Organic Intermediates in the Degradation of 2,4-Dichlorophenoxyacetic Acid by Fe^{3+}/H_2O_2 and $Fe^{3+}/H_2O_2/UV$

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The transient products formed during mineralization of 2,4-D by Fe^{3+}-catalyzed hydrogen peroxide in the dark or under 350-nm UV were identified in connection with studies of these advanced oxidation processes for wastewater treatment. Ethyl acetate extracts revealed 2,4-dichlorophenol as the major product ($\leq 15\%$ yield) and $\leq 3\%$ each of 2,4-dichlorophenyl formate, 2,4-dichloro-1-(chloromethoxy)-benzene, and 6,8-dichloro-2H-1,4-benzodioxan-3-one. The aqueous phase contained oxalic acid in dark reactions and oxalic and formic acids in photoassisted reactions, identified as their 1-propanol esters. In the light oxalate and formate were found in $\leq 1\%$ yield based on total carbon, but in the dark oxalate accumulated to about 60% yield. Experiment and numerical simulation showed that in the dark oxalate was unreactive toward the oxidizing species (hydroxyl radical) owing to its complexation with ferric ion, while in the light the ferric oxalate complex photolyzes to CO_2.

INTRODUCTION

Fenton-type systems employing Fe^{2+} or Fe^{3+} and H_2O_2 are a source of hydroxyl radicals (OH•) and therefore of interest as "advanced oxidation processes" for treatment of wastewaters containing hazardous organic compounds (Pignatello, 1992; Sun and Pignatello, 1992, 1993, and references cited therein). One potential application is the treatment of small-scale pesticide wastes, since the reagents are relatively safe and easy to handle.

The basis of this chemistry is the Fenton reaction (Fe^{2+} + H_2O_2) which produces OH• stoichiometrically and results in oxidation of the iron to Fe^{3+}. However, in excess peroxide, OH• continues to form, albeit at a much slower rate, by an Fe^{3+}-to-Fe^{2+} catalytic redox cycle involving hydrogen peroxide. The use of iron as a catalytic as opposed to a stoichiometric reagent would be an obvious advantage in practice. It has been found that the rate and extent of mineralization of organic compounds in Fe^{3+}-catalyzed reactions can be greatly increased by irradiating reaction mixtures with UV light from sunlight or a blacklamp. A number of ferric-sensitized photoreactions take place that generate Fe^{2+} in situ and cause photodecomposition of organic intermediates (Sun and Pignatello, 1993). The broadleaf herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (Pignatello, 1992; Sun and Pignatello, 1993) and several other compounds (unpublished data) are rapidly and completely mineralized by $Fe^{3+}/H_2O_2/UV$ in slightly acidic water. The chlorophenoxy herbicides required as little as 7 molar equiv of peroxide to be quantitatively oxidized to HCl and CO_2.

Up to this point we have been concerned mainly with inorganic and photochemical reactions that occur. The only intermediate that was identified during chlorophenoxy herbicide degradation was the corresponding di- or trichlorophenol. For mechanistic as well as toxicological considerations we carried out a more thorough investigation of 2,4-D intermediates in both dark (Fe^{3+}/H_2O_2) and irradiated ($Fe^{3+}/H_2O_2/UV$) systems.

MATERIALS AND METHODS

Materials. Acetyl chloride was purchased from Sigma Chemical Co., 14% (w/w) boron trifluoride in 1-propanol from Kodak, sodium formate from Sigma, $Fe(ClO_4)_3$ from GFS

Chemicals, 2,4-D from Aldrich Chemical Co., and [14C]oxalic acid (4.5 mCi/mmol; stated purity, $\geq 98\%$) from Sigma.

2,4-Dichlorophenyl formate was prepared from the phenol and acetic formic anhydride (Sofuku et al., 1967), which in turn was prepared fresh from sodium formate and acetyl chloride (Krimen, 1970).

Procedures. Details of the oxidation reactions can be found in previous publications (Pignatello, 1992; Sun and Pignatello, 1993). Typical conditions used in this work are as follows: [2,4-D] = 0.1 mM, [Fe^{3+}] = 1.0 mM, [H_2O_2] = 10 mM, pH = 2.8, T = 25 ± 1 °C. The light source was four 15-W black light tubes (F15T8/BLB, General Electric). Reaction solutions received 9 × 10^{17} photons s^{-1} L^{-1} (300–400 nm) as measured by potassium ferrioxalate actinometry.

