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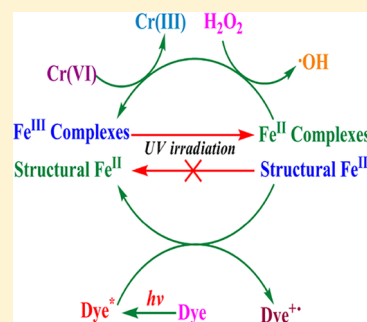
Photochemical Coupling of Iron Redox Reactions and Transformation of Low-Molecular-Weight Organic Matter

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ABSTRACT: The photoreactions between Fe(III)/Fe(II) and low-molecular-weight organic matter (LMWOM) under solar irradiation have significant implications for many biogeochemical cycles on the Earth and for the fates of environmental pollutants. In this Perspective, we focus on several fundamental aspects of the photochemical processes that couple the redox cycling of iron species and transformation of organic substrates. The primary photoprocesses (e.g., intramolecular electron transfer or photodissociation) are first highlighted by introducing the recently disputed observations on the photolysis of ferrioxalate complexes. The effects of LMWOM and its daughter radicals on the photochemical redox cycling of iron species are discussed with special attention given to the example of Fe–malonate complexes. These processes and mechanisms would provide us some refreshed understanding of environmental photochemistry of LMWOM and the iron species and would be helpful for our assessment of photochemical decontamination of organic pollutants.



As one of the most abundant transition metals on the Earth's surface, iron plays an essential role in the biogeochemical cycle. Many of its biogeochemical functions are based on its valence variability. In the environment, solar irradiation has been found to be one of the vital factors that control the chemical states of the iron species in natural aquatic bodies.^{1–4} It has also been recognized that the naturally abundant soluble small organic matter such as low-molecular-weight carboxylates can profoundly influence the photochemical transformation of iron species. The interplay of photochemical redox cycling of iron and low-molecular-weight organic matter (LMWOM) may have important implications for environmental chemical processes. Particularly, the photochemical redox interaction between Fe and LMWOM can generate and consume reactive radical species and significantly influence the redox transformation of many important environmental species (such as $\text{SO}_3^{2-}/\text{SO}_4^{2-}$, As(III)/As(V) , and Cr(III)/Cr(VI)), the degradation of natural organic matter and anthropogenic contaminants, and phytoplankton blooms in natural aquatic bodies.^{5–11} Photochemical coupling between the iron and organic substrates (e.g., the photo-Fenton reaction) can also find its promising applications in environmental remediation.¹² These intriguing effects and applications have motivated scientists to explore the linkage between iron-based photochemistry and a variety of biogeochemical processes. However, compared to the remarkable progress in macroscopic field survey and concentration analysis of the involved species, the advances in the understanding of the molecular basis and radical chemistry for photochemical coupling of iron and LMWOM are not matched.

The photoinduced ligand to metal charge transfer (LMCT) of the Fe(III) complex with inorganic ligands such as hydroxyl

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and sulfate plays an essential role in the photochemical transformation of iron species.^{13,14} For example, in the photoassisted Fenton reaction, the enhanced $\text{Fe(III)} \rightarrow \text{Fe(II)}$ transformation is ascribed to the excitation of Fe(III) hydroxide complexes.¹⁵ There is increasing evidence that the complexes between iron and organic ligands, such as the carboxylates in the LMWOM, can be another kind of important photoactive species for the transformation from Fe(III) to Fe(II). Under sunlight irradiation, the LMCT from the organo ligand to the Fe(III) would result in the reduction of Fe(III) to Fe(II) and the oxidation of the ligand to a radical form. Photochemistry of such organo–iron complexes should have more environmental significance than that of the inorganic ones because they usually exhibit considerable LMCT absorption at longer wavelength

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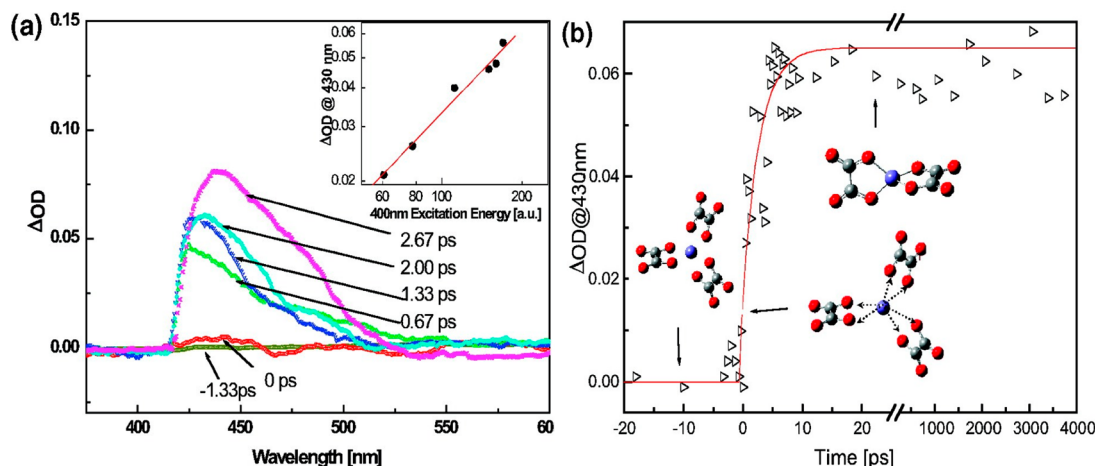


