

# Ferric Ion Promoted Photodecomposition of Triazines<sup>†</sup>

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The aqueous photodegradation rates of the triazines atrazine, ametryn, prometon, and prometryn were greatly enhanced by the addition of 20–300  $\mu\text{M}$  amounts of ferric perchlorate or ferric sulfate. The hydroxyl radical,  $\text{HO}^\bullet$ , derived from the photoreaction of the complex  $\text{Fe}(\text{OH})^{2+}$ , is likely to be the active reactant. Known quenchers of  $\text{HO}^\bullet$  as well as constituents of buffers expected to react with  $\text{HO}^\bullet$  diminished the rate of reaction. Furthermore, photodegradation products of the atrazine/ferric iron system were the same as those for a Fenton reaction (known to involve  $\text{HO}^\bullet$ ). In the absence of oxygen, the reaction rate decreased; it increased at higher added iron concentrations and decreased in natural water (vs distilled water), implying that some dissolved constituents found in natural waters had a retarding effect on the photodegradation by competing for  $\text{HO}^\bullet$ . Results obtained indicate that these iron salts may be of value in the cleanup of contaminated groundwaters.

The use of light-induced reactions in wastewater treatment has drawn increasing attention recently (Eisenberg et al., 1987; Zepp, 1988; Larson et al., 1989). Triazine herbicides, which have been found in many groundwater samples (cf. Junk et al., (1980)), are almost inert to direct photolysis because of their weak absorption of sunlight. However, Burkhard and Guth (1976) determined that the rate of degradation of some triazines under the artificial light of a photochemical reactor was increased 3–11 times when acetone was used as a photosensitizer.

Iron(III) salts effectively promote some photoreactions. For example, illumination with light of wavelengths greater than 310 nm destroys several pyrimidine bases in the presence of ferric iron as a promoter (Cernohorský and Blackburn, 1971). In dilute  $\text{FeCl}_3$  and  $\text{Fe}(\text{NO}_3)_3$  solutions, the insecticide parathion was photodegraded to paraoxon and *p*-nitrophenol (Bowman and Sans, 1980). Free iron(III) cations absorb weakly in the solar UV region (290–400 nm), but the absorption spectra of hydrated or otherwise complexed iron species (ion pairs) are shifted toward the visible (Calvert and Pitts, 1966; Knight and Sylva, 1975), which might make their use in sunlight possible.

There are several possible photochemical mechanisms by which iron(III) salts could generate reactive species that could cause the photodestruction of organic compounds. Complexed iron(III) can undergo photoinitiated electron-transfer reactions in which the iron becomes reduced and the ligand is oxidized (Balzani and Carassiti, 1970). For example, hydroxyl radical ( $^\bullet\text{OH}$ ) is produced by electron transfer between an excited ferric ion and a water molecule (Weiss, 1969). Recent kinetic evidence (Faust and Hoigné, 1990) confirms that  $\text{HO}^\bullet$  is efficiently formed in the photolysis of dilute ferric ion solutions at weakly acidic pHs in which the complex  $\text{Fe}(\text{OH})^{2+}$  is the predominant species.

We have investigated the aqueous degradation rates of the triazines atrazine (AZ), ametryn (AY), prometryn (PY),

and prometon (PO) (Figure 1) with salts of ferric iron added as photopromoters. Rates in distilled and natural waters were compared, and the effects of pH, concentration of iron, promoters, and inhibitors were studied. The results indicate that iron salts may be of value in the cleanup of some contaminated waters.

## MATERIALS AND METHODS

**Reagents.** Atrazine and *p*-nitroanisole (PNA) were obtained from the U.S. Environmental Protection Agency, Athens, GA. D-Mannitol (99+%) and potassium superoxide were purchased from Aldrich Chemical Co. (Milwaukee, WI). Ferric and ferrous sulfate (analytical reagents) were purchased from Mallinckrodt (St. Louis, MO). Ferric and ferrous perchlorate (95+%) were obtained from Alfa Products (Danvers, MA). 2-Deoxy-D-ribose was obtained from Sigma Chemical Co. (St. Louis, MO), and all triazines (except atrazine) were purchased from Supelco, Inc. (Bellefonte, PA). Thiobarbituric acid (TBA) was obtained from Kodak (Rochester, NY). Natural water samples from the Boneyard Creek (Urbana, IL) were filtered and refrigerated prior to use.