For identification of hydrophobic products, 100 mL of reaction solution was extracted with 100 mL of ethyl acetate. The extract was dried over anhydrous Na_2SO_4 and evaporated in a rotary evaporator at about 20–25 °C. The residue was then dissolved in 2 mL of chloroform and analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).

For identification of organic acid products, a 10-mL aliquot of the reaction mixture was withdrawn and the reaction quenched by adding 1 mL of methanol. The mixture was brought to pH 6–8 with NaOH and the ferrihydr(oxide) precipitate removed by passing through a 0.2-μm pore size filter. The supernatant was then freeze-dried prior to esterification. Experiments using ring-14C-labeled 2,4-D showed no evaporative or other loss of the 14C label due to these manipulations.

A variety of methods are available for esterification of organic acids prior to GC/MS analysis (Knapp, 1979). We obtained the best results using the 1-propyl esterification method of Appleby and Mayne (1967), with slight modifications. Freeze-dried reaction samples were ground together with 1 mL of 1-propanol and 3 drops of 85% phosphoric acid. A solution (2 mL) of $BF_3/$1-propanol was added and the mixture sealed in a vial with a PTFE-lined septum cap and heated at 100 °C for 2.5 min. After immediate cooling on ice, 20 mL of ice-cold distilled water was added and the mixture extracted with 0.5 mL of chloroform. The extract was dried over anhydrous Na_2SO_4 prior to GC or GC/MS analysis. [In preliminary tests on several organic acids anticipated as products, extraction by petroleum ether or cyclopentane, as originally recommended (Appleby and Mayne, 1967), failed to extract very polar esters like tartrate that contain hydroxy groups. Although methyl esters could be prepared in similar fashion (Harmon and Doelle, 1969), 1-propyl esters are preferred due to their lower volatility and water solubility.]

Analysis. GC/MS analysis was carried out on a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard

Table I. GC/MS Operating Conditions

components	description	operating conditions
gas chromatograph		
instrument	Hewlett-Packard 5890	
capillary column	DB-1, 0.25 μm, 30 m × 0.25 mm	
injection mode	splitless	
carrier gas	helium	20 psi
temp	transfer line	260 °C
	injection	250 °C
	oven initial	70 °C
	oven final	250 °C
	rate	5 °C/min
time	at initial temp	0 min
	at final temp	10 min
mass spectrometer		
instrument	Hewlett-Packard 5970	
ion source	electron impact	70 eV
	source temp	250 °C
full scan	m/z	50–300 or 25–300
detection	mass selective detector	

5970 mass spectrometer with mass selective detector. Operating conditions are given in Table I.

Product quantitation was done by GC on a DB-1 30 m × 0.25 mm, 0.25-μm film capillary column (J&W Scientific) with flame ionization detection. Helium was the carrier gas, and N_2 at 30 mL min^{-1} was the auxiliary gas. The splitless injection mode was used, with the injection port temperature at 250 °C. The temperature program was as follows: 50 °C initial temperature, raised at 10 °C min^{-1} to 250 °C, which was held for 10 min.

RESULTS

Solvent-Extractable Products. The total ion chromatogram (TIC) of ethyl acetate extracts of Fe^{3+}/H_2O_2 or $Fe^{3+}/H_2O_2/UV$ reactions showed one major and three minor peaks, all of which were absent at time zero or in 2,4-D standards. Table II lists the TIC retention times and major MS fragments. The molecular assignments are illustrated in Figure 1.

Intermediate **A** is 2,4-dichlorophenol (DCP) ($C_6H_4Cl_2O$, MW = 162), which was positively identified earlier as the major product (Pignatello, 1992).

Intermediate **B** has a weak molecular ion cluster at m/z 190 and an intense cluster at 162, each of which contains two Cl. The fragmentation pattern of **B** is identical to that of the compound synthesized from DCP and acetic formic anhydride. It is also similar to the fragmentation pattern of 2,4,5-trichlorophenyl formate formed during TiO_2 photocatalytic degradation of 2,4,5-T (Barbeni et al., 1987) except for the difference of one Cl for H substitution. Thus, compound **B** is identified as 2,4-dichlorophenyl formate ($C_7H_4Cl_2O_2$, MW = 190). The major fragments are m/z 190 (M), 162 (M – CO), 133 (M – CO – COH), 127 (M – CO – Cl), and 98 (M – CO – CHO – Cl). Note that the pattern below m/z 162 is identical to that of DCP (**A**).

