Inorg. Chem. **2008**, *47*, 6314−6321

Inorganic Chemistry

Article

Influence of Fluoride on the Reversible Binding of NO by $[Fe^{II}(EDTA)(H_2O)]^{2-}$. Inhibition of Autoxidation of $[Fe^{II}(EDTA)(H_2O)]^{2-}$

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Received February 28, 2008

The promising BioDeNO$_x$ process for NO removal from gaseous effluents suffers from an unsolved problem that results from the oxygen sensitivity of the Fe^{II}−aminopolycarboxylate complexes used in the absorber unit to bind NO(g). The utilized $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex is extremely oxygen sensitive and easily oxidized to give a totally inactive $[Fe^{III}(EDTA)(H_2O)]^{-}$ species toward the binding of NO(g). We found that an in situ formed, less-oxygen-sensitive mixed-ligand complex, $[Fe^{II}(EDTA)(F)]^{3-}$, still reacts quantitatively with NO(g). The formation constant for the mixed ligand complex was determined spectrophotometrically. For $[Fe^{III}(EDTA)(F)]^{2-}$ we found $\log K_{MLF}^{F} = 1.7 \pm 0.1$. The $[Fe^{II}(EDTA)(F)]^{3-}$ complex has a smaller value of $\log K_{MLF}^{F} = 1.3 \pm 0.2$. The presence of fluoride does not affect the reversible binding of NO(g). Even over extended periods of time and fluoride concentrations of up to 1.0 M, the nitrosyl complex does not undergo any significant decomposition. The $[Fe^{III}(EDTA)(NO^{-})]^{2-}$ complex releases bound NO on passing nitrogen through the solution to form $[Fe^{II}(EDTA)(H_2O)]^{2-}$ almost completely. A reaction cycle is feasible in which fluoride inhibits the autoxidation of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ during the reversible binding of NO(g).

Introduction

Environmental problems that arise from industrial emissions are still a serious risk to global life. One specific problem concerns the so-called NO$_x$ effluents. They are generated during energy production from coal, oil, or gas. Poisonous NO$_x$ can be found in the flue gas of, for example, coal-fired power plants in concentrations of 500 to 2000 mg/m^3. The release of NO$_x$ during combustion cannot be prevented due to the presence of molecular nitrogen in the air/fuel mixtures. The nitrogen oxides produced are mainly NO and NO_2, of which NO is present in a higher concentration (95%) than NO_2.[1,2] These species are involved in acid-rain formation and photochemical processes involving smog and ozone.[3] Modern power plants are equipped with catalytic DeNO$_x$ systems to reduce the concentration of these hazardous gases. A promising technical process for the small scale removal of NO$_x$ is based on the BioDeNO$_x$ process (Figure 1). It consists of two main parts: one for the chemical absorption and the other for the biological reduction of nitrogen oxides (NO$_x$).

As a result of the poor solubility of NO(g) in water as compared to the high solubility of NO_2, a special technique has been developed to increase the solubility of NO(g) by several orders of magnitude. For this purpose, the BioDeNO$_x$ process uses an absorber unit, the so-called "scrubber", in which an aqueous $[Fe^{II}(EDTA)(H_2O)]^{2-}$ solution is used to absorb NO(g). This is in principle an efficient approach because a very stable and highly soluble $[Fe^{III}(EDTA)(NO^{-})]^{2-}$ complex is formed during this reaction.[4,5]

$$[Fe^{II}(EDTA)(H_2O)]^{2-} + NO \rightleftharpoons [Fe^{III}(EDTA)(NO^{-})]^{2-} + H_2O \quad (1)$$

In the second part of the process (biological reactor), bacteria are used to reduce NO to dinitrogen. The aqueous solution from the absorber containing $[Fe^{III}(EDTA)(NO^{-})]^{2-}$ is fed into the reactor where it is finally reduced to dinitrogen.

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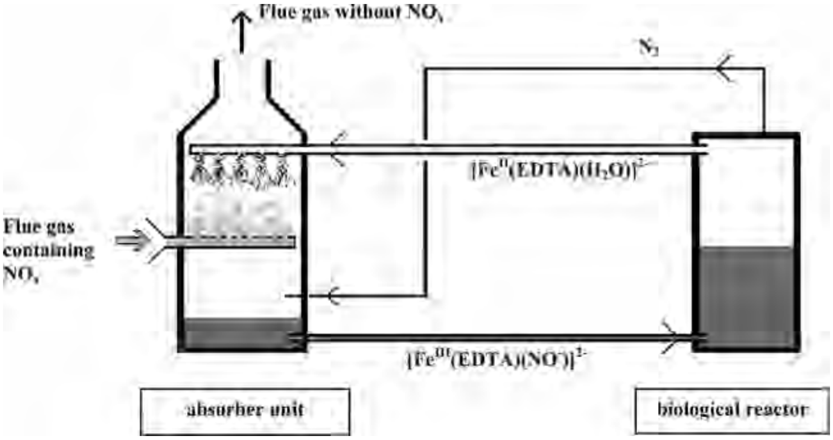

Figure 1. Principal components and operation mode of the BioDeNO$_x$ process.

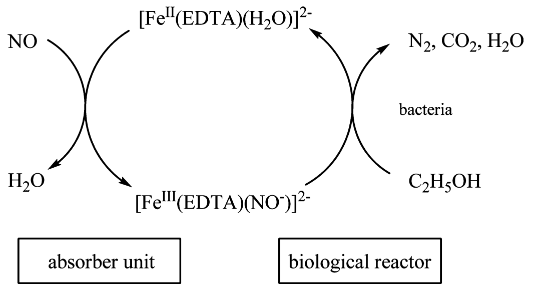

Figure 2. Reaction cycle in the BioDeNO$_x$ process.

