Photochemistry of Aqueous Iron(III)–Polycarboxylate Complexes: Roles in the Chemistry of Atmospheric and Surface Waters

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Photochemical redox reactions of Fe(III) complexes of polycarboxylates (e.g., citrate, malonate, oxalate) occur on time scales of minutes in sunlight and are potentially important sources of Fe(II), 'O2-/HO2*, H2O2, and 'OH in atmospheric water drops and surface waters. Quantum yields for Fe(II) formation, determined from experiments and equilibrium speciation calculations, are (i) 0.28 for Fe(OH)(citrate)− at 436 nm, (ii) 0.027 for Fe(malonate)2− at 336 nm, and (iii) 1.0 for Fe(oxalate)3− and 0.6 for Fe(oxalate)3+ at 436 nm. Competitive reactions of O2 and Fe(III) with the polycarboxylate radicals and/or the carbon-centered radicals derived from decarboxylation, as well as the speciation of Fe(II) and Fe(III), affect the experimental quantum yields of Fe(II) formation.

Introduction

The carboxylate group [R-C(0)O−] is one of the most common functional groups of the dissolved organic compounds present in natural waters (1, 2). Polycarboxylates (i.e., molecules that have more than one carboxylate functional group), including citrate, malonate, and oxalate, are common constituents of precipitation (3, 4), fog (4), urban (5, 6) and remote (7) tropospheric aerosols, surface waters (1, 8), and soil solutions (9). Polycarboxylates form strong complexes with Fe3+ that undergo rapid photochemical reactions in sunlight (10).

Photolysis of Fe(III)–polycarboxylates affects the speciation of iron in atmospheric and surface waters, which in turn affects numerous iron-dependent biogeochemical processes (10). Sunlight photolysis of naturally occurring Fe(III)–carboxylate moieties is also responsible for the iron-mediated photochemical production of CO2 and consumption of O2 in humic-colored natural waters (11). Esterification of carboxylate groups in the natural organic matter decreased oxygen consumption rates by 50% (11).

Since the 1950s, numerous investigations have found that Fe(III)–oxalate complexes photolyze with high efficiency (10-18, and references cited therein). Little is known, however, about the effect of oxygen on the experimental quantum yields of Fe(II) formation for this reaction. Moreover, scant information is available on the quantum yields of Fe(1I) formation, determined from experiments and equilibrium speciation calculations, are (i) 0.28 for Fe(OH)(citrate)− at 436 nm, (ii) 0.027 for Fe(malonate)2− at 336 nm, and (iii) 1.0 for Fe(oxalate)3− and 0.6 for Fe(oxalate)3+ at 436 nm. Competitive reactions of O2 and Fe(III) with the polycarboxylate radicals and/or the carbon-centered radicals derived from decarboxylation, as well as the speciation of Fe(II) and Fe(III), affect the experimental quantum yields of Fe(II) formation.

Conceptual Model

Figure 1 illustrates a reaction scheme that is consistent with observations from this study. Absorption of a photon by an Fe(III)–polycarboxylate species initiates the formation of short-lived intermediates (15, 16) that ultimately yield Fe(II) and a free polycarboxylate radical outside of the solvent cage (Figure 1). Several competing processes can affect the fate of the polycarboxylate radical (Figure 1): (i) back-reaction with Fe(II) to re-form Fe(III) (not shown in Figure 1); (ii) reaction with O2 to form 'O2-/HO2*; (iii) reduction of another Fe(III)–polycarboxylate species, which is rapid for reaction of C204− with Fe(III)–oxalate species (k > 5 x 10^7 M−1 s−1 (15, 16)); or (iv) decarboxylation, which is a rapid process for C204− (half-life ∼ 0.3 μs (19)), to form carbon-centered radicals. Carbon-centered radicals also react at near-diffusion-controlled rates with O2 and Fe(III)–carboxylate species (20, 21).