Figure 1. Structures of solvent-extractable 2,4-D degradation products.

Compound **C**, 2,4-dichloro-1-(chloromethoxy)benzene ($C_7H_5Cl_3O$, MW = 210), gives a molecular ion cluster at m/z 210 indicating the presence of three chlorines. The cluster at m/z 175 is due to the loss of one chlorine from the molecular ion. Other major fragments are m/z 161 (M – CH_2Cl), 145 (M – OCH_2Cl), and 133 (M – CH_2Cl – CO), a pattern consistent with ethers of this type.

Intermediate **D** has an intense molecular ion cluster at m/z 218 that indicates a formula containing two fewer hydrogens than the 2,4-D molecule. The major fragments are m/z 190 (M – CO) and 189 (M – CHO). The fragmentation pattern is analogous to that of 5,6,8-trichloro-2H-1,4-benzodioxan-3-one, which was observed during the photocatalytic degradation of 2,4,5-T on TiO_2 (Barbeni et al., 1987), with a difference of one Cl for H substitution. On this basis intermediate **D** is identified as 6,8-dichloro-2H-1,4-benzodioxan-3-one ($C_8H_4Cl_2O_3$, MW = 218).

The changes in concentration of **A–D** with time are shown in Figures 2 (Fe^{3+}/H_2O_2 reaction) and 3 ($Fe^{3+}/H_2O_2/UV$ reaction). Bell-shaped curves typical of transient intermediates are evident. The yields of **B–D** are all minor compared with that of **A** (DCP). Reactivity of all products was greater in the light than in the dark, accordant with the observed reactivity of 2,4-D itself (lifetimes of about 3 and 20 min, respectively) (Pignatello, 1992).

Water-Soluble Products. Table II gives GC/MS data on the 1-propyl esterified products in the aqueous phase of reaction mixtures. Their yields with time are depicted in Figure 2 for the dark and in Figure 3 for the light reaction.

(a) *Dark Reaction.* The major product from Fe^{3+}/H_2O_2 reactions was identified as oxalic acid, whose assignment was confirmed by esterification and GC/MS analysis of authentic oxalic acid. Di-1-propyl oxalate has no molecular ion peak but gives the fragments m/z 133 (M – C_3H_5), 89 (M – $COOC_3H_5$), 59 (OC_3H_7), 43 (C_3H_7), 41 (C_3H_5), and 27 (C_2H_3). The peak at m/z 133 arises from the characteristic "McLafferty + 1" rearrangement for propyl and higher esters.

Oxalate appeared after a few minutes' lag and built up to an eventual yield of 60% after about 1.5 h. Since degradation of ring- and carboxy-labeled 2,4-D in the dark gave about 40% yield of $^{14}CO_2$ by that time (Pignatello,

