Sensitized Photodecomposition of Organic Compounds Found in Illinois Waterways

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Sensitized Photodecomposition of Organic Compounds Found in Illinois Wastewaters

by

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University of Illinois
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Urbana, Illinois

Printed May 1990
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Abstract

Although some dissolved pollutants are susceptible to direct photodecomposition by simple exposure to sunlight, their photolysis is often facilitated by addition of photosensitizing additives. We report laboratory experiments that suggest that both organic and inorganic sensitizing agents may have potential usefulness for the treatment of some contaminated waters.

Several triazine herbicides were rapidly photodecomposed in ferric perchlorate or sulfate solutions, and reducible compounds like nitrobenzene disappeared rapidly in ferrous ion-containing solutions exposed to Pyrex-filtered mercury arc light whose UV intensity was approximately twice that of sunlight. Although ferric ion was more effective than ferrous ion, both increased the degradation rate significantly. Photodegradation products of the atrazine/ferric iron system were the same as those for a Fenton reaction (known to involve HO·), suggesting that the hydroxyl radical, HO·, derived from the photoreaction of hydrated Fe3+, was the active reactant. In the absence of oxygen, the reaction rate decreased, it increased at higher added iron concentrations and decreased in natural freshwater samples (compared to the rate in distilled water), implying that some dissolved constituents found in natural waters have a retarding effect on the photodegradation by competing for HO·.

Riboflavin, when initially added at 5 μM to solutions of phenols or anilines (structurally related to common environmental contaminants) greatly accelerated the rate of their disappearance in the presence of light. The sensitized photolysis rates increased in the absence of oxygen, suggesting a mechanism involving direct energy or electron transfer between flavin excited states and acceptor molecules. A preliminary kinetic model was developed to calculate loss rates. Riboflavin itself was rapidly converted to products which had variable efficiencies as sensitizers.

The effects of organic and inorganic solutes on the desired photodecomposition processes vary greatly, but in many cases some common solutes strongly inhibit the reactions.
Executive Summary

For about fifteen years, some water engineers and chemists have been evaluating the usefulness of light energy as a potential treatment system for contaminated waters. A variety of light sources have been tested over the years. Approximately four percent of the total energy contained in sunlight occurs in the ultraviolet (UV); this radiation has a high potential for inducing chemical reactions due to its elevated energy content relative to visible and infrared (IR) radiation. Light can also be provided by artificial lamps; a wide variety are available, ranging from simple tungsten-filament bulbs that emit strongly in the visible region of the spectrum, to mercury arcs that produce high intensity UV light of even more energetic wavelengths than are found in sunlight. For waste treatment purposes, however, it would be desirable to make maximum use of solar UV if possible. Many organic compounds have been shown to be photolytically decomposed upon uptake of solar UV, however, many other compounds resist this type of treatment.

The use of sunlight dye-sensitized photodecomposition for treatment of effluents appears to be a promising technique. In sensitized photolysis, a light-absorbing solute (photosensitizer) is able to efficiently transfer the absorbed light energy to another dissolved chemical such as a pollutant. Common organic sensitizers are dyes such as methylene blue and rose bengal and natural pigments such as riboflavin. This type of system using methylene blue as a sensitizer has reached the pilot-plant scale at Tennessee Technological University in research directed by V. D. Adams (Eisenberg et al., 1987). The purpose of our study was to investigate the potential of three types of sensitizing agents—riboflavin, ferric ion, and ferrous ion—to sensitize the decomposition of common types of water pollutants.

Knowledge of the chemical mechanisms by which these sensitizers act is advantageous for the design of effective photochemical treatment systems. Dissolved ferric salts in acidic solution absorb light and produce hydroxyl radicals, potent oxidants. In contrast, ferrous salts produce hydrated electrons, powerful reductants. Riboflavin readily forms complexes with certain classes of pollutants, such as anilines and phenols, and is a potent energy-transfer agent in the presence of light.

The photooxidation of organic substrates by aqueous ferric ion with simultaneous reduction of the iron has been studied intermittently for over 30 years. In its aqueous chemistry, the most important oxidation states of iron are Fe(II) (ferrous) and Fe(III) (ferric). There are several photochemical mechanisms by which iron salts could generate reactive species that could cause the photodestruction of organic compounds. Ferric ion, when exposed to light, produces hydroxyl radical (OH−), by direct electron transfer (charge transfer) between an excited ferric ion and a water molecule. In contrast, the principal pathway for ferrous ion photolysis is the cation photoionization process. It has been proposed that the ferrous ion releases a hydrated electron (e−aq) when exposed to light.
In the presence of oxygen, superoxide (O$_2^-$) would be generated and ultimately a hydroxyl radical could be produced by the Fenton reaction, a dark reaction between ferrous ion and hydrogen peroxide.

In our photochemical experiments with iron salts, (using Pyrex-filtered mercury lamps whose intensity was about twice that of sunlight) the most dramatic results were obtained with ferrous and ferric perchlorate. The addition of ferrous perchlorate in a distilled-water system at a concentration of 260μM (about 14 mg/L iron) decreased the degradation half-life of atrazine by a factor of about 100, from 1500 min to 14 min. Ferric perchlorate was even more effective at the same iron concentration, the half-life of atrazine was decreased to approximately 1 min when this salt was added. The reactions performed with atrazine were repeated with other triazines—ametryn, prometryn and prometon; the half-lives of these triazines were also significantly reduced with the addition of ferric perchlorate. Ferric and ferrous sulfates were also effective photodegradation agents under these conditions. In natural freshwater or in buffered solutions, the efficiency of these sensitizers was greatly diminished, however, due to the interception of the active hydroxyl radicals by other dissolved substances. These effects are similar to those observed in those types of photochemical treatment methods that generate hydroxyl radicals, such as titanium dioxide, ozone-UV, or ozone-H$_2$O$_2$ systems.

Riboflavin, a known photosensitizer, when initially added at 5 μM (about 1.8 mg/L) to solutions of added phenols or anilines (structurally related to common environmental contaminants) greatly accelerated the rate of their loss in the presence of light, by factors of 100 or more in several instances. The sensitized photolysis rates increased in the absence of oxygen, suggesting a mechanism involving direct energy or electron transfer between flavin excited states and acceptor molecules. A preliminary kinetic model was developed to calculate loss rates. Riboflavin itself was rapidly converted in aqueous solution by Pyrex-filtered mercury arc light to products which had variable efficiencies as sensitizers. In each series of compounds, no simple relationship was apparent between electronic parameters of the substituents and rates of photoreaction with riboflavin. A working hypothesis for the primary mechanism of photodecomposition of anilines and phenols is: 1) electron transfer from a heteroatom (or an aromatic ring orbital) of the substrate to the flavin (flavin photoreduction), 2) transfer of the electron from the reduced flavin to oxygen, if present, with the restoration of the original flavin and formation of superoxide, which may take part in subsequent reactions, and 3) reaction of the radical cation of the oxidized substrate with ground-state oxygen or other species to form oxidized products. Other processes (for example, pathways involving $^1$O$_2$) may be important for some substrates, but did not appear to contribute significantly to the rate of photodecomposition of the compounds we studied.

To determine whether riboflavin or iron salts could be successfully used in a treatment process for removal of pollutants from contaminated waters, further experiments were performed in systems more closely resembling actual polluted environments. One such
sample was obtained from Central Illinois Power Service from the site of a former coal
gasification plant at Taylorville, Illinois. Analysis of this sample showed that the majority
of the compounds in it are aromatic compounds (hydrocarbons and a few phenols), and are
accordingly electron-rich compounds of the type expected to be treatable by riboflavin. The
groundwater was exposed to light from the mercury arc lamp both with and without
riboflavin present. The results indicated that several classes of compounds were partially
removed by light alone, but that riboflavin significantly improved the rates of loss.

To test the relative effectiveness of the various potential methods of photochemical
treatment on another common environmental contaminant, we measured the rates of loss
of the herbicide trifluralin (2,6-dinitro-4-trifluoromethyl-N,N-dipropylaniline). Under our
conditions, the \( t_{1/2} \) for 5 \( \mu M \) trifluralin without added sensitizer was 14.5 min. Addition
of ferrous perchlorate, contrary to expectation, did not significantly decrease the half-life
(13.6 min). Ferric perchlorate decreased it to 9.8 min, however, and riboflavin was the best
of all sensitizers tested, with a \( t_{1/2} \) of 5.1 min.

Further studies on the use of all these treatment systems in actual polluted water
samples is necessary, however, these preliminary findings suggest that the use of sensitizing
agents for water treatment may be a promising technique.
CHAPTER 1

INTRODUCTION

Sunlight and UV Light

In addition to visible light and infrared (IR) radiation (heat), the sun emits radiation in the 290-400 nm (ultraviolet, UV) region that reaches the earth's surface. Approximately four percent of the total energy contained in sunlight occurs in the UV region. This radiation has a high potential for inducing chemical reactions due to its elevated energy content relative to visible and IR radiation. Distinctions are sometimes made between the "UV-A" (400-320 nm) and the more energetic "UV-B" (320-290 nm) radiation that is more strongly absorbed by many pollutants and biomolecules. In both cases, however, the fundamental mechanisms of photochemical damage are similar, although different receptor molecules (chromophores) are involved. UV radiation, because of its potent chemical energy content, has a potential for causing direct damage to biochemically important molecules that absorb it and also to destroy dissolved pollutants in water under some conditions. The intensity of solar UV irradiance at the earth's surface varies greatly with season, time of day, latitude, ozone layer thickness, altitude, and cloud cover.

Light can also be provided by artificial lamps, a wide variety are available, ranging from simple tungsten-filament bulbs that emit strongly in the visible region, to mercury arcs that produce high intensity UV light of even more energetic wavelengths than are found in sunlight. For waste treatment purposes, however, it would be desirable to make maximum use of solar UV, whenever possible.

Photochemically damaging events are initiated by the uptake of the electronic energy of a photon by a UV-absorbing molecule. In the UV region of the electromagnetic spectrum, the energy of such photons is sufficient to break covalent bonds, although it is unusual for their energy to be absorbed that efficiently. Usually, the absorbed energy converts the target molecule in its ground state to an electronically excited state, whose excess energy manifests itself in a different and often quite unstable electron configuration. The initial excited state, a short-lived singlet having fully paired electrons, may be deactivated by fluorescence (the emission of a photon having a longer wavelength than the exciting radiation) and return to the ground state, it may react with neighboring molecules (although this is not common with singlets since their lifetimes are normally too short for them to diffuse over many molecular diameters), or it may undergo internal rearrangement to a longer-lived triplet excited state. The triplet state is much more likely to react chemically with surrounding molecules.
A potential route for the formation of a reactive species from a photochemically activated triplet state is the transfer of triplet energy to molecular oxygen. The product of the energy transfer reaction is singlet oxygen, $^1\text{O}_2$ (Foote, 1981). This substance is more reactive than ground-state triplet oxygen with some classes of organic compounds, but its lifetime in water is very short and, for most molecules, other reactive oxygen species are more likely to be involved in environmental transformation processes.

Although the direct oxidation of most organic compounds with ground-state oxygen (a diradical) is quite slow, if the oxidation is initiated by some source of more reactive free radicals, the degradation of some compounds can occur in a very short time (Malaiyandi et al., 1980). Advantage is taken of these techniques in the so-called "advanced oxidation processes," in which combinations of short-wave UV, ozone, and hydrogen peroxide are exploited. When used in water in the presence of ultraviolet light, these systems initiate degradation of organic compounds due to the heterolytic cleavage of the O-O bond of either ozone or $\text{H}_2\text{O}_2$ that produces the hydroxyl radical (OH$^-$) (Schumb et al., 1955). This radical is extremely reactive with almost all organic compounds. Polar organic substances are very susceptible to OH$^-$ attack and undergo oxidative degradation, especially in the presence of UV light (Walling, 1975, Koubek, 1975).

Other possible mechanisms for light-induced pollutant decomposition include direct electron transfer between dissolved pollutants and photochemically activated redox agents, or formation of hydrated electrons by photoionization of substrates that could then attack reducible solutes such as oxygen or electron-poor organic compounds in water.