A very important consideration is the competition between O2 and Fe(III) species for the polycarboxylate radical (RCOO•−) and the carbon-centered radical (>C•) derived therefrom (12). If the RCOO•− and >C• radicals react with Fe(III), then additional Fe(II) is formed; however, if they react with O2, then a sequence of oxidants ('O2-/HO2*, H2O2, 'OH, ROO*, ROOH) are formed, each of which can oxidize Fe(II) (Figure 1). As will be seen, this can reduce substantially the experimental quantum yield for Fe(II) formation, relative to the Fe(II) quantum yield for the primary photochemical step.

Experimental and Computational Methods

Except where noted, all reagents, purified water, apparatus and equipment, analytical and experimental procedures and conditions, protocols for preparation and irradiation of solutions, kinetic analyses, and speciation computations were identical to those previously described (17). The solution composition and speciation calculations were previously described (298 K, 0.01 M ionic strength, 1 atm; see Tables I and III of ref 17); the only differences being that scavengers and probe molecules (e.g., 1-octanol, 2-methyl-2-propanol, nitrobenzene, anisole, etc.) were not present in these solutions. More information regarding the stoichiometries and stability constants (22-28) of species considered in the equilibrium speciation computations are given in Table I. All ionic strength corrections were made using the Davies equation (29). All Fe(III)–polycarboxylate solutions were freshly prepared within 1 h of the time of irradiation.

Monochromatic illumination utilized a Schoeffel Reaction Chemistry System equipped with a monochromator (17). Solutions were either saturated with air or purged with argon prior to irradiation. Solutions were irradiated in stopped rectangular quartz cuvettes that were stirred continuously with a Teflon-coated magnetic stir bar.

Potassium ferrioxalate, synthesized and recrystallized as described elsewhere (30), was used as a chemical.
Figure 1. Reaction scheme for the photolysis of Fe(III) complexes of polycarboxylates (oxalate$^{2-}$, malonate$^{2-}$, citrate$^{3-}$). The symbol $>$ represents the carbon-centered radical derived from the decarboxylation of the polycarboxylate radical, or $\mathrm{O}_2^-$ in the case of oxalate. Note that not all polycarboxylate-derived Fe(II) will necessarily form $\mathrm{O}_2^-$ upon reaction with $\mathrm{O}_2$; some Fe(II) species could form organic peroxy radicals ($>\mathrm{COO}^{\cdot}$, or more generally, $\mathrm{ROO}^{\cdot}$) that could form organic peroxides rather than $\mathrm{H}_2\mathrm{O}_2$. Values of $\Phi_{\text{Fe(III)-polycarboxylates}}$ were determined from the initial slope of a plot of $[\text{Fe(III)}]$ versus irradiation time (30). All thermodynamic data are for 298 K, 1 atm, with ionic strength → 0. $\Delta$ is the molar activity of the species/component; $i$, $j$, ... are stoichiometric coefficients for the corresponding component; and $\beta$ is the equilibrium constant for formation of the species. $pK_a$ values (22): (1) 1.25 and 4.27 for $\mathrm{H}_{\text{ox}}$, (2) 2.85 and 5.70 for $\mathrm{H}_{\text{mal}}$, (3) 3.18, 4.76, and 6.40 for $\mathrm{H}_{\text{cit}}$, and (4) 2.15, 7.20, and 12.35 for $\mathrm{H}_2\mathrm{PO}_4$. $[\text{H}^+]$ and $[\text{OH}^-]$ were obtained by various methods. The activity (mole fraction) of solid phases is $a$, with $a$ values in the table are zero.

