

Activation of Hydrogen Peroxide by Iron(III) Chelates for Abiotic Degradation of Herbicides and Insecticides in Water

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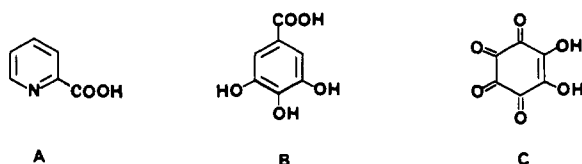
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Degradation of selected pesticides was carried out in water at pH 6 using hydrogen peroxide and soluble Fe(III) chelates of picolinic acid, gallic acid, or rhodizonic acid as catalysts and with or without near-UV irradiation. The catalysts were selected on the basis of an earlier screening. Without UV light, transformation of baygon, carbaryl, picloram, 2,4-D, 2,4,5-T, and atrazine was complete within a few minutes to about 2 h. Trifluralin reacted slowly. Ring- and carboxy-labeled [^{14}C]-2,4-D and ring-labeled [^{14}C]-2,4,5-T were 70–80% mineralized to $^{14}\text{CO}_2$ in 2–4 h. Ring-labeled [^{14}C]atrazine yielded no $^{14}\text{CO}_2$. UV light accelerated degradation by the above chelates, as well as by thermally inactive oxalate and citrate chelates. UV acceleration is most likely due to charge-transfer photoreduction of the chelate to give Fe(II), which then reacts with H_2O_2 to generate hydroxyl radical in the Fenton reaction. These reactions are potentially useful for detoxifying pesticide wastes.

INTRODUCTION

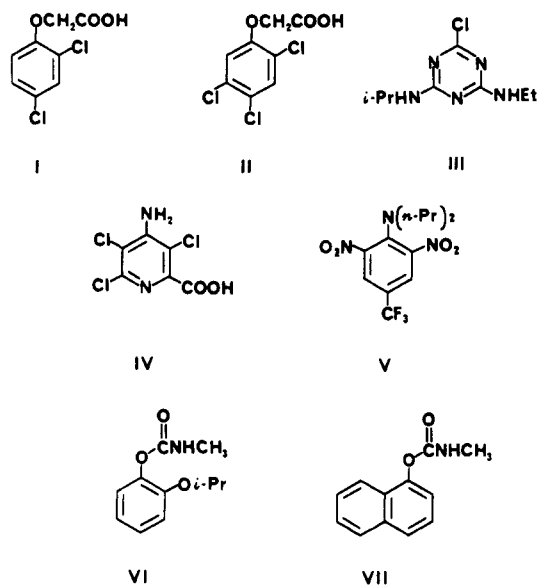
The application of millions of pounds of pesticides each year generates rinsate, waste product, and contaminated soil at hundreds of thousands of application sites. The disposal of such wastes faces ever tougher regulations. Land disposal threatens water supplies (Habecker, 1989), and incineration is costly because of the large volume of water accompanying the waste and the high transport costs. A possible treatment option is chemical or photochemical degradation. A viable method must convert the original compound to less toxic or more biodegradable intermediates or, ideally, should result in mineralization to simple inorganic compounds, such as CO_2 , H_2O , Cl^- , and NH_3 .

Ferric-catalyzed hydrogen peroxide under acidic conditions has been shown to readily mineralize organic compounds—for instance, 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (Pignatello, 1992)—by producing highly oxidizing species such as the hydroxyl radical (OH^\bullet) in Fenton-type reactions. However, above pH 3, ferric ions exist as inactive oxyhydroxide solids. To circumvent the drawbacks of working under acidic conditions, especially for treating contaminated soil, we screened a number of ferric chelates that were soluble at pH 6 for activity in degrading 2,4-D (Sun and Pignatello, 1992a). We found 20 or so chelates that were effective in mediating the transformation and mineralization of 2,4-D. Virtually all active chelators were themselves unstable in such strong oxidizing media, so they are not truly catalysts. On the basis of reactivity and stability, picolinic acid (A), gallic acid (B), and rhodizonic



acid (C) appeared to be good candidates for further study of activity toward other pesticides. They are most likely bidentate ligands.