Photodegradation of Chemical Compounds

Direct Photolysis Direct and indirect photolysis are important degradative pathways for some contaminants in the aqueous environment (Miller, 1983, Zafiriou et al., 1984). Energy absorption is the primary prerequisite for a photochemical reaction, and only those contaminants exhibiting significant light absorption overlapping with solar spectral output can undergo direct photolysis in sunlight. In the UV region, absorption of energy causes excitation of electrons, which may result in breakage and/or formation of chemical bonds, fluorescence or loss of energy as heat (Crosby, 1976). During direct photolysis, the chemical absorbs the incident radiation directly and this can be followed by degradation (Zepp and Cline, 1977). Of course, not all compounds that absorb light undergo chemical reactions at useful rates.

Indirect Photolysis (Photosensitization) Many environmental pollutants are poor solar light absorbers (wavelengths >290 nm). For these chemicals, indirect (photosensitized) and photocatalyzed reactions must be evaluated in order to establish the importance of photolysis as a degradative pathway. Indirect (sensitized) photolysis requires an additional solute as a photosensitizer to transfer the absorbed energy to another dissolved chemical. Such a sensitizer must have a long-enough-lived excited state for energy transfer to take place in competition with other deactivating mechanisms. During sensitization, the excited
molecules of a substance that is an efficient absorber of light energy, collide with a weak or non-absorber (the contaminant substrate) with a subsequent transfer of energy (Crosby, 1976). The sensitizer may remain unchanged and return to the ground state to absorb another quantum of light energy, or it may undergo irreversible transformation due to chemical reactions (Crosby, 1976). In another indirect photolysis mechanism, the sensitizer photochemically generates reactive oxygen species which promote the decomposition of the substrate (Draper and Crosby, 1981).

Iron Photochemistry The photooxidation of organic substrates by aqueous ferric ion with simultaneous reduction of the iron has been studied intermittently for over 30 years (Balzani and Carassiti, 1970). Bowman and Sans (1980) found that dilute FeCl₃ and Fe(NO₃)₃ solutions degraded parathion to paraoxon and p-nitrophenol, DDT was also degraded. An increased FeCl₃ concentration afforded an increased disappearance rate for parathion. The near UV (>300 nm) photolysis of 0.15 M solutions of Fe(ClO₄)₂ in a series of primary alcohols led to a variety of products (Walling and Humphreys, 1981). It was concluded that the photooxidation of the alcohols by ferric iron involved the excitation of the charge-transfer band and that dissociation to the various products involved the initial production of alkoxy radicals from the alcohols.

The photodegradation of the herbicides 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (1) and picloram (2) was investigated by Skurlatov et al (1983). They found that iron (III) species (at concentrations observed in natural waters) can induce rapid transformation of 2,4,5-T, especially if trace concentrations of H₂O₂ are present. The photocatalytic effect of iron (III) is probably attributable to the oxidation of 2,4,5-T by oxygen-containing free radicals that are generated upon sunlight absorption by hydroxy or humic complexes of the iron (III) (Balzani and Carassiti, 1970). The authors also found that the reaction proceeded more slowly in natural waters due to changes in the iron (III) speciation or to scavenging of free radicals by fulvic acids and carbonate.

In its aqueous chemistry, the most important oxidation states of iron are Fe (II) and Fe (III). There are several photochemical mechanisms by which iron salts could generate reactive species that could cause the photodestruction of organic compounds. Ferric ion, when exposed to light in the presence of water or OH ligands, produces a hydroxyl radical (OH⁻). The hydroxyl radical could be produced by direct electron transfer (charge transfer) between an excited ferric ion and a water molecule (Weiss, 1969). Recent kinetic evidence (Faust and Hoigné, 1990) confirms that OH⁻ is formed in the photolysis of dilute ferric ion solutions at acidic pH (<4.0), where the cation exists principally either as the simple hydrate or as the complex Fe(OH)ₓ²⁺. In highly acidic solutions, the reaction proceeds as follows:
\[ \text{Fe}^{3+} \cdot \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} \cdot \text{H}_2\text{O}^+ \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{OH} \quad (1) \]

In reaction (1), a fraction of the hydroxyl radicals may be scavenged by ferrous ions or other species present in the solution (Balzani and Carassiti, 1970). In less acidic solutions \((\text{pH} > 3)\), the reaction is:

\[ \text{Fe}^{3+} \cdot \text{OH}_{\text{aq}} \cdot \rightarrow \text{Fe}^{2+} \cdot \text{OH} \quad (2) \]

The oxidation of organic compounds by irradiation in the presence of ferric ions has been reported by several authors (for a summary of early references see Balzani and Carassiti, 1970). This process is due to a secondary reaction between organic molecules and \(\text{OH}^-\) produced in reactions (1) and (2). In the absence of organic substrates, oxygen is evolved but the quantum yields are low due to the back-reaction with \(\text{Fe}^{3+}\) (Walling and Humphreys, 1981). Production of oxygen occurs upon UV irradiation of \(\text{Fe(ClO}_4)_3\) solutions, hydroxyl radicals can combine to give oxygen (Balzani and Carassiti, 1970). In the presence of organic substrates, \(\text{OH}^-\) is scavenged and oxidation products from such photooxidations are typical of \(\text{OH}^-\) reactions: aromatic compounds undergo ring hydroxylation or side-chain oxidation and alcohols are oxidized to carbonyl compounds (Walling and Humphreys, 1981). Hydroxyl and alkylperoxy radicals have been shown to be capable of breaking down several persistent pesticides (Draper and Crosby, 1984). If the substrate complexes with iron, photooxidation may occur at longer wavelengths and it appears that the photoexcited state may collapse directly to \(\text{Fe}^{2+}\) and radical products derived from the substrate (Balzani and Carassiti, 1970).

The principal pathway for ferrous ion photolysis is the cation photoionization process. It has been proposed that the ferrous ion releases a hydrated electron \((e_{\text{aq}}^-)\) when exposed to light (Airey and Dainton, 1966, Dainton and Jones, 1965).

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e_{\text{aq}}^- \quad (3) \]

In the presence of oxygen, superoxide could be generated and ultimately a hydroxyl radical could be produced by the Fenton reaction (reaction 6), as shown in the following sequence:

\[ \text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+} + \text{O}_2^- \quad (4) \]
\[ 2\text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (5) \]
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}^- + \text{HO}^- + \text{Fe}^{3+} \quad (6) \]

If complexing anions are present (for example, \(\text{Cl}^-\)), iron species can undergo electron
transfer processes between the metal and its ligands in the solvent cage. For instance, several ion pairs were found to photochemically initiate polymerization of vinyl compounds by radical formation when irradiated with visible light (Evans et al., 1951). Thus, organic pollutants, such as the triazines studied during the course of this project, could be attacked and degraded by these species or by the free radicals produced in the oxidation reactions described above.

**Photochemistry in Wastewater Treatment**

For some time water engineers and chemists have been considering the usefulness of light energy as a treatment system for contaminated waters. A variety of light sources have been tested over the years.

Exposure to UV light (at 254 nm, a wavelength not found in sunlight) kills or renders bacteria incapable of reproduction by photochemically altering DNA as well as other targets in the cell. Thus, the use of UV light for sterilization of potable water is possible. Oliver and Carey (1976) used UV light exclusively for wastewater disinfection and found that 99% of the indicator organisms could be killed with fairly low doses of UV light. The effluent of UV-treated water was found to be much less toxic to aquatic life than a chlorinated effluent. Whitby et al. (1984) also found that UV light treatment led to reduction in numbers of indicator bacteria from secondary wastewater effluents. The UV-irradiated effluent exhibited no toxicity to fish compared to unirradiated wastewater.

Malaiyandi et al. (1980) found that the total organic carbon (TOC) content of distilled water samples was reduced by about 88% and of tap water by 98% when a combination of UV light and ozone was used. They also determined that ozone treatment of up to 8 hours without UV light was much less effective than H$_2$O$_2$ plus UV light for the removal of non-polar organic compounds in water. They concluded that small amounts of H$_2$O$_2$ in water in the presence of UV light could be a very simple and efficient method of obtaining purified water.

The use of UV light and ozone for pesticide degradation in farm-generated pesticide wastewater was investigated by Kearney et al. (1984). 2,4-D (1086 ppm) and atrazine (4480 ppm) [sic, the generally accepted solubility of atrazine is about 35 ppm] in aqueous solutions were >80% degraded in 2-3 hours with UV light (254 nm) and ozone. The two most important parameters affecting the degree of completeness of degradation were concentration of pesticide and residence time (time that the molecule was actually in the reactor). The product analysis revealed that most products identified were considerably more biodegradable and less toxic than the parent materials.

As mentioned previously, high-intensity short-wavelength UV lamps can be used to catalyze the formation of OH from H$_2$O$_2$. It reacts with organic contaminants, theoretically oxidizing chemicals such as hydrocarbons to CO$_2$, and halogenated materials.
to halides. Oxidation of herbicides with UV light and ozone has been shown to be successful when the influent organic carbon concentration is in the ppm to low ppb range (Nyer, 1988). The hydroxyl radical is an intermediate in this treatment process.

In addition, many investigators have proposed the use of suspended, photocatalytically active oxides such as TiO₂ and ZnO to treat polluted waters. These techniques are quite interesting but, in practice, may be less useful than the use of soluble sensitizers, because of attenuation of light by the suspension and the necessity for removal of the spent oxide.

The use of sunlight dye-sensitized photodecomposition for treatment of effluents appears to be a promising technique. Takahashi et al. (1988) reported that pesticides can be substrates for reactive oxygen species: several pesticides reacted with singlet molecular oxygen to yield various degradation products and others experienced enhanced decomposition by the hydroxyl radical via radical addition, hydrogen transfer, or electron transfer. Acher (1978) investigated the use of solar energy and dye-sensitized photooxidation for recovering municipal wastewater for crop irrigation. In experiments with methylene blue, increased dye concentrations led to increased destruction of coliforms and decreased COD and methylene blue-active substances (detergents). Methylene blue has also been used to photosensitize the degradation of 2,4,5-tribromoimidazole (3), a potent biocide. The photolysis of an 8 mM solution of this chemical in methanol and in the presence of singlet oxygen, using methylene blue as a sensitizer, affords an 80-85% yield of parabanic acid (4) after 4 h (Wamhoff et al., 1988). Oxygen was essential for rapid photodegradation. In the sensitized photodegradation of several triazines with riboflavin, Rejto et al. (1983) found that when both oxygen and riboflavin were present in the irradiation mixture, the triazines were photochemically degraded with the major products being de-ethylated triazines. The indirect photolysis of 3,4-dichloroaniline in the presence of riboflavin gave products such as 3,4,3',4'-tetrachloroazobenzene (Rosen et al., 1970). Plimmer and Klingebiel (1971) also found riboflavin to be an effective sensitizer, sensitized photooxidation of 2,4-dichlorophenol gave several dimeric products. Again, the presence of both oxygen and riboflavin was necessary to obtain measurable amounts of products in water. In the presence of photoexcited dyes, decomposition reactions may occur through intermediate phenoxy radicals (Matsuura et al., 1965). It was suggested that riboflavin may participate in hydrogen abstraction reactions.

Acher et al. (1981) and Acher and Saltzman (1980) studied the dye-sensitized photodegradation of several herbicides using both riboflavin and methylene blue as
sensitizers. The degradation of the herbicide terbacil (5) was studied by Acher et al (1981). They determined that in alkaline solution, methylene blue and riboflavin gave the same reaction products in similar relative amounts though the rates were slightly different. In acidic solutions, methylene blue was ineffective since the efficiency of singlet oxygen production sensitized by methylene blue is reduced at acid pH (Bonneau et al., 1975), whereas riboflavin sensitized down to pH 3 with different products (not characteristic of singlet oxygen) being formed. Acher and Saltzman (1980) found that the herbicide bromacil (6) was degraded in the presence of light and methylene blue or riboflavin: the maximum efficiency was 90% degradation in 15 to 30 minutes of irradiation.

Eisenberg et al (1987) indicated that sensitized photooxidation (with methylene blue) is an effective treatment process for wastewater disinfection and detoxification. At a methylene blue concentration of 1 mg/L and pH=9, influent coliform numbers of 500,000 to 5,000,000 per 100 mL were consistently reduced to less than 500 per 100 mL with a detention time of 2 hours. Methylene blue concentrations of 1 to 10 mg/L were sufficient to photooxidize a 30 mg/L bromacil solution. Results from both bench scale and pilot plant studies showed that this process was effective for wastewater disinfection and detoxification in full scale systems.