Figure 1. Picosecond transient absorption spectra of an aqueous ferrioxalate solution with a concentration of 1.6 M (a) and formation kinetics (b) for -20 – 25 ps ($c = 0.115$ M, excited at 400 nm) and 250 ps– 4 ns ($c = 9.3 \times 10^{-3}$ M, excited at 355 nm). (a, inset) linear dependence of the transient absorbance on the excitation intensity at 430 nm. The three structures illustrated represent the ground state (-20 to -1 ps), the excited state (0 to $+2$ ps), and the tetrahedral-like $[\text{Fe(III)}(\text{C}_2\text{O}_4)_2]^-$ transient (10 ps– 4 ns), respectively. Reprinted from ref 18.

and can thus extend their light response in the visible spectrum. Also, these ubiquitous organo-coordinated Fe(III) species are often highly soluble in water, which significantly increases their availability in surface waters. However, our present understanding on the organo–iron-based photochemistry, such as the primary photochemical events and the relationship between the organic ligand with photoactivity, is rather poor and is still disputed.

Besides photoinduced inner-sphere charge transfer (LMCT) in the organo-coordinated Fe(III) species, outer-sphere charge transfer from excited organic chromophores to iron species can initiate photochemical reactions, representing another important photochemical coupling pathway between iron species and organic matter. In these processes, the organic matter, rather than the complexes, absorbs light. Electron transfer between the formed excited states of the organic molecule and Fe species initiates the transformation of the Fe species and the formation of organic radicals. As colored-dissolved organic matter (CDOM) such as organic dye pollutants and much naturally occurring conjugated organic matter are abundant in the environment with a broad range of visible light absorption, in principle, CDOMs are expected to remarkably influence the state of iron species. However, their significance in the transformation of iron species was overlooked to a large extent in the past studies of light-induced redox transformation of environmental iron species.

After the initial photoinduced charge separation, secondary reactions are complex and always involve a series of complicated radicals, in which other molecules such as H_2O_2 , molecular oxygen, and water are incorporated. It is these reactions that determine the photochemical fates of the iron species, the involved LMWOM, and their environmental effects. Because of their short lifetimes, their low steady concentration, and the complexity of the reaction processes of the reactive species, experimental studies on their formation and role is still a challenge.

In this Perspective, we will focus on several fundamental aspects of the photochemical processes that couple the redox cycling of the iron species and the transformation of organic substrates. In particular, the primary photochemical steps of the organo–Fe complexes, secondary radical events, and their

relationship with the redox chemistry of iron species and oxidation of organic substrates are highlighted. Although most of these works were carried out in synthetic systems on a laboratory scale, this Perspective provides useful insight into iron-based photochemistry and is helpful for the understanding of the interaction between iron species and LMWOM under sunlight irradiation and their environmental effects.

Electron-Transfer Mechanism of Ferrioxalate Complexes. The photolysis of ferrioxalate plays an important role in environmental photochemistry and represents a typical model of the photochemical interactions between iron species and (poly)-carboxylates, which are abundant in the environment. Photo-reactions of ferrioxalate result in generation of Fe(II) at the expense of the oxidation of the oxalate ligand, followed by a release of ligand radicals from the coordination entity. These radicals together with the Fe(II)/Fe(III) cycling of Fenton-like reactions can initiate the formation of a series of oxygen-bearing species ($\cdot\text{OH}$, $\text{HO}_2\cdot$, and H_2O_2), which can further influence the redox properties of natural water systems. However, the primary charge separation mechanism for its photolysis is still not fully understood. Traditionally, the charge separation process is regarded as a consequence of the LMCT transition,^{16,17} in which photoinduced intramolecular electron transfer from the oxalate ligand to the Fe(III) ion immediately after irradiation generates the radical complex $[(\text{C}_2\text{O}_4)_2\text{Fe}^\text{II}(\text{C}_2\text{O}_4\cdot)]^{3-}$ or the $\text{C}_2\text{O}_4\cdot^-$ radical. The recent studies by Rentzepis's group^{18–20} showed that intramolecular electron transfer is not always the dominant process that occurs after excitation in the “charge-transfer band”. There could be another primary photoprocess following the excitation. During their study on the photoredox reaction of ferrioxalate in water by time-resolved extended X-ray absorption fine structure (EXAFS) in conjunction with ultrafast optical transient spectroscopy and DFT and UHF calculations, a fast transient absorption band was observed after excitation at 400 nm, whose maximum wavelength, interestingly, shifted to 430 nm from -1.33 to 2.67 ps (Figure 1a). This transient spectrum reached its maximum intensity at 2.6 ps after excitation and then remained constant for at least 4 ns, as illustrated in Figure 1b.

