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THE PHOTOLYSIS OF p-XYLENE IN AN AQUEOUS ENVIRONMENT

BY

JOSEPH DANIEL LINTOTT

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

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1973

ABSTRACT

The photolysis of p-xylene in several aqueous solutions was studied as a model for removing refractory organic pollutants from water, and to demonstrate that photochemical reaction of these compounds may be an important factor in their degradation in the environment.

Solutions of p-xylene in deaerated water, water saturated with oxygen, 0.05M sodium phosphate tribasic, 0.1M sodium nitrate and 3.28×10^{-4}M ferric sulfate were exposed to ultraviolet and visible radiation. p-Xylene in 3.28×10^{-4}M ferric sulfate was also exposed to sunlight. The reaction rate was determined by measuring the disappearance of the p-xylene.

In all of the photolyses, except in the sodium nitrate solution, the major product was insoluable in water. The presence of oxygen and ferric sulfate increased the reaction rate while the sodium phosphate and sodium nitrate were found to slow down the reaction rate. p-Xylene, which does not absorb radiation above 280 mμ was found to undergo reaction when exposed to light of wavelengths greater than 280 mμ when sodium nitrate or ferric sulfate was present. p-Xylene in ferric sulfate solution was found to undergo

reaction when exposed to sunlight passing through ordinary window glass.

APPROVAL OF THESIS

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BY

JOSEPH DANIEL LINTOTT

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

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INTRODUCTION

I. Trace Organics in Water

Water is considered to be polluted when it contains substances which make it unsuitable for its intended use. The extent to which a compound will pollute water depends upon its chemico-physical nature and its concentration in the body of receiving water. Many pollutants are readily degraded by chemical, biological and physical processes. Conventional waste treatment processes are usually satisfactory in reducing the concentration of these pollutants to acceptable levels. However some pollutants are very resistant to degradation by conventional methods. Therefore, these so-called refractory pollutants pose a threat to the environment even when they are discharged in small amounts because they will accumulate in the environment.

Compounds which have a low solubility in water are often removed from waste streams by use of phase separators. This removes most of the pollutants but small quantities (in the ppm range) often remain dissolved in the water and are discharged into the environment. When these compounds are refractory they can cause a pollution problem.

Many pollutants undergo chemical reactions after they are introduced into the environment. These reactions may lead to intermediates and products which are more toxic than the original compound. The presence of other compounds in the aquatic environment complicates the problem of predicting which reactions will occur. An understanding of these environmental complexities may not result in a numerical formulation for determining the possible fates, but it can provide important background material for decision making and should lead to a better evaluation of the hazard associated with a given substance (7).

Since most bodies of water are exposed to sunlight, photochemical processes may play an important part in the decomposition of refractory organic compounds in the environment. The products of the photochemical reactions may be more easily metabolized by microorganisms. Photochemical treatment of waste streams could provide an effective method of removing photochemically reactive refractory organics from water before it is discharged into the environment.

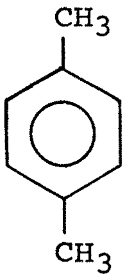
This research was directed towards the study of the photochemical reactions of a selected hazardous poluting substance (HPS) in an aqueous environment (8). In this study p-xylene was selected as a model organic pollutant since it is classified as being a HPS (7).

Xylenes are listed as being among the fifty chemicals which are produced in the largest amounts in the United States (10). p-Xylene is the primary raw material for the production of dimethyl terephthalate and terephthalic acid which are used in the manufacture of polyester fibers (40).

p-Xylene can be oxidized by microorganisms which have been acclimated to aniline (27), but its biochemical oxygen demand (BOD) in normal sewage is 0.0 (17). Thus p-xylene can be considered as being a refractory organic pollutant. Some physical and biological properties of p-xylene are given in Table 1.

Table 1.