Riboflavin Photochemistry. Riboflavin (Vitamin B₂) occurs in natural waters and has been implicated in abiotic aquatic redox processes such as the photogeneration of hydrogen peroxide and the photooxygenation of amino acids and organic free radicals (Mopper and Zika, 1987). In general, it has been found that flavins (compounds containing the isoalloxazine ring system) are photochemically reactive toward electron-rich aromatic compounds. Thus, in reactions of substituted phenylalanines, electron-donating substituents increase the rate of photodegradation, whereas electron-withdrawing groups deactivate the ring to attack (Rizzuto et al., 1986). Riboflavin produces both singlet oxygen (¹⁰O₂) and superoxide radical (O₂⁻) when irradiated with visible or solar UV light in the presence of oxygen (Joshi, 1985). Hydroxyl radicals have also been postulated in some of its reactions (Ishimitsu et al., 1985). In addition, excited flavins take part in energy-transfer processes and hydrogen atom abstraction (Chan, 1977).
CHAPTER 2

RESULTS AND DISCUSSION

Direct Photolysis of Triazines

The direct photodegradation of the herbicides (atrazine, 7; ametryne, 8; prometone, 9, prometryne, 10) exposed to UV (λ=290-380 nm) was expected to proceed slowly, because triazines absorb weakly in the solar UV region. The absorbance maxima of the triazines studied (Table 1) are in the lower UV range, at around 220 nm. As predicted, the half-lives were similar, on the order of about a day (Table 2). The half-life of atrazine in aqueous solution had previously been reported as 25±2 hrs (first-order indoor photolysis using a mercury arc lamp similar to ours) by Burkhard and Guth (1976). Our data for atrazine closely agree with this result.

![Chemical structures](image)

Table 1. Absorbance Maxima and Extinction Coefficients for Triazines

<table>
<thead>
<tr>
<th>Triazine</th>
<th>λ_{max} (nm)</th>
<th>ε (l/cm mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>223</td>
<td>34,000</td>
</tr>
<tr>
<td>Ametryn</td>
<td>221</td>
<td>48,000</td>
</tr>
<tr>
<td>Prometon</td>
<td>217</td>
<td>49,000</td>
</tr>
<tr>
<td>Prometryn</td>
<td>222</td>
<td>31,000</td>
</tr>
</tbody>
</table>
Table 2  Half-Lives and Rate Constants of Triazines

<table>
<thead>
<tr>
<th>Triazine</th>
<th>Iron salt (0.26 mM)</th>
<th>$t_{1/2}$ (min)</th>
<th>$k$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>none</td>
<td>1500</td>
<td>0.00046</td>
</tr>
<tr>
<td>Ametryn</td>
<td>none</td>
<td>1600</td>
<td>0.00042</td>
</tr>
<tr>
<td>Prometon</td>
<td>none</td>
<td>1400</td>
<td>0.00049</td>
</tr>
<tr>
<td>Prometryn</td>
<td>none</td>
<td>1200</td>
<td>0.00060</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Fe(ClO$_4$)$_3$  xH$_2$O</td>
<td>1.4</td>
<td>0.51</td>
</tr>
<tr>
<td>Ametryn</td>
<td>Fe(ClO$_4$)$_3$  xH$_2$O</td>
<td>1.6</td>
<td>0.43</td>
</tr>
<tr>
<td>Prometon</td>
<td>Fe(ClO$_4$)$_3$  xH$_2$O</td>
<td>1.7</td>
<td>0.41</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Fe(ClO$_4$)$_3$  xH$_2$O</td>
<td>2.7</td>
<td>0.26</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Fe$_2$(SO$_4$)$_3$  5.6H$_2$O</td>
<td>24</td>
<td>0.029</td>
</tr>
<tr>
<td>Ametryn</td>
<td>Fe$_2$(SO$_4$)$_3$  5.6H$_2$O</td>
<td>1.4</td>
<td>0.50</td>
</tr>
<tr>
<td>Prometon</td>
<td>Fe$_2$(SO$_4$)$_3$  5.6H$_2$O</td>
<td>6.4</td>
<td>0.11</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Fe$_2$(SO$_4$)$_3$  5.6H$_2$O</td>
<td>31</td>
<td>0.023</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Fe(NO$_3$)$_3$  9H$_2$O</td>
<td>450</td>
<td>0.0015</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Fe$_4$H$_5$O$_7$</td>
<td>270</td>
<td>0.0026</td>
</tr>
</tbody>
</table>
Iron Salts

*Indirect Photolysis Experiments.* Several groups have previously reported that the photodegradation of numerous organic compounds can be significantly increased by adding iron salts: alcohols (Walling and Humphreys, 1981), formaldehyde (Murphy et al., 1989), chlorophenols (Barbeni et al., 1987) and several pesticides (Bowman and Sans, 1980, Skurlatov et al., 1983). We have investigated the aqueous photodegradation rates of four triazines with ferrous or ferric iron added to promote the reaction. The absorption spectra of all iron salts used are shown in Figs. 1-6. The observed spectrum of ferric perchlorate closely matches that of the hydrated complex, Fe(OH)\textsuperscript{2+}, as measured by Faust and Hoigné (1990). Wescrler et al. (1986) indicate that photolysis of this complex is an important source of OH radicals in rain.

I. FERROUS AND FERRIC PERCHLORATE

The most dramatic results were obtained with ferrous and ferric perchlorate. The addition of ferrous perchlorate (Fe[ClO\textsubscript{4}]\textsubscript{2} \cdot 6H\textsubscript{2}O) at a concentration of 0.26 mM to distilled water decreased the degradation half-life of atrazine from 1500 min to 14 min. Ferric perchlorate (Fe[ClO\textsubscript{4}]\textsubscript{x}H\textsubscript{2}O) was even more effective at the same iron concentration, the half-life of atrazine was decreased to approximately 1 min when the ferric salt was added. Table 2 and Figure 7 indicate that the half-lives of triazines 7-10 were also significantly reduced (by a factor of about 1000) by added ferric perchlorate. (In Fig 7 and subsequent graphs, what is plotted is the decrease in the concentration of the triazine, plotted logarithmically, versus time.) A control experiment run with atrazine, sodium perchlorate (NaClO\textsubscript{4}) and light indicated no changes in the atrazine concentration; thus any direct role of perchlorate in the photolysis reaction can be ruled out. Dark control experiments (reactions run without exposure to a light source) indicated no significant changes in triazine concentrations. In order to examine the effect of varying iron concentrations, [Fe\textsuperscript{3+}] was added to give initial concentrations ranging from 0.026 mM to 0.26 mM (Figure 8). It is apparent that the reaction rate increased (and therefore the half-life decreased) with increasing ferric ion concentration. Another important and related factor is pH. As the iron concentration increased, the pH of the reaction solutions decreased, increasing the concentration by a factor of ten increased [H\textsuperscript{+}] by a factor of ten (pH went from 4.3 to 3.3, see Table 6). Figure 8 also shows that rather small changes in iron concentration result in large changes in reaction rates. This seems to indicate that H\textsuperscript{+} promotes the reaction. The speciation of iron complexes in water is known to be strongly affected by pH (Faust and Hoigné, 1990). Further investigation is required to determine the importance and role of pH in the mechanisms of these photoreactions.
II. Ferrous and Ferric Sulfate

Ferrous sulfate (FeSO₄ 7H₂O), at 0.26 mM (as above), decreased the photodegradation half-life of atrazine from 1500 to 69 min. Ferric sulfate (Fe₃(SO₄)₃·56H₂O, assuming 20% water content), at 0.21 mM, decreased the half-life of atrazine to 24 min. The half-lives of ametryn, prometryn and prometon were also decreased with the addition of ferric sulfate (Table 2). Both ametryn and prometon reacted faster with the ferric ion added than did atrazine, while prometryn reacted slower than atrazine (Figure 9). No degradation in the dark was observed.

Again, an increase in the ferric sulfate concentration caused an increased rate of atrazine degradation. Figure 10 illustrates the effect of varying the final iron concentration from 0.042 to 0.42 mM.

III. Other Iron Salts

In order to compare the effects of adding various ferric salts on the degradation of atrazine, ferric nitrate (Fe(NO₃)₃, 9H₂O) and ferric citrate (undetermined composition, FeC₆H₄O₇ assumed for molarity calculations) were added in separate experiments, both at 0.26 mM (Table 2). The addition of the citrate salt promoted atrazine photodegradation better than did the nitrate salt, although neither did as well as either the perchlorate or the sulfate salts (Figure 11). The slowing of the degradation could be due to the reaction of nitrate or citrate with the hydroxyl radical. If this radical were attacking and degrading atrazine, any competition for OH⁻ would slow the reaction. The molar ratio of the nitrate ion to atrazine is 150:1 and for the citrate ion to atrazine is 50:1, so that more competition from the nitrate ion for the hydroxyl radical on a molar basis would be expected. On the other hand, nitrate reacts with OH⁻ with a second order rate constant of ≈5x10⁸ L/mol sec, while citrate reacts with OH⁻ with k = 5.4x10⁸ L/mol sec (Farhataziz and Ross, 1977). This would indicate that the reaction of atrazine with ferric nitrate should go faster than the reaction with ferric citrate, however, the reverse was the case. One explanation might be that citrate forms another radical species during photolysis that could attack atrazine, perhaps an alkyl radical. Also, the presence of nitrate in the solvent cage surrounding iron could be influencing radical formation by possibly producing a nitrate radical (NO₃⁻).
Figure 1  Absorption Spectrum of Ferric Perchlorate (0.001 M)

Figure 2  Absorption Spectrum of Ferrous Perchlorate (0.01 M)
Figure 3. Absorption Spectrum of Ferric Sulfate (0.001 M)

Figure 4. Absorption Spectrum of Ferrous Sulfate (0.01 M)
Figure 5. Absorption Spectrum of Ferric Citrate (0.0005 M)

Figure 6. Absorption Spectrum of Ferric Nitrate (0.001 M)
Figure 7. Triazine Photodegradation with Ferric Perchlorate

![Figure 7](image)

Figure 8. Effect of Varying Ferric Perchlorate Concentration on Atrazine Disappearance

![Figure 8](image)
Figure 9. Triazine Photodegradation with Ferric Sulfate

Figure 10. Effect of Varying Ferric Sulfate Concentration on Atrazine Disappearance
Figure 11. Effect of Several Iron Salts on Atrazine Disappearance
IV. RIBOFлавIN AND METHYLENE BLUE

Dye-sensitized photolysis of the triazines was evaluated in solutions 5 \( \mu M \) in riboflavin or methylene blue. The addition of these photosensitizing dyes decreased three of the four triazine half-lives as seen in Table 3. Although the reduction in the half-lives was not as dramatic as with the addition of iron salts, it was still significant: the atrazine half-life was reduced from 1500 min to 690 and 780 min by the addition of riboflavin and methylene blue, respectively. Both ametryn and prometryn had a shorter half-life with riboflavin than did atrazine. The prometon half-life apparently increased by about a factor of 2, for reasons that are not presently obvious.

Mechanistic Studies. It is clear that iron salts had a powerful degradative effect on atrazine and the other triazines studied under certain conditions. We studied the mechanisms of the photolysis reactions in more detail using atrazine in order to validate the parameters and pathways under which triazines photodegraded. Our data from these studies, summarized in the sections below, suggest that both hydroxyl radical (OH) and superoxide radical (\( O_2^- \)) are produced by photolysis of ferric perchlorate, but that only OH is important for the photodestruction of the triazines. The hydroxyl radical is a very strong, non-selective oxidant that attacks nearly all organic substrates. A tentative mechanism for the photolysis of iron salts is shown in Figure 12.

I. HYDROXYL RADICAL

Mannitol is known to scavenge hydroxyl radicals (Misra and Fridovich, 1976; Gutteridge and Halliwell, 1982). Goldstein and Czapski (1984) measured the rate constant for this reaction at (1.8±0.4)x10^9 L/mol·sec. Mannitol is much less reactive toward many other free radicals, such as alkoxy radicals (Halliwell and Gutteridge, 1985). Therefore, if OH is involved in the photoreaction of Fe\(^{3+}\) and atrazine, the presence of mannitol would scavenge HO and cause the reaction to slow down. Addition of mannitol at various concentrations to both the atrazine/ferric sulfate and atrazine/ferric perchlorate reaction mixtures, had a diminishing effect on the rate. Figure 13 illustrates a 2-fold increase in the half-life when 5x10^-4 \( M \) mannitol was added to atrazine/ferric sulfate and an even greater increase in the half-life (to 850 min) when mannitol was added at 5 x 10^-3 \( M \). The half-life of the atrazine/ferric perchlorate system also increased upon the addition of mannitol (Figure 14): \( t_{1/2} = 2.4 \text{ min with 5x10^{-5} M mannitol added and 16 min with 5x10^{-4} M mannitol added.} \) Thus, the involvement of OH is suggested. Without knowledge of the exact rate constant of HO with atrazine, one cannot assess whether the observed inhibition by mannitol is in the expected range, but assuming a rate constant of about 10^6 for atrazine (in the range observed for aniline and N,N-dimethylaniline; Farhataziz and Ross, 1977), the observed values would fit well with those calculated. The OH could be coming either directly from solvated Fe\(^{3+}\) or from a dark (Fenton-type) reaction involving H\(_2\)O\(_2\), as discussed previously.

