-2} s^{-1} (L = edta), k_2K_1 = 8.4 ± 0.3 M^{-1} s^{-1}, and k_3K_1 = (3.6 ± 0.7) × 10^4 M^{-2} s^{-1} (L = dtpa). These values are in good agreement with k_c ($=k_2K_1$) in Table I and also with the value of k_3K_1 determined in the presence of an excess of O$_2$ for L = edta.

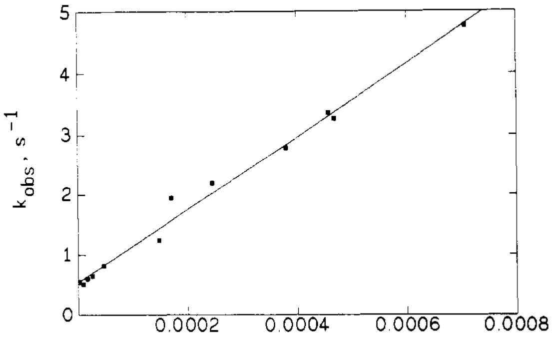

Figure 7. k_{obs} as function of [H$^+$] for the autoxidation of Fe^{II}(edta) in the pH range 4.6–3.1.

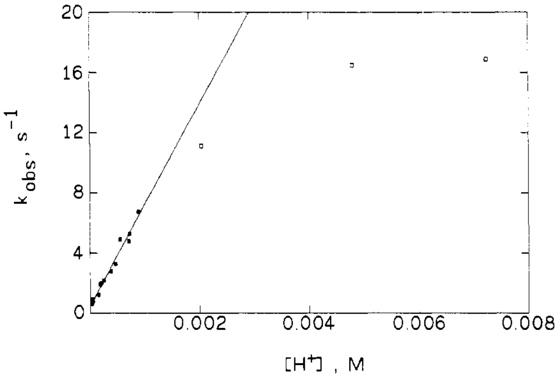

Figure 8. k_{obs} as function of [H$^+$] for the autoxidation of Fe^{II}(edta) in the presence of excess edta in the pH range 4.6–2.1.

The significantly higher oxidation rates observed in the presence of uncoordinated edta (Figure 2) could be due to a general-acid catalysis by a protonated species of the edta ligand. Such general-acid-catalyzed reactions have been reported for Fe^{III}(edta) complexes involving protonated buffer species.[13] However, plots similar to those in Figure 6 for the kinetic data at higher [edta] show that this effect cannot account for the very significant increase in k_{obs} with increasing [edta] reported in Figure 2, since k_3K_1 merely increases to (2.7 ± 0.1) × 10^6 M^{-2} s^{-1} for L = edta. Alternatively, the excess edta can stabilize the Fe^{II}(edta) species at lower pH by preventing protonation of the complex, which is accompanied by dechelation and a decrease in reactivity. This will also result in a shift in the bell-shaped curve to lower pH in the presence of a large excess of edta, as seen in Figure 2. The very significant increase in k_{obs} is then due to a more effective contribution from the acid-catalyzed reaction path (see (3)) under such conditions, made possible through the stabilization of the Fe^{II}(edta) complex by the excess edta in acidic medium. A plot of k_{obs} versus [H$^+$] for the data at pH > 2 under such conditions (Figure 8) clearly demonstrates the linear [H$^+$] dependence observed at lower [H$^+$] before (Figure 7), as well as a limiting rate at higher [H$^+$]. The latter could partly be due to the interference of the protonation/dechelation process mentioned above or could indicate the operation of a protonation equilibrium prior to the rate-determining electron-transfer step. Under such circumstances the acid-catalyzed electron-transfer reaction in (3) should be written as in (8), and (6) should be modified to (9). At low [H$^+$],

$$\mathrm{Fe^{II}(L)O_2 + H^+ \overset{K_4}{\rightleftharpoons} Fe^{II}(L)O_2H^+ \xrightarrow{k_5} Fe^{III}(L) + HO_2} \tag{8}$$

$$k_{\mathrm{obs}} = \left\{\frac{k_2 + k_5K_4[\mathrm{H^+}]}{1 + K_4[\mathrm{H^+}]}\right\}K_1[\mathrm{Fe^{II}(L)}] \tag{9}$$