The herbicides tested were 2,4-D (I), 2,4,5-T (II), atrazine (III), picloram (IV), and trifluralin (V), which are commonly used to control broadleaf weeds in grass and various



crops (WSSA, 1983; *Farm Chemicals Handbook*, 1990). The insecticides included baygon (VI) and carbaryl (VII), commonly used on row crops and orchards. Previously reported research on chemical or photochemical treatment methods for these pesticides includes the following: ozone/UV [atrazine (Kearney et al., 1988)], titanium dioxide heterogeneous photocatalysis [atrazine (Pelizzetti et al., 1990) and 2,4,5-T (Barbeni et al., 1987)], ferric-sensitized photodegradation [atrazine (Larson et al., 1991)], and others cited earlier for 2,4-D (Sun and Pignatello, 1992a).

In addition, we tested the effects of UV light. The reactivity of simple Fe^{3+} -catalyzed H_2O_2 in acid increases greatly under UV illumination due to several ferric-sensitized reactions. These reactions include increased production of OH^\bullet from photoreduction of $\text{Fe}(\text{OH})^{2+}$ and photoreduction of Fe(III) complexes of substrate (chlorophenoxy acid) and/or its intermediate oxidation products (Pignatello, 1992; Sun and Pignatello, 1992b). Recently, Zepp et al. (1992) photoreduced ferric oxalate and citrate complexes in the presence of H_2O_2 and showed that the Fe(II) product reacted with H_2O_2 to produce OH^\bullet in the Fenton reaction. We found that, in the dark, oxalate and citrate chelates were only weakly active toward peroxide

Table I. HPLC Conditions for Pesticide Determinations

pesticide	solvent, %			flow, mL/min	retn t, min	wavelength, nm
	H ₂ O	MeOH	TFA			
2,4-D	40	60	0.08	1.5	6.7	230
2,4,5-T	30	70	0.06	1.5	10.2	230
atrazine	35	65	0.07	1.0	7.5	240
trifluralin	40	60	0.08	0.8	6.2	200
picloram	52	48	0.06	0.8	5.9	220
baygon	40	60	0.08	1.0	5.9	210
carbaryl	40	60	0.08	1.5	6.0	230

oxidation of 2,4-D (Sun and Pignatello, 1992a). In view of the above results, therefore, we decided to test Fe(III) chelates of citrate and oxalate, as well as A-C, in a photocatalytic mode for oxidation of the pesticides.

MATERIALS AND METHODS

Materials. Chemicals were used as purchased. Hydrogen peroxide was from Mallinckrodt. Fe(ClO₄)₃ was from GFS Chemicals. Picolinic, gallic, and rhodizonic acids were from ICN Biochemicals. The pesticides and their sources are as follows: 2,4-D (2,4-dichlorophenoxyacetic acid) (Aldrich); 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) (Aldrich); atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine] (Aldrich); trifluralin [*N,N*-dipropyl-2,6-dinitro-4-(trifluoromethyl)aniline] (Lilly); picloram (4-amino-3,5,6-trichloropicolinic acid) (Aldrich); baygon (2-isopropoxyphenylmethylcarbamate) (Velsicol Chemical Laboratory, Chicago, IL); carbaryl (1-naphthyl *N*-methylcarbamate) (Riedel-de Haën, Germany). [*ring*-UL-¹⁴C]-2,4-D (10.0 mCi/mmol), [*carboxy*-¹⁴C]-2,4-D (9.0 mCi/mmol), [*ring*-UL-¹⁴C]-2,4,5-T (7.1 mCi/mmol), and [*ring*-UL-¹⁴C]atrazine (4.0 mCi/mmol) were from Sigma.