Physical and Biological Properties of *p*-Xylene

Property	Value	Reference
Structure		24
Formula	$C_6H_4(CH_3)_2$	24
Formula weight	106.16	24
Melting point	13.3°C	24
Boiling point	138.4°C	24
Refractive index (n_D)	1.4958 @ 20°C	24
Specific gravity	0.861 $\frac{20^\circ C}{4}$	24
Solubility in water	198 $^{mg}/_{l}$ @ 25°C	39
BOD_5 (sewage seed)	0.0	17
Toxicity to sunfish	lethal in 1 hour (47-48 $^{mg}/l$)	36

II. Photochemistry

Photochemistry deals with the interaction between matter and light in the 200-800 mμ region of the electromagnetic spectrum. The energy of a photon, E_p, is related to its wavelength, λ, in the following manner:

$$E_p = hc/\lambda$$

where h is Planck's constant (6.6×10^{-27} erg-sec) and c is the velocity of the radiation. Ultraviolet radiation (200-400 mμ) corresponds to an energy of 143-72 kcal/mole.

Quantum theory states that a molecule can only increase its energy in discrete amounts. A molecule in its ground state may absorb a photon only if the energy difference between the ground state and an excited state is equal to the energy of the photon.

Absorption of ultraviolet radiation leads to electronic excitation of a molecule in which an electron in a bonding molecular orbital is promoted to an anti-bonding molecular orbital. If the spin of the electron is unchanged the excited state is a singlet state (S) and if the spin is reversed it is called a triplet state (T). These excited electronic states are shown in Figure 1.

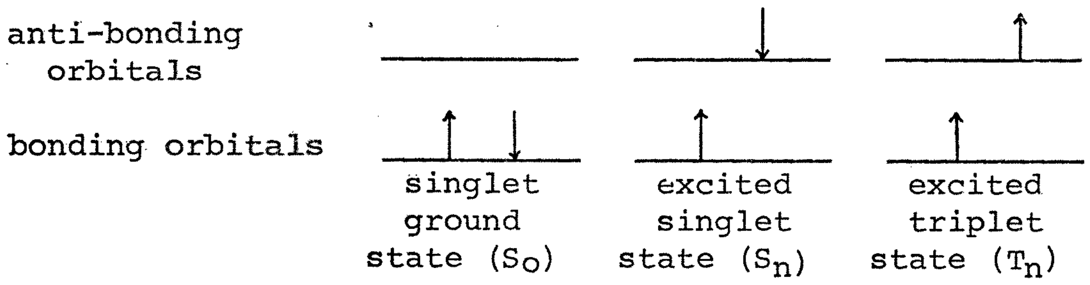


Figure 1. Singlet and Triplet Excited Electronic States

Transitions in which the spin of the electron is reversed are spin-forbidden processes, yet it is the singlet ⟶ triplet transition which makes the triplet state an important intermediate in photochemistry.

Usually electrons in upper excited states will rapidly dissipate their excess vibrational energy by radiationless processes until they reach the low-lying singlet or triplet states (S_1 and T_1). A molecule in the low-lying singlet state will be deactivated by one of the following processes:

(1) - fluoresence - emission of a photon during transition from S_1 to S_2,

(2) - chemical reaction,

(3) - radiationless decay - transfer of thermal energy to the surroundings,

(4) - intersystem crossing - transfer from S_1 to T_1 by spin inversion.

A molecule in the low-lying triplet state will undergo deactivation by one of the following paths:

(1) - phosphorescence - emission of a photon during transition from T_1 to S_o,

(2) - chemical reaction,

(3) - radiationless decay - transfer of thermal energy to the surroundings.

These events are shown in Figure 2.

A useful parameter for measuring the rate of a photochemical process is the quantum yield. The quantum yield, ϕ, is defined as the number of molecules following a certain process, divided by the number of photons absorbed by the system. The sum of all of the primary quantum yields is unity.

A more indepth discussion of photochemical processes can be found in the books by Depuy and Chapman (9), and Turro (41), and in the articles by Noyes and Burton (31), and Owen (33).