### Times and Discussion

Iron(II) Quantum Yield for Fe(III)–Polycarboxylates: Argon-Saturated Solutions. Table II summarizes results for the Fe(III)–citrate system for a pH range (pH 4–6) that is typical of natural waters having high concentrations of carboxylic acids (1, 2). Table II shows that the experimental quantum yield for Fe(II) formation ($\Phi_{\text{Fe(II)-citrate}}$) decreases slightly: (i) from 0.28 at pH 4 to 0.21 at pH 6 and (ii) from 0.28 at 1:1 Fe(III)/citrate stoichiometry.
Table II. Effects of pH and Citrate Concentration on the Experimental Quantum Yields for Fe(II) Formation at 436 nm (Φ_{Fe(II),436}) in the Fe(III)-Citrate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Total [citrate] (mM)</th>
<th>Φ_{Fe(II),436}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.10</td>
<td>0.28</td>
</tr>
<tr>
<td>5.0</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>6.0</td>
<td>0.10</td>
<td>0.21</td>
</tr>
<tr>
<td>4.0</td>
<td>0.10</td>
<td>0.28</td>
</tr>
<tr>
<td>4.0</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>4.0</td>
<td>1.00</td>
<td>0.24</td>
</tr>
</tbody>
</table>

0 \{Fe(III)\} = 0.10 mM; ionic strength 10 mM; temperature 298 K; argon purged. *Total [orthophosphate] = 5.0 mM. **pH adjusted by dropwise addition of an aqueous bicarbonate solution; orthophosphate was not added.

Figure 2. Measured experimental Fe(III)-based decadic molar absorptivity at 436 nm, for each Fe(III)-oxalate solution versus the calculated equilibrium fraction of Fe(III) present as Fe(oxalate)\(^2-\) for the same solution. The least-squares linear regression of the data is given by the line. The right intercept (f_{1,2} = 1) and left intercept (f_{1,3} = 0, f_{1,3} = 1) are the decadic molar absorptivities (value ± SE) of Fe(oxalate)\(^2-\) (f_{1,2} = 62 ± 6 M\(^{-1}\) cm\(^{-1}\)) and Fe(oxalate)\(^3-\) (f_{1,3} = 24 ± 4 M\(^{-1}\) cm\(^{-1}\)).

Figure 3 illustrates the product of the experimental quantum yield and experimental Fe(III)-based molar absorptivity is linearly related to the fraction of Fe(III) present as Fe(oxalate)\(^2-\).

It is noteworthy that the quantum yield for Fe(II) formation of Fe(malonate)\(^2-\) at 366 nm is only 2.7% of that for Fe(oxalate)\(^2-\) at 436 nm (vide infra). Several factors could contribute to this large difference in quantum yields, including variability in the relative rates of different polycarboxylate radical reactions (e.g., decarboxylation and recombinantion with Fe(II)) as well as differences in the photoinduced ligand-to-metal charge transfer of the Fe(III) complexes. Sorting out the different contributing factors was beyond the scope of this study.

As a similar analysis was carried out for the photochemistry of Fe(III)-oxalate solutions (17), the absorbance and photochemistry at 436 nm is dominated by Fe(oxalate)\(^2-\) and Fe(oxalate)\(^3-\); the sum of the concentrations of Fe(oxalate)\(^2-\) and Fe(oxalate)\(^3-\) is calculated to be much larger than the sum of concentrations of all other Fe(III) species (more than 5000 times larger for half of the solutions and more than 100 times larger for all but one of the solutions). In other words, the sum of the calculated equilibrium fractions of Fe(III) present as Fe(oxalate)\(^2-\) (f_{1,2}) and Fe(oxalate)\(^3-\) (f_{1,3}) are approximately unity (f_{1,2} + f_{1,3} ≈ 1).

Figure 2 shows the linear relationship between the experimental Fe(III)-based decadic molar absorptivities and the calculated equilibrium fraction of Fe(III) present as Fe(oxalate)\(^2-\). This linear relationship is consistent with the view that the absorbance of these Fe(III)-oxalate solutions is dominated by Fe(oxalate)\(^2-\) and Fe(oxalate)\(^3-\).