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(9) simplifies to (6), with $k_3K_1 = k_5K_4K_1 = 2.7 \times 10^6$ M^{-2} s^{-1} from the data in Figure 8. At high [H$^+$], i.e. where $1 + K_4[\mathrm{H}^+] \approx K_4[\mathrm{H}^+]$, (9) simplifies to $k_{\mathrm{obs}} = k_5K_1[\mathrm{Fe^{II}(L)}]$, which is independent of [H$^+$] and can account for the limiting rate constant in Figure 8. It follows that $k_5K_1 = 6.8 \times 10^3$ M^{-1} s^{-1} and, combined with the quoted value for $k_5K_4K_1$, results in $K_4 = 4.0 \times 10^2$ M^{-1}. This in turn corresponds to a pK_a value of 2.6 for the protonated Fe$^{\mathrm{II}}$(L)O$_2$H$^+$ species, which is quite realistic, taking into account that the pK_a value for HO$_2$ is 4.7.[46] Furthermore, this suggestion also accounts for the fact that increased [edta] does not affect the observed kinetics at pH > 4, resulting in a common intercept for k_{obs} versus [H$^+$], viz. k_2K_1.

For the reactions with O$_2$ in excess, the reaction scheme in (3) can fully account for the observed kinetics. However, in the presence of an excess of Fe$^{\mathrm{II}}$(L), the additional reactions in (10)

$$\mathrm{Fe(L)O_2 + Fe^{II}(L) \xrightarrow{k_6} (L)Fe^{III}\text{–}O_2^{2-}\text{–}Fe^{III}(L)}$$

$$\mathrm{(L)Fe^{III}\text{–}O_2^{2-}\text{–}Fe^{III}(L) + H^+ \xrightarrow{fast} 2Fe^{III}(L) + H_2O_2} \qquad (10)$$

must be included to account for the square dependence on [Fe$^{\mathrm{II}}$(L)].[30,31] To complete the oxidation process, the O$_2^-$, HO$_2$, and H$_2$O$_2$ produced in reactions 3, 8, and 10 undergo subsequent reduction according to the reactions in (11). Values reported

$$\mathrm{Fe^{II}(L) + O_2^- \xrightarrow{k_7} Fe^{III}(L)O_2^{2-}}$$

$$\mathrm{Fe^{III}(L)O_2^{2-} + H^+ \xrightarrow{fast} Fe^{III}(L) + H_2O_2}$$

$$\mathrm{2Fe^{II}(L) + H_2O_2 \xrightarrow{H^+} 2Fe^{III}(L) + 2H_2O} \qquad (11)$$

in the literature for k_7 (L = edta) range between 2×10^6 and 1×10^7 M^{-1} s^{-1} at 25 °C.[13,15,47] Rate constants for the reaction of Fe$^{\mathrm{II}}$(L) with H$_2$O$_2$ are 2×10^4 M^{-1} s^{-1} (L = edta),[13,48] and 1.37×10^3 M^{-1} s^{-1} (L = dtpa).[12] Although it was originally thought that this reaction proceeds via the formation of OH$^\bullet$ radicals, recent work indicates that this reaction probably involves a two-electron reduction step and an Fe(IV) intermediate.[12,18]

The suggested formation of a μ-peroxo complex in (5) and a peroxo complex in (6) is based on work performed on related Co(II) and Fe(II) complexes.[36,49–52] Such species are only stable in basic medium and undergo acid-catalyzed aquation.[13,15–17] The formation of the μ-peroxo complex is, according to the results in Figure 5, of most significance for the hedtra complex, as reflected by almost only a square dependence on [Fe$^{\mathrm{II}}$(hedtra)]. This may be correlated with the ease of bridging this complex, which contains at least one coordinated water molecule. The absence of such a water molecule or the more crowded packing of the coordination sphere may account for the less importance of this reaction route in the case of the dtpa complex.

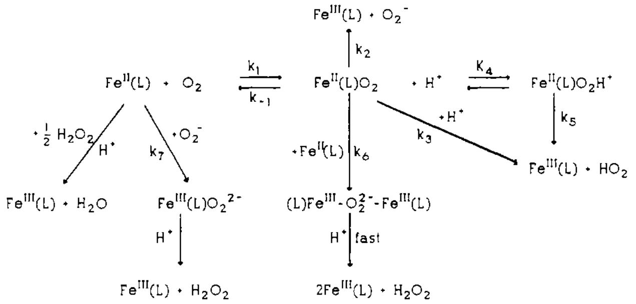
It follows that in the presence of an excess of Fe$^{\mathrm{II}}$(L), reactions 3 and 10 can account for the observed kinetics and the overall rate expression is given in (12), which in the absence of acid catalysis (high pH) reduces to (13). Equation 13 is in agreement