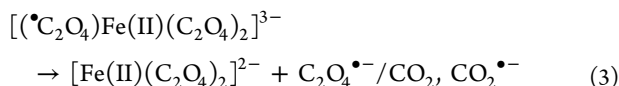
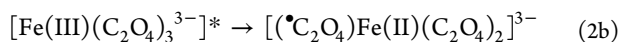
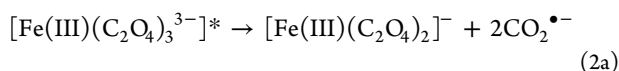
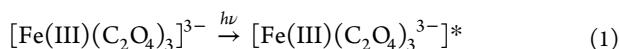
Their EXAFS experiments with 2 ps resolution and 0.04 Å accuracy showed a transient species with an Fe–O distance of

2.16 Å within the first 2 ps after excitation (Table 1), which was assigned to an excited state of the parent Fe(III) complex. They

Table 1. Fe–O Bond Length at Different Delay Times before and after Excitation Obtained by Time-Resolved EXAFS and Quantum Chemistry Calculations¹⁸

time	assignment	ligand	R(Å)/exp	R(Å)/UHF	R(Å)/DFT
–20 ps	[Fe(III)(C ₂ O ₄) ₃] ^{3–}	C ₂ O ₄ ^{2–}	2.02	2.04	2.01
1–2 ps	[Fe(C ₂ O ₄) ₃] ^{3–} *	C ₂ O ₄ ^{2–}	2.16	n/a	n/a
4 ps	[C ₂ O ₃ O–Fe(C ₂ O ₄) ₂] ^{3–}	C ₂ O ₃ O ^{2–}	1.93–2.09	1.87	1.87
		C ₂ O ₄ ^{2–}		2.01	2.02
9–115 ps	[Fe(III)(C ₂ O ₄) ₂] [–]	C ₂ O ₄ ^{2–}	1.87–1.93	1.90	1.90

also observed several intermediates between 4 and 115 ps after the excitation. Combined with the experimental Fe–O bond lengths with results of DFT theoretical calculations, these intermediates were assigned to the five-coordinated [C₂O₃O–Fe(III)(C₂O₄)₂]^{3–} and the tetrahedral-like four-coordinated [Fe(III)(C₂O₄)₂][–]. Therefore, they concluded that sequential cleavage of an Fe(III)–O bond between Fe(III) and one oxalate ligand and the C–C bond of oxalate takes place before electron transfer, whereas Fe(III) remains in its +3 oxidation state (eqs 1 and 2a).



However, supported by nanosecond flash photolysis experiments, Pozdnyakov et al. argued that the intramolecular electron transfer (eqs 1, 2b, and 3) should be responsible for the primary photoredox reactions of ferrioxalate instead of the photodissociation mechanism.^{21,22} Their finding interestingly showed that the yields of the CO₂^{•–} and C₂O₄^{•–} radicals were less than 6% relative to the depletion of the Fe(III) complex (Figure 2). They concluded that this was an important piece of experimental evidence for the electron transfer from the ligand

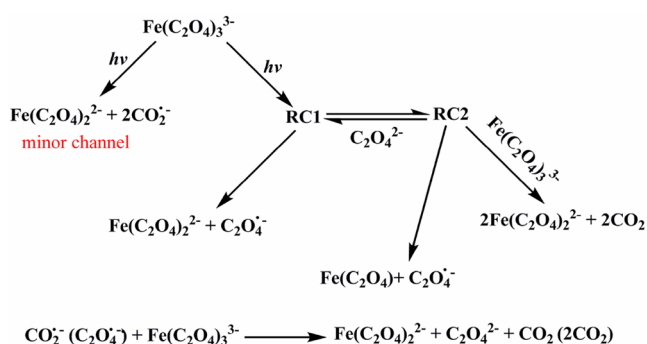


Figure 2. Proposed scheme of [Fe^{III}(C₂O₄)₃]^{3–} photolysis by the Pozdnyakov group. Reprinted from ref 21.

to Fe(III) that occurs immediately after excitation (eq 2b).²¹ They also gave their alternative explanations for the EXAFS results by Rentzepis et al.¹⁸ It was proposed that the primary short-lived transient observed at the times of 1–2 ps should be the excited state of [Fe(III)(C₂O₄)₃]^{3–} in which partial Fe(III) reduction occurs because the reported Fe–O bond length (2.16 Å) observed by EXAFS corresponds to the bond lengths of the Fe(II) complex (2.1–2.2 Å). The successive formation of two intermediates observed in nanosecond flash photolysis were believed to be the primary and secondary radical complexes [(C₂O₄)₂Fe(II)(C₂O₄[•])]^{3–} (RC1 in Figure 2) and [(C₂O₄)Fe(II)(C₂O₄[•])][–] (RC2), respectively.