**Equipment.** All kinetic analyses were carried out by high-pressure liquid chromatography (HPLC) using a 250  $\times$  4.1 mm i.d. reverse-phase column packed with PRP 1 resin, 10  $\mu\text{m}$  (Hamilton, Reno, NV). Acetonitrile-water (60/40 v/v) was used as the eluting solvent. Triazine samples were injected with an external standard: 2,6-diethylaniline ( $5 \times 10^{-5}$  M) for atrazine, ametryn, and prometon and *p*-toluidine ( $1 \times 10^{-5}$  M) for prometryn. The detector was adjusted to the wavelength of maximum absorbance (approximately 225 nm) of the triazine. A medium-pressure Pyrex-filtered mercury arc lamp was used for indoor light experiments, using a "merry-go-round" reactor (Ace Glass) to obtain uniform exposure of the samples. A Perkin-Elmer 552A UV-visible spectrophotometer was used for absorbance measurements. A Hewlett-Packard 5985A gas chromatograph/mass spectrometer (GC/MS) with a DB-1 capillary column (0.25- $\mu\text{m}$  film thickness), 30 m  $\times$  0.32 mm i.d. (J&W Scientific, Placerville, CA), was used for product analysis. After sample injection, the oven temperature was held at 60  $^\circ\text{C}$  for 10 min and then increased from 60 to 280  $^\circ\text{C}$  at 5  $^\circ\text{C}/\text{min}$ .

**Experimental Procedures.** Reaction solutions were prepared in Pyrex tubes (10-mm diameter) to give a final concentration of 5.2  $\mu\text{M}$  (1.12 mg/L) for atrazine and  $2.6 \times 10^{-5}$  to  $2.6 \times 10^{-4}$  M (1.47–14.7 mg/L  $\text{Fe}^{3+}$ ) for the iron salts. The pH of these solutions were all moderately acidic, ranging from 3.3 to 5.7. In general, unless buffers were used, increasing the iron concentration 10-fold caused a pH decrease of 1 unit. The ultraviolet spectra of the ferric salt solutions were consistent with the  $\text{Fe}(\text{OH})^{2+}$  ion being the principal species present (Knight and Sylva, 1975).

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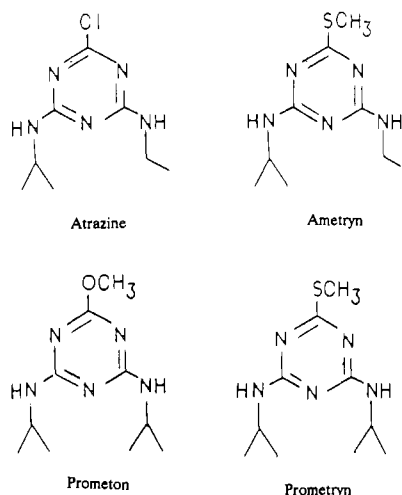


Figure 1. Structures of triazine herbicides.

Outdoor photochemical experiments were conducted by exposing the reaction tubes, mounted on a test tube at about a 90° angle to the incident solar radiation, to full midday sunlight (June/July at Urbana, IL, latitude 40° N). Indoor experiments were carried out with the mercury arc lamp. The iron compounds were the only light-absorbing species. Previous experiments using these conditions had indicated that outdoor photolysis half-lives were usually about twice as long as indoor photolysis half-lives, and these experiments gave similar data. For both indoor and outdoor experiments, PNA was used as the actinometer (Dulin and Mill, 1982). The PNA samples were exposed in exactly the same manner as the other reaction solutions. Dark control experiments indicated no significant changes in triazine concentrations. The Fenton reaction was carried out by slowly adding reduced iron (100 mL of 3.5 mM ferrous sulfate solution) to 700 mL of a solution of atrazine (70  $\mu$ M) and H<sub>2</sub>O<sub>2</sub> (0.5 mM), while stirring. The reaction was allowed to continue for 15 min, and then the solution was adjusted to pH 6 with 1 M NaOH, filtered (Büchner funnel), applied to an XAD-2 resin column, and eluted with 100 mL of methylene chloride. After drying (MgSO<sub>4</sub>), the sample was concentrated to about 0.5 mL using a Kuderna-Danish apparatus. Anthracene was then added as an external standard, and the sample was analyzed by GC/MS.