To test the hypothesis of OH generation from a Fenton-type reaction, catalase was added to the atrazine/ferric perchlorate system. Catalase, which is known to destroy hydrogen peroxide and react quickly with hydrated electrons, had a diminishing effect on
Table 3. Dye-Sensitized Photolysis of Triazines

<table>
<thead>
<tr>
<th>Triazine</th>
<th>Dye*</th>
<th>Special Conditions</th>
<th>$t_{th}$ (min)</th>
<th>$k$(min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>RF</td>
<td></td>
<td>690 †</td>
<td>0.0010</td>
</tr>
<tr>
<td>Ametryne</td>
<td>RF</td>
<td></td>
<td>480</td>
<td>0.0014</td>
</tr>
<tr>
<td>Prometryn</td>
<td>RF</td>
<td></td>
<td>600</td>
<td>0.0012</td>
</tr>
<tr>
<td>Prometon</td>
<td>RF</td>
<td></td>
<td>2700</td>
<td>0.00025</td>
</tr>
<tr>
<td>Atrazine</td>
<td>MB</td>
<td></td>
<td>780 †</td>
<td>0.00089</td>
</tr>
<tr>
<td>Atrazine</td>
<td>RF</td>
<td>Degassed</td>
<td>4600</td>
<td>0.00015</td>
</tr>
<tr>
<td>Atrazine</td>
<td>MB</td>
<td>Natural Water (Boneyard Creek)</td>
<td>7100</td>
<td>0.000097</td>
</tr>
</tbody>
</table>

* RF = riboflavin (5 $\mu M$)  
  MB = methylene blue (5 $\mu M$)

† These are average values of several experiments
Figure 12. Mechanism of Iron Photolysis
Figure 13. Mannitol Inhibition of Ferric Sulfate-Sensitized Atrazine Photolysis

![Graph showing the effect of mannitol on ferric sulfate-sensitized atrazine photolysis.](image)

Figure 14. Mannitol Inhibition of Ferric Perchlorate-Sensitized Atrazine Photolysis

![Graph showing the effect of mannitol on ferric perchlorate-sensitized atrazine photolysis.](image)
the atrazine degradation rate. Figure 15 illustrates that at a concentration of 10 µg/mL, catalase had only a slight diminishing effect on the atrazine/ferric perchlorate system, but strongly inhibited degradation at a concentration of 100 µg/mL. This experiment with catalase could indicate that there is a significant dependence on H₂O₂ in the reaction mechanism, or alternatively that catalase, by reacting non-catalytically with •OH, is siphoning away these reactive intermediates.

Several experiments with superoxide dismutase (SOD) were performed. SOD catalyzes the disproportionation ("dismutation") of superoxide to H₂O₂, therefore promoting H₂O₂ production:

\[ \text{O}_2^\cdot \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \]  \hspace{1cm} (7)

If the photodegradation of atrazine is indeed partly dependent on H₂O₂, as postulated, the addition of SOD should have decreased the half-life; in fact, it was increased. In various experiments performed with atrazine, iron salts and SOD (10 µg/mL), the increase in the half-life ranged from a factor of 2 to about 20. Reaction rates of several experiments with degassed solutions and SOD were also quite variable. When control reactions were run with denatured (boiled, presumably destroying its enzymatic activity) SOD plus atrazine and iron, one experiment showed a decreased half-life, one showed an increased half-life and two showed no effect (i.e. same as with active SOD). As the data accumulated with SOD seems to be quite inconsistent, the effect of SOD is judged to be inconclusive. Personal communication with Diane Cabelli of Brookhaven National Laboratory, Upton, LI, NY (1988) revealed that no known data regarding reactions of SOD at low pHs (below about 5) had been accumulated. At pHs below 4.8, superoxide is predominantly in its conjugate acid form (HOO•) and it is therefore difficult to measure the superoxide radical absorbance in order to determine the reaction rate of the above reaction with SOD at these pHs. Another possible explanation for the apparent inconsistency of our data was also suggested; at the low pHs of the reaction solutions, catalytically active copper may be removed from SOD.

Strong evidence for the mechanism involving attack by HO• was found by performing analyses of reaction products (by GC/MS) to compare the products obtained with the atrazine/ferric perchlorate and atrazine/ferrous perchlorate systems to those observed when atrazine was allowed to react with OH• generated by a known OH•-producing reaction (Fenton reaction). If the same products were obtained for each reaction, then the theory would be supported. The atrazine/ferric perchlorate experiment was performed on a larger scale. The Fenton reaction was performed with fivefold molar excesses of ferrous ion and H₂O₂ to atrazine, in the dark. The same products were observed in all three reactions and were tentatively identified as de-ethylated atrazine, de-isopropylated atrazine and an oxidized product (Figure 16). Rejto et al. (1983) found both the de-ethylated and the oxidized product from the riboflavin-sensitized photooxidation of atrazine. It seems logical to postulate that the hydroxyl radical is the active reactant for the atrazine destruction in all three experiments.
Figure 15. Effect of Catalase on Ferric Perchlorate-Sensitized Atrazine Photolysis
Another result which substantiates the involvement of OH⁻ was an experiment with the sugar deoxyribose (2-deoxy-D-ribose), which has often been used to measure the formation of OH⁻ in biochemical systems (Gutteridge, 1981; Halliwell and Gutteridge, 1981). Deoxyribose is attacked by OH radicals to form a product that reacts upon heating with thiobarbituric acid (TBA) at acidic pH to form a chromogen which can be measured by visible spectroscopy (λ=532nm). An experiment conducted in this manner with ferric perchlorate (0.26mM) and deoxyribose in water resulted in a strongly absorbing chromogen, indicating OH radicals were formed during the ferric ion photolysis (Table 4). When the same experiment was conducted with ferrous perchlorate, no chromogen developed and the absorbance was minimal.

Hydroxyl radical production was also supported by the similarity in iron-promoted half-lives of several triazines. Ametryn and prometryn have an -SCH₃ group and prometon has an -OCH₃ group at the ring position where atrazine has a -Cl group. Aromatic -OCH₃ and -SCH₃ substituents are more electron-donating than a -Cl substituent, making the ring more electron-rich and thus presumably more susceptible to electrophilic (oxidative) attack. This can be seen in Table 3, both prometryn and ametryn plus riboflavin degrade faster than atrazine with riboflavin. Therefore, one would expect these triazines to be photooxidized somewhat faster than atrazine. Experiments conducted with ferric perchlorate indicated, however, that this was not the case (Table 2). This would be expected if OH⁻ is involved, since the OH radical is quite unselective in its attack. In experiments conducted with ferric sulfate, atrazine had a longer half-life than ametryn and prometon (expected), but the half-life of prometon was somewhat longer than that of atrazine (Table 2). Again, an unselective attack on the triazines may be occurring, although the ferric sulfate photolysis may involve sulfate radical, in part, rather than hydroxyl radical.

II. SUPEROXIDE RADICAL

Production of O₂⁻ during Fe³⁺ photolysis was inferred in kinetic experiments with anisole and nitrobenzene. Zepp and Hoigné (1987) demonstrated that anisole is 2.6 times more reactive than nitrobenzene toward hydroxyl radicals. However, when ferric perchlorate photolysis was performed with these two compounds, nitrobenzene disappeared about 2.4 times as fast as anisole (Figure 17). This indicates that O₂⁻ (or some other nucleophilic species) must have been formed. Further work is necessary to assess the extent and importance of O₂⁻ formation in these photoreactions.

To test the extent of atrazine degradation when only O₂⁻ was present, excess potassium superoxide (KO₂) was added to atrazine (in the absence of iron) as a superoxide radical generator. The pKₐ of O₂⁻ is 4.7, so that above pH = 4.7, the ionized form dominates versus the conjugate acid (HOO⁻) form. Since HOO⁻ is the active species that undergoes disproportionation (dismutates) to hydrogen peroxide and oxygen, O₂⁻ is very stable at high pH (Bielinski and Allen, 1977). Both at pH 4 and 9, the atrazine was not degraded; therefore, we conclude that O₂⁻ by itself was not important in the degradation of atrazine.
Figure 16. Photodecomposition Products of Atrazine

Deethylated Atrazine (R=Cl)

De-isopropylated Atrazine (R=Cl)

Oxidized Atrazine (R=Cl)
Table 4. Deoxyribose Experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color Before Test</th>
<th>Color After Test</th>
<th>Absorbance at 532 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank*</td>
<td>Yellow</td>
<td>Yellow</td>
<td>0.104</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}$/Ascorbate Deoxyribose</td>
<td>Yellow</td>
<td>Dark Pink</td>
<td>2.64</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}$/Ascorbate Deoxyribose</td>
<td>Yellow</td>
<td>Yellow</td>
<td>0.161</td>
</tr>
</tbody>
</table>

* The blank consisted of ascorbate and deoxyribose only

Figure 17. Nitrobenzene and Anisole Photodegradation by Ferric Perchlorate
III. SULFATE RADICAL

It is possible that the formation of sulfate radicals (SO$_4^-$) occurs during the photolysis of the sulfate salts; iron complexed to sulfate anion could take part directly in electron transfer reactions, or hydroxyl radical formed initially could subsequently react with sulfate anion. Sulfate radicals are potent oxidants (Behrens et al., 1988) and may play a role in the degradation of the triazines. The concentration of the sulfate ion (SO$_4^{2-}$) in the atrazine/sulfate salt reaction solutions was about 100 times that of atrazine, so that SO$_4^{2-}$ may partially compete with the triazine for the hydroxyl radical, since the rate constant for sulfate ion with OH$^-$ is 2 to 3 orders of magnitude smaller than that for OH$^-$ with heterocyclic aromatic compounds (Table 5). Further studies with added sulfate will be required to answer this question.

IV. OXYGEN

To assess the dependence of the reaction on oxygen, it was removed from the reaction solutions by bubbling argon gas into the solutions for about one minute. The saturation value of dissolved oxygen in water exposed to air is 8.5 mg/L (2.7x10$^{-4}$ M) at 24°C (Viessman and Hammer, 1985), and thus its concentration far exceeds that of the other reactants in these systems. In the absence of oxygen, the iron-promoted half-life of atrazine increased significantly. This effect was seen with ferrous sulfate, ferric perchlorate and riboflavin. Degassing the atrazine/ferrous sulfate system increased the half-life by about 8 times, as seen in Figure 18. Figure 19 illustrates the 6-fold increase in the atrazine half-life when the atrazine/ferric perchlorate solutions were degassed. When the atrazine/riboflavin reaction solutions were degassed, the half-life increased over 6-fold (Table 3). Oxygen may promote the reaction by scavenging hydrated electrons and by providing H$_2$O$_2$ (see Figure 12). In order to determine if increased oxygen concentrations would enhance degradation, oxygen gas was bubbled through the atrazine/ferric perchlorate reaction mixtures. Figure 20 shows that there was virtually no difference in the reaction rates.

It is apparent that oxygen was necessary for the reaction to proceed efficiently but that adding oxygen above the ambient level produced little or no additional benefit.

Natural Systems. The experiments conducted in the laboratory employed artificial conditions: distilled water and non-buffered reaction solutions which were often quite acidic. If the proposed mechanism is important and OH$^-$ is responsible for the triazine photodegradation, examination of the usefulness of this process must be conducted in more realistic systems, which contain dissolved substances that could interfere with the triazine degradation by a variety of mechanisms. In order to simulate ground-water conditions, both buffers and natural waters were used in experiments. Although obviously light does not penetrate into groundwater, some techniques for restoring its quality depend on pumping it to the surface, treating it by some means such as (conceivably) photolysis, and pumping it back into the aquifer.
Table 5. Rate Constants of Various Species with OH⁻.