Such discrepancies could have been due to differences in experimental conditions. Pozdnyakov et al. used an initial K₃Fe(C₂O₄)₃ concentration of (1–12) × 10^{–3} M,²¹ compared to 1.6 M (NH₄)₃Fe(C₂O₄)₃, which was used in EXAFS experiments by the Rentzepis group.¹⁸ It is very likely that dimeric or even polynuclear Fe(III) species besides [Fe(III)(C₂O₄)₃]^{3–} dominate the Fe(III) speciation at larger Fe salt concentrations.²² From the present experimental evidence, it is not possible to reconcile the results from both sides without further experimental or theoretical work.

Carboxylate Dependence of Photochemical Cycling of Fe Species: Special Case of Malonate. In addition to oxalate, the effects of other di- or monocarboxylates on the photochemical reactions of the iron species are of interest due to their abundances in atmospheric liquids and surface waters. For example, malonic and succinic acids are also dominant dicarboxylic acids only inferior to oxalic acid in carbon-rich atmospheric waters.^{23,24}

The influences on the photochemically reduced Fe budget are preferentially dependent on their coordinate capacities of organic matter with Fe(III). Any organic ligand (L) that outcompetes hydroxide for Fe(III), such as oxalate and malonate, can form its own Fe(III) complexes instead of the Fe(III)–OH complex, thereby fundamentally altering the photo-reduction pathways of Fe(III).

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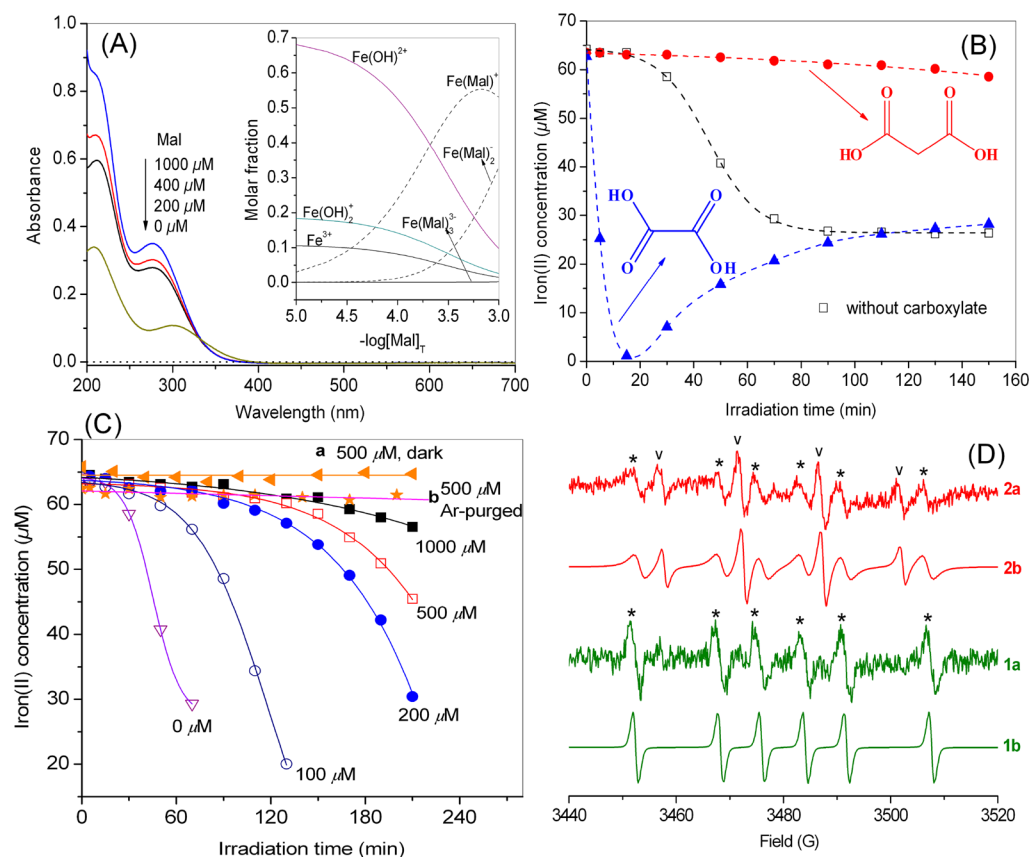


Figure 3. Photochemistry of Fe(III)–malonate (Mal) complexes at pH = 3.0. (A) UV–vis absorption spectra for solutions containing 100 μM Fe(III) and Mal ligand with different concentrations. (Inset) Speciation (molar fraction) of 100 μM Fe(III) in solutions as a function of total malonate concentration ($[\text{Mal}]_T$) between 10 and 1000 μM . (B) Photo-oxidation of Fe(II) in the presence of malonate and oxalate. (C) Effect of $[\text{Mal}]_T$ (marked beside the lines) on photo-oxidation of Fe(II). (D) ESR spectra of DMPO radical adducts formed during the photolysis of Fe(III)/Mal solution under argon-purged conditions. (1a) Experimental data, Mal, 1000 μM ; (1b) simulated data of 1a; (2a) experimental data, Mal, 200 μM ; (2b) simulated data of 2a. (*) DMPO $\cdot\text{CH}_2\text{COOH}$, (V) DMPO $\cdot\text{OH}$. Reprinted from ref 25.