Here, a reducing agent, for example ethanol, is required as shown in the following reaction.

$$6[\mathrm{Fe^{III}(EDTA)(NO^-)}]^{2-} + \mathrm{C_2H_5OH} + 3\mathrm{H_2O} \rightarrow 6[\mathrm{Fe^{II}(EDTA)(H_2O)}]^{2-} + 3\mathrm{N_2} + 2\mathrm{CO_2} \quad (2)$$

The regenerated, active [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ can be used again for NO uptake. Thus, the role of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ is to reversibly bind NO(g), for which the reaction cycle can be formulated as shown (Figure 2).

In the technical application of this process, a basic problem exists with the extreme oxygen sensitivity of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ because oxygen present in the flue gas can rapidly oxidize [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ to form [Fe^{III}(EDTA)(H$_2$O)]$^-$.

$$4[\mathrm{Fe^{II}(EDTA)(H_2O)}]^{2-} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 4[\mathrm{Fe^{III}(EDTA)(H_2O)}]^{-} + 4\mathrm{OH^-} \quad (3)$$

[Fe^{III}(EDTA)(H$_2$O)]$^-$ formed during oxidation is totally inactive toward the binding of NO(g) and so no further NO uptake is possible. Thus, the presence of oxygen leads to a tremendous loss of active Fe^{II} species. Thus, not the reduction of NO, but the reduction of [Fe^{III}(EDTA)(H$_2$O)]$^-$, was identified as the rate-limiting factor of the process.[6] The formed inactive [Fe^{III}(EDTA)(H$_2$O)]$^-$ can be reduced by dissimilatory iron-reducing bacteria (e.g., *Escherichia coli*) under the consumption of additional reducing agent (ethanol, glucose) to regenerate the active [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ complex. However, it was found that the presence of [Fe^{III}(EDTA)(NO$^-$)]$^{2-}$ and [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ leads to a significant decrease in cell growth of the iron-reducing bacteria, *Escherichia coli* FR-2, with an almost complete inhibition of cell growth at 3.7 mM [Fe^{III}(EDTA)(NO$^-$)]$^{2-}$.[7] Thus, in practice the active [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ species can only be recovered to a small degree, so that in some cases sulfide must be used as an additional reducing agent.[8] Consequently, the reformation of the active [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ complex increases the cost of the process considerably. Besides this, a further problem concerns the oxidation of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ to [Fe^{III}(EDTA)(H$_2$O)]$^-$ by dioxygen that involves the formation of radicals, which in turn cause irreversible damage to the EDTA chelate. Therefore, the oxidation of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ by dioxygen should be prevented in such a way that the reversible binding of NO is not affected.

This goal could in principle be achieved by displacing the labile aqua ligand on [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ by a halogenide anion, which could lead to a lowered oxygen sensitivity because of a hindered reaction with dioxygen. Only little is known about the behavior of mixed-ligand complexes of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$. The systems studied so far are mainly Fe^{III} chelate complexes.[9–11] The complex-formation constant for [Fe^{III}(EDTA)(H$_2$O)]$^-$ with fluoride ion was measured by Yuchi et al.[12] to be log $K_{MLF}{}^{F} = 1.7$. In general, it can be expected that the Fe^{II}−chelate will exhibit a smaller stability constant. The value of log $K_{MLNO}{}^{F} = 6.31$ for complex formation with NO suggests that the binding of NO should not be affected by the presence of fluoride. This means that fluoride in [Fe^{II}(EDTA)(F)]$^{3-}$ is most likely displaced entirely by NO but not by the weak nucleophile dioxygen. To investigate this suggestion, we studied the reactions of

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$[Fe^{II}(EDTA)(H_2O)]^{2-}$ with NO and dioxygen in the presence of different concentrations of fluoride. We performed combined experiments close to the experimental situation in the BioDeNO$_x$ process to clarify the influence of mixed-ligand complex formation with fluoride on the reversible binding of NO.

Experimental Section

Materials. Chemicals of analytical quality and doubly distilled water were used throughout this study. The $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex was prepared in solution from $Fe^{II}SO_4 \cdot 7H_2O$ (Fluka Chemika) and ethylenediaminetetraacetic acid H_4EDTA (Merck). $K[Fe^{III}(EDTA)(H_2O)] \cdot 1.5H_2O$ was synthesized as described elsewhere.[13] Potassium fluoride for the formation of the mixed-ligand complex was of ≥99% (Merck) purity. Acetic acid/acetate buffer was prepared from acetic acid (Fisher Chemicals) and potassium hydroxide (Fluka) and was used to control the pH of the solution. NO(g), delivered by Air−Liquide in a purity of at least 99.5 vol %, was cleaned from trace amounts of higher nitrogen oxides (e.g., N_2O_3 or NO_2) by passing it through an Ascarite II column (NaOH on silica gel, Sigma-Aldrich). For drying purposes, the gas was then passed through a phosphorus pentoxide column.

Preparation of the Solutions. All experiments with $[Fe^{II}(EDTA)(H_2O)]^{2-}$ were performed under strict exclusion of air. The buffer solutions were prepared as described in the literature.[5a] In the reported procedure, the buffer solutions containing the EDTA ligand were deaerated for extended periods (1 min per mL solution) with pure nitrogen before $Fe^{II}(SO)_4 \cdot 7H_2O$ was added for in situ preparation of the chelate complex. Through a gas inlet pipe, purified NO(g) and air ($p(O_2) = 254$ mbar) were directly bubbled through the sample solutions. A gas pressure regulator preserved a constant positive operating pressure of 200 mbar throughout the gas inlet experiments. The samples are placed in special cuvettes with a directly attached round flask and a separate nitrogen inlet to keep the solutions under an inert gas atmosphere before, during and after the gas exposures. A subsequent treatment with inert gas was performed to remove unreacted oxygen and NO from the sample solutions.[5b]

Measurements. UV−vis spectra were recorded on Cary 1E and 5E spectrophotometers from Varian. Because of the extreme oxygen-sensitivity of the $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex, quartz cuvettes (2 and 10 mm optical path length) with directly attached 50 mL round flasks with gas inlets were employed. pH measurements were performed on a Metrohm 713 pH meter with the aid of a Metrohm pH electrode filled with 3 M KCl.