The deoxyribose experiment was conducted as described in Halliwell and Gutteridge (1981): atrazine (2  $\mu$ M), ascorbate (92  $\mu$ M), deoxyribose (2.55 mM), EDTA (95  $\mu$ M), and iron (90  $\mu$ M) solutions were added to 12  $\mu$ M phosphate buffer to a total volume of 1.1 mL. The reaction was run in 10-mL Pyrex tubes in the mercury arc lamp reactor (35 °C) for 1 h. The tubes were then removed and 1 mL of 1% (w/v) thiobarbituric acid and 1 mL of 2.8% (v/v) hydrochloric acid were added to each sample, after which they were heated at 100 °C (water bath) for 15 min. After the samples were cooled to room temperature, the absorbance at 532 nm was measured.

**Analysis of Data.** The rates of disappearance of the triazines were determined by removing aliquots periodically and analyzing their concentrations by HPLC. An external standard was used with the triazines to normalize the peak heights by determining the ratio of the triazine peak height to the external standard peak height. The logarithm of the ratio of the initial concentration to the concentration at a given time ( $t$ ) vs time was plotted and the (pseudo-first-order) rate constant ( $k$ ) determined by calculating the slope of the line obtained. The rate constant for PNA was obtained in the same manner. The half-lives could then be determined by eqs 1 and 2.

$$t_{1/2} = \ln 2/k \quad (1)$$

$$t'_{1/2} = t_{1/2, \text{triazine}} t_{1/2, \text{PNA(av)}} / t_{1/2, \text{PNA}} \quad (2)$$

A mean value for the PNA half-life was calculated from the data of all actinometer experiments. From this, a "normalized" half-life ( $t'_{1/2}$ ) for the triazine reactions was calculated by eq 2. In

Table I. Rate Data for Triazine Photodegradation in the Presence and Absence of Ferric Salts<sup>a</sup>

triazine	iron salt (0.26 mM)	$t_{1/2}$ , min	$k$ , min <sup>-1</sup>
atrazine	none	1500	0.000 46
ametryn	none	1600	0.000 42
prometon	none	1400	0.000 49
prometryn	none	1200	0.000 60
atrazine	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1.4	0.51
atrazine <sup>b</sup>	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	900	0.000 77
atrazine <sup>c</sup>	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1400	0.000 49
ametryn	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1.6	0.43
prometon	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1.7	0.41
prometryn	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	2.7	0.26

<sup>a</sup> In distilled water except as noted. <sup>b</sup> Boneyard Creek water. <sup>c</sup> pH 3.7 acetate buffer, 0.01 M.

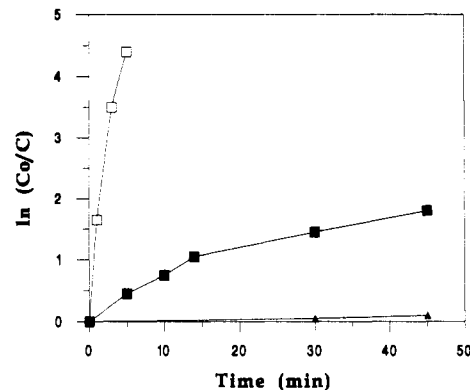


Figure 2. Effect of varying ferric perchlorate concentration on atrazine disappearance. (Open squares) 0.26 mM; (solid squares) 0.18 mM; (solid triangles) 0.08 mM.