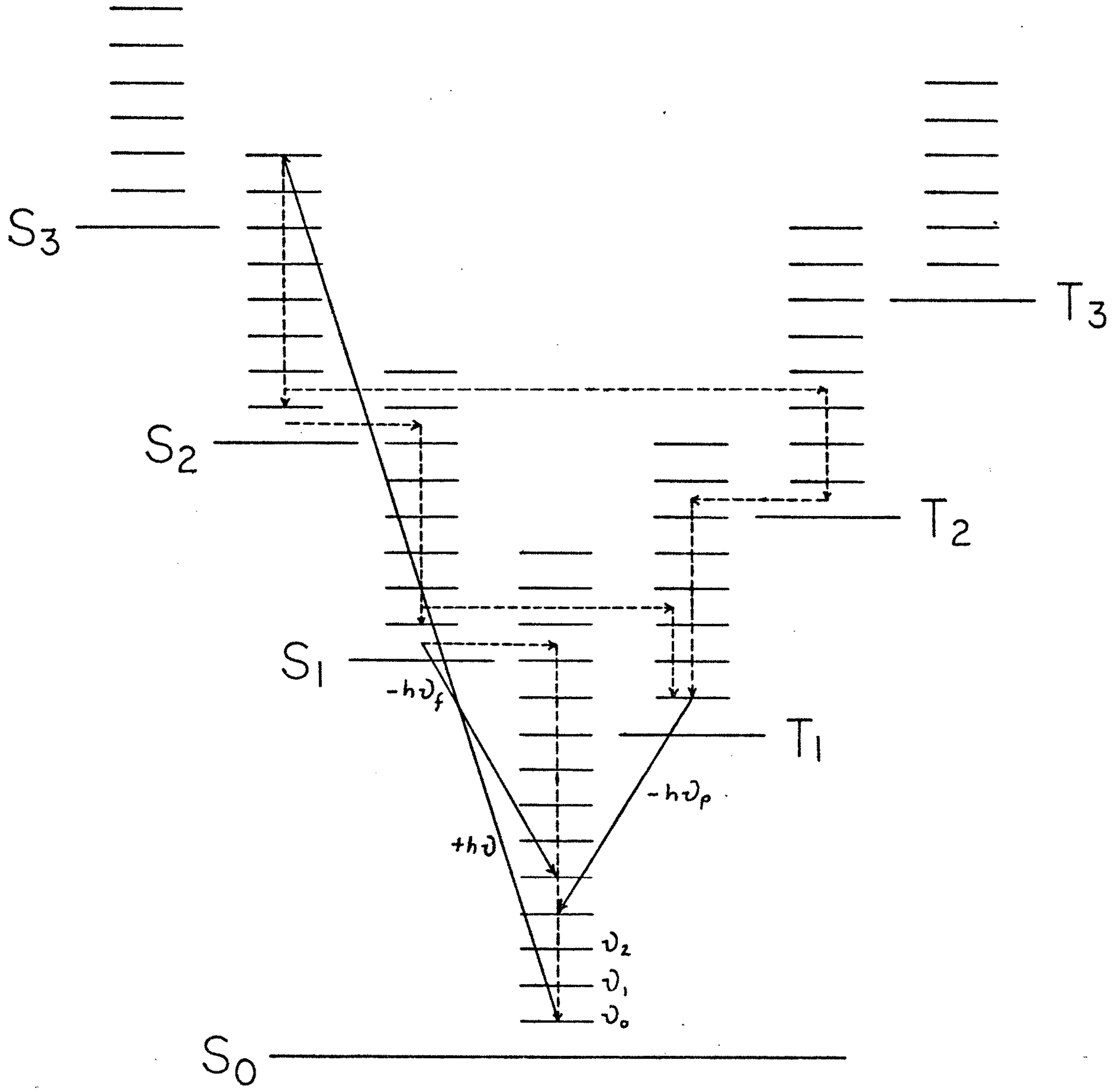
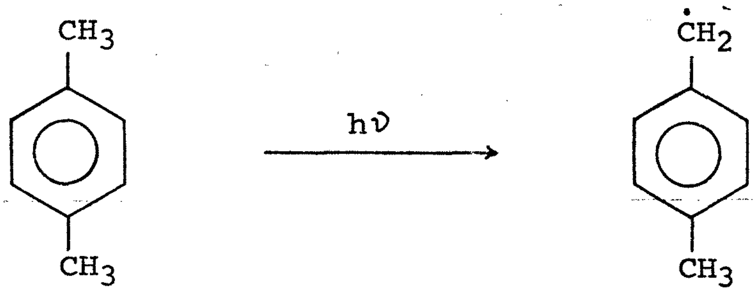