$$k_{\mathrm{obs}} = \{k_2 + k_3[\mathrm{H}^+] + k_6[\mathrm{Fe^{II}(L)}]\}K_1[\mathrm{Fe^{II}(L)}] \qquad (12)$$

$$k_{\mathrm{obs}} = \{k_2 + k_6[\mathrm{Fe^{II}(L)}]\}K_1[\mathrm{Fe^{II}(L)}] \qquad (13)$$

with eq 2, from which it follows that $k_6K_1 = k_d$ (see Table I for the values of k_d). The most effective reaction is observed for L = hedtra, in line with the expected trends outlined above. On the other hand, the edta and dtpa complexes exhibit the similar acid-catalyzed oxidation route and similar redox potentials, viz. 0.117 and 0.169 V, respectively.[12,33]

Scheme I



The reactions outlined in (3), (8), (10), and 11), suggested to account for the observed kinetic trends, are all forward processes and cannot account for the intercepts observed in the plots in Figure 4. The intercepts can be due to a reverse reaction of the product species Fe$^{\mathrm{III}}$(L) and O$_2^-$/H$_2$O$_2$ as outlined in (14).

$$\mathrm{Fe^{III}(L) + O_2^- \xrightarrow{k_8} Fe^{II}(L) + O_2}$$

$$\mathrm{Fe^{III}(L) + H_2O_2 \xrightarrow{k_9} Fe^{II}(L) + O_2^- + 2H^+} \qquad (14)$$

Typical values for the rate constants for L = edta are $k_8 = 2 \times 10^6$ M^{-1} s^{-1},[13] and k_9 = 250, 350, 500 M^{-1} s^{-1}.[13,15,53] These reactions are only of significance when an excess of O$_2$ is used, since then all Fe$^{\mathrm{II}}$(L) is oxidized by reactions 3 and 8 to Fe$^{\mathrm{III}}$(L). In the presence of an excess of Fe$^{\mathrm{II}}$(L), the reverse reactions in (14) do not contribute to the overall observed kinetics because the secondary reactions outlined in (11) are preferred under such conditions, since they are significantly faster than the reactions in (14).

The activation parameters reported in Table II are for k_2K_1 and k_6K_1, depending on the selected [Fe$^{\mathrm{II}}$(L)]. In the case of L = edta, the activation parameters are reported for k_2K_1 and k_6K_1 at the low and high concentrations, respectively. ΔH^* is significantly lower for k_6 than for k_2 (L = edta), indicating that the μ-peroxo complex formation is the favored reaction path under such conditions. For the interpretation of ΔS^* and ΔV^*, it should be noted that these are composite functions, viz. $\Delta V^* = \Delta V^*(k_2) + \Delta \bar{V}(K_1)$, where the latter term is the reaction volume for the formation of the dioxygen complex. It is reasonable to expect that $\Delta \bar{V}(K_1)$ will have a significantly negative value. On the basis of available data for addition and oxidative addition reactions,[54] along with a recently determined reaction volume for the formation of oxymyoglobin,[55] we predict that $\Delta \bar{V}(K_1) \approx -20$ cm^3 mol^{-1}. This would mean that both $\Delta V^*(k_2)$ and $\Delta V^*(k_6)$ have positive values, with $\Delta V^*(k_6) > \Delta V^*(k_2)$, which can be interpreted in terms of intrinsic and solvational volume changes during the electron-transfer process.[56] For instance, in the case of L = edta, electron transfer (k_2 in (3)) results in charge dilution, since the dioxygen complex carries an overall 2– charge. Such charge dilution will result in a decrease in electrostriction and a significant increase in volume ($\Delta V^*(k_2)$). During the redox process in (10), bond formation is followed by electron transfer, and the overall effect is a volume increase that depends on the nature of L. The largest $\Delta V^*(k_6)$ is observed for L = dtpa, i.e. where two Fe(dtpa)$^{3-}$ species are oxidized to Fe(dtpa)$^{2-}$, which will be accompanied by a significant decrease in electrostriction and an increase in volume. Although the reactions are too complex to draw detailed conclusions regarding other effects that may contribute to the overall negative ΔV^* and ΔS^* values reported in Table II, the data underline the importance of bond formation between Fe$^{\mathrm{II}}$(L) and

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O_2 during the overall redox process.