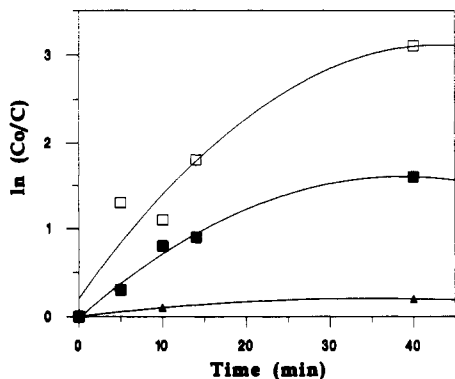
eq 2,  $t_{1/2, \text{PNA(av)}}$  is 146 min and  $t_{1/2, \text{PNA}}$  was the half-life for a particular experiment.

## RESULTS AND DISCUSSION

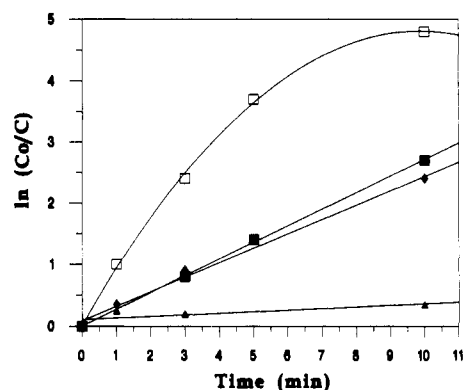
**Photodegradation Kinetics.** Burkhard and Guth (1976) reported that the half-life of an aqueous atrazine solution (about 50  $\mu$ M) exposed to artificial light was about 25 h. Experiments conducted in our laboratory at lower concentrations of atrazine closely agreed with these data. (In outdoor experiments in full summer sunlight, the half-life was considerably longer, on the order of 39 h.) We also tested other triazine herbicides—prometryn, ametryn, and prometon. As expected because of their similar light absorption characteristics (very weak absorption at >290 nm), the photodegradation of these triazines proceeded very slowly with approximately the same half-life as atrazine (Table I).

Addition of dissolved iron salts to the triazine solutions resulted in greatly enhanced degradation rates. The reaction rate increased with increasing ferric ion concentration. The most dramatic results were obtained with 0.26 mM ferric perchlorate, where the atrazine half-life decreased by 3 orders of magnitude, from 1500 to about 1 min (Figure 2). Ferric sulfate was also a good promoter of atrazine degradation; when added at a concentration of 0.21 mM, the half-life decreased from 25 h to 24 min. Again, the rate increased with increasing concentration of iron (Figure 3).

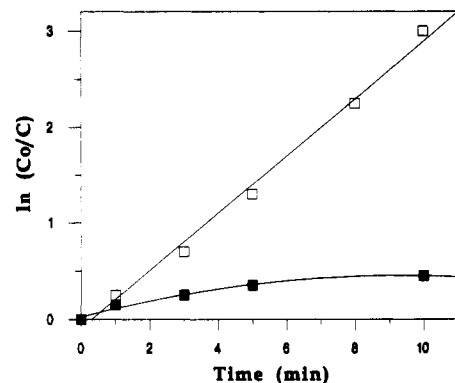
Initial pHs were lower in the samples with the higher iron concentrations; increasing the iron concentration by a factor of 10; from 0.026 to 0.26 mM, increased [H<sup>+</sup>] by a factor of 10 (pH went from 4.3 to 3.3). Figure 2 also shows that rather small changes in iron concentration resulted in large changes in reaction rates. The speciation of iron complexes in water is known to be strongly



**Figure 3.** Effect of varying ferric sulfate concentration on atrazine disappearance. (Open squares) 0.42 mM; (solid squares) 0.21 mM; (solid triangles) 0.04 mM.



**Figure 4.** Triazine photodegradation with ferric sulfate. (Open squares) ametryn; (solid squares) atrazine; (solid diamonds) prometon; (solid triangles) prometryn.