Results and Discussion

The investigated $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex reacts rapidly with dioxygen to form $[Fe^{III}(EDTA)(H_2O)]^{-}$, as has been studied in detail before.[14] The observed rate constants show a linear dependence on the oxygen concentration:

$$k_{obs} = k_a + k_b[O_2] \text{ with } k_a = 0.058 \pm 0.007 \text{ s}^{-1} \text{ and } k_b = 302 \pm 8 \text{ M}^{-1}\text{s}^{-1} \text{ at 298 K} \quad (4)$$

More complicated is the dependence of k_{obs} on the complex concentration. At low $[Fe^{II}(EDTA)(H_2O)]^{2-}$ concentrations, a linear dependence of k_{obs} on the complex concentration was found. At higher concentrations of $[Fe^{II}(EDTA)(H_2O)]^{2-}$, a quadratic dependence was observed.

$$k_{obs} = k_c[Fe^{II}\text{-EDTA}] + k_d[Fe^{II}\text{-EDTA}]^2 \text{ with } k_c = 187 \pm 3 \text{ M}^{-1}\text{s}^{-1} \text{ and } k_d = (1.87 \pm 0.03)10^4 \text{ M}^{-2}\text{s}^{-1} \text{ at 298 K} \quad (5)$$

To understand the oxidation mechanism, the solution structure of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ is of great importance. In the case of Fe^{III}, the solid-state structure showed that the EDTA ligand is bound with all six donor atoms to the metal center, and a water molecule occupies the seventh coordination site.[15] Several indications for a similar structure in the aqueous solution were obtained from NMR and Raman measurements.[16–20] X-ray measurements on $[Fe^{II}(EDTA)(H_2O)]^{2-}$ show a solid-state structure with a 6-fold coordinated EDTA ligand and a water molecule in the seventh position.[21,22] It is generally assumed that the dissolved $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex exists in solution as a heptacoordinate species with hexadentate EDTA and a bound water molecule that exhibits fast exchange kinetics.[23] Indeed, our ^1H and ^{13}C NMR experiments and variable-temperature and -pressure ^{17}O NMR measurements proved the existence of the proposed solution structure and fast water exchange kinetics, with $k_{ex} = (2.7 \pm 0.1) \times 10^6$ s^{-1} at 298.2 K.[24] The activation parameters for the water exchange process on $[Fe^{II}(EDTA)(H_2O)]^{2-}$ strongly support a dissociative interchange (I_d) mechanism. These kinetic and structural findings substantiate earlier mechanistic suggestions that the first step in the oxidation process is the displacement of the labile water ligand in the seventh coordination site by elementary dioxygen.[25]

$$[Fe^{II}(EDTA)(H_2O)]^{2-} + O_2 \rightleftharpoons [Fe^{II}(EDTA)(O_2)]^{2-} + H_2O \quad (6)$$

This is followed by an inner-sphere electron-transfer reaction, leading to the superoxo species.

$$[Fe^{II}(EDTA)(O_2)]^{2-} \rightarrow [Fe^{III}(EDTA)(O_2^{-})]^{2-} \quad (7)$$

The superoxo species binds a second $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex and substitutes the water ligand followed by electron transfer to form a peroxo-bridged $[Fe^{III}(EDTA)(H_2O)]^{-}$ dimer.

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$$[Fe^{III}(EDTA)(O_2^{-})]^{2-} + [Fe^{II}(EDTA)(H_2O)]^{2-} \rightarrow [(EDTA)Fe^{III}\text{-}(\mu\text{-}O_2^{2-})\text{-}Fe^{III}(EDTA)]^{4-} + H_2O \quad (8)$$

The dimer undergoes a fast decomposition reaction leading to monomeric $[Fe^{III}(EDTA)(H_2O)]^-$ and H_2O_2, which immediately reacts with $[Fe^{II}(EDTA)(H_2O)]^{2-}$ to produce $[Fe^{III}(EDTA)(H_2O)]^-$.

$$[(EDTA)Fe^{III}\text{-}(\mu\text{-}O_2^{2-})\text{-}Fe^{III}(EDTA)]^{4-} + H^+ + H_2O \rightarrow 2[Fe^{III}(EDTA)(H_2O)]^- + H_2O_2 \quad (9)$$

It is our objective to hinder the autoxidation reaction by replacing the labile water molecule by a ligand that cannot be substituted that easily by the dioxygen molecule. In this way, the formation of the dioxygen complex as well as the formation of the dimer will be affected. UV−vis spectroscopy was employed to determine the extent of autoxidation. The absorbance of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ differs significantly from that of $[Fe^{III}(EDTA)(H_2O)]^-$ at a wavelength of 255 nm. In Figure 3, it is shown that oxidation (**1** → **5**) leads to a notable increase in absorbance. A comparison of the in situ oxidized $[Fe^{II}(EDTA)(H_2O)]^{2-}$ spectrum (left) with that of synthesized $K[Fe^{III}(EDTA)(H_2O)]\cdot 1.5H_2O$ (right) shows a similar absorbance after passing air for 2 min through the solution (Figure 3, trace 2). This comparison clearly shows that oxidation of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ is complete within the 2 min contact period with oxygen, and further contact with oxygen does not lead to significant spectral changes. The measured value of $\epsilon = 8504\ M^{-1}\ cm^{-1}$ at 255 nm is in excellent agreement with that reported by Zang et al. ($\epsilon = 8500\ M^{-1}\ cm^{-1}$).[26]