Concluding Remarks

The overall reaction scheme including all primary and secondary redox reactions can be summarized as shown in Scheme I. The rate constants of the secondary redox processes, i.e. the reactions with O_2^- and H_2O_2, are significantly larger than those of the primary reactions, such that the latter steps are rate-determining. There seems to be a fine balance between the forward reactions in Scheme I and the reverse reactions in (14). The produced O_2^- can either react with $Fe^{II}(L)$, as shown in (11), or react with $Fe^{III}(L)$, as shown in (14), depending on the concentration ratios employed. The literature values of k_7 and k_8 for L = edta are such that reaction 11 is preferred over reaction 14. A similar trend exists for the corresponding reactions with H_2O_2. In this way the secondary redox reactions lead to the formation of $Fe^{III}(L)$ such that the reverse reactions in (14) contribute little to the overall observed kinetics. This balance may depend on the pH of the medium, i.e. the possible protonation of O_2^- to HO_2, for which the pK_a value is 4.7.[46] In this respect it is interesting to note that recent studies on the redox behavior of HO_2 and O_2^- have reported a greater reactivity for HO_2 than for O_2^-.[57,58] It was suggested that HO_2 participates in an outer-sphere electron-transfer process, whereas O_2^- reacts via a hydrogen atom transfer process involving the amine ligand.

This investigation has revealed a very significant acid-catalyzed reaction path for the autoxidation reaction of $Fe^{II}(L)$ complexes, especially for L = edta. The role of this path can be enhanced by stabilizing the complex with excess edta at low pH. In this way, protonation of such complexes, accompanied by dechelation and a decrease in reactivity, is prevented in favor of acid-catalyzed autoxidation reactions. Such effects will be ligand specific and controlled by the intimate nature of the $Fe^{II}(L)O_2$ complex. Interestingly enough, a similar acid-catalyzed electron-transfer reaction was reported for the $Fe^{II}(edta)/HONO/NO_2^-$ system.[1] Although the nature of the protonated $Fe^{II}(L)O_2H^+$ species is unknown, it is logical to assume that its catalytic redox behavior is related to the formation of HO_2, i.e. protonated O_2^-.[57,58] The fine balance between acid-catalyzed dechelation and autoxidation as found for the Fe^{II}(edta) complex is most probably related to a number of dynamic equilibria involving ring opening of the multidentate ligand and solvent-exchange processes. In this respect, a seven-coordinate structure, as found for Fe^{III}(edta), in which six coordination sites are occupied by the edta ligand and the seventh is occupied by a solvent molecule, could account for all the observed kinetic results. From a comparison of the different investigated complexes, it follows that O_2 (and presumably also O_2^-) can interact with the d orbitals of transition metals, even in cases where the complexes are coordinatively saturated.[57]

The results of this study demonstrate that the oxygen sensitivity of Fe^{II}(edta) and Fe^{II}(hedtra) can be ascribed to the presence of a labile water molecule in the coordination sphere of these complexes. On the contrary, the Fe^{II}(dtpa) complex is significantly less oxygen sensitive and is not expected to have a coordinated water molecule. A labile solvent molecule enables rapid coordination of O_2 to produce $Fe^{II}(L)O_2$, which is followed by three parallel reaction steps outlined above (see Scheme I). The intermediate $Fe^{II}(L)O_2$ species can act as oxidation agents for species like sulfur(IV) oxides (viz. the catalytic role of such complexes in the simultaneous removal of SO_2 and NO_x[1-8]) or in the cleavage of DNA.[9-11]

Finally, the formation of μ-peroxo complexes is suggested to account for the square dependence on the $[Fe^{II}(L)]$ observed at higher $[Fe^{II}(L)]$. A similar result was reported[36] for iron(II) porphyrin and heme complexes,[59] where $Fe^{II}(P)O_2$ and $Fe^{II}(P)$ react to produce $(P)Fe^{III}(O_2^{2-})Fe^{III}(P)$.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Stiftung Volkswagenwerk, and the Max Buchner Forschungsstiftung.

Supplementary Material Available: Listings of k_{obs} as a function of pH for various $Fe^{II}(L)$ complexes (Table A), k_{obs} as a function of $[Fe^{II}(L)]$ for various L (Table B), and k_{obs} as a function of $[O_2]$ for Fe^{II}(edta) and Fe^{II}(hedtra) (Table C) (5 pages). Ordering information is given on any current masthead page.

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