Equation 1 is consistent with this observed linear relationship and relates the experimental Fe(III)-based molar absorptivity to the molar absorptivities of Fe(oxalate)\(^2-\) and Fe(oxalate)\(^3-\):
formation of $'02-/HO_2'$ is the first step in generating a Fe(I)$_1$ formation in two ways (see Figure 1 for more detail). With Fe(II), as shown in Figure 1.

The decrease in experimental Fe(II) quantum yields in air-saturated solutions was substantially lower, by as much as a factor of 10, than those for identical argon-purged solutions. The quantum yields for Fe(II) formation in air-saturated Fe(II)-oxalate solutions were substantially lower, by as much as a factor of 10, than those for identical argon-purged solutions. The quantum yields for Fe(II) formation are shown in Figure 2 and the molar absorbivities ($\epsilon_{1:2,436}$ and $\epsilon_{1:3,436}$) given previously (Figure 3).

Figure 3. Product of the independently measured experimental quantum yield for Fe(II) formation ($\Phi_{\text{Fe(II),436}}$) and the experimental Fe(II)-based decadic molar absorbivity ($\epsilon_{\text{Fe(II),436}}$) at 436 nm for each Fe(II)-oxalate solution versus the calculated equilibrium fraction of Fe(II) present as Fe(oxalate)$_2^-$ for the same solution. The least-squares linear regression of the data is given by the line. The right intercept ($I_{1:2}$ = 1) and left intercept ($I_{1:3}$ = 0, $I_{2:3}$ = 1) are the quantities (value ± SE) for the individual complexes. ($\Phi_{\text{Fe(II),436}}$,$I_{1:2}$,436) = 54 ± 14 and ($\Phi_{\text{Fe(II),436}}$,$I_{1:3}$,436) = 15 ± 1 ± 1 M$^{-1}$ cm$^{-1}$, respectively. See eq 2 and the text for further explanation.

The experimental quantities to the fundamental quantum yields and molar absorbivities of Fe(oxalate)$_2^-$ and Fe(oxalate)$_3^-$ are:

$$\Phi_{\text{Fe(II),436}}(I_{1:2}) (\text{Fe(II),436}) \approx \Phi_{\text{Fe(II),436}}(I_{1:3}) (\text{Fe(II),436}) + [(\Phi_{\text{Fe(II),436}} (I_{1:2}) (\text{Fe(II),436}) - (\Phi_{\text{Fe(II),436}} (I_{1:3}) (\text{Fe(II),436}) (I_{2:3}) \tag{2}\)$$

where $\Phi_{\text{Fe(II),436}}$ (I$_{1:2}$) and $\Phi_{\text{Fe(II),436}}$ (I$_{1:3}$) are the quantum yields for Fe(II) formation at 436 nm of Fe(oxalate)$_2^-$ and Fe(oxalate)$_3^-$, respectively. Using the information given in Figure 2 and the molar absorbivities ($\epsilon_{1:2,436}$ and $\epsilon_{1:3,436}$) given previously (Figure 3), we calculated (eq 2) quantum yields for Fe(II) formation at 436 nm to be $\Phi_{\text{Fe(II),436}}$ (I$_{1:2}$) = 1.0 ± 0.25 for Fe(oxalate)$_2^-$ and $\Phi_{\text{Fe(II),436}}$ (I$_{1:3}$) = 0.60 ± 0.46 for Fe(oxalate)$_3^-$. It should be emphasized that these quantum yields are not those of the primary photochemical process, but that they also include contributions from secondary reactions involving the oxalate radical. The decrease in experimental Fe(II) quantum yields in air-saturated solutions cannot be attributed to thermal oxidation of Fe(II) by O$_2$ because micromolar concentrations of Fe(II) added to air-saturated unirradiated Fe(II)-oxalate solutions were oxidized on time scales that were slow (half-life of Fe(II) 50 min) compared to the time scales of these photolysis experiments (10 min) (32).