To decrease the oxygen sensitivity of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ and prevent the formation of $[Fe^{III}(EDTA)(H_2O)]^-$, we used fluoride to substitute the labile coordinated water. Fluoride seems to be a promising candidate for this purpose. Potentiometric measurements for mixed-ligand complex-formation of $[Fe^{III}(EDTA)(H_2O)]^-$ with fluoride reported by Yuchi et al. revealed a value of $\log K_{MLF}^{F} = 1.7$, which is significantly larger than for other halides.[12] Nothing was known for the $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex, and we therefore measured the formation constant for both cases.

In Figure 4, plots of the absorbance at 255 nm (A_{255nm}) of $[Fe^{III}(EDTA)(H_2O)]^-$ (left) and $[Fe^{II}(EDTA)(H_2O)]^{2-}$ (right) versus fluoride concentration are shown. The measured absorbances (A_x) at variable fluoride concentrations, $[F^-]$, were fitted according to eq 1, where the parameters A_0 and A_∞ represent the absorbances at zero and infinite fluoride concentration, respectively, and K_{MLF}^{F} is the formation constant of the fluoride complex (Schemes 1 and 2, horizontal reactions).

$$A_x = A_0 + \frac{(A_\infty - A_0)K_{MLF}^{F}[F^-]}{(1 + K_{MLF}^{F}[F^-])} \quad (10)$$

The fits yielded a value for the formation constant $\log K_{MLF}^{F} = 1.7 \pm 0.1$ for $[Fe^{III}(EDTA)(F)]^{2-}$, which is in excellent agreement with that reported in the potentiometric measurements by Yuchi et al.[12] We also applied this

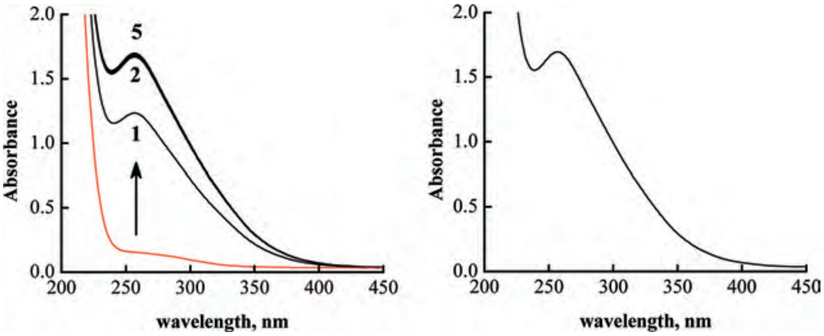


Figure 3. Left: UV−vis spectra of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ before (—) and after oxidation (**1**−**5**; 1−5 min oxygen contact period). Right: UV−vis spectrum of dissolved $K[Fe^{III}(EDTA)(H_2O)]\cdot 1.5H_2O$. Experimental conditions: 1 mM $FeSO_4\cdot 7H_2O$ and 1.25 mM EDTA (left); 1 mM $K[Fe^{III}(EDTA)(H_2O)]\cdot 1.5H_2O$ (right); 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 2 mm optical path length.

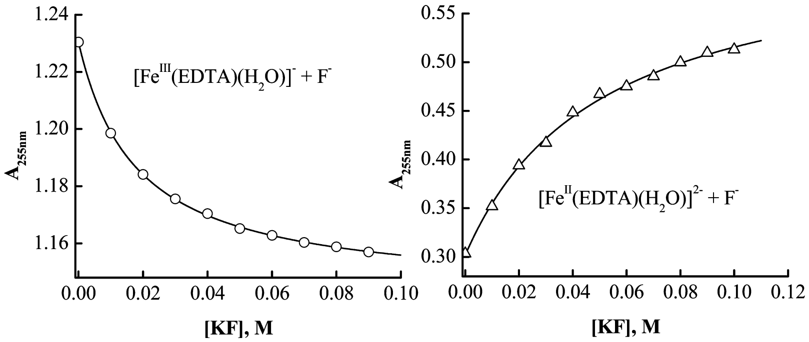
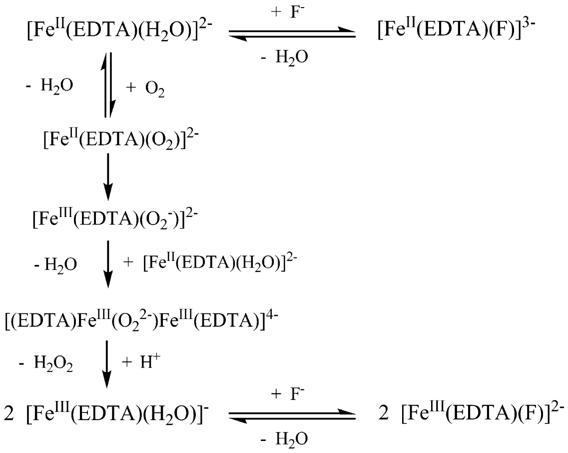
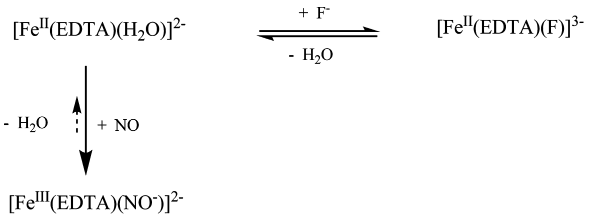


Figure 4. Absorbance change at 255 nm for $[Fe^{III}(EDTA)(H_2O)]^-$ as a function of fluoride concentration (○, left) and corresponding spectral changes for the $[Fe^{II}(EDTA)(H_2O)]^{2-}$ complex (Δ, right). The solid line represents a nonlinear fit of the data with eq 1. Experimental conditions: 0.75 mM $K[Fe^{III}(EDTA)(H_2O)]\cdot 1.5\ H_2O$ (left); 0.75 mM $FeSO_4\cdot 7H_2O$ and 1 mM EDTA (right); 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 10 mm optical path length.