Figure 2. Jablonski Diagram

III. Literature Survey

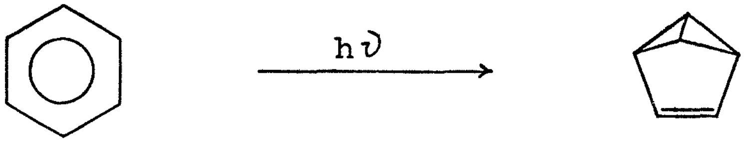
1. The photochemistry of alkyl benzenes. Braun, Kato and Lipsky (3) studied the efficiency of the internal conversion (radiationless decay) from the upper electronic states to the first excited singlet state in some alkyl benzenes. They found that alkyl benzenes excited in their second and third absorption bands are capable of deactivation by processes other than internal conversion to the first excited singlet state, especially in the vapor phase. In the condensed phase internal conversion becomes a more competitative process to deplete the upper states. Increasing methyl substitution, and dilution of the pure aromatic with cyclohexane seems to further enhance the internal conversion efficiency to the first excited singlet state.

Porter and Wright (34) reported the formation of free radicals from the vapor phase photolysis of aromatic molecules. p-Xylene was found to form a p-methylbenzyl radical.

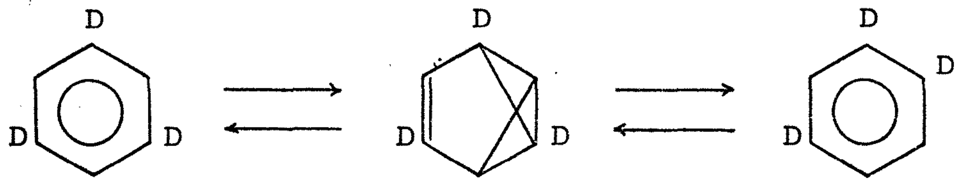


Johnson and Rice (18) showed that the dissociation of a methyl hydrogen atom from a methylbenzene by light is an intramolecular process. They found that irradiation of p-xylene in a solid argon matrix with 275 mμ light produced the known radical emission.

Kaplan, Wilzbach, Brown and Yang (21) suggested the formation of benzvalene as an intermediate during the vapor phase photolysis of alkyl benzenes. Wilzbach, Ritscher and Kaplan (45) reported that benzvalene is formed by the photolysis of benzene in the liquid phase at 2537 Å.

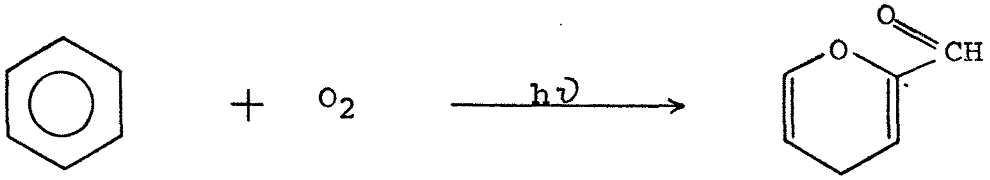


The photochemical rearrangement of benzene-1,3,5-d_3^1 in both the vapor phase and in solutions of hexadecane has been investigated by Wilzbach, Harkness and Kaplan (43). The rearrangement seems to occur through a benzvalene intermediate. Photolysis was carried out with light in the region

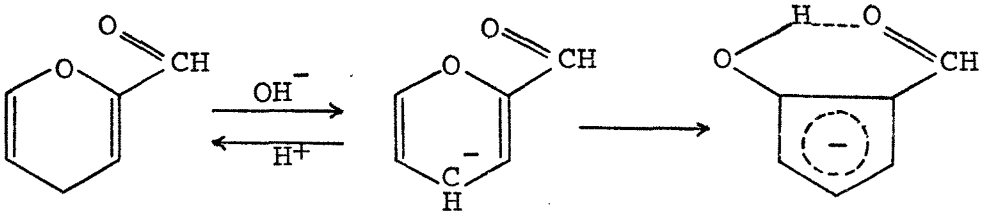


of 2500 Å.