Table II. GC/MS Data for 2,4-D Degradation Intermediates

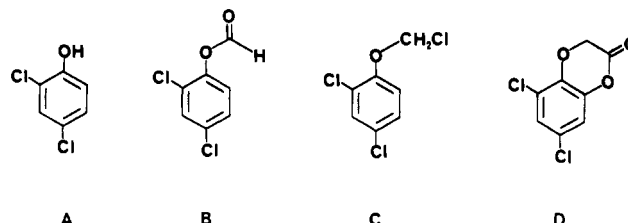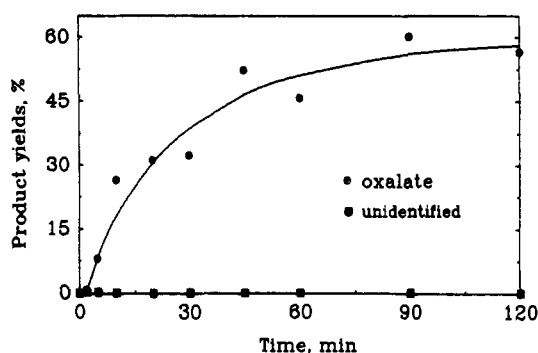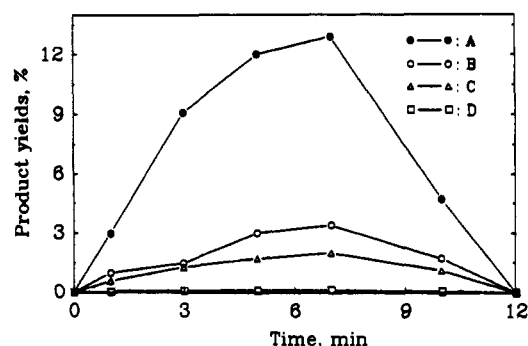| compound	TIC retention time	MS peaks
2,4-dichlorophenol (**A**)	8.4	166 (16), 164 (75), 162 (100), 135 (9), 133 (12), 127 (14), 98 (36), 73 (19), 63 (46), 29 (24)
2,4-dichlorophenol formate (**B**)	9.7	192 (4), 190 (6), 164 (64), 162 (100), 133 (12), 129 (6), 127 (10), 100 (8), 98 (30), 73 (15), 63 (40), 29 (23)
2,4-dichloro-1-(chloromethoxy)benzene (**C**)	14.7	214 (19), 212 (66), 210 (57), 177 (42), 175 (61), 163 (58), 161 (100), 147 (28), 145 (42), 135 (36), 133 (50), 111 (20), 109 (24), 75 (27), 74 (27), 63 (18)
6,8-dichloro-2H-1,4-benzodioxan-3-one (**D**)	18.3	220 (44), 218 (63), 193 (30), 192 (40), 191 (98), 190 (73), 189 (100), 119 (35), 97 (41)
oxalic acid (as dipropyl ester)	8.1	133 (4), 89 (3), 73 (2), 71 (3), 59 (4), 43 (100), 41 (44), 27 (32)
unidentified product	10.3	147 (9), 129 (68), 105 (97), 87 (40), 43 (100), 42 (41), 27 (36)
formic acid (as tripropyl orthoformate)	16.1	131 (47), 119 (10), 103 (9), 89 (100), 59 (13), 43 (100), 41 (42)

Figure 2. Product yields with time for degradation of 2,4-D in the dark. Yields of B-D were calculated under the assumption that their FID response factors are the same as that of A (DCP). Oxalate and formate were quantified from a calibration curve established with authentic materials and are based on total 2,4-D carbon.
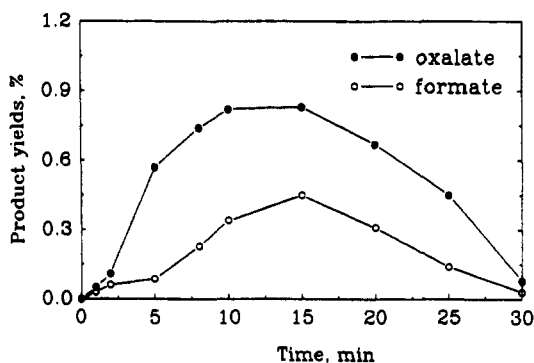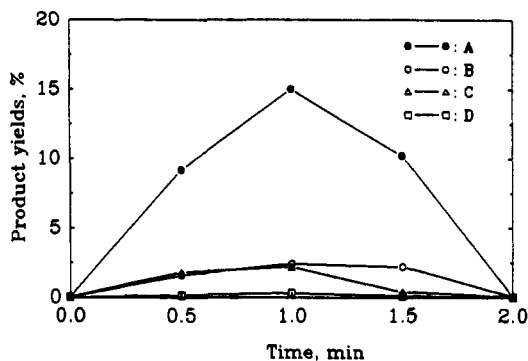

Figure 3. Product yields with time for degradation of 2,4-D in the light. See legend to Figure 2.

1992), it seems clear that oxalic acid makes up virtually all of the organic carbon in solution at that point.