Scheme 1. Reaction Pathways for the Oxidation of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ by Dioxygen in the Presence of Fluoride



Scheme 2. Reaction of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ to $[Fe^{III}(EDTA)(NO^-)]^{2-}$ in the Presence of Fluoride



technique to determine the mixed-ligand, complex-formation constant for $[Fe^{II}(EDTA)(H_2O)]^{2-}$ with fluoride. As expected, the value of the formation constant $\log K_{MLF}{}^{F} = 1.3 \pm 0.2$ is smaller than in the case of the $[Fe^{III}(EDTA)(H_2O)]^-$ complex. This seems reasonable because the total charge on the complex changes from -1 to -2, which causes a hindered attack of the negatively charged nucleophile F^- and weaker bonding to the Fe^{II} center as compared to the Fe^{III} complex. However, a consequence of the low formation constant for the mixed complex is the requirement of high concentrations of fluoride to obtain high concentrations of $[Fe^{II}(EDTA)(F)]^{3-}$ in aqueous solution. On the other hand, weak binding of fluoride will be helpful for the binding of NO. It follows that the reaction with dioxygen needs to be significantly inhibited to make fluoride protection efficient. Therefore, we performed the oxidation experiments at different fluoride concentrations.

In Figure 5, the recorded spectra show clearly that the more fluoride present in solution, the less $[Fe^{III}(EDTA)(H_2O)]^-$ is formed. We account for these observations in terms of the increased formation of the less oxygen-sensitive $[Fe^{II}(EDTA)(F)]^{3-}$ complex with increasing fluoride concentration (Scheme 1, upper horizontal reaction). The oxidized species, $[Fe^{III}(EDTA)(H_2O)]^-$, is able to react with fluoride to give the mixed-ligand complex $[Fe^{III}(EDTA)(F)]^{2-}$. As a consequence, the two equilibria between the mixed-ligand complexes are coupled through the autoxidation process (Scheme 1, vertical reaction).

Fluoride inhibition of the autoxidation reaction will only be useful if a nonhindered reaction of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ with NO will still occur in the presence of fluoride. For practical applications, the oxidation of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ should be inhibited as much as possible, whereas the nitrosylation reaction should be affected as little as possible in the presence of fluoride. We found that even high concentrations of fluoride did not lead to a decreased formation of the nitrosyl complex. In Figure 6, it can be seen that even at concentrations of up to 1.0 M potassium fluoride, the $[Fe^{III}(EDTA)(NO^-)]^{2-}$ complex is still formed completely.

The calculated values for ϵ are summarized in Table 1. A comparison with those given as a reference indicate that even high concentrations of fluoride do not have a significant influence on the formation of $[Fe^{III}(EDTA)(NO^-)]^{2-}$.

We account for this observation in terms of the large formation constant for the $[Fe^{III}(EDTA)(NO^-)]^{2-}$ complex. This value was measured by Hishinuma et al. and Schneppensieper et al. to be $K_{MLNO}{}^{F} = 1 \times 10^6$ and $(2.1 \pm 0.5) \times 10^6$ M^{-1}, respectively.[27,28] Theoretical studies on the binding of NO and O_2 in $\{FeNO\}^7$ and $\{FeO_2\}^8$ complexes, respectively, also showed that although NO is more difficult to reduce, the resulting NO^- species forms a more-stable bond to Fe^{III} than $O_2{}^-$ because of different bonding interactions. Only one bonding interaction in the superoxo species compared to σ- and π-type interactions in the $Fe^{III}-NO^-$ bond makes O_2 binding less favorable.[29]

A combined experiment clearly showed the effect of lowered oxygen sensitivity on protecting $[Fe^{II}(EDTA)(H_2O)]^{2-}$ through complexation by fluoride. We first performed the reaction of the mixed-ligand complex with NO, and then repeated it with samples that had been in contact with dioxygen prior to the reaction with NO. In the latter case, only the nonoxidized $[Fe^{II}(EDTA)(H_2O)]^{2-}$ can then react with NO to give $[Fe^{III}(EDTA)(NO^-)]^{2-}$.

A comparison of the nitrosyl product spectra, after different contact times with oxygen (0, 1, 2 min) as a function of fluoride concentration, clearly shows an increase in the degree of nitrosylation with increasing fluoride concentration (Figure 7). To prove the suggestion that lowered oxygen sensitivity is responsible for the increased formation of the nitrosyl complex at higher fluoride concentrations, we plotted the measured absorbances at characteristic wavelengths for the oxidation reaction (A_{255nm}) and for the formation of the nitrosyl complex (A_{435nm}) as a function of fluoride concentration (Figure 8). Lower absorbances at 255 nm (less oxidation) are found along with higher absorbances at 435 nm (increased NO formation) with increasing fluoride concentration. The relationship between reduced oxidation and increased nitrosyl complex formation is obvious.