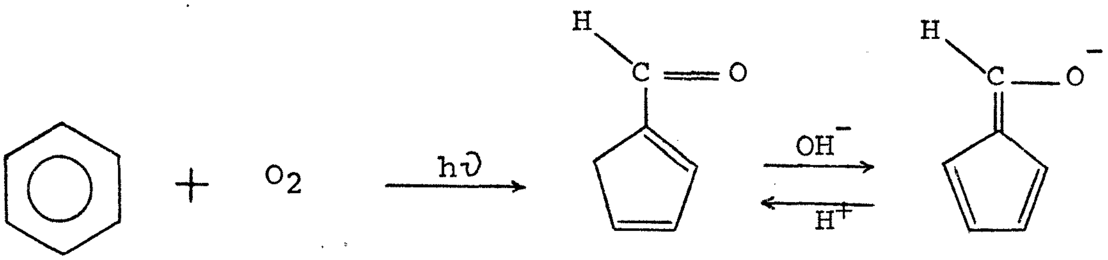
Farenhorst (11) investigated the photooxidation of benzene in aerated water and tentatively proposed that the product was 4H-pyran-2-carboxaldehyde.



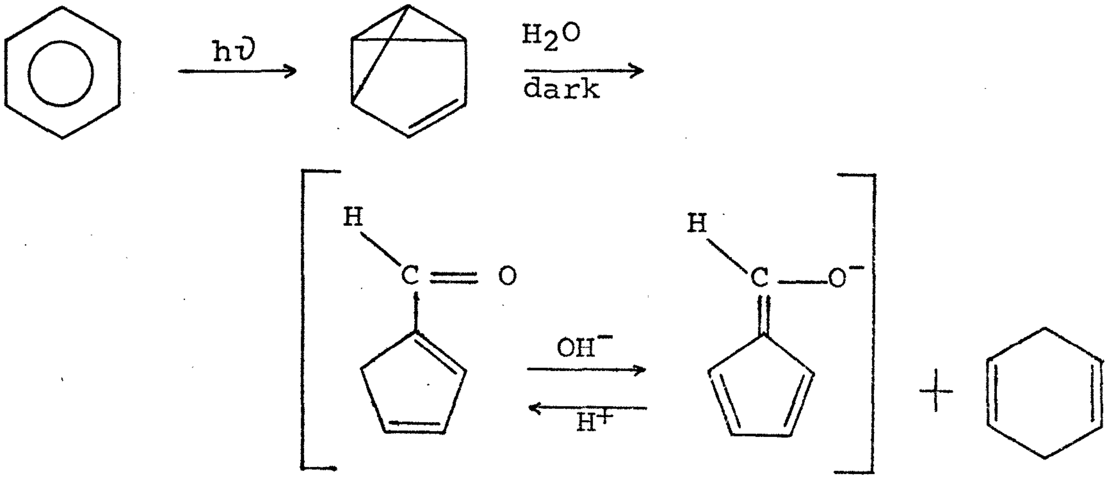
This was confirmed to be the only major photoproduct in neutral aqueous solutions of benzene in the presence of oxygen by Luria and Stein (25,26). They irradiated the solution with 2537 Å light. Luria and Stein also proposed that the product is stabalized further by the formation of the cyclopentadienyl anion.