Procedure. Detailed experimental procedures are given elsewhere (Pignatello, 1992; Sun and Pignatello, 1992a) but are briefly described here. Ferric ion solution was prepared in 0.1 M HClO₄ to minimize iron(III) hydrolysis and polymerization (Flynn, 1984; Sylva, 1972). Iron(III) chelates were made by directly mixing the Fe³⁺ solution with a solution of the corresponding chelator. The solution pH was then adjusted to 6.0 with NaOH. Reactions were conducted with continuous vigorous magnetic stirring to keep the solutions aerated.

The normal reaction conditions are as follows: [pesticide] = 0.1 mM; [Fe³⁺] = 1.0 mM; [chelator] = 1.0 mM except oxalate, which was 10.0 mM; [H₂O₂] = 10.0 mM; pH 6.0; *T* = 25 ± 2 °C; and ionic strength at 0.2 M NaClO₄. Radioactive compounds were added at about 1 × 10⁴ dpm/mL. Conditions that deviate from these will be noted in the figures and tables.

Photolysis was carried out in a temperature-controlled room (25 ± 1 °C). UV illumination was provided by four 15-W black light blue (BLB) tubes from General Electric. The lights emit in the 300–400-nm region (Pignatello and Sun, 1992). A Pyrex glass Erlenmeyer flask (250 mL) covered with a Pyrex watchglass was used for all photoreactions. The light intensity was 9 × 10¹⁷ quanta L⁻¹ s⁻¹, as determined by ferrioxalate actinometry.

Analyses. The concentrations of parent pesticides and phenol intermediate products of 2,4-D and 2,4,5-T were determined by HPLC on a C-18 reversed-phase silica gel column (4.6 mm i.d. × 250 mm, ODS-25 Micro, Alltech), using a mobile phase of water-methanol-trifluoroacetic acid (TFA), and detected by UV. Table I lists for each pesticide the HPLC conditions, retention time, and detector wavelength. Under the conditions used for their respective parent compounds, 2,4-dichlorophenol (DCP) and 2,4,5-trichlorophenol (TCP) had retention times of 8 and 14 min, respectively. Aliquots of the reaction mixture (2 mL) for HPLC analysis were mixed with 0.05 mL of 2 M HClO₄ and 3 mL of methanol, which quenched the reaction. Mineralization was assessed by loss of solution radioactivity, which was assumed to parallel ¹⁴CO₂ evolution (Pignatello, 1992).

RESULTS

Thermal Degradation. 2,4-D. Thermal catalytic activity of ferric chelates was investigated under ordinary room fluorescent light intensity. Such light had little or

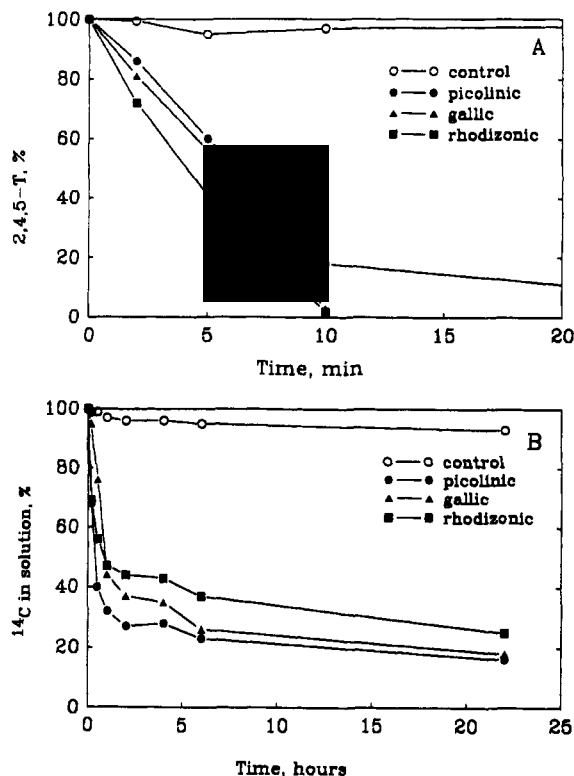


Figure 1. Transformation (A) and mineralization (B) of ring-labeled 2,4,6-T by Fe(III) chelates and hydrogen peroxide. Control is precipitated ferric oxyhydroxides suspension.