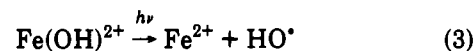
**Figure 5.** Effect of argon on ferric perchlorate sensitized atrazine photodegradation. (Open squares) air-saturated solution; (solid squares) argon-purged solution. Ferric perchlorate concentration was 0.26 mM.

affected by pH (Faust and Hoigné, 1990). Triazines are also protonated in acidic solutions, with a first  $pK_a$  of about 1.7 (Knuesli et al., 1969). Further investigation is required to determine the importance and role of pH in the mechanisms of these photoreactions.

The reactions performed with atrazine were repeated with the other triazines, ametryn, prometryn, and prometon. When ferric perchlorate ( $[Fe^{3+}] = 0.26$  mM) was added, the rate increased by a factor of about 1000, as with atrazine, although the half-lives were somewhat longer than that of atrazine (Table I). With ferric sulfate, both ametryn and prometon reacted faster with the ferric ion added than did atrazine, while prometryn reacted slower than atrazine (Figure 4).

A significant effect of oxygen on the reaction was observed. In the absence of oxygen, both atrazine/ferric sulfate and atrazine/ferric perchlorate reaction rates decreased. Figure 5 illustrates the 30-fold increase in the half-life when the atrazine/ferric perchlorate solutions were degassed with argon.

**Reaction Mechanism.** Ferric ions have long been known to undergo ligand-to-metal charge-transfer reactions in the excited state (Evans et al., 1951). In pure water, hydrated ferric cations are photoreduced with the production of  $HO^\bullet$  radicals, with this process being especially favorable for the  $Fe(OH)^{2+}$  complex, which is predominant at somewhat acidic pHs (Faust and Hoigné, 1990). Starting with an aqueous solution containing only atrazine and excess ferric perchlorate (no oxygen or other reactant), photolysis of this complex at low pH would produce ferrous ion and  $^\bullet OH$ .

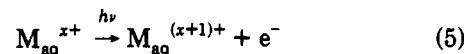


The fate of the  $^\bullet OH$  will either be back-reaction with the  $Fe^{2+}$  or attack on atrazine (AZ in eq 4).



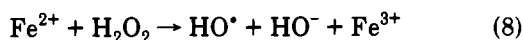
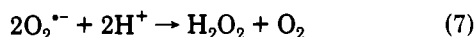
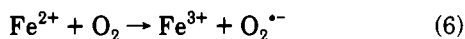
Although no rate data for the reaction between  $HO^\bullet$  and atrazine have been reported, the hydroxyl radical reacts very unselectively and rapidly with many other aromatic compounds with second-order rate constants ranging from  $10^9$  to  $10^{10}$  L/(mol·s) (Dorfman and Adams, 1973). The rate of reaction of  $^\bullet OH$  with  $Fe^{2+}$  has been determined as  $3 \times 10^8$  L/(mol·s) (Farhatziz and Ross, 1977). At the beginning of the reaction [AZ] would far exceed  $[Fe^{2+}]$ , but as  $Fe^{2+}$  concentrations build up during photolysis, the reverse reaction in eq 4 would become more important and the rate of atrazine loss would be expected to reach a steady, low rate. This phenomenon was in fact observed in argon-purged solutions (Figure 5).

The fate of  $Fe^{2+}$  in the system will have important consequences for the kinetics of the reaction and the products observed. In water, reduced transition-metal cations such as ferrous ion can undergo photodetachment of an electron from the hydrated ion to produce a higher valent metal ion and a hydrated electron (Fox, 1984):



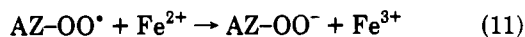
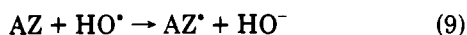
The molar extinction coefficient (at 300 nm) of ferrous ion, however, is more than 2 orders of magnitude lower than that of ferric ion; therefore, in sunlight one would expect the photolysis of ferric ion to predominate, assuming similar quantum yields of the two competing photoprocesses.