Kaplan, Wendling and Wilzbach (19) reported that irradiation of benzene at 2537 Å in aerated water at pH 4-8 yielded 1,3-cyclopentadiene-1-carboxaldehyde. They also reported (20) that the formation of the cyclopentadienecarbox-



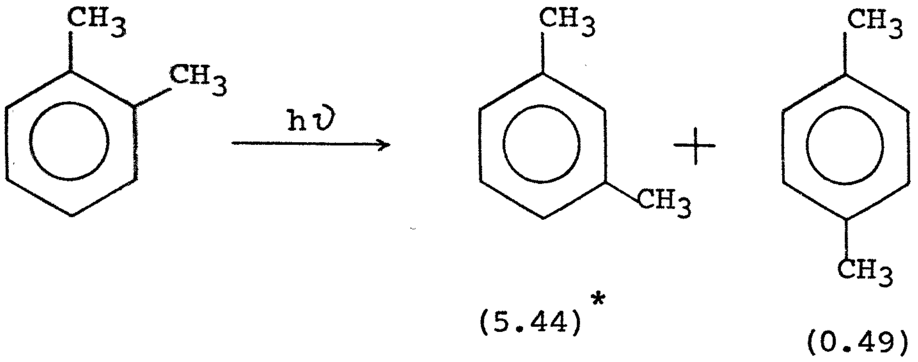
aldehyde does not require dissolved oxygen to be present. The product is formed from the reaction of benzvalene with water. In deaerated water one molecule of benzvalene is oxidized to the aldehyde while a second is reduced to 1,4-cyclohexadiene.

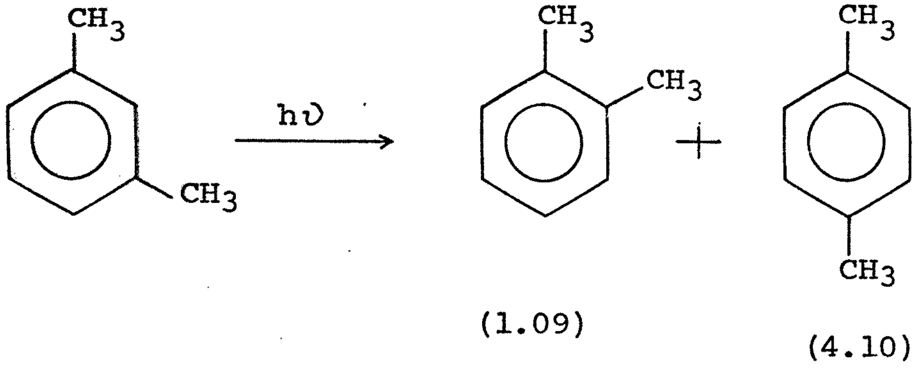


In aerated water a peroxide is formed instead of the 1,4-cyclohexadiene.

Wilzbach and Kaplan (44) have investigated the photoisomerization of dialkylbenzenes in the vapor phase at 2500 Å.

Ortho and meta xylene were found to isomerize as follows:





Several other volatile products were detected but the major product seemed to be polymer. Anderson (1) studied the photoisomerization of the xylenes in solutions of n-hexane, EPA (a 5:5:2 mixture of diethyl ether, isopentane and ethanol) and perfluorohexane at 248 and 275 mμ and found that isomerization accounts for only a fraction of the parent compound lost, polymer probably being the major product.

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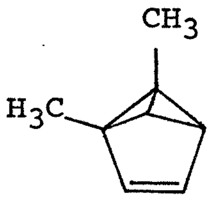
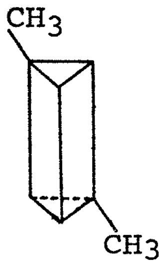
*yields in mole percent

Noyes and Harter (32) report that *p*-xylene has been found to isomerize to *m*-xylene when exposed to 240 - 274 mµ light in the vapor phase but the quantum yield is extremely low. *p*-Xylene seems to have a considerably greater photochemical stability than the other xylenes.

Noyes and Harter also report that the predominant intermediates for isomerization of the xylenes are almost certainly dimethyl benzvalenes and perhaps dimethyl prismanes. The quantum yields for isomerization of the three xylenes are much smaller than the quantum yields for the formation of the intermediates. Thus the intermediates must deactivate by a variety of processes.