A second trace product with TIC retention time of 10.3 min is presently unidentified. Assuming a response factor equal to that of oxalate, its yield was always below 0.2%. It is possibly the di-1-propyl ester of pyrocarbonic acid (di-1-propyl dicarbonate, $C_8H_{14}O_5$, MW = 190), as sug-
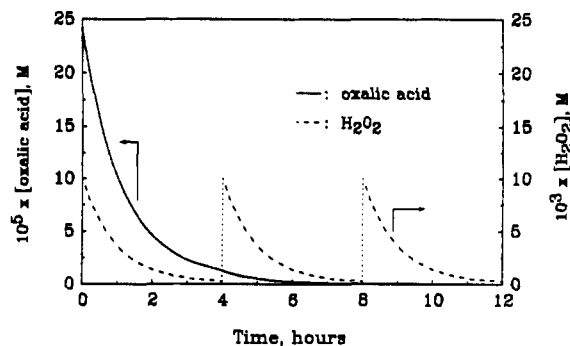

Figure 4. Simulation of the oxidation of oxalic acid by Fe^{3+}/ H_2O_2 (dark) without Fe–oxalate complexation.

gested by the peak at m/z 147 (M – C_3H_7), although pyrocarbonic acid is rapidly hydrolyzed in water.

(b) *Irradiated Reaction.* Oxidation by $Fe^{3+}/H_2O_2/UV$ afforded oxalic and formic acids. Hydrated formic acid forms the tripropylorthoformate ester in BF_3/propanol. The tripropyl ester has peaks at m/z 131 (M – OC_3H_7), 59 (OC_3H_7), 43 (C_3H_7), and 41 (M – C_3H_5), among others. Its assignment was confirmed with a derivatized sample of authentic formic acid. None of the unidentified product with retention time 10.3 min was detected in light reactions.

Unlike the dark reaction, oxalic acid was transient and found in low yield throughout the reaction (Figures 2 vs 3). We note that 2,4-D is completely mineralized in about 45 min by $Fe^{3+}/H_2O_2/UV$ under the same conditions (Sun and Pignatello, 1993).

DISCUSSION

Intermediate **D** probably results from lactonization following ortho-hydroxylation of the ring by OH•. That additional hydroxylated intermediates were not detected is likely due to the activating effect of the hydroxyl group on the ring; indeed, dechlorination is nearly concurrent with 2,4-D transformation, showing that ring-oxidized intermediates react more rapidly than starting material (Pignatello, 1992).

The products **A–C** result from side-chain oxidation of 2,4-D. Attack of OH• on the side chain gives intermediate radicals I and II that may be further oxidized and hydrolyzed to yield **A** and **B**:

$$Ar-O-CH_2CO_2H + OH^• \rightarrow$$

$$\underset{I}{Ar-O-\overset{•}{C}HCO_2H} + \underset{II}{Ar-O-CH_2CO_2^•} \quad (1)$$
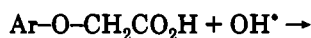
C was unexpected but could form by reaction of an intermediate such as $[Ar-O-CH_2]^+$ with liberated Cl^-. A minor route to **A** is photodecarboxylation of a Fe(III)–2,4-D complex (Sun and Pignatello, 1993).

$$[Ar-O-CH_2CO_2-Fe]^{2+} \overset{h\nu}{\rightarrow} Ar-O-CH_2^• + CO_2^• + Fe^{2+} \quad (2)$$
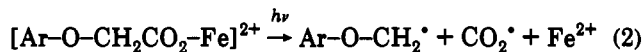
Oxalate and formate are products of advanced degradation, and therefore their exact (perhaps multiple) pathways are obscure.