formation,²¹ and initiate other radical reactions by coupling with other species in the system. As for other di- or monocarboxylates, they are usually regarded to act mainly as $\cdot\text{OH}$ scavengers to avoid reoxidation of Fe(II) from photo-reduction of $\text{Fe}^{\text{III}}(\text{OH})^{2+}$, depending on their rate constants for $\cdot\text{OH}$ oxidation. Interestingly, a recent study of the photochemistry of Fe(III)–malonate complexes (FMCs) uncovered a unique effect of malonate that was ignored before.²⁵ Although both malonate and oxalate can form strong complexes with Fe(III) and the formed complexes have strong molar absorbance (Figure 3A), their photochemical effects on Fe cycling are quite different. It was found that Fe(II) was rapidly oxidized to Fe(III) in the presence of oxalate during the initial stage of irradiation, whereas photocatalyzed oxidation of Fe(II) proceeded rather slowly in the malonate system (Figure 3B). Further investigation showed that the initial concentration of malonate can present a significant effect on the photo-oxidation of Fe(II). In the absence of malonate, Fe(II) was rapidly oxidized, whereas quite a long induction period for the photo-oxidation of Fe(II) was observed in irradiated aerobic malonate-containing solutions. Higher initial concentrations of malonate led to longer induction periods (Figure 3C). The presence of induction periods demonstrates another special effect of the malonate. Intriguingly, spin-trapping ESR spectra showed that the formed radical species and their abundance under UV irradiation in the Fe/malonate system are dependent

on the concentration of malonate. At a low malonate concentration, two major kinds of radicals, DMPO $\cdot\text{CH}_2\text{COOH}$ ($\alpha_{\text{H}} = 23.01$ G, $\alpha_{\text{N}} = 15.34$ G) and DMPO $\cdot\text{OH}$ ($\alpha_{\text{N}} = \alpha_{\text{H}} = 14.8$ G) were detected (2a in Figure 3D). The $\cdot\text{CH}_2\text{COOH}$ should have been derived from malonate decarboxylation following LMCT excitation, while $\cdot\text{OH}$ arose from the photolysis of $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ species. However, at high malonate concentrations, only the $\cdot\text{CH}_2\text{COOH}$ adduct signal was observed (1a in Figure 3D).

Both the presence of an induction period and the dependence of radical species formation on malonate concentration can be well explained by the iron complexes' distribution. In the aqueous solution containing Fe(III) and malonate, the equilibrium between the $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ species and the FMCs is controlled by the concentration of malonate and Fe(III). At high malonate concentration, FMCs should dominate the Fe(III) speciation. The photochemical reaction in this situation gives $\cdot\text{CH}_2\text{COOH}$ as the main radical species. At low malonate concentrations, both $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ species and FMCs should coexist in the solution, and consequently, both $\cdot\text{CH}_2\text{COOH}$ and $\cdot\text{OH}$ can be formed. During photochemical reactions, $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ becomes dominant gradually due to the rapid degradation of malonate, which results in the enhanced oxidation of Fe(II), as in the $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ system (Figure 3B). This argument was further supported by the experimental observation that the degradation of malonate is still rather fast

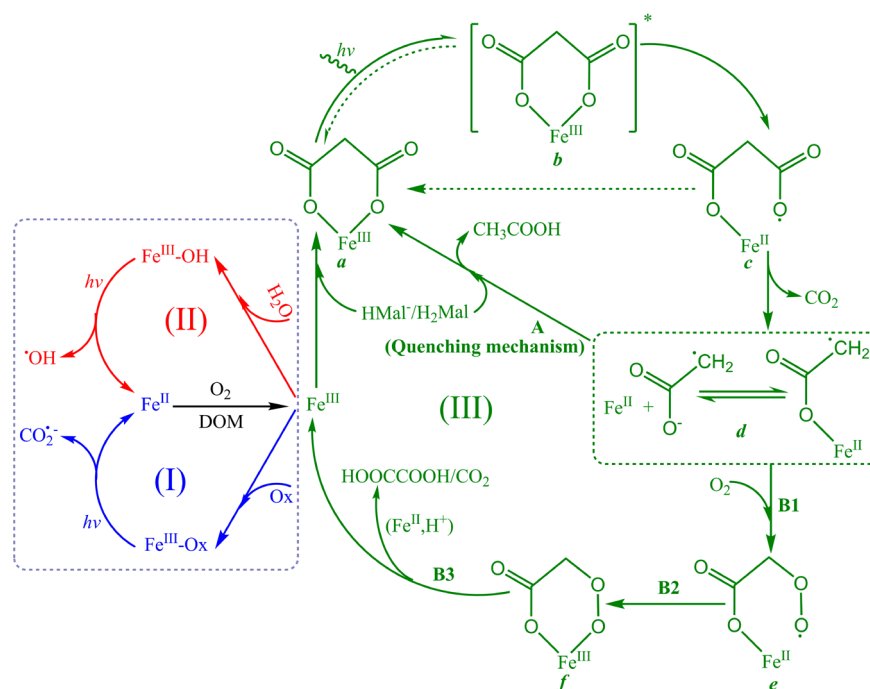


Figure 4. Proposed pathways for photodecomposition of FMCs. Reprinted from ref 25.

during the induction period and that the induction period was shortened considerably after addition of more Fe(III).