no effect on reactivity compared to total darkness. Details concerning thermal degradation of 2,4-D using these chelates can be found in an earlier publication (Sun and Pignatello, 1992a). To summarize briefly here, the transformation of 2,4-D with 1 mM gallate, picolinate, and rhodizonate chelates and 10 mM hydrogen peroxide was complete after only 10–30 min. Chloride was released quantitatively in the case of gallate. About 80% mineralization of ring-labeled 2,4-D occurred in about 2 h, but further mineralization was difficult. Reactions with the oxalate and citrate chelates were much slower, requiring a few hours to a day to achieve complete loss of 2,4-D.

2,4,5-T. The transformation of 2,4,5-T was similar to that of 2,4-D. Within minutes of the addition of hydrogen peroxide, 100% of 2,4,5-T was removed (Figure 1A). A minor amount of the byproduct 2,4,5-trichlorophenol (TCP)—whose identity was confirmed by GC/MS in this laboratory in an earlier study (Pignatello, 1992)—was formed but rapidly converted to other products. Chloride ion determined gravimetrically using AgNO₃ was produced quantitatively.

Mineralization occurred on a slower time scale (Figure 1B). Gallate and picolinate chelates showed about the same activity and were slightly faster than rhodizonate chelate. Substantial mineralization took place in the first 2–4 h. After extended times, solution radioactivity was reduced about 80% for gallate and picolinate and 70% for rhodizonate. Additional supplements of H₂O₂ (10 mM each) were not helpful; in fact, supplementation hastened formation of rust-colored precipitates (ferric oxyhydroxides), indicating decomposition of the chelates.

Atrazine. Transformation of atrazine was complete in 30–90 min (Figure 2). Gallate proved to be much better than the others. A number of peaks were observed in HPLC chromatograms that have not yet been identified. No loss of solution radioactivity occurred from [*ring*-UL-¹⁴C]atrazine. This is not surprising, since the *s*-triazine

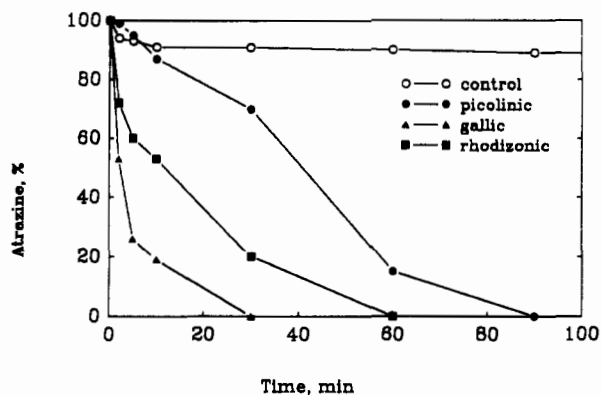


Figure 2. Transformation of atrazine by Fe(III) chelates and hydrogen peroxide.

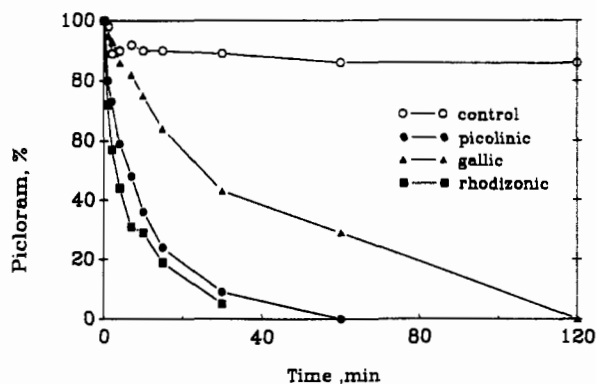


Figure 3. Transformation of picloram by Fe(III) chelates and hydrogen peroxide.

ring is resistant to hydroxyl radical generated by Fenton's reagent (Plimmer et al., 1971), ozone (Kearney et al., 1988), and TiO_2 heterogeneous photocatalysis (Pelizzetti et al., 1990). Atrazine mainly undergoes dealkylation, dechlorination, and deamination reactions resulting in a series of *s*-triazine intermediates, with cyanuric acid (1,3,5-trihydroxy-*s*-triazine) as the terminal product (Pelizzetti et al., 1990).