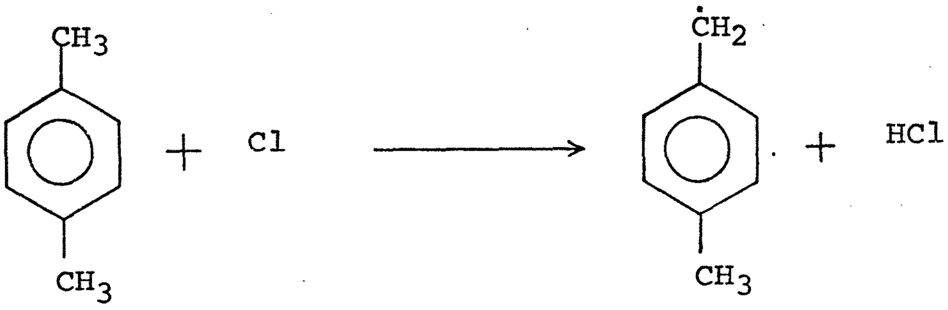
DIMETHYL BENZVALENE



DIMETHYL PRISMANE

Kryukov and Opanasenko (23) investigated the role of iron(III) chloride in the photochemical oxidation of *p*-xylene in acetic acid. The solution was exposed to light of wavelengths exceeding 300 mμ. They reported that in the absence of oxygen *p*-methylbenzyl radicals are obtained from *p*-xylene by the abstraction of a hydrogen atoms from the methyl groups by chlorine atoms formed by the photoreduction of the iron(III) chloride.

$$Fe^{3+}Cl^{-} \xrightarrow{h\nu} \left[Fe^{2+}\ Cl\right] \longrightarrow Fe^{2+} + Cl$$



The *p*-methylbenzyl radicals then react with iron(III) chloride to form a chloro-derivative of *p*-xylene.

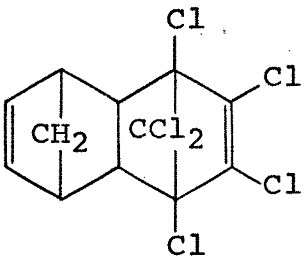
2. Photochemical Treatment. Matsuura and Smith (30) studied the pholodecomposition kinetics of formic acid in an aqueous solution at 25-60° C as a model reaction for removing organic pollutants from water. The products of the photolysis, were carbon dioxide, carbon monoxide, hydrogen and water. They found that the reaction rate was first order in absorbed light intensity and between zero and first order in formic acid. These results show that both chain and nonchain kinetics occur simultaneously. They also found that ferric and ferrous ions act as oxidation-reduction catalysts in the presence of ultraviolet light. Addition of these sensitizers to the solution increased the rate of decomposition by 20 to 60 times.

Schorr, Boval, Hancil and Smith (37,38) studied the photooxidation kinetics of organic pollutants in municipal waste water. They found that the removal of the pollutants does not appear to be hindered by the production of refractory intermediates. The reaction rate was found to be first order in the amount of radiation absorbed, directly proportional to the oxygen concentration when the oxygen concentration is low and independant of the oxygen concentration when the oxygen concentration is high.

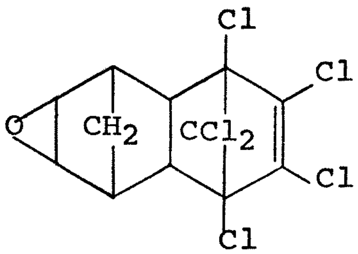
Hancil and Smith (13) studied the chlorine-sensitized photochemical oxidation of soluble organics in municipal waste water. They found that the addition of chlorine can increase the rate of decomposition of the pollutants by more than 20 times the unsensitized rate. The rate of decomposition of the pollutants was found to be directly proportional to the chlorine concentration when the chlorine concentration is less than $1.5^{mg}/l$, and independant of the chlorine concentration when the chlorine concentration is greater. The rate of removal of free chlorine was directly proportional to the light absorbed by the chlorine and independant of the pollutants present. The contribution of the chlorine was not affected by oxygen as long as the concentration of the oxygen was greater than 10% of the concentration corresponding to saturation of the reaction solution with air.