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>7</td>
<td>(3.0±0.6)x10⁹ (1)</td>
</tr>
<tr>
<td>2-Chloropyridine</td>
<td>9</td>
<td>1.75x10⁹ (1)</td>
</tr>
<tr>
<td>Sodium Acetate-Acetic Acid (Buffer)</td>
<td>5</td>
<td>7x10⁷ (1)</td>
</tr>
<tr>
<td>Phosphate (Buffer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>3.85-4.0</td>
<td>2.2x10⁶ (1)</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>9-12.3</td>
<td>(7.9±0.4)x10⁸ (1)</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>7</td>
<td>&lt;1.0x10⁷ (2)</td>
</tr>
<tr>
<td>Borate (Buffer)</td>
<td>9</td>
<td>&lt;1x10⁶ (2)</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>7</td>
<td>1.6x10⁶ (1)</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>9</td>
<td>&lt;5x10⁵ (1)</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>2-2.2</td>
<td>5.4x10⁸ (1)</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>11</td>
<td>3.5x10⁸ (1)</td>
</tr>
</tbody>
</table>

(1) Farhataziz and Ross, 1977.
(2) Buxton et al., 1988.
Figure 18. Effect of Argon on Ferrous Sulfate-Sensitized Atrazine Photolysis

![Graph showing effect of argon on ferrous sulfate-sensitized atrazine photolysis.](image)

Figure 19. Effect of Argon on Ferric Perchlorate-Sensitized Atrazine Photolysis

![Graph showing effect of argon on ferric perchlorate-sensitized atrazine photolysis.](image)
Figure 20. Effect of Added Oxygen on Ferric Perchlorate-Sensitized Atrazine Photolysis
I. BUFFERED SOLUTIONS

Experiments in buffers were initially attempted in order to study the effect of varying pH on the photochemical reactions of iron salts. (The pH of several experimental reaction solutions is given in Table 6.) It is apparent that addition of iron salts to distilled water caused the solution pH to drop into a fairly acidic range. In oxygenated water or solutions, ferrous iron is rapidly oxidized to ferric iron at pHs above 5.5 (Snoeyink and Jenkins, 1980):

\[ 4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2(\text{aq}) \Leftrightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (8) \]

The \( \text{Fe}^{3+} \) may then precipitate as ferric hydroxide:

\[ \text{Fe}^{3+} + 3\text{OH}^- \Leftrightarrow \text{Fe(OH)}_3(\text{s}) \quad (9) \]

Ferric hydroxide is sparingly soluble in waters with a pH greater than 5 to 6, so that most of the iron would precipitate out as the hydroxide in these conditions. If ferrous iron is present in solution, it may also precipitate:

\[ \text{Fe}^{2+} + 2\text{OH}^- \Leftrightarrow \text{Fe(OH)}_2(\text{s}) \quad (10) \]

At pHs much above those given for reaction solutions in Table 6, only a small fraction of the iron would be in solution; the majority would be in the form of insoluble hydrous oxides. As distilled and natural waters are usually in the neutral pH range, the question was whether the reaction would proceed at these pHs. Also, the pH of natural waters (especially surface waters) varies seasonally and changes with the constituents of the water (i.e. humic materials, wastes, microorganisms, etc.). The atrazine/ferric sulfate system was studied using a sodium acetate-acetic acid buffer, a phosphate buffer and a borate buffer, for pH of 5, 7 and 9, respectively. All buffered reaction solutions proceeded much more slowly than unbuffered solutions (Table 7) and no definite correlation of reaction rate with pH could be established. It seemed, though, that lower buffer concentrations gave faster reaction rates.

Two buffer systems were used to study pH effects on the atrazine/ferric perchlorate reaction: an acetate buffer and a tetramethylpyrazine buffer (Me₄-pyr) (Table 7). Adding sodium acetate to give a final acetate concentration of 0.0033 \( M \) (pH=3.7), gave a half-life of 1450 min. A 0.01 \( M \) sodium acetate-acetic acid buffer (pH=4.4), gave a half-life of 2210 min. Again, these reactions were much slower than those in unbuffered solutions. The Me₄-pyr buffer system was chosen for its supposed non-complexing tendencies with metals (Bips et al., 1983). A 0.01 \( M \) buffer was prepared and the pH was adjusted to 4.2 using perchloric acid. Experiments conducted with the buffer alone indicated, however, that the atrazine/buffer control reacted faster than this system with ferric perchlorate added, a
Table 6. pHs of Various Reaction Solutions

<table>
<thead>
<tr>
<th>Reaction Solution</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine in glass distilled water</td>
<td>7.5</td>
</tr>
<tr>
<td>Atrazine in Boneyard Creek water</td>
<td>8.15 *</td>
</tr>
<tr>
<td>Atrazine/Ferrous Sulfate (0.26 mM)</td>
<td>5.7 *</td>
</tr>
<tr>
<td>Atrazine/Ferrous Perchlorate (0.26 mM)</td>
<td>5.1</td>
</tr>
<tr>
<td>Atrazine/Ferric Perchlorate (0.26 mM)</td>
<td>3.35</td>
</tr>
<tr>
<td>Atrazine/Ferric Perchlorate (0.18 mM)</td>
<td>3.75</td>
</tr>
<tr>
<td>Atrazine/Ferric Perchlorate (0.026 mM)</td>
<td>4.3</td>
</tr>
</tbody>
</table>

All pH measurements were made with an Orion pH meter and electrode except for those marked with *, these were made with a Corning pH meter and an Orion electrode.
### Table 7. Effects of Buffered Reaction Solutions on Atrazine Photolysis

<table>
<thead>
<tr>
<th>Iron Salt</th>
<th>Buffer</th>
<th>buffer conc.</th>
<th>pH</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous Sulfate</td>
<td>-</td>
<td>-</td>
<td>5.7</td>
<td>69</td>
</tr>
<tr>
<td>Ferrous Sulfate</td>
<td>Acetic Acid-Na Acetate</td>
<td>0.001</td>
<td>5</td>
<td>970</td>
</tr>
<tr>
<td>Ferrous Sulfate</td>
<td>Phosphate</td>
<td>0.01</td>
<td>7</td>
<td>2400</td>
</tr>
<tr>
<td>Ferrous Sulfate</td>
<td>Borate</td>
<td>0.01</td>
<td>9</td>
<td>2500</td>
</tr>
<tr>
<td>Ferric Perchlorate</td>
<td>-</td>
<td>-</td>
<td>3.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Ferric Perchlorate</td>
<td>Na Acetate</td>
<td>0.003</td>
<td>3.7</td>
<td>1400</td>
</tr>
<tr>
<td>Ferric Perchlorate</td>
<td>Acetic Acid-Na Acetate</td>
<td>0.01</td>
<td>4.4</td>
<td>2200</td>
</tr>
<tr>
<td>Ferric Perchlorate</td>
<td>Me₄-pyr</td>
<td>0.01</td>
<td>4.2</td>
<td>74</td>
</tr>
<tr>
<td>None</td>
<td>Me₄-pyr</td>
<td>0.01</td>
<td>4.2</td>
<td>48</td>
</tr>
</tbody>
</table>


Figure 21. Tetramethylpyrazine Buffer as a Photosensitizer
very unexpected result (Figure 21). The buffer, even at this concentration, was, however, not as effective as ferric perchlorate in pure water at much lower concentrations. The UV spectrum of Me₄-pyr indicates significant absorption at wavelengths of 206 nm, 275 nm and 295 nm. Thus, the buffer absorbed nearly all of the short-wave UV light in the system, shielding the much lower concentrations of iron from being excited, and may have taken part on its own in photochemical reactions, possibly involving electron transfer. (Its structure shares some elements with riboflavin, which does act in this manner.) Dark samples of both systems (with and without ferric iron added) were essentially non-reactive. Samples that were degassed with argon reacted with the same half-life as those that were not degassed, indicating that oxygen was not required for the degradation to proceed in the Me₄-pyr buffer system. To determine the reasons for the rate acceleration by the pyrazine will require further study. A search of the literature revealed no citations to photochemical investigations of this class of compounds.

As the rates of all reactions in buffers were slowed significantly relative to unbuffered solutions, the cause of this slowing of the rate may be common to all buffers. If the hydroxyl radical is in fact involved in the degradation of the triazines, reaction of the buffer with OH· would slow down the rate. It is well known that the hydroxyl radical adds very rapidly to aromatic compounds related to atrazine, with second order rate constants ranging from 10⁸ to 10¹⁰ (Dorfman and Adams, 1973); however, at high enough concentrations, species such as buffer salts might be able to compete for HO·, despite lower rate constants, and prevent attack of the radical on the desired substrate. The rate constants for the reaction of several species, including the buffers used, with OH· are given in Table 5. Especially in the case of the acetate buffer, competition for the OH· radical by the buffer could be the cause of the rate reduction. Also, a lower buffer concentration affords a faster rate; this also suggests that the buffer is interfering in some manner, presumably by competing for OH·.

II. NATURAL WATERS

The dissolved substances found in natural waters, such as humic and fulvic acids, can influence photolysis rates by either promoting or retarding photochemical and photophysical processes. Miller et al. (1980) showed that light attenuation is a retarding effect while mediation of indirect photoprocesses can be an accelerating effect. Zepp et al. (1985) reported that humic materials sensitize photoreactions of several organic chemicals. In experiments with tryptophan and methylene blue (used as a sensitizer), Guy and Narine (1980) found that the amount of tryptophan degraded was significantly reduced when humic acid was present. The authors stated that this could be due to different light absorption and emission properties of methylene blue bound to the colloid or due to
quenching by humic acid of the $^1\text{O}_2$ produced. The reaction of OH with carbonate (CO$_3^{2-}$) is also an important factor. In natural freshwaters, OH$^-$ is consumed within a few microseconds by dissolved organic carbon and by carbonate (Hoigné and Bader, 1977, 1979); the reaction of OH with carbonate is very rapid (Table 5). Although this rate constant is somewhat lower than the rate constant for the reaction of OH with many organic compounds, the concentration of CO$_3^{2-}$ in drinking water and wastewater is usually greater than the trace organic compounds found in these waters (Hoigné and Bader, 1979), thus, the scavenging of OH by carbonate becomes the determining reaction in such waters. Carbonate radical itself is not particularly reactive with most classes of dissolved organic compounds (Larson and Zepp, 1988) and its fate in natural waters is at present uncertain.

Several experiments with atrazine plus iron salts were conducted in natural water samples from a local stream (Boneyard Creek, Urbana, IL). Although organic carbon analyses of this water was not performed, dissolved organic matter was present in the stream, as indicated by an optical density of 0.264 at 223 nm. In all cases, atrazine in this natural water was degraded much more slowly than in distilled water in both direct and indirect photolysis (Table 8). The reaction of ferrous sulfate and atrazine in natural water proceeded even slower than the direct photolysis of atrazine in distilled water. In order to eliminate interferences from larger particles in the natural water, it was filtered through a glass filter using Anspec nylon 66 filter membranes (47 mm, 0.45 μm). Even this did not effectively decrease the half-life. Increased degradation was observed when ferric sulfate (instead of ferrous sulfate) was added to the reaction mixtures, although the half-life was still very long. Finally, the addition of ferric perchlorate to atrazine in natural water caused the greatest decrease in the half-life from the unsensitized reaction, as with reactions done in distilled water.

Experiments with atrazine and methylene blue were also conducted in natural water (Boneyard Creek). Again, the reaction was slowed greatly. Table 3 indicates that the average half-life in natural water was 7100 min, versus 780 min in distilled water.