Oxygen will react with  $Fe^{2+}$  in the dark to produce  $O_2^{\bullet -}$  (reaction 6). Although the oxidation of ferrous ion by  $O_2$  is quite slow at low pH, it is reportedly promoted at interfaces and by light (Stumm and Morgan, 1981). Therefore, oxidation of ferrous ion (in the presence of reasonable levels of oxygen) would generate superoxide ( $O_2^{\bullet -}$ ), which as its conjugate acid  $HOO^\bullet$  ( $pK_a = 4.8$ ) is susceptible to disproportionation to hydrogen peroxide and oxygen (reaction 7; Bielski, 1978). Ultimately, additional  $HO^\bullet$  could be produced by the Fenton reaction of  $H_2O_2$  with  $Fe^{2+}$ . The overall process is summarized by reaction 3 and the following three reactions:



Scavenging of  $\text{Fe}^{2+}$  by oxygen would have the dual effect of removing  $\bullet\text{OH}$ -reactive material from the equilibrium and also producing another reactive oxygen species, namely  $\text{O}_2^{\bullet -}$ , whose fates could include electron donation to  $\text{Fe}^{3+}$  or self-dismutation to  $\text{H}_2\text{O}_2$  and oxygen. The net effect should be to increase the rate of loss of atrazine (Figure 5).

Another possible explanation for the dependence on oxygen involves the reaction of peroxy radicals ( $\text{ROO}^{\bullet}$ ) with ferrous ion to produce ferric ion and a hydroperoxy anion ( $\text{ROO}^-$ ). The peroxy radical would be formed from attack on organic substrates by  $\text{HO}^{\bullet}$ , followed by reaction with dissolved  $\text{O}_2$ . This reaction would provide another mechanism for removing  $\text{Fe}^{2+}$ . The scheme as illustrated for atrazine would be as follows:



Ingold (1969) determined that similar fast reactions take place in photochemical reactions of several other transition-metal ions. Thus, there are several points in the overall mechanism (Figure 6) where the presence of oxygen could promote the loss of atrazine.

The intermediacy of  $\text{HO}^{\bullet}$  in our experimental system containing ferric perchlorate and atrazine was demonstrated by five sets of results. First, the sugar alcohol mannitol is known to scavenge  $\bullet\text{OH}$  radicals (Misra and Fridovich, 1976; Gutteridge and Halliwell, 1982). Goldstein and Czapski (1984) measured the rate constant for this reaction at  $(1.8 \pm 0.4) \times 10^9 \text{ L}/(\text{mol}\cdot\text{s})$ . Mannitol is much less reactive toward many other free-radical species such as alkoxy radicals (Halliwell and Gutteridge, 1985). Addition of mannitol to the atrazine/ferric perchlorate reaction mixture had a diminishing effect on the atrazine degradation rate (Figure 7):  $t_{1/2} = 2.4 \text{ min}$  with  $5 \times 10^{-5} \text{ M}$  mannitol added and 16 min with  $5 \times 10^{-4} \text{ M}$  mannitol added. Without knowledge of the exact rate constant of  $\text{HO}^{\bullet}$  with atrazine, one cannot assess whether the observed inhibition by mannitol is in the expected range, but if a rate constant of about  $10^{10}$  is assumed for atrazine [approximately that observed for thymine (Buxton et al., 1988), aniline, and  $N,N$ -dimethylaniline (Farhatziz and Ross, 1977)], the observed values fit well with those calculated.

Second, it was found that the products observed (by GC/MS) in the ferric perchlorate photoreaction were the same as those formed in a Fenton reaction ( $5\times$  excess  $\text{H}_2\text{O}_2$  and ferrous iron, dark). The Fenton reaction (reaction 8 above; Walling, 1975) is a known producer of  $\text{HO}^{\bullet}$  radicals. The products observed were tentatively identified as dealkylated atrazine derivatives and an oxidized product (Figure 8) as also found by Rejto et al. (1983).