A closer look at the observed absorbances for the characteristic nitrosyl complex band at 435 nm shows a substantially diminished oxidation at high fluoride concentrations. This is an inevitable consequence of the small formation constant for the mixed ligand complex [Fe^{II}(ED-

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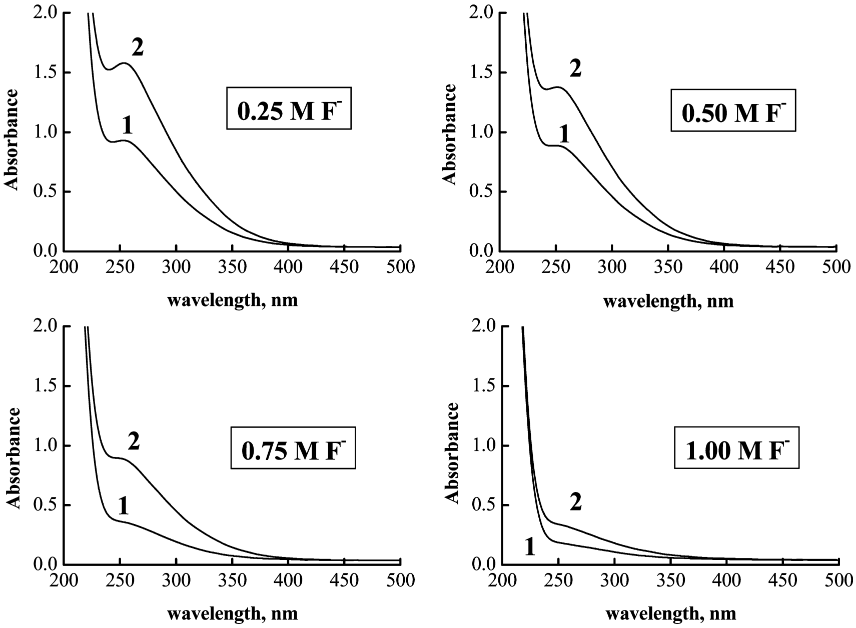


Figure 5. Spectra of a $[Fe^{II}(EDTA)(H_2O)]^{2-}$ solution recorded after 1 min (**1**) and 2 min (**2**) contact with oxygen at different fluoride concentrations. The absorbance at 255 nm, a sensitive probe for the degree of oxidation, shows less autoxidation at higher fluoride concentrations. Experimental conditions: 1 mM $FeSO_4 \cdot 7H_2O$; 1.25 mM EDTA; 0.25−1.0 M potassium fluoride; 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 2 mm optical path length.

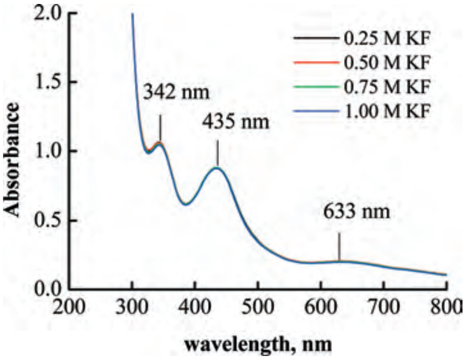


Figure 6. Spectra of $[Fe^{II}(EDTA)(H_2O)]^{2-}$ recorded at different fluoride concentrations following 1 min contact with NO gas. An identical absorbance was found for each fluoride concentration at the characteristic nitrosyl complex bands. Experimental conditions: 1 mM $FeSO_4 \cdot 7H_2O$; 1.25 mM EDTA; 0.25 − 1.0 M potassium fluoride; 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 10 mm optical path length.

Table 1. Molar Extinctions Coefficients of the $[Fe^{III}(EDTA)(NO^-)]^{2-}$ Complex for Different Concentrations of Potassium Fluoride

	ϵ [$M^{-1}cm^{-1}$]					
wavelength, nm	ref 5	0 M F^-	0.25 M F−	0.5 M F^-	0.75 M F^-	1.0 M F−
342	1080	1031	1065	1064	1052	1045
435	820	809	881	877	881	876
633	130	190	202	207	202	198

TA)(F)]$^{3-}$ (Table 2). High concentrations of fluoride are required to drive the equilibrium to the product side. However, at a concentration of 1 M F^- the oxidation rate can be reduced up to 57%, leading to an increase in nitrosyl complex formation of up to 43%. Under the same conditions, but in the absence of fluoride, $[Fe^{II}(EDTA)(H_2O)]^{2-}$ is completely oxidized, and no nitrosyl complex formation occurs at all.

Mechanistically, it seems reasonable to assume that nitrosylation and oxidation proceeds via substitution of the labile water molecule of the aqua complex in equilibrium with the ternary fluoride complex. The water exchange data for $[Fe^{II}(EDTA)(H_2O)]^{2-}$ suggest that these substitution reactions will follow a dissociative interchange (I_d) mechanism.[24] The equilibrium with the NO complex needs to be considered to lie nearly entirely on the product side, due to the large formation constant for the nitrosyl complex (Scheme 3, left). Consequently, the connected equilibrium with the fluoride complex will be shifted to the reactant side, that is, to the aqua complex. This explains the observed complete formation of the nitrosyl complex at different fluoride concentrations. On the other hand, the less-favored formation of the dioxygen complex will not shift the pre-equilibrium to a comparable extent (Scheme 3, right).

With this model, both observations, namely, complete conversion to the nitrosyl complex and inhibition of autoxidation, can be successfully explained. However, the possible direct substitution of fluoride by NO or O_2 cannot be entirely ruled out. Thus, at this stage we do not know whether the lower concentration of the aqua complex or a hindered substitution of fluoride by dioxygen, is the criterion that is responsible for the observed inhibition of the oxidation process. Important is that a less-oxygen-sensitive species is formed in situ that shows an unrestricted reaction toward NO(g). Nevertheless, to work efficiently in the BioDeNO$_x$ process, the effect of fluoride on the binding and release kinetics of NO needs to be evaluated. Furthermore, it must be assured that no significant decomposition of the nitrosyl complex is caused by the application of fluoride. Thus, we performed repetitive binding and release experiments of NO by $[Fe^{II}(EDTA)(H_2O)]^{2-}$ in the presence of fluoride, and observed the formation of a stable nitrosyl complex over extended periods of time.