As summarized in Figure 4, on the basis of their coordinating capacity with Fe(III), the photoactivity of their Fe(III) complexes, and their role during secondary radical reactions, the carboxylates can be classified into three groups. Complexes of Group I (represented by the oxalate, which has strong coordinating ability to Fe(III)) with Fe(III) exhibit high absorption and undergo efficient LMCT in the near-UV region. The radical species formed after the LMCT have a strong reductive ability. Group II complexes (for example, mono-carboxylates) have weak interactions with the Fe(III). The function of these carboxylates in the photochemical cycling of iron species is to couple with the radicals formed by the photolysis of other photoactive species. For example, both formate and acetate exhibit poor coordinating capacity with Fe(III), though they are very ubiquitous in atmospheric water droplets where the dissolved iron coexists at a comparable concentration. In this case, the well-known photochemistry of the Fe(III)–OH complex is predominant. The photolysis of $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ under UV irradiation leads to generation of Fe(II) and $\bullet\text{OH}$ (eq 4). The formate and acetate can act as $\bullet\text{OH}$ traps to participate in the photochemical reaction.



Group III is represented by malonate in this Perspective. As those in Group I, the carboxylates' coordinating ability to Fe(III) is strong, and their complexes with Fe(III) can absorb the sunlight to undergo efficient direct photolysis. In contrast with those in Group I, the radical species formed by photolysis of Fe(III)–malonate complexes have a strong oxidative ability.

Photostationary State of the Photochemical Cycling of Iron Species. At first glance, the presence of LMWOMs should help to maintain a high Fe(II) level because (1) LMWOMs are expected to scavenge the active oxygen radicals to protect

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Fe(II) from oxidation, (2) LMWOMs can directly coordinate with Fe(III) to enhance its photochemical transformation to Fe(II), and (3) direct reduction of Fe(III) can occur by itself and/or with its daughter reducing radicals. However, the picture of the effect of LMWOM on the distribution of the iron species is apparently not so simple. For example, the photochemical reaction of the Fe complex of the reductive oxalate would form a strongly reductive $\text{CO}_2^{\bullet-}$ radical. Fe(II) is unexpectedly oxidized to Fe(III) at the early stages of photoreactions when it is carried out in the air-saturated solutions, although malonate is found to keep high concentration of Fe(II) (Figure 3B). Compared to photoreduction processes of Fe(III), our understanding of photochemical oxidation mechanisms of Fe(II) is still in its infancy.

Because of their relative stability (with a half-life of 285 days in the dark) and the lack of near-UV (>300 nm) absorption of their complexes,²⁵ photochemical Fe(II) oxidation should be driven by the radical reactions initiated from the excitation of $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ species or other photoactive complexes. Accordingly, Fe(II) oxidation kinetics are greatly affected by reactivity of LMWOM and their intermediates/radicals with Fe(III)/Fe(II), dioxygen, and reactive oxygen species. For example, the presence of malonate greatly limits the formation of the

Fe(III)–OH complex, thereby indirectly preventing Fe(II) from oxidizing in Figure 3B, whereas in the presence of oxalate, Fe(II) was rapidly oxidized by secondary $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ radicals generated from photolytic reaction of ferrioxalate.²⁵

Photodriven reduction and oxidation of Fe species occur simultaneously in the same system. Therefore, competition between the oxidation and reduction can lead to an interesting photochemical oscillation in the ratio of Fe(II) to total Fe [Fe(t)] [i.e., Fe(II)/Fe(t)], rather than a monotonous increase in Fe(II) concentration, when organic substrates are periodically added (Figure 5A).²⁶ For each cycle, the Fe(II)/Fe(t) ratio increased notably at the beginning stage of LMWOM feeding and then decreased with extended irradiation through a maximum. During this process, the total organic carbon (TOC) of the system exhibited a continuous decrease. Once LMWOM present in the system was completely mineralized, a photostationary state, where the photo-oxidation rate of Fe(II) equaled to that of Fe(III) photoreduction, was approached.

The oscillation period and amplitude, which reflect the competition between Fe(II) oxidation and Fe(III) reduction, were strongly dependent on the LMWOM structure, as depicted in Figure 5A and B. Relatively slow depletion of Fe(II) was observed in the presence of salicylic acid, benzoic acid, and 2,4-dichlorophenol, owing to the reductive properties of the resulting quinone-like intermediates. As far as the aliphatic compounds (oxalic acid, citric acid, and formaldehyde) were concerned, their photoproduct intermediate radicals are apt to generate active oxidizing species by reaction with dioxygen, resulting in a short period of the Fe(II)/Fe(III) cycle.