The increase in the half-life of atrazine in natural water with iron salts added, when compared to distilled water, is most likely due to competition for the hydroxyl radical, although in some cases light attenuation of the incident radiation may play a role. Dissolved materials in creek water (probably carbonate or organic compounds) may be scavenging the hydroxyl radicals produced in the photoreaction, thereby leaving a lower flux of radicals to attack and break down the atrazine.
Table 8. Half-Lives of Atrazine in Boneyard Creek Water Containing Iron Salts

<table>
<thead>
<tr>
<th>Iron Salt Added</th>
<th>[Fe]</th>
<th>(t_{1/2}) (min)</th>
<th>(k) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous Sulfate</td>
<td>0.26 mM</td>
<td>1900</td>
<td>0.00037</td>
</tr>
<tr>
<td>Ferric Sulfate</td>
<td>0.42 mM</td>
<td>990</td>
<td>0.0007</td>
</tr>
<tr>
<td>Ferric Perchlorate</td>
<td>0.26 mM</td>
<td>900</td>
<td>0.00077</td>
</tr>
<tr>
<td>None</td>
<td></td>
<td>1500</td>
<td>0.00046</td>
</tr>
</tbody>
</table>

**Proposed Mechanism.** As shown in Figure 12, there are at least two routes for producing hydroxyl radical in these systems, ferrous ion photolysis and ferric ion photolysis. Photolysis of ferric ion at low pH produces ferrous ions and OH

\[
\text{Fe}^{3+}(\text{H}_2\text{O}) \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{OH}^- \quad (11)
\]

Production of a hydroxyl radical from ferrous ion is more complicated, and may even be of negligible importance in systems exposed to sunlight because of the low absorbance of \(\text{Fe}^{2+}\). Transition metal cation spectra have been described as arising from photodetachment of an electron from the hydrated ion (Fox, 1984):

\[
M_{\text{aq}}^{x+} \rightarrow M_{\text{aq}}^{(x+1)+} + e^- \quad (12)
\]

where \(M_{\text{aq}}^{x+}\) is a solvated cation. Here, the loss of an electron from a lower-valent metal ion (\(\text{Fe}^{2+}\)), affords a higher-valent metal ion (\(\text{Fe}^{3+}\)) and a hydrated electron. In the presence of oxygen, this process could generate superoxide (\(\text{O}_2^-\)) (reaction 13), which as its conjugate acid \(\text{HO}^-\) is susceptible to disproportionation to hydrogen peroxide and oxygen at pHs above 4.8 (reaction 14). A hydroxyl radical (\(\text{HO}^-\)) can then be produced by the Fenton reaction (reaction 6). The process can thus be summarized by the following three reactions:

\[
\begin{align*}
\text{Fe}^{2+} + \text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{O}_2^- \quad (13) \\
2\text{O}_2^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (14) \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}^- + \text{HO}^- + \text{Fe}^{3+} \quad (6)
\end{align*}
\]

The dependence of the reaction on oxygen may be explained by several mechanisms. First, when oxygen is available, it can react with the \(\text{Fe}^{2+}\) from reaction (11) and go on to produce \(\text{HO}^-\) by (13)-(14) and (6). The oxidation of ferrous ion by \(\text{O}_2\) is quite slow at low pH but is promoted by light (Stumm and Morgan, 1981). Thus the hydroxyl radical is produced by (11) and (6) in the presence of oxygen in sufficient quantities to prevent the back-reaction of (11) and to promote atrazine degradation. When there is no oxygen available, the \(\text{Fe}^{3+}\) produced in (11) is not "scavenged" and can back-react, therefore reducing the concentration of \(\text{HO}^-\) available to degrade the atrazine. In addition, it is well.
Table 9. Summary of Photolysis of Anilines and Phenols at pH 7

<table>
<thead>
<tr>
<th>Anilines</th>
<th>Sensitized</th>
<th>Direct</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$t_{A/2}^2$ (min)</td>
</tr>
<tr>
<td>aniline</td>
<td>0.11</td>
<td>1.8</td>
</tr>
<tr>
<td>p-chloroaniline</td>
<td>0.042</td>
<td>2.3</td>
</tr>
<tr>
<td>p-nitroaniline</td>
<td>0.13</td>
<td>0.4</td>
</tr>
<tr>
<td>4-bromo-3-chloroaniline</td>
<td>0.017</td>
<td>66</td>
</tr>
<tr>
<td>p-toluidine</td>
<td>0.26</td>
<td>0.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phenols</th>
<th>Sensitized</th>
<th>Direct</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>0.11</td>
<td>2.1</td>
</tr>
<tr>
<td>2,4-dichlorophenol</td>
<td>0.032</td>
<td>7.0</td>
</tr>
<tr>
<td>2,4,6-trichlorophenol</td>
<td>0.080</td>
<td>3.0</td>
</tr>
<tr>
<td>pentachlorophenol</td>
<td>0.040</td>
<td>5.5</td>
</tr>
<tr>
<td>p-cresol</td>
<td>0.38</td>
<td>0.36</td>
</tr>
<tr>
<td>4-cyanophenol</td>
<td>0.032</td>
<td>150</td>
</tr>
<tr>
<td>1-naphthol</td>
<td>0.46</td>
<td>0.26</td>
</tr>
</tbody>
</table>

2 This quantity refers to the time required for the acceptor to reach one-half its initial concentration. It differs from a half-life for riboflavin-sensitized photoreactions because the photolysis mechanism changes as riboflavin is converted to photoproducts during the reaction. Methods for calculating $t_{A/2}$ are given elsewhere (Larson et al., 1989).
known that the hydroxyl radical adds very rapidly to aromatic compounds, with second order rate constants ranging from $10^9$ to $10^{10}$ (Dorfman and Adams, 1973). The rate of reaction of OH· with Fe$^{2+}$ has been determined as $3 \times 10^9$ L/mol·sec (Dorfman and Adams, 1973, Farhataziz and Ross, 1977). Therefore, we would expect that if the Fe$^{2+}$ was lowered, the atrazine degradation would proceed more rapidly, as competition between atrazine and Fe$^{2+}$ for OH· would decrease. Thus, if O$_2$ scavenges Fe$^{2+}$, a positive effect on the reaction should have been, and was, seen when solutions contained oxygen versus no oxygen.

**Riboflavin**

 Riboflavin Reactions. Riboflavin is rapidly destroyed by sunlight in natural waters; we confirmed that the half-life of riboflavin in our system was approximately 1.5 min, in reasonable agreement with the previously reported (Dunlap and Susic, 1986) value of 3.2 min for distilled water exposed to sunlight. However, one of the major photoproduents of riboflavin in water is lumichrome (Dunlap and Susic, 1986), and its half-life (>8 hr) was much longer than riboflavin’s in our experiments. Under our conditions, lumichrome in the presence of oxygen was also a very efficient sensitizer; for example, $t_{1/2}$ for the photolysis of 5µM phenol with 6.2 µM lumichrome was 2.2 min at pH 5. The conversion of riboflavin to lumichrome (in distilled water) did not proceed in a single step, an intermediate compound was formed as riboflavin began to disappear. As the reaction continued, this intermediate was itself photolyzed, and lumichrome was formed. In pH 7 buffer, however, the results were much different. Riboflavin was destroyed at a higher rate, but lumichrome was not produced during the duration of the experiment (8 min). The previously observed intermediate was formed at this pH also.

 Experiments with riboflavin and anilines at pH 7 are summarized in Table 9. Aniline itself was not very susceptible to direct photodegradation by light, but it was much more rapidly destroyed in the presence of riboflavin and Pyrex-filtered mercury arc light. In the absence of sensitizer the half-life of aniline was 3 hr or more, depending on pH, at pH 5, where it would largely have been in the protonated -NH$_3^+$ form, it was virtually inert. With riboflavin, half the original aniline disappeared at pH 7 in approximately 2 min. The photosensitized rate was strongly dependent on pH, increasing from pH 5 to pH 8.

 Although p-toluidine, which has an electron-donating substituent, was virtually inert to direct photolysis, it was photodegraded rapidly in the presence of riboflavin ($t_{1/2} = 0.7$ min).

 At pH 7, 4-chloroaniline was very rapidly destroyed by mercury arc light alone (half-life about 5 min) but riboflavin increased the rate of destruction by a factor of 2 under our conditions. Correcting for the rate of direct photolysis, it appeared that 4-chloroaniline, as expected on the basis of electron availability, was somewhat less reactive than aniline to riboflavin attack. Sensitizers had little or no effect on the photodegradation of 4-bromo-3-chloroaniline (BCA, Table 9). BCA is present in combined (amide) form in the widely used herbicide, chlorbromuron. The half-life for its direct photolysis was 61 min.
at pH 7; in the presence of riboflavin, \( t_{1/2} \) was 66 min, perhaps reflecting some minor inhibition due to light absorption by the sensitizer. The results with aniline and its alkylated or halogenated derivatives could not be simply extrapolated, using simple electron density arguments, to other substituted anilines. For example, although 4-nitroaniline carries a strongly electron-withdrawing group and was virtually inert to direct photolysis, it appeared to have a reactivity with riboflavin comparable to aniline. Since 4-nitroaniline has significant absorption in the visible range (its solutions are yellow), it may be that photoreactions are occurring that involve the excited states of the aniline as well as those of riboflavin.

Previous workers have identified a variety of mechanisms by which riboflavin might react with substrates like anilines; production of singlet oxygen, photoionization to afford superoxide radical anion and thus hydrogen peroxide, hydrogen abstraction, and energy or electron transfer. Under our conditions, mechanisms requiring reactive oxygen species were ruled out by the observation that oxygen was not required for the photoreaction of anilines. For example, if oxygen was completely removed from the photoreaction between riboflavin and aniline, the rate of aniline disappearance increased significantly (Fig. 22.) These results suggest a "Type I" sensitized reaction (Foote, 1981) where energy is transferred directly between the sensitizer and the substrate, perhaps via a charge-transfer complex (Isenberg and Szent-Gyorgi, 1958). In this mechanism, oxygen would compete for the energy of the excited riboflavin molecules and decrease the rate of loss of aniline. Previous workers (for example Ishimitsu et al., 1985) have suggested this mechanism for other riboflavin-sensitized photoreactions. Experiments with riboflavin and phenolic compounds are summarized in Table 9. Phenol itself was not susceptible to direct photolysis by wavelengths present in sunlight except at very high pHs (>10) where the phenolate anion, which absorbs solar light more strongly, is present. However, in the presence of riboflavin, phenol was rapidly destroyed (Fig. 23). At pH 5, the photodegradation of phenol involved two different processes. For the first two minutes, riboflavin played the greater role in sensitizing the photolysis of phenol. After three minutes, the rate of photolysis slowed down, and lumichrome, which was efficiently formed at this pH, had the larger role in sensitizing this degradation. At pH 7 in the presence of phenol, riboflavin was destroyed more rapidly than at pH 5. The loss of phenol was accordingly slower at pH 7 during the first two minutes when riboflavin was disappearing. Thus, there are two principal reasons for the slower photolysis of phenol at pH 7. The first was the more rapid destruction of riboflavin; the second is that at pH 7 little or no lumichrome was formed to continue the photolysis (the intermediate product was apparently not an efficient photosensitizer). The disappearance of phenol at pH 5 continued to be rapid as lumichrome became the most abundant flavin.

Chlorophenols, and in particular their anions, absorb solar UV rather strongly and are known to be susceptible to direct photolysis (Hwang et al., 1986). 2,4-Dichlorophenol is a fairly acidic compound (pKa = 7.7) that had under our conditions a direct photolysis half-life of about 25 min in the protonated form (pH 5) and 3 min as an anion (pH 9).
Figure 22 Riboflavin-sensitized aniline photolysis

Figure 23 Riboflavin-sensitized phenol photolysis (pH 7)
Riboflavin increased the rate of photodegradation of 2,4-dichlorophenol to a 7-min $t_{\lambda/2}$ at pH 7. The rate of this photolysis increased with increasing pH. Experiments with 4-chlorophenol and more highly chlorinated phenols at pH 7 showed that the more highly chlorinated phenols were at least as susceptible if not more susceptible to riboflavin-sensitized photodegradation. All chlorinated phenols tested had roughly similar reactivities at pH 7 ($t_{\lambda/2}$, corrected for direct photolysis, was 3-8 min for phenols bearing one, two, three, or five chlorine atoms). The results may reflect more efficient light absorption or energy transfer by the anions of the more acidic, more highly chlorinated isomers. 4-Cyanophenol, a very electron-poor substrate, was somewhat unreactive with riboflavin ($t_{\lambda/2}$ about 150 min) although direct photolysis was still slower. The sensitized rate was many times slower than that of phenol under our conditions. In contrast, $p$-cresol, which has an electron-donating substituent, was much more reactive with riboflavin ($t_{\lambda/2}$ less than 1 min).

In each series of compounds, no simple relationship was apparent between electronic parameters of the substituents and the rates of photoreaction with riboflavin. A working hypothesis for the primary mechanism of photodecomposition of anilines and phenols is: 1) electron transfer from a heteroatom (or an aromatic ring orbital) of the substrate to the flavin (flavin photoreduction), 2) transfer of the electron from the reduced flavin to oxygen, if present, with the restoration of the original flavin and formation of superoxide (Korycka-Dahl and Richardson, 1980), which may take part in subsequent reactions, and 3) reaction of the radical cation of the oxidized substrate with ground-state oxygen or other species to form oxidized products. The mechanism is synopsized in Figure 24, a summary of the competing photoreactions of flavins (F) in the presence of substrates (A) and/or oxygen. In the figure, reaction 1 is the first-order oxygen-independent photolysis of flavins to products P: 2, energy transfer from excited flavin to oxygen with formation of $^{1}\text{O}_2$: 3, electron transfer between flavin and substrate: 4, reversible electron transfer to oxygen with formation of $\text{O}_2^\cdot$; and 5, reactions of substrate radical cation with oxygen or other reactants M to form products.