The fleeting existence of oxalate in the irradiated reactions is in accord with the well-known photodecomposition of ferric oxalate complexes to give CO_2 and Fe(II) (Parker, 1954; Parker and Hatchard, 1959). The quantum yield for ferric trioxalate, for example, is around 1 between 250- and 509-nm wavelengths. Considering that oxalic acid itself is fairly reactive toward OH• [k_{ox} = 4.7 × 10^7 M^{-1} s^{-1} at pH 3 (Buxton et al., 1988; Getoff et al., 1971)], its persistence in dark reactions (Figure 2) is at first surprising. In fact, even after multiple additions of
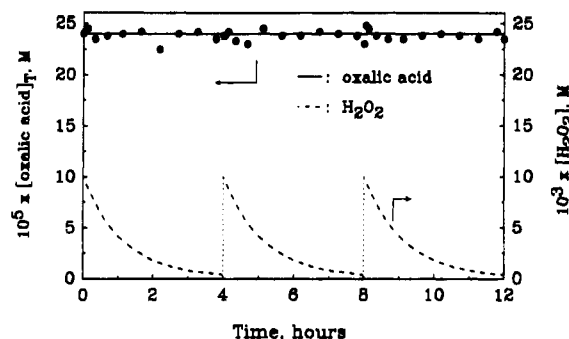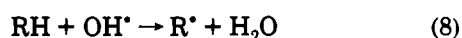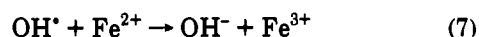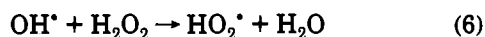
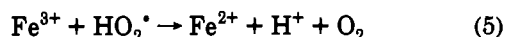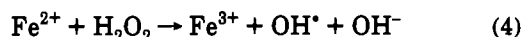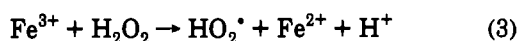**Figure 5.** Simulation of oxalic acid oxidation by Fe^{3+}/H_2O_2 (dark) with Fe–oxalate complexation and assuming complexed oxalate is unreactive toward OH•. Solid circles represent experimental decay of solution radioactivity starting with [^{14}C]oxalate.

peroxide to [$ring$-^{14}C]-2,4-D, 50–60% of the ^{14}C (presumably as oxalate) remains in solution (Sun and Pignatello, 1993). In the dark, OH• is generated and consumed by

$$Fe^{3+} + H_2O_2 \rightarrow HO_2{}^• + Fe^{2+} + H^+ \qquad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^• + OH^- \qquad (4)$$

$$Fe^{3+} + HO_2{}^• \rightarrow Fe^{2+} + H^+ + O_2 \qquad (5)$$

$$OH^• + H_2O_2 \rightarrow HO_2{}^• + H_2O \qquad (6)$$

$$OH^• + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (7)$$

$$RH + OH^• \rightarrow R^• + H_2O \qquad (8)$$

where RH is an organic substrate such as oxalate.

Using the multistep kinetic program GEAR (PC version 1.11; Project Seraphim, Department of Chemistry, University of Wisconsin, Madison, WI 53706) that we used earlier in another context (Sun and Pignatello, 1993), we simulated the oxidation of oxalic acid by 10 mM H_2O_2 added every 4 h for a period of 12 h in the presence of 1 mM Fe^{3+} (Figure 4). The maximum yield of oxalate obtained in the experiment of Figure 2 (0.24 mM) was taken as the initial oxalate concentration in the simulation. The following rate constants were used in the simulations (units of $M^{-1} s^{-1}$; pH ~3 except where noted): $k_3 = 2 \times 10^{-2}$; $k_{-3} = 1.2 \times 10^6$; $k_4 = 53$; $k_5 = 2.9 \times 10^4$; $k_6 = 2.7 \times 10^7$ (pH 7); $k_7 = 4.3 \times 10^8$; and $k_8 = k_{ox}$. The simulation (Figure 4) shows that, despite competition for OH• from reactions 6 and 7, about 95% of initial oxalate will be mineralized in 4 h.

Oxalate, however, strongly complexes with Fe(III) (Martell and Smith, 1982). The formation constants for 1, 2, and 3 oxalates per Fe are $K_1 = 3.80 \times 10^7$, $K_2 = 1.60 \times 10^6$, and $K_3 = 6.17 \times 10^5 M^{-1}$. At oxalate between 0.01 and 1.0 mM, only 0.003–0.5% of oxalate will be uncomplexed. It may be hypothesized that coordination to iron greatly reduces the reactivity of oxalic acid toward OH•. This is verified in Figure 5, where the simulation was repeated inclusive of the equilibria represented by K_1–K_3

and assuming that only uncomplexed oxalate reacts with OH•. The simulation predicts about 0.3% decomposition, in agreement with experiment using [^{14}C]oxalic acid (solid circles), where no significant loss of solution radioactivity in the dark occurred. From this we conclude that dark oxidation of oxalic acid by Fe^{3+}/H_2O_2 is inhibited due to its complexation with Fe(III). Although complexation by oxalate may also reduce the reactivity of Fe(III) toward H_2O_2, this must be less important, since most (76%) of the initial iron remains uncomplexed under the conditions used (0.24 mM initial oxalate).

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