A comparison of the effects of LMWOM and inorganic redox species on the photochemical cycling of iron species may be interesting because the oxidation of LMWOM is irreversible, while the inorganic species with different valences should always be present. An examination of the coupling between the Cr(III)/Cr(VI) and Fe(II)/Fe(III) photochemical cycles showed that,⁷ unlike in the LMWOM system, where the same photostationary state is reached regardless of the kind of organic substrate and concentration, the ultimate photostationary concentration of Fe(II) was greatly dependent on the state of Cr species. The photoreaction initially from the Cr(III) gives a higher photostationary concentration of Fe(II) than that from the Cr(VI), and both are higher than the Cr-free system (Figure 5C).⁷ These results suggested that LMWOM and inorganic redox species can exhibit different effects on the photoredox cycling of iron. It is known that LMWOM is irreversibly degraded to CO_2 and then has no further effects on the photostationary states, whereas the chromium species should still be active due to its redox cycling. Cr(VI) is readily reduced to the stable Cr(III), a good $\bullet\text{OH}$ scavenger, thus protecting Fe(II) against $\bullet\text{OH}$ oxidation. Thus, chromium species can alter the redox equilibrium of iron species, resulting in the shift of the photostationary state toward Fe(II).

Photochemical Processes Initiated by CDOM-to-Fe Outer-Sphere Electron Transfer. Besides the direct photolysis of organo–iron species, the excitation of chromophores in CDOM can initiate another important photochemical redox reaction of iron species. After the absorption of sunlight, an excited state of the CDOM molecule can be a better oxidant or reductant than its ground state. It can donate an electron to Fe(III) or accept an electron from Fe(II) and thus initiate the photochemical reactions of both the CDOM itself and the iron species. Such a sensitization process should be quite common in the natural environment and would also be relevant in cases where

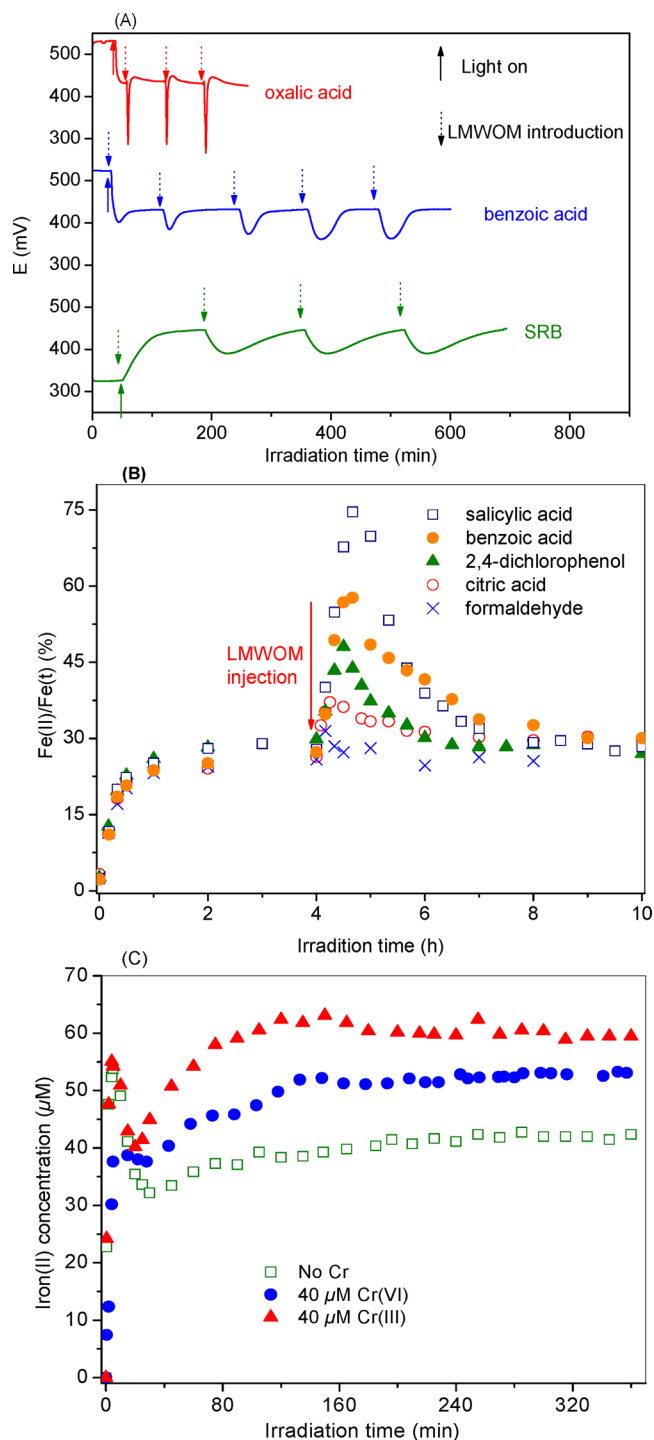


Figure 5. (A) Periodic changes in the ratio of Fe(III)/Fe(II) as demonstrated by the potential (E) in the presence of various LMWOMs measured by the in situ potential method. (B) Change in the Fe(II)/Fe(t) ratio in the presence of various LMWOMs: salicylic acid, benzoic acid, 2,4-dichlorophenol, citric acid, and formaldehyde. (C) Effects of Cr species on Fe(II) photoproduction during UV irradiation. Reprinted from refs 7 and 26.