Oxygen Effects on Experimental Fe(II) Quantum Yields. For the Fe(III)-oxalate system, the experimental quantum yields for Fe(II) formation in air-saturated solutions were substantially lower, by as much as a factor of 10, than those for identical argon-purged solutions. The effect of air is attributed to the reaction of aqueous O$_2$ (ca. 0.25 mM in air-saturated aqueous solutions) with C$_2$O$_4^{2-}$ and CO$_2$ to form 'O$_2$-/HO$_2$'. Reactions of C$_2$O$_4^{2-}$/CO$_2$ with O$_2$ decrease the experimental quantum yield for Fe(II) formation in two ways (see Figure 1 for more detail). One, O$_2$ competes with Fe(III) for C$_2$O$_4^{2-}$/CO$_2$-, which limits the formation of additional Fe(II) from reactions of C$_2$O$_4^{2-}$/CO$_2$- with Fe(III). Two, more importantly, the formation of 'O$_2$-/HO$_2$' is the first step in generating a series of oxidants (e.g., HO$_2^+$, H$_2$O$_2$, *OH) that can oxidize Fe(II), as shown in Figure 1.

Thus, other oxidants, such as 'O$_2$-/HO$_2$' in the early stages of the reaction and also H$_2$O$_2$ and *OH later in the reaction, probably re-oxidized the photoformed Fe(II). Re-oxidation of Fe(II) lowered the experimental quantum yield for Fe(II) formation. Addition of H$_2$O$_2$ to preirradiated Fe(III)-oxalate solutions resulted in the rapid oxidation of Fe(II) [half-life < 1 min (17)].

The speciation of Fe(II) is expected to affect the rate of Fe(II) oxidation by H$_2$O$_2$ (33, 34). For the oxalate system, the calculated equilibrium speciation of Fe(II) was dominated by Fe$^{2+}$, Fe(oxalate)$^{5-}$, and Fe(oxalate)$_2^{3-}$; FeOH$^+$ represented less than 0.002% of the total Fe(II) in these oxalate solutions. Numerous studies (see Table I of ref 33) have found that H$_2$O$_2$ reacts 10-1000 times faster with Fe(II)-polycarboxylate complexes than with Fe$^{2+}$. Thus for air-saturated Fe(III)-oxalate solutions (which form H$_2$O$_2$ upon photolysis (18)), it is expected that as the fraction of Fe(II) present as Fe$^{2+}$ increases, the rate of Fe(II) oxidation by H$_2$O$_2$ decreases, and correspondingly, the experimental quantum yield for Fe(II) formation increases. Figure 4 is consistent with this hypothesis and illustrates that the experimental quantum yields for Fe(II) formation in air-saturated Fe(III)-oxalate solutions approach the values of their corresponding argon-saturated solutions as the fraction of Fe(II) present as Fe$^{2+}$ increases.

An important consideration in the formation of H$_2$O$_2$ (and other O$_2$-derived oxidants) is the competitive reactions of Fe(III) species and O$_2$ with C$_2$O$_4^{2-}$/CO$_2$- (Figure 1). If C$_2$O$_4^{2-}$/CO$_2$- reacts with Fe(III), then additional Fe(II) is formed: however, if C$_2$O$_4^{2-}$/CO$_2$- reacts with O$_2$, then a "cascade" of oxidants (including H$_2$O$_2$) is formed which can oxidize Fe(II) (Figure 1). The Fe(III) speciation is expected to affect the competition between Fe(III) and O$_2$ for C$_2$O$_4^{2-}$/CO$_2$- and, therefore, the experimental quantum yields for Fe(II) formation in air-saturated solutions. Specifically, it is likely that C$_2$O$_4^{2-}$/CO$_2$- will transfer an electron to Fe(oxalate)$^{3-}$ more slowly than they will to Fe(oxalate)$_2^{2-}$ or Fe(oxalate)$^{4+}$, due to electrostatic repulsion.