Third, we carried out an experiment with the sugar deoxyribose (2-deoxy-D-ribose), often used to measure the formation of  $\bullet\text{OH}$  in biochemical systems (Halliwell and

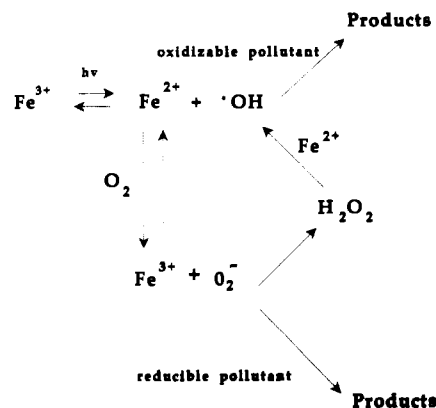


Figure 6. Proposed mechanism of  $\text{Fe}^{3+}$ -sensitized photodegradation.

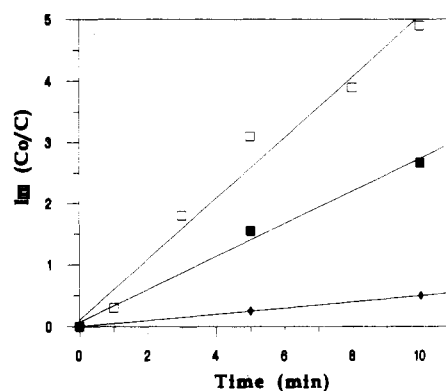


Figure 7. Mannitol inhibition of ferric perchlorate sensitized atrazine photodegradation. (Open squares) no mannitol; (solid squares)  $5 \times 10^{-5} \text{ M}$  mannitol; (solid diamonds)  $5 \times 10^{-4} \text{ M}$  mannitol.

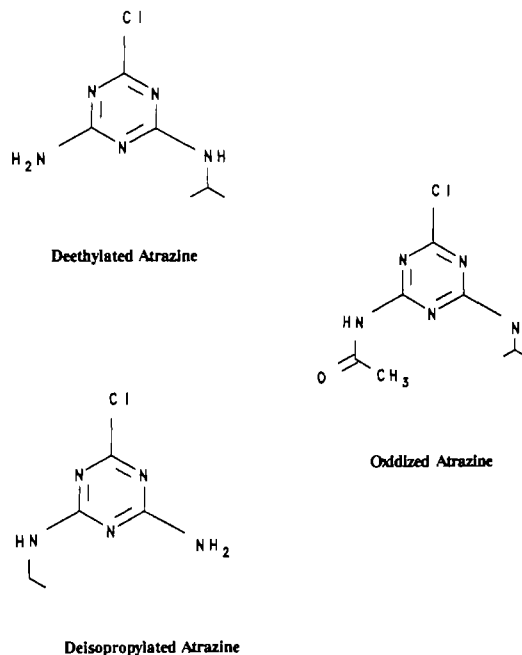


Figure 8. Photodecomposition products of atrazine.

Gutteridge, 1981). Deoxyribose is attacked by  $\bullet\text{OH}$  radicals to form one or more products that react upon heating with thiobarbituric acid (TBA) at low pH to form a colored material that can be measured by visible spectroscopy ( $\lambda = 532 \text{ nm}$ ). Exposure of ferric perchlorate ( $0.26 \text{ mM}$ ) in water and deoxyribose to light resulted in the formation of strongly absorbing colored material. When the same

Table II. Deoxyribose Experiments

sample	color before test	color after test	absorbance at 532 nm
blank <sup>a</sup>	yellow	yellow	0.104
Fe <sup>3+</sup> /ascorbate deoxyribose	yellow	dark pink	2.64
Fe <sup>2+</sup> /ascorbate deoxyribose	yellow	yellow	0.161

<sup>a</sup> The blank consisted of ascorbate and deoxyribose only.

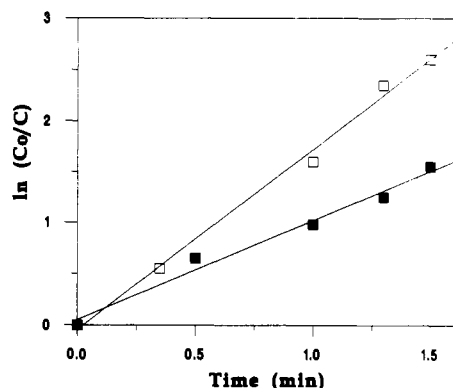


Figure 9. Nitrobenzene and anisole photodegradation by ferric perchlorate. (Open squares) anisole; (solid squares) nitrobenzene.

experiment was conducted with ferrous perchlorate, little or no color developed and the absorbance was minimal (Table II).