Other processes (for example, pathways involving $^{1}\text{O}_2$) may be important for some substrates, but did not appear to contribute significantly to the rate of photodecomposition of the compounds we studied.

Use of Riboflavin to Treat Actual Contaminated Waters

To determine whether riboflavin could be successfully used in a treatment process for removal of pollutants from contaminated waters, further experiments will be required in systems more closely resembling actual polluted environments. Also, work on photolysis products will be necessary in order to assess whether more or less hazardous compounds are being produced. Preliminary laboratory tests were made to determine the usefulness of riboflavin sensitized photolysis in the treatment of actual waste samples. Two different samples were investigated. The first was a groundwater that had been contaminated with coal gasification wastes. The second was the effluent from an anaerobic waste treatment column containing various chlorophenols. Detailed chemical characterization of these
Figure 24. Mechanism of Riboflavin Photolysis
wastewaters was not undertaken since the purpose of examining them was in the nature of a screening rather than a full understanding of all the factors affecting the process.

The first sample was obtained from Central Illinois Power Service from the site of a former coal gasification plant at Taylorville, Illinois. GC/MS analysis of this sample showed that the majority of the compounds in it are aromatic compounds (hydrocarbons and a few phenols), and are accordingly electron-rich compounds of the type expected to be treatable by riboflavin. The groundwater was exposed to UV light from the mercury arc lamp both with and without riboflavin present. The results indicated that several classes of compounds were partially removed by light alone, but that riboflavin significantly improved the rates of loss. Results for three major classes of compounds, alkylbenzenes, naphthalenes, and benzothiophenes, are summarized in Figs. 25-27. In these figures, the normalized area (relative to an internal standard) of each compound type was summed and the total areas obtained were plotted.

The second sample was obtained from Professor Makram Suidan of the Environmental Engineering Department of the University of Illinois. The major constituents, as determined by HPLC, were 2-chlorophenol (2.2 X 10^{-4} M), 4-chlorophenol (5.4 X 10^{-4} M), and 2,4-dichlorophenol (9.7 X 10^{-4} M). The pH of this sample was approximately 8.5. Experiments were carried out to determine the rate of direct and riboflavin sensitized photolysis under air saturated conditions and with O_2 removed by bubbling argon through the sample. The results of these experiments are summarized in Table 10. For all three compounds in this sample, riboflavin sensitized air-saturated photolysis proceeded the most rapidly. The results from these experiments conflict with earlier experiments carried out with aniline where O_2 was found to slow down the photolysis.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>direct/air</th>
<th>rf/vn/air</th>
<th>direct/Ar</th>
<th>rf/vn/Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chlorophenol</td>
<td>19.2</td>
<td>7.33</td>
<td>23.7</td>
<td>15.9</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>36.6</td>
<td>13.6</td>
<td>61.0</td>
<td>26.5</td>
</tr>
<tr>
<td>2,4-dichlorophenol</td>
<td>6.67</td>
<td>5.76</td>
<td>8.68</td>
<td>6.66</td>
</tr>
</tbody>
</table>

There are two possible explanations for this. The aromatic ring in aniline is electron-rich whereas the ring in chlorophenols is electron-poor. A second difference is the fact that the chlorophenols are largely anionic at pH 8.5. We have also carried out experiments with this sample using the flow-through reactor shown in Fig. 28. The above mentioned effluent was pumped at a fixed rate (approx. 3 L/day) through the tube and 1.5 X 10^{-4} M solution of riboflavin was pumped in at 0.6 L/min (final concentration of riboflavin 42 \muM). The Pyrex glass tubes of this reactor were placed in close conjunction with two Westinghouse FS-40 sunlamps, which emit light mostly in the medium-range UV region around 300 nm. These lamps were used because of their configuration (they are used in
Figure 26. Riboflavin Effect on Compounds in Taylorville Groundwater – Naphthalenes
Figure 27. Riboflavin Effect on Compounds in Taylorville Groundwater – Benzo[a]thiophenes
10^{-4} M RIBOFLAVIN

.75L/day

EFFLUENT

COLUMN #3
3L/day

Pyrex tubing
exposed to UV
approx. 3.5mm X 4ft
94 mL
0.8 hrs residence time

Figure 28. Flow-through Reactor Design
standard fluorescent lamp fittings) and because they emit very little infrared (heat) and so can be placed in close contact with the flow-through tubing of the reactor. Results of these experiments indicated that even in the absence of sensitizer, 2-and 4-chlorophenol were partly destroyed (37% in the case of 2- and 16% of the 4-isomer over a period of about 3 hr), but that in the presence of riboflavin somewhat more degradation occurred (42% and 21%, respectively). In batch tests using mercury lamps, 2-chlorophenol was much more rapidly degraded in the presence of riboflavin; half-lives were 19 min in the absence and 7.3 min in the presence of riboflavin, respectively. Thus, the flow-through reactor appears inefficient relative to the batch process. The differences may be due to the different spectral characteristics of the lamps used, to intensity disparities, contact times, or other variables.

**Comparative Experiments: Trifluralin (Treflan\textsuperscript{*}) and Parathion**

To test the relative effectiveness of the various potential methods of photochemical treatment on another common environmental contaminant, we measured the rates of loss of the herbicide trifluralin (2,6-dinitro-4-trifluoromethyl-N,N-dipropylaniline). Trifluralin is well known to react rapidly in sunlight to produce a variety of products (Crosby and Leitis, 1973). We anticipated that this compound's substitution pattern would make it highly susceptible to nucleophilic (O\textsuperscript{2-} \cdot) attack. On the other hand, as an aniline derivative, it might also be liable to riboflavin-sensitized energy transfer. Under our conditions, the $t_{1/2}$ for 5 $\mu$M trifluralin without added sensitizer was 14.5 min. Addition of ferrous perchlorate, contrary to expectation, did not significantly decrease the half-life (13.6 min). Ferric perchlorate decreased it to 9.8 min, however, and riboflavin was the best of all sensitizers tested, with a $t_{1/2}$ of 5.1 min.

In a similar experiment, the insecticide parathion (O,O-diethyl-p-nitrophenyl phosphorothioate) was found to be unreactive to UV light alone. Both riboflavin-sensitized and ferrous ion ($\text{Fe(\text{ClO}_4)}_2$) sensitized photolysis also proved to be ineffective against it. It was, however, rapidly photodegraded in the presence of ferric ion ($\text{Fe[ClO}_4]_3^-$; $t_{1/2} = 14.3$ min). The reason for the difference between the ferrous and ferric ion results are not yet fully understood, although the formation of hydroxyl radicals by ferric ion photolysis would certainly account for its loss. Why ferrous ion is capable of producing a species that reacts with nitrobenzene and not parathion will require further study with differently substituted derivatives.
CHAPTER 3
MATERIALS AND METHODS

Atrazine and p-nitroanisole (PNA) were obtained from the U.S. Environmental Protection Agency, Athens, Georgia. d-Mannitol (99+%), anisole (99%) and potassium superoxide were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin). Ferrous sulfate, ferric sulfate, ferric nitrate, and sodium perchlorate (reagent grades) were purchased from Mallinckrodt (Paris, KY). Ferrous and ferric perchlorate (95+%%) were obtained from Alfa Products (Danvers, MA). Ferric citrate (purified), nitrobenzene and hydrogen peroxide were purchased from Fisher Scientific (Fair Lawn, NJ). Superoxide dismutase, catalase, methylene blue and 2-deoxy-D-ribose were obtained from Sigma Chemical Company (St. Louis, MO) and all triazines (except atrazine) were purchased from Supelco, Inc. (Bellefonte, PA). Riboflavin was purchased from Eastman Organic Chemicals (Rochester, NY). Thiobarbituric acid (TBA) was a gift from Elizabeth Jeffery (Institute for Environmental Studies, Urbana, IL). Anilines and phenols were obtained commercially and were used without further purification. Lumichrome was from Sigma (St. Louis, MO). Glass distilled water and HPLC grade acetonitrile (Fisher Scientific) were used as solvents for high-pressure liquid chromatography (HPLC). Glass distilled methylene chloride (Burdick and Jackson, Muskegon, MI) was used for the elutions in product determination studies. Natural water grab samples from the Boneyard Creek (Urbana, IL) were collected in glass beakers, filtered through a glass filter holder using Anspec (Ann Arbor, MI) nylon 66 filter membranes (47 mm, 0.45 μm) and refrigerated prior to use.

Reaction solutions were prepared from more concentrated stock solutions (made up in glass distilled water with minimal amounts of acetonitrile as a co-solvent for the triazine solutions when necessary) in 10 mL pyrex test tubes (10 mm diameter) to give a concentration of 5.2 μM (1.2 mg/L for atrazine). The diluted stock solutions contained either no acetonitrile or amounts that were too low to interfere even with hydroxyl radical reactions. Riboflavin and methylene blue were both added at 5 μM (1.88 mg/L and 1.87 mg/L, respectively); the reaction volume was 4.0 mL. Concentrations of the iron salts in solution ranged from 2.6×10^{-4} M to 4.2×10^{-4} M (1.47 mg/L to 23.4 mg/L Fe); the actual reaction volume in these experiments was 3.8 mL. The molarity of ferric perchlorate (Fe(IO₄)₃·xH₂O) was determined by assuming 20% water by weight. Optical densities of ferric perchlorate solutions in the pH 4 range were within 6% of the literature value (Faus and Hoigné, 1990) at the maximum absorbance of around 310 nm. Indoor kinetic experiments were carried out using a medium-pressure 500-W Pyrex-filtered mercury arc lamp and immersion well (Ace Glass, Vineland, NJ). The Pyrex filter serves to filter out wavelengths below 290 nm so that the lamp more closely simulates sunlight. A "merry-go-round" reactor (Ace Glass) was used to obtain uniform exposure of the samples to the lamp. Previous experiments indicated that indoor photolysis half-lives were approximately half as long as outdoor photolysis half-lives; thus, the lamp system intensity was approximately twice that of sunlight. p-Nitroanisole (PNA) was used as the actinometer system (Dulin and Mill, 1982) in order to compensate for changes in the intensity of the light source. The PNA samples were exposed in exactly the same manner as the other reaction solutions. Dark control experiments were conducted to test for any degradation
which may proceed in the absence of light. No significant changes in the triazine concentrations were observed for any dark experiments.

The rate of disappearance of the triazines was determined by removing aliquots periodically and analyzing the concentration by HPLC. A variable wavelength absorbance detector (ABI Analytical Kratos Division, Ramsey, NJ) and a Waters pump (Milford, MA) or a Beckman pump (San Ramon, CA) made up the HPLC system with a 250 x 4.1 mm i.d. reverse phase column packed with PRP 1 resin, 12-30 µm (Hamilton, Las Vegas, NV) was used. The detector wavelength was adjusted to the wavelength of maximum absorbance (approximately 223 nm) of the triazine. Triazine samples were injected with an external standard (added after the reaction was completed): 2,6-diethylaniline (5x10⁻⁵ M) for atrazine, ametryn and prometon; p-toluidine (1x10⁻⁵ M) for prometryn. The external standard was used in order to normalize the peak heights, as they may vary with changes in temperature, solvent composition, etc. The peaks were normalized by determining the ratio of the triazine peak height to the external standard peak height.

In order to determine the pseudo-first order rate constant for the degradation of the triazines (k), the logarithm of the ratio of the initial concentration to the concentration at a given time was plotted versus time. The slope of the line obtained gave the value of k. The rate constant for PNA was determined in the same manner, except no external standard was used. The respective half-lives could then be determined by the following equation:

\[ t_{\frac{1}{2}} = \ln 2 \frac{k}{k} \]

An average value for the PNA half-life \( t_{\frac{1}{2},\text{PNA(ave)}} \) was calculated from the data of all actinometer experiments. From this, a "normalized" half-life \( t'_{\frac{1}{2}} \) for the triazine reactions was calculated by the following equation:

\[ t'_{\frac{1}{2}} = \frac{t_{\frac{1}{2},\text{triadine}} \cdot t_{\frac{1}{2},\text{PNA(ave)}}}{t_{\frac{1}{2},\text{PNA}}} \]

In this equation, \( t_{\frac{1}{2},\text{PNA(ave)}} \) is 145.8 min and \( t_{\frac{1}{2},\text{PNA}} \) was the half-life for a particular experiment. All half-lives in this paper are given as the normalized half-lives.