photochemical reactions of iron species without visible light absorption become possible in the visible light region, providing an alternative pathway to promote the iron redox reactions. The previous investigations indicated that excited chromophores can transfer an electron to visible-light-insensitive Fe(III), which leads to regeneration of Fe(II) and

an enhanced cycle of Fe(III)/Fe(II) under visible light irradiation.^{27–29} This photosensitization scenario was recently used to initiate the redox reactions of photoinert structural iron in clay, in which Al atoms in the octahedral lattice are partly substituted by iron.^{30–33} Figure 6 illustrates simplified pathways

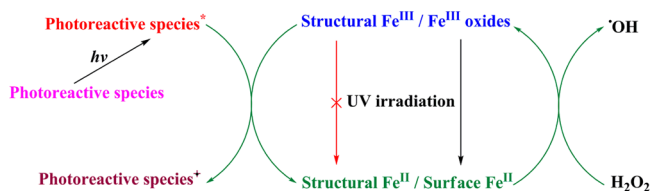


Figure 6. Proposed pathways of H₂O₂ decomposition catalyzed by iron oxides and structural iron of montmorillonite in the presence of photoreactive substances. Reprinted from ref 31.

for enhanced Fe cycling in the iron-bearing clay by sensitization. It was found that the photolysis of free iron oxide on the clay surface can generate Fe(II) species, which contributes to H₂O₂ decomposition by Fenton reactions. However, the structural iron in clay could hardly be photoreduced to structural Fe(II) under UV irradiation and thus exhibits poor photoactivity to decompose H₂O₂. Interestingly, introduction of organic chromophores like *N,N*-dimethylaniline (DMA), Rhodamine B (RhB) or Malachite green (MG), whose excited state donates electrons to structural iron or reduces structural Fe(III) to Fe(II) via outer-sphere electron-transfer pathways, greatly promotes the redox cycling of structural iron under UV or visible light irradiation.^{31,33}

Future Prospects. In this Perspective, we highlight several key photochemical processes involving the photochemical coupling of the iron redox reaction and the transformation of organic matter. Despite the concerted efforts, a clearly understood picture of the interplay among iron, LMWOM, light, and even dioxygen has not yet emerged. Many questions remain unanswered from a physical chemistry perspective. First, the primary charge-transfer mechanism for photolysis of organo-Fe(III) complexes is not well understood. Thanks to the advances in analytical tools and methods available for the study of photochemistry, the wealth of knowledge on the molecular basis for light-induced iron redox reactions has already been enriched. For example, the EXAFS experiments led Rentzepis and co-workers to propose a new pathway for the primary photochemistry of ferrioxalate, though their conclusions are controversial to those from Pozdnyakov's group. Further studies are called for to bridge the gap between the two pathways.

Second, the effects of carboxylates on photoinduced Fe redox cycling deserve further investigations. In particular, the relationship between the carbon chain length/substituents of the dicarboxylate homologue and the nature of secondary radicals generated from photocarboxylation is not fully elucidated. In this Perspective, carboxylates are divided into three categories. Indeed, oxalate, formate, and malonate are the major photo-oxidation intermediates of aromatics and long-chain aliphatics in the environment. Malonate as an example of Group III is highlighted because such photochemistry of Fe-malonate complexes can impact atmospheric chemistry, aquatic redox chemistry, and biogeochemistry in ways that are only beginning to be fully understood.

Third, effects of LMWOM on iron speciation are of great interest. Concentration profiles of various Fe species are largely

determined by ligand abundance and its coordination ability with Fe(III). The gap in knowledge remains for further insight into the impact of dynamic speciation change during the photolysis process, particularly with regard to the change in nature (e.g., coordination capacity and photoabsorptivity) and concentration of the primary chromophore with irradiation time and pH.^{5,34} Compared to extensive investigations on Fe(III) photoreduction, which unusually drives the photochemical Fe cycle, Fe(II) photo-oxidation remains unresolved, even though Fe(II) oxygenation kinetics has been well established. The roles of dioxygen in Fe(II) photo-oxygenation at acidic pH and the mechanism of the Fe(II) oxidation in the presence of irradiated Fe(III) complexes deserve study further.

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Finally, we also highlight the importance of photochemical processes initiated from electron transfer between the excited states of CDOM and iron species in solution or on the surface of Fe-bearing materials (such as clay). In this aspect, understanding of the primary electron-transfer processes, the effects of the iron specimen, and the types of chromophores on these processes should be the first things that deserve investigation.

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