Fourth, because ametryn, prometryn, and prometon, with their electron-donating oxygen and sulfur substituents, have more electron-rich rings than atrazine, they should have been more susceptible to electrophilic (oxidative) attack. However, there was little difference in the iron-promoted half-lives for photodecomposition of the four triazines. This would be expected if  $\cdot\text{OH}$  were involved, since the  $\cdot\text{OH}$  radical is quite unselective.

Fifth,  $\cdot\text{OH}$  formation was inferred in a kinetic competition experiment. Zepp et al. (1987) demonstrated that anisole is 2.6 times more reactive than nitrobenzene toward hydroxyl radicals. When ferric perchlorate photolysis was performed under our conditions with these two compounds, anisole disappeared about 2.4 times as fast as nitrobenzene (Figure 9).

The mechanism of triazine photodecomposition from the ferric sulfate based system is less certain. Hydroxyl radicals react with sulfate (actually bisulfate) ions at low pH to produce the sulfate radical,  $\text{SO}_4^{\cdot-}$ , which is also a potent oxidant but not quite as unselective as  $\text{HO}\cdot$  (Behrens et al., 1988; Farhataziz and Ross 1977). Because the concentrations of sulfate in the triazine-sulfate salt reactions were up to 100-fold higher than that of triazine,  $\text{SO}_4^{\cdot-}$  may partially compete with the triazine for the hydroxyl radical, since the rate constant for sulfate ion with  $\text{OH}\cdot$  is 2-3 orders of magnitude smaller than that for  $\text{OH}\cdot$  with heterocyclic aromatic compounds, and this may partially explain the differences in rate observed in ferric sulfate promoted photolysis compared to those for ferric perchlorate. Further studies with added sulfate will be required to answer this question.

**Realistic Systems.** If the proposed mechanism is important and  $\cdot\text{OH}$  is responsible for the triazine degradation, examination of this process, like other treatment processes involving  $\text{HO}\cdot$ , should be conducted in realistic systems containing dissolved substances typical of natural waters. Photoinduced reactions of atrazine with iron salts studied in natural water samples from a local stream proceeded much more slowly than in distilled water (Table I). This increase in the half-life can be attributed to the

scavenging of  $\cdot\text{OH}$  by dissolved materials in the water such as dissolved organic matter and/or bicarbonate anion.

Attempts were made to study the effect of varying pH on the loss of atrazine using buffered solutions. All photoinduced degradations in buffered reaction solutions proceeded much more slowly than in unbuffered solutions, and no definite correlation of reaction rate with pH could be established. For example, an acetate buffer system was used to study pH effects on the atrazine/ferric perchlorate reaction. Even at a buffer concentration of 0.01 M, the half-life of atrazine was much longer than without the added buffer (Table I). If  $\cdot\text{OH}$  was in fact involved, the slowing of the rate was almost certainly due to the reaction of the buffer with  $\cdot\text{OH}$ . [Farhataziz and Ross (1977) report a rate constant of  $7 \times 10^7$  for reaction of acetate with  $\cdot\text{OH}$ .]

## CONCLUSIONS

Ferric perchlorate and sulfate greatly promote the photodegradation of atrazine and related triazines in moderately acidic aqueous solution. In oxygen-free solutions, the rate of triazine disappearance was greatly reduced. The degradation was due to the formation of the hydroxyl radical by an electron-transfer process involving hydrated iron(III) complexes. Dissolved solutes (organic compounds, buffer salts,  $\text{HO}\cdot$  quenchers) inhibited the reaction by competing with the triazine for  $\cdot\text{OH}$ . The degradation products of environmental contaminants may be more or less toxic than the starting materials (Larson et al., 1979); thus, it would be desirable to have toxicity data on products of partial degradation of compounds such as atrazine.

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