Picloram. Picloram is a derivative of picolinic acid. The introduction of three chlorines on the ring was expected to reduce ring electron density and hence its reactivity toward the electrophilic OH^\bullet . Nevertheless, the transformation of picloram was complete in about 60 min for picolinate and rhodizonate chelates and in 2 h for gallate chelate (Figure 3). Despite the presence of chlorine, picloram degraded more quickly than the picolinate chelate decomposed.

Trifluralin. Trifluralin is only sparingly soluble in water (2.4 mg/L, 7.2×10^{-3} mM at 20 °C) and could not be studied at the 0.1 mM level used for all of the other compounds. A saturated solution of trifluralin reacted extremely slowly (Figure 4), presumably because (1) the trifluoromethyl and nitro groups greatly reduce the ring electron density and (2) trifluralin was much lower in concentration than the chelate itself, making it less competitive for the oxidant.

Baygon. The carbamate insecticide baygon reacted in less than 2 min with gallate (Figure 5). The rhodizonate chelate failed to convert baygon completely in 1 h, while the picolinate was intermediate in reactivity. No major peaks attributable to intermediates appeared in HPLC chromatograms.

Carbaryl. Carbaryl, also a carbamate insecticide, is extremely reactive. At 10 mM H_2O_2 , the reaction with all three chelates was complete before the first sampling

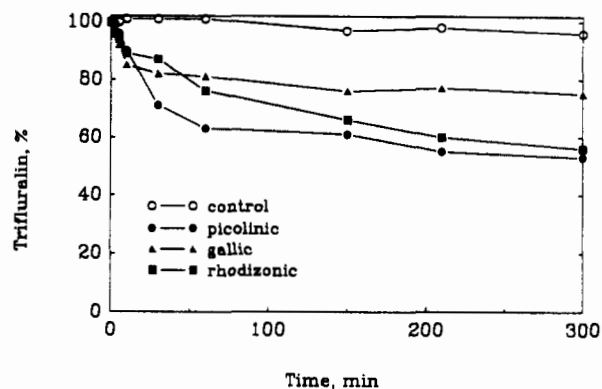


Figure 4. Transformation of trifluralin by Fe(III) chelates and hydrogen peroxide. [Trifluralin] = 7.2×10^{-3} mM.

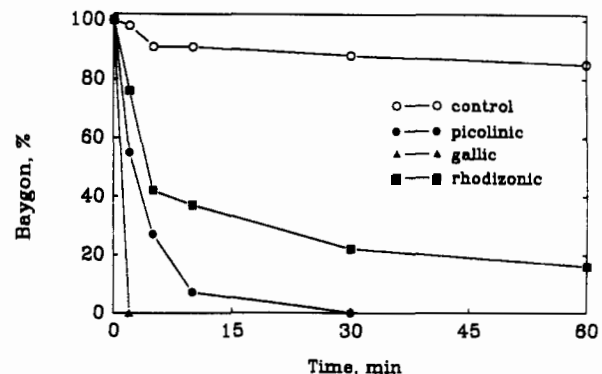


Figure 5. Transformation of baygon by Fe(III) chelates and hydrogen peroxide.