Thus in the Fe(III)-oxalate solutions, as the fraction of Fe(III) present as Fe(oxalate)$^{3-}$ increases, a greater fraction of C$_2$O$_4^{2-}$/CO$_2$- reacts with O$_2$ rather than with Fe(III), and consequently the formation rates and concentrations of the O$_2$-derived oxidants (e.g., H$_2$O$_2$) increase. This change in Fe(III) speciation accelerates the rates of
Fe(II) oxidation and lowers the experimental quantum yield for Fe(II) formation. Figure 5 is consistent with this hypothesis and shows that the experimental quantum yield for Fe(II) formation in air-saturated solution, relative to that for the identical argon-saturated solution, decreases as the calculated equilibrium fraction of Fe(III) present as Fe(oxalate)$_3^{2-}$ increases.

Significance to Atmospheric and Surface Waters.

The half-lives of Fe(III)-polycarboxylate species in sunlight (latitude $34^\circ$ N, midday, June) are $0.2$ min for Fe(malonate)$_2$/Fe(malate)$_2^-$ (12, 33), $5$ min for Fe(malolate)$^2$/Fe(malate)$^{2-}$ (this work), and $0.9$ min for Fe(OH)$_2$(citrate)$^-$ (this work). With half-lives on the order of minutes, the photolysis of Fe(III)-polycarboxylates represents a potentially important daytime source of Fe(II) to atmospheric and surface waters and could easily account for much of the Fe(II) formation in many natural waters (10).

Photolysis of Fe(III)-polycarboxylates is a sink for the polycarboxylates and, through decarboxylation of the polycarboxylate radical, is a source of CO$_2$ to the system (Figure 1). The iron-mediated photomineralization of natural organic compounds has received little study (11) but could be an important mechanism for the cycling of carbon in natural waters having appreciable concentrations of dissolved organic carbon (DOC) and iron (10). Furthermore, in such natural waters, photoredox reactions of Fe(III)-polycarboxylates could represent a significant sink for dissolved O$_2$ (11).

The reduction of O$_2$ through photolysis of Fe(III)-polycarboxylates forms $\cdot$OH/H$_2$O$_2$, which in turn forms H$_2$O$_2$ (Figure 1). Given the high photoactivity of Fe(III)-polycarboxylates, their photolysis could represent an important source of H$_2$O$_2$ to some atmospheric and surface waters (10, 18).

For atmospheric and surface waters having significant concentrations of Fe(III)-polycarboxylates, the simultaneous and rapid photof ormation of Fe(II) and H$_2$O$_2$ could represent a significant thermal source of hydroxyl radical ($\cdot$OH), through Fenton's reaction of Fe(II) with H$_2$O$_2$ (Figure 1). In this model, polycarboxylates have three important roles. One, polycarboxylates increase the concentration of dissolved Fe(III) because they form strong complexes with Fe$^{3+}$; two, Fe(III)-polycarboxylates photolyze rapidly, which reduces Fe(III) to Fe(II) and simultaneously reduces O$_2$ to H$_2$O$_2$ (Figure 1). Three, H$_2$O$_2$ reacts much faster with Fe(II)-polycarboxylates than with Fe$^{2+}$ (33); therefore, polycarboxylates apparently increase the rate of $\cdot$OH formation in the photo-Fenton reaction, because one $\cdot$OH is formed for every Fe(III) oxidized by H$_2$O$_2$ in irradiated Fe(III)-polycarboxylate solutions (17).

Finally, the results reported here are for the pH range 3.0-6.0, which is typical of atmospheric waters and of surface waters with high DOC concentrations. Depending on the exact conditions of a natural water (e.g., pH, [Fe(III)], [DOC]), precipitation of ferricydrate [amorphous Fe(OH)$_3$] could occur (10, 29), and this would, of course, affect the photochemistry of the Fe(III) (10).

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Literature Cited


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