For experiments with anisole and nitrobenzene, both reagents were made up in glass distilled water to 1x10⁻⁵ M. Reaction solutions were prepared and run in the lamp as described. The rate of disappearance of anisole and nitrobenzene was determined by removing aliquots periodically, as with the triazines, and analyzing them by HPLC. The detector wavelength was set at 220 nm for anisole and at 267 nm for nitrobenzene. Half-lives and rate constants were determined as described.

To determine the products of the atrazine/ferric perchlorate reaction, a larger reaction volume and higher atrazine concentration was necessary due to the lower sensitivity of the GC/MS as compared to HPLC. Atrazine was made up to a final concentration of 1x10⁻⁴ M in glass distilled water (no co-solvent used) in a 1 L flask. Ferric perchlorate was
added to give a final concentration of 0.26 mM, as before. The reaction was carried out in a 1 L glass reaction vessel (Ace Glass) into which a medium-pressure, Pyrex-filtered mercury arc lamp fit. This vessel was used for preparative purposes and no comparisons between the rates of reaction in this vessel (vs. the earlier test tube experiments) could be made, but HPLC analyses showed no new types of products formed. (Samples were taken and analyzed by HPLC at 10 min intervals in order to follow the extent of degradation.) After 60 min, the lamp was turned off and removed from the reactor; the reaction solution temperature was 28°C. A column of precleaned Amberlite XAD-2 resin (Sigma Chemical Co.) was packed in a buret (2 cm diameter) and rinsed with about 1 L of glass distilled water to remove traces of methanol, in which the resin had been stored. The reaction solution was then applied to the column and the eluent discarded. To elute the products, 100 mL of methylene chloride was run through the resin. Magnesium sulfate was added to the eluent to remove any water. The sample was concentrated to about 0.5 mL using a Kuderna-Danish apparatus. Finally, anthracene (4 x 10^{-4} M) was added as an external standard before the sample was analyzed by gas chromatography/mass spectroscopy (GC/MS).

A 5985A Hewlett-Packard GC/MS with a DB-1 capillary column, 30 m x 0.31 mm i.d. (J. and W. Scientific, Placerville, CA), was used for product analysis. The film thickness was 0.25 μm. The temperature program used was as follows: hold at 60°C for 10 min, 60 to 280°C @ 5°C per min.

The Fenton reaction was run with the concentrations of hydrogen peroxide (5x10^{-4} M) and ferrous ion (3.5x10^{-4} M) about five times that of atrazine (7x10^{-5} M). The iron was added as the solid, all at once, to the 1 L solution of atrazine and H_2O_2, while stirring. The reaction was allowed to continue for 15 minutes and then was adjusted to about pH 6 with 1M NaOH in order to precipitate the iron. After filtering the reaction mixture through a Büchner funnel, it was applied to a column of Amberlite XAD-2 resin (Sigma Chemical Co.), and worked up by the procedure described above. Anthracene (4x10^{-4} M) was used as an external standard and the sample was analyzed by GC/MS as described.

The deoxyribose experiments were conducted as described in Halliwell and Gutteridge (1981). Deoxyribose is attacked by OH· to form a product that can be measured spectroscopically. To test whether hydroxyl radicals were being produced in our experiments, only ascorbate, deoxyribose and iron salt were added for a total volume of 1.1 mL. The reaction was run in 10 mL test tubes in the mercury arc lamp (35°C) for one hour. The test tubes were then removed and 1 mL 1% (w/v) thiobarbituric acid and 1 mL 2.8% (v/v) hydrochloric acid were added to each sample. Following these additions, the test tubes were heated to 100°C in a boiling water bath for 15 min. After cooling the samples to near room temperature, the absorbance at 532 nm was measured on a Perkin-Elmer 522A UV-Vis Spectrophotometer (Oak Brook, IL). A yellow color (low absorbance) indicated that OH· was not involved in the reaction, while a pink color (high absorbance) indicated that hydroxyl radicals had attacked and converted the deoxyribose.

The disappearance of the anilines, phenols, and riboflavin and the appearance of product peaks, if any, were followed by reverse phase high-pressure liquid
chromatography (HPLC) using a Hamilton PRP-1 column and a Kratos Spectroflow 757 variable wavelength absorbance detector. Aliquots of 200μl were injected, and mixtures of acetonitrile and water were used as mobile phases. Concentrations of both sensitizer and substrate were usually 5μM. Reactions were carried out in 1 x 20 cm (10-ml) Kimax screw-capped tubes; the light source was a Pyrex-filtered, water-cooled 200 W medium pressure mercury arc lamp (merry-go-round photoreactor, Ace Glass). The principal lines emitted by this lamp which are also present in solar UV radiation are the 313-nm and 365-nm lines. The tubes were 5 cm from the lamp and the temperatures of the reaction mixtures remained constant throughout the course of the reactions. The rate constants of all reactions were normalized to that of a standard reaction, the photodecomposition of valerophenone (Zepp et al., 1985). This first-order reaction had under our conditions a rate constant (kiloc) of 0.058/min, and thus a half-life of about 12 minutes. (In general, midday summer sunlight photolysis rate constants at our latitude were approximately one-half of those determined under these conditions.) Photolysis rates for flavin-sensitized reactions, which were not kinetically simple, were calculated by the method described in the appendix. The quantity t1/2 was defined as the time required for the concentration of a substrate to decrease to one-half of its initial concentration as calculated using this procedure.

Experiments at pH 7 were carried out in 0.02M phosphate buffer; at pH 5, in 0.02 M acetate buffer; and at pH 9, in 0.02 M borate buffer. Changes in oxygen concentration were not monitored.
CONCLUSIONS

Exposure of contaminated water samples to light in the presence of a sunlight-absorbing photosensitizer, either riboflavin or an iron salt, may lead to photochemical reactions that can aid in the removal of certain organic pollutants from these waters. In this study, we performed kinetic experiments in buffered, riboflavin-containing aqueous solutions with anilines and phenols whose structures are closely related to some herbicides commonly found in groundwater and other contaminated waters. Neither phenol nor aniline are very susceptible to direct photodestruction by light alone, but both were much more rapidly destroyed in the presence of riboflavin and sunlight or Pyrex-filtered mercury arc light. For example, in our arc lamp setup aniline had a half-life of 15 hr by light alone and 1.8 min in the presence of 20 µM riboflavin. We also carried out experiments with phenols and anilines bearing electron-withdrawing or electron-donating substituents; most of these experiments have suggested that riboflavin reacts faster with more electron-rich compounds, but there were some indications of other types of mechanisms for some compounds. The sensitized photolysis rates increased in the absence of oxygen, suggesting a mechanism involving direct energy or electron transfer between flavin excited states and acceptor molecules. A preliminary kinetic model was developed to calculate loss rates. Riboflavin itself was rapidly converted in aqueous solution by Pyrex-filtered mercury arc light to products which had variable efficiencies as sensitizers. We suggest that riboflavin forms charge-transfer complexes with these compounds that undergo electron transfer; subsequent reactions, still not well understood but probably not requiring oxygen, led to the disappearance of the substrates from solution.

Iron salt-promoted photochemical reactions follow a different mechanistic pathway. When iron was added to atrazine solutions, in the form of ferrous (Fe^{2+}) or ferric (Fe^{3+}) salts, the rate of atrazine degradation was greatly increased, with or without added riboflavin. Furthermore, the aqueous photodegradation rates of the triazines ametryn, prometon and prometryn were also greatly enhanced by the addition of ferrous and ferric iron. While ferric ion was more effective than ferrous ion, both increased the degradation rate significantly. The photodegradation rate was increased by using higher added iron concentrations and was diminished when natural water versus distilled water was used, indicating that the dissolved constituents found in natural waters have a retarding effect on the photodegradation. Photodegradation products of the atrazine/iron system were the same as those for a Fenton reaction (known HO· producer), suggesting that HO· may be the active reactant. In the absence of oxygen, the reaction is also slowed, indicating a dependence on oxygen.

In preliminary experiments in which both riboflavin and iron methods were applied, the photodecomposition of the herbicide trifluralin was accelerated significantly by riboflavin, to a minor extent by ferric ion, and hardly at all by ferrous ion. The insecticide parathion, in contrast, was readily photodegraded by ferric ion and not at all by ferrous iron or riboflavin.
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APPENDIX

Modeling of Riboflavin-sensitized Reactions
The kinetics of riboflavin sensitized photolysis are complicated by the fact that riboflavin is photodecomposed by ultraviolet light. This destruction can also result, under some conditions, in the formation of lumichrome which is also an efficient photosensitizer. A brief summary of the equations describing this photolysis follows.

The first order rate equation for the sensitized photolysis of a substrate A is

\[-d[A]/dt = k [A]\]

in which \( k \) contains terms for sensitizer light absorption, triplet quantum yield, and quantum yield of singlet oxygen formation or electron transfer.

However, this equation assumes that the concentration of the sensitizer (S) remains constant. If this is not the case, the equation must include [S]:

\[-d[A]/dt = k_1 [S][A] \quad \text{(Equation 1)}\]

(In order for this equation to be correct, [S] must be low enough so that the light intensity is not affected.) In the case of riboflavin:

\[-d[R]/dt = k_2 [R]
\]

\[ [R] = [R_0]e^{-k_2t} \]

where \( R_0 \) is the initial concentration of riboflavin. (Under our conditions, using the mercury lamp, \( k_2 = 0.56/\text{min at pH} 7 \) and 0.29/min at pH 5.)

This changes equation 1 to

\[-d[A]/dt = k_1 [A][R_0]e^{-k_2t} \quad \text{(Equation 2)}\]

This, however, is still incomplete since riboflavin may degrade to lumichrome which is also a good photosensitizer. The contribution of lumichrome to the photolysis of A is

\[-d[A]/dt = k_3 [L][A]
\]

\[ [L] = X([R_0] - [R]) \]

where \( X \) equals the ratio of lumichrome formed to riboflavin destroyed. At pH 5 under our conditions, \( k_3 = 0.21/\text{min} \) and the ratio of the lumichrome formed to riboflavin destroyed was 0.35. Lumichrome was not formed during the duration of our experiments at pH 7, so both \( k_3 \) and \( X \) were set to zero for calculations at this pH. Adding this term to
equation 2 gives

\[-d[A]/dt = k_1 [A][R_0]e^{k_2 t} + k_3 [A]X[R_0](1 - e^{-k_2 t})\]

The contribution of direct photolysis is

\[-d[A]/dt = k_4 [A]\]

Adding this to the above yields the following differential equation to describe riboflavin-sensitized photolysis

\[-d[A]/dt = k_1 [A][R_0]e^{k_2 t} + k_3 [A]X[R_0](1 - e^{-k_2 t}) + k_4 [A]\]

Solving this equation yields

\[\ln([A_0]/[A]) = (k_1 R_0/k_2)(1-e^{-k_2 t})+(Xk_3 R_0t)+(Xk_3 R_0/k_2)(e^{-k_2 t}-1)+k_4 t\]

The equation can be rearranged to solve for \(k_1\):

\[\ln([A_0]/[A])+(Xk_3 R_0 t)+(Xk_3 R_0/k_2)(e^{-k_2 t}-1)+k_4 t = (k_1 R_0/k_2)(1-e^{-k_2 t})\]

This equation is of the form \(y = mx + b\) where

\[y = \ln([A_0]/[A])+(Xk_3 R_0 t)+(Xk_3 R_0/k_2)(e^{-k_2 t}-1)+k_4 t\]
\[m = -(k_1 R_0/k_2)\]
\[b = (k_1 R_0/k_2)\]
\[x = e^{-k_2 t}\]

Therefore, a plot of \(y\) versus \(x\) will have a slope of \(-(k_1 R_0/k_2)\). Since all of the constants in these equations can be determined from other experiments (\(k_2\) from the direct photolysis of riboflavin, \(k_3\) and \(X\) from lumichrome sensitized photolysis of the acceptor, and \(k_4\) from direct photolysis of the acceptor), \(k_1\) can be determined from this slope.

An example of the fit of this description to experimental data is shown in Fig. 23, where the solid line represents the calculated loss of phenol and the points are the measured data.