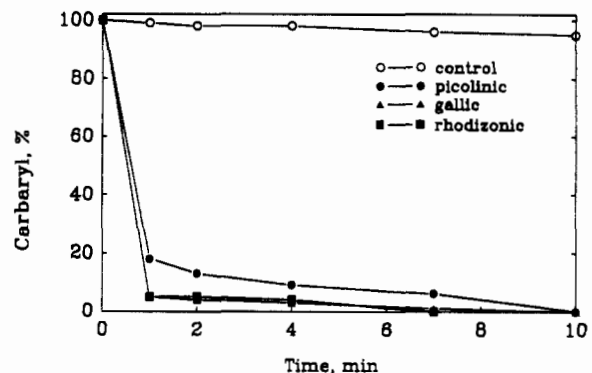


Figure 6. Transformation of carbaryl by Fe(III) chelates and hydrogen peroxide. [H_2O_2] = 1.0 mM.

(about 30 s). At 1.0 mM H_2O_2 , the reaction was complete in less than 10 min (Figure 6). In the absence of chelating agents, carbaryl complexed with iron(III), forming a pink solution at pH 3.0 and a brown precipitate at pH 6. Therefore, the control experiment in Figure 6 was done by precipitating ferric ion first at pH 6 and then adding carbaryl.

UV-Assisted Degradation. Figure 7 shows the transformation of 2,4-D by iron(III) chelates at pH 6.0 under black light UV irradiation with and without hydrogen peroxide. In the absence of peroxide, it was shown that 2,4-D could be degraded by UV-irradiated Fe^{3+} in acid solution due to generation of OH^\bullet by photoreduction of $\text{Fe}(\text{OH})^{2+}$ (Sun and Pignatello, 1992b). In contrast, irradiated picolinate and gallate chelates were inactive without peroxide, and the rhodizonate chelate yielded only about 50% transformation in 2 h (Figure 7A). As a strongly absorbing polyketone, rhodizonic acid is itself a potential photosensitizer. Irradiated reaction solutions containing rhodizonic acid alone at pH 6, however, gave only 25%

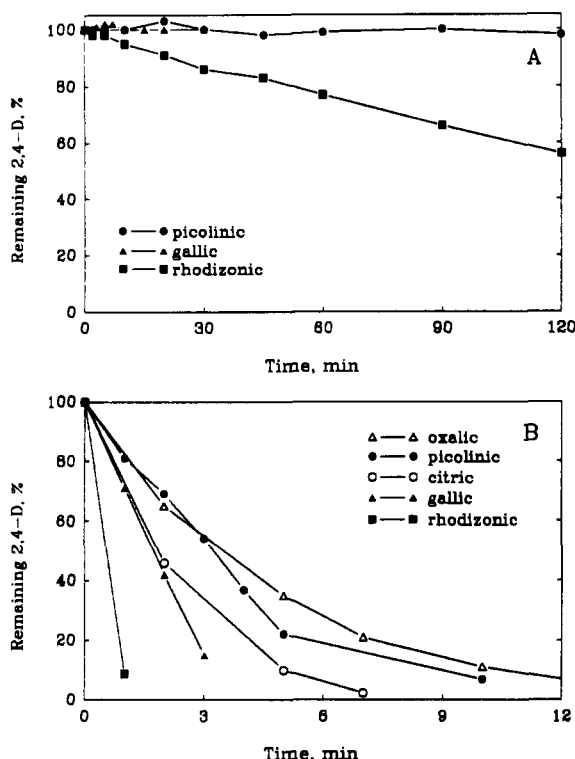


Figure 7. UV-assisted 2,4-D transformation of 2,4-D by Fe(III) chelates at 0 (A) and 10 mM (B) H₂O₂.

Table II. Comparison of the Extent of Ring ¹⁴C 2,4-D Degradation with and without UV Irradiation^a

chelates	transformation after 2 min, %		mineralization after 120 min, %	
	no UV	UV	no UV	UV
Fe(III) only	<1	2	<1	<2
picolinate	40	41	64	90
gallate	41	58	73	85
rhodizonate	65	100	54	87
oxalate ^a	4	35	12	74
citrate	<1	54	2	75

^a [Oxalate] = 10.0 mM.

loss of 2,4-D in 2 h (not shown), despite near total bleaching of its orange color.