In Figure 9, the results of an experiment are shown that monitor to some extent the reactions of the BioDeNO$_x$ process. The absorption catalyst $[Fe^{II}(EDTA)(H_2O)]^{2-}$ is

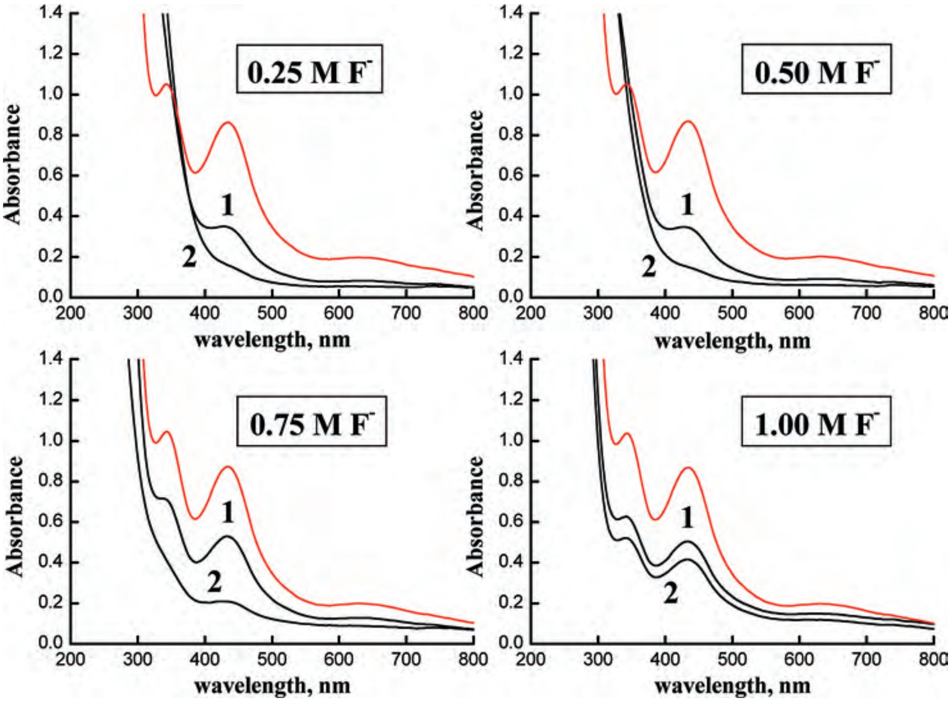


Figure 7. Spectra of $[Fe^{III}(EDTA)(NO^-)]^{2-}$ recorded for different fluoride concentrations under oxygen-free conditions (—) and after 1 min (**1**) and 2 min (**2**) contact with oxygen. Experimental conditions: 1 mM $FeSO_4 \cdot 7H_2O$; 1.25 mM EDTA; 0.25−1.0 M potassium fluoride; 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 10 mm optical path length.

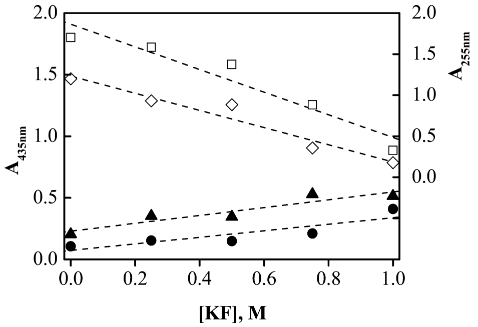
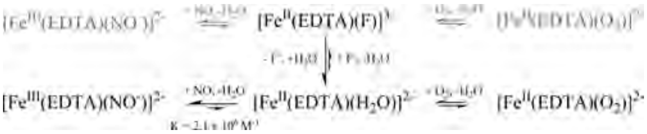


Figure 8. Comparison of the observed absorbances at the characteristic wavelength for the formation of $[Fe^{III}(EDTA)(H_2O)]^-$ (A_{255nm}), after 1 min (◇) and 2 min (□), and the formation of the nitrosyl complex (A_{435nm}), after 1 min (Δ) and 2 min (●) contact with oxygen. Experimental conditions: 1 mM $FeSO_4 \cdot 7H_2O$; 1.25 mM EDTA; 0.0−1.0 M potassium fluoride; 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 10 mm optical path length.

Table 2. Absorbances at Characteristic Wavelengths for the Oxidation (A_{255nm}), and Nitrosylation Process (A_{435nm}) after 1 min (**1**) and 2 min (**2**) Contact with Dioxygen

	A_{255nm}		A_{435nm}		NO Complex Formation	
$[F^-]$, M	**1**	**2**	**1**	**2**	**1**	**2**
0	1.199	1.703	0.203	0.106	13%	0%
0.25	0.930	1.583	0.347	0.153	33%	6%
0.50	0.883	1.374	0.344	0.149	33%	6%
0.75	0.356	0.882	0.529	0.210	60%	14%
1.00	0.178	0.329	0.513	0.410	57%	43%

Scheme 3. Mechanistic Scheme of Equilibria Connected with the Ternary Fluoride and Nitrosyl Complex (Left) and the Dioxygen Complex (Right)[a]



[a] The proposed reaction pathway proceeds via the substitution of the labile water molecule of the $[Fe^{II}(EDTA)(H_2O)]^{2-}$ species (black); alternatively a direct substitution of fluoride is conceivable (gray).