In the presence of H₂O₂ (10 mM) (Figure 7B), irradiated reactions resulted in complete removal of 2,4-D within minutes in all cases and were faster than the thermal reaction, except for picolinate (Table II). Thermally inactive oxalate and citrate chelates were much more active under UV, as expected from the results of Zepp et al. (1992).

The extent of 2,4-D mineralization was also accelerated by UV, especially for oxalate and citrate (Figure 8; Table II). Ring- and carboxy-labeled 2,4-D evolved ¹⁴CO₂ at virtually the same rate in the case of gallate (Figure 8).

Chelates were generally less stable under UV. In 10 mM H₂O₂, the deep blue color of gallate chelate disappeared in 7 min and the dark brown color of rhodizonate faded completely in 2 min. The same color changes require about 30 and 10 min, respectively, without UV. Also, while gallate and citrate chelates were stable to precipitation of ferric oxides for days after initial addition of 10 mM H₂O₂ under room light, precipitation began in 60 min under UV. Picolinate, rhodizonate, and oxalate chelate solutions showed precipitation within 0.5 h.

DISCUSSION

Inspection of Figures 1–7 reveals no clear choice among the chelates in terms of "catalytic" activity toward pesticide

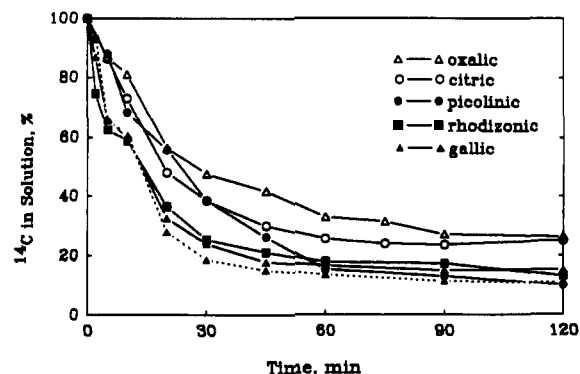
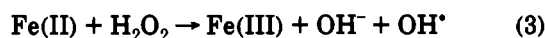
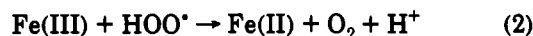
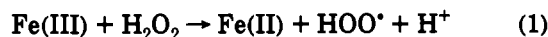


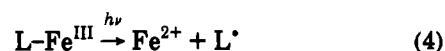
Figure 8. UV-assisted mineralization of 2,4-D by Fe(III) chelates at 10 mM H₂O₂. Solid lines represent ring-labeled and dashed line represents carboxy-labeled 2,4-D.

oxidation. At this time there is no firm explanation for the variable order. Dual pathways of thermal hydrogen peroxide activation seem to exist with Fe(III) chelates. One is OH[•] formation by a mechanism analogous to the uncomplexed Fe³⁺/H₂O₂ system:



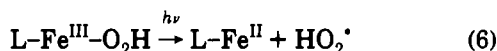
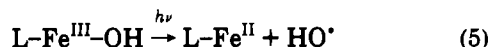
The key step, eq 3, is referred to as the Fenton reaction. The behavior of Fe(III) chelates is less clear. Production of OH[•] from various Fe(II) chelates has been shown by spin trapping (Yamazaki and Piette, 1990), but the yield of OH[•] depended on the ligand. There is now growing evidence that many Fe(II) and Fe(III) chelates react thermally with H₂O₂ to form ferryl complexes, (L)Fe^{IV}=O, or one electron ligand-oxidized ferryl complexes (L⁺)Fe^{IV}=O [Leising et al., 1991; citations in Pignatello (1992)]. Like OH[•], these species can be strong and nonselective oxidizing agents. Thus, activity may depend on chelate and substrate in a complex manner. In any case, it is expected that OH[•] and ferryl are so reactive that they have only fleeting existence.