exposed to oxygen for 1 min in the presence of 1.0 M KF. Inhibited oxidation leads to increased nitrosyl complex formation (viz. +44% compared to fluoride-free conditions). No matter if fluoride is simultaneously present in the solution, the $[Fe^{III}(EDTA)(NO^-)]^{2-}$ complex is formed within 1 min contact with NO. After the release of NO on passing nitrogen through the sample solution, the absorption catalyst is fully regenerated, and the same concentration of the nitrosyl complex is formed during a second exposure to NO. Repeated reversible binding of NO with no significant loss of the active species, $[Fe^{II}(EDTA)(H_2O)]^{2-}$, was found. Furthermore, the required, high concentrations of fluoride do not lead to a significant decomposition reaction of $[Fe^{III}(EDTA)(NO^-)]^{2-}$ even over extended periods of time, for example after more than 17 h $[Fe^{II}(EDTA)(H_2O)]^{2-}$ can be regenerated quantitatively.

Conclusions

The investigated effect of fluoride inhibition of autoxidation seems promising. We could observe a considerably reduced oxygen sensitivity, without any limiting effect on the formation of $[Fe^{III}(EDTA)(NO^-)]^{2-}$ or the reversibility of the NO binding process. However, the experiments only partially simulate the situation in the absorber unit of the BioDeNO$_x$ process. Different from our study, dioxygen and NO gas are simultaneously present in the flue gas of the technical process. So, there is a competition between both gases to bind to $[Fe^{II}(EDTA)(H_2O)]^{2-}$. We predict that the observed fluoride inhibition of the autoxidation process will

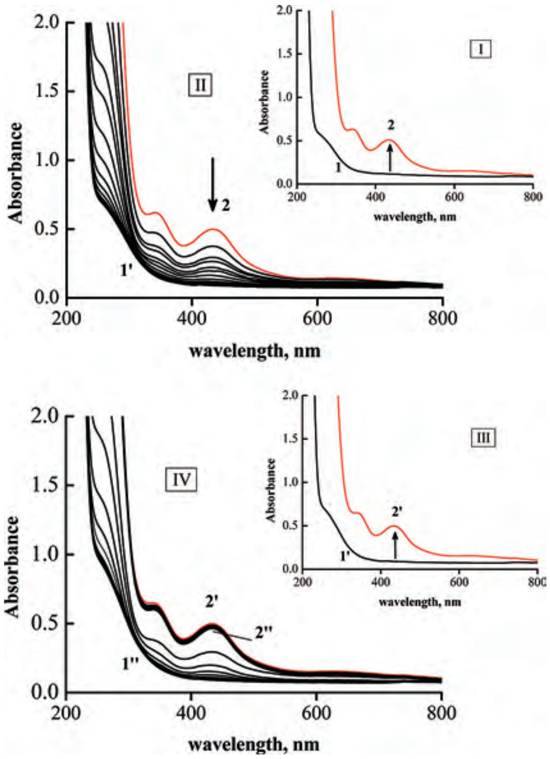


Figure 9. Spectra recorded for partially oxidized [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ resulting from 1 min contact with oxygen (I, 1) and following nitrosylation (I, 2) in the presence of 1.0 M F$^-$. The formed [Fe^{III}(EDTA)(NO$^-$)]$^{2-}$ complex (II, 2) releases the bound NO on bubbling nitrogen through the solution (II, 2 → 1′) to give [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$. The regenerated [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ can react again to form [Fe^{III}(EDTA)(NO$^-$)]$^{2-}$ (III, 1′ → 2′). Over a time period of 1040 min, this complex does not undergo significant decomposition (IV, 2′ → 2″). After this extended period, approximately the same amount of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ can be obtained by bubbling nitrogen through the solution (IV, 2″ → 1″). Experimental conditions: 1 mM FeSO$_4$·7H$_2$O; 1.25 mM EDTA; 1.0 M potassium fluoride; 0.5 M potassium acetate buffer; pH = 5.0; 25 °C; 10 mm optical path length.

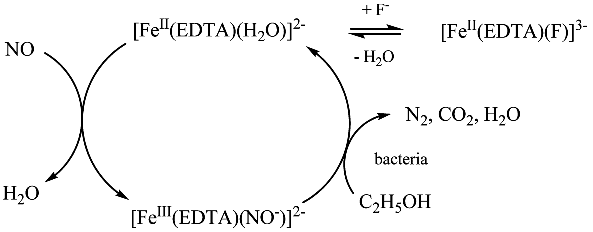


Figure 10. Proposed extended reaction cycle for the BioDeNO$_x$ process by employing fluoride inhibition of the autoxidation reaction.

in this case lead to an even higher activity of [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ because NO is a more effective nucleophile, and the dioxygen concentration in the flue gas will be lower than in air. Another advantage of our approach is that fluoride will not be consumed in this process. The fluoride present in solution will protect the active [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ species by in situ formation of the mixed ligand complex whenever this species is formed in the BioDeNO$_x$ process. A modified reaction cycle for the BioDeNO$_x$ process with fluoride induced protection can now be proposed (Figure 10).

A high formation constant for the mixed-ligand complex $K_{MLF}{}^{F}$ could lead to an even higher autoxidation inhibition level for the present Fe^{II} species. On the other hand, a nucleophile that binds stronger to [Fe^{II}(EDTA)(H$_2$O)]$^{2-}$ may not be displaced effectively by NO. So far, fluoride seems to be the best candidate for this purpose, with a bonding strong enough to inhibit displacement by dioxygen but weak enough to be displaced by NO.

Acknowledgment. The authors gratefully acknowledge financial support from the Deutsche Forschungs-gemeinschaft as part of SFB 583 “Redox-active Metal Complexes”. R.M. is grateful to the DFG for financial support within the framework of project ME 1148/7–1.

IC800378C