The most likely explanation for UV enhancement is photodissociation of the chelate by ligand-to-metal charge-transfer excitation (Baxendale and Magee, 1955; Balzani and Carassiti, 1970)



followed by reaction of the photoreduced iron with peroxide in the Fenton reaction (eq 3). Reaction 4 is known for a variety of carboxyl- or hydroxyl-containing ligands (Balzani and Carassiti, 1970) and explains the high photoactivities of oxalate and citrate chelates, which are practically unreactive without UV. The photoreduction of ferric oxalate and citrate complexes proceeds with high quantum efficiency in the near UV (Balzani and Carassiti, 1970; Zepp et al., 1992). The quantum yield of Fe²⁺ from ferrioxalate is near unity, whereas that of the citrate is somewhat less. The resulting ferrous ion reacts with hydrogen peroxide to generate OH[•] according to Zepp et al. (1992), who pointed out the potential utility of this photoreaction for waste treatment. The lack of significant reactivity in the absence of peroxide indicates that reaction of pesticide with L[•] is unimportant.

Two additional reactions may be considered:



Reaction 5 generates HO^{\bullet} directly. It may be important, and then only marginally so, only in the case of rhodizonate, which gives some reaction in the absence of peroxide (Figure 7A); however, photosensitization by the chelator itself may explain part of its activity under this condition. In any case, reaction 5 is much faster in simple ferric systems when L is water (Sun and Pignatello, 1992b), probably because photoinitiated charge transfer to iron from a suitable organoligand (eq 4) is favored over charge transfer from a hydroxide ligand.

Reaction 6 is analogous to the thermal reaction 1. Reaction 6 has been proposed for ferric ion (Behar and Stein, 1966) but has not been demonstrated in chelated systems. The organoligand will affect the formation constant of the peroxy complex, as well as whether electron transfer to the metal occurs from HO_2^- or L.

Other potential mechanisms for UV enhancement include photolysis of H_2O_2 itself, photosensitization by the chelator or chelate in the absence of peroxide, and photolytic reactions involving hydrogen peroxide within the coordination sphere of the metal ion. Owing to the weak absorbance of H_2O_2 above 300 nm, direct photolysis of H_2O_2 to OH^{\bullet} is unimportant at the UV wavelengths used in this study (Sun and Pignatello, 1992b). Reaction with the chelate in the absence of peroxide was much slower (Figure 7A), ruling out photosensitization by the chelate. Rhodizonic acid alone was even less reactive than its Fe(III) chelate, ruling out photosensitization by the ligand alone. A photoreaction producing a reactive metal oxidant from a metal-peroxide complex is unlikely but cannot be eliminated by the data.

For 2,4-D, there seems to be a practical limit of roughly 80% mineralization (Figure 8). We demonstrated that mineralization of intermediates formed in later stages of UV-assisted Fe^{3+} -catalyzed oxidation occurs by reaction 4 and thus requires their complexation with ferric ion (Sun and Pignatello, 1992b). The presence of chelating agents (and/or their breakdown products) could prevent such complexation. Indeed, in acidic media EDTA inhibited the last ~60% mineralization of 2,4-D ring carbons (Sun and Pignatello, 1992b).

In conclusion, hydrogen peroxide rapidly transformed and in some cases mineralized 2,4-D, 2,4,5-T, atrazine, baygon, carbaryl, and picloram when activated by Fe(III) picolinate, gallate, and rhodizonate complexes. Trifluralin reacted slowly. Oxidation of 2,4-D was accelerated by 300–400-nm UV, especially with thermally inactive Fe(III) oxalate and citrate complexes. These systems show potential for treating pesticide wastes and possibly other organic wastes. The reagents are inexpensive, the reactions are rapid, and the technology is apparently simple. Gallic, citric, and oxalic acids are natural products; the toxicities of picolinic and rhodizonic acids are not well-known. In any case, the chelates are unstable. Use of a chelating agent eliminates the need for acidification, hence simplifying the process and, as will be reported elsewhere, making it more suitable for soil remediation.

ACKNOWLEDGMENT

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