Ligninsulfonates are biologically recalcitrant pollutants which are produced in the manufacturing of paper. The chemical nature of lignin has not been definitely established but the basic building block is felt to be a phenyl propane unit, with hydroxyl and methoxyl aromatic functions, and connected by ether and carbon-carbon bonds. Klein (22) studied the effect of exposing ligninsulfonates to ultraviolet light. He found that after photolysis, the ligninsulfonates were more easily metabolized by microorganisms. The effective wavelength range for modifying the ligninsulfonates was below 210 mu. He also found that it was necessary for a free radical acceptor such as oxygen to be present for degradation of the lignin materials to occur.

Bulla and Edgerley (4) studied the photolysis of the chlorinated hydrocarbon pesticides aldrin, dieldrin and endrin which is the endo-endo isomer of dieldrin.



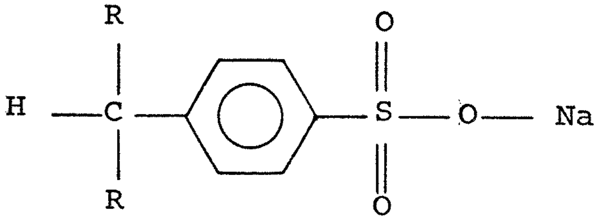
ALDRIN



DIELDRIN

They reported that exposure of aqueous solutions of aldrin to 253.7 mμ light decreased their toxicity. The reaction rate was found to be independant of temperature in the 20-40°C range. They also report that the rate of degradation was directly proportional to the concentration of the unreacted pesticide.

Matsuura and Smith (28,29) studied the kinetics of the photodecomposition of a linear alkyl benzene sulfonate (LAS).



LINEAR ALKYL BENZENE SULFONATE

They irradiated aqueous solutions of dodecyl benzene sulfonate (DBS) with light in the 200-450 mμ range. They report that the activated DBS molecules undergo a second-order deactivation which leads to a rate equation one-half order in light intensity and DBS concentration.

$$\mathrm{DBS} \xrightarrow{h\nu} \mathrm{DBS}^*$$

$$2\ \mathrm{DBS}^* \xrightarrow{\text{fast}} 2\ \mathrm{DBS}$$

$$\mathrm{DBS}^* \xrightarrow{\text{slow}} \text{decomposition products}$$

They also studied the effect of adding ferric ions to the reaction solution. The reaction rate was greater than first order in light intensity, but first order in ferric ion concentration. The reaction probably involves hydrogen abstraction by hydroxyl radicals produced by the photolysis of the ferric ion.

$$\mathrm{Fe}^{3+}(\mathrm{OH}^-) \xrightarrow{h\nu} \mathrm{Fe}^{2+}(\mathrm{OH}\cdot) \longrightarrow \mathrm{Fe}^{2+} + \mathrm{OH}\cdot$$

$$\mathrm{OH}\cdot + \mathrm{DBS} \longrightarrow \mathrm{H_2O} + \begin{array}{c}\text{free}\\ \text{radical}\end{array} \longrightarrow \begin{array}{c}\text{decomposition}\\ \text{products}\end{array}$$

The sensitizer increased the reaction rate by two orders of magnitude. The final oxidation product, carbon dioxide, fromed more slowly than the DBS disappeared suggesting the formation of intermediates. Analysis of the products indicated that the aromatic ring structure was destroyed.

IV. Kinetics

The first step in any photochemical reaction is the excitation of a molecule by the absorption of light. The molecule may then be deactivated by several processes. All of the primary photo-chemical processes must be known before a rate equation can be derived from theory. When the reaction mechanism is unknown an empirical equation is used in the formulation of a rate equation.

A complication in kinetic studies of photochemical reactions is that except for certain special cases (5), the reaction rate is not homogeneous over the volume of the reactor. This is caused by the variation of the light intensity in the reactor.

In the system which was studied the intensity and wavelength of the light, the temperature, and the pressure were conatant during the irradiation period. For this reason the measured reaction rate was assumed to be a function of reactant concentration only. The following equation was used:

$$-{}^{dC}/_{dt} = kC^{a}$$

where k and a are constants, and C is the reactant concentration. When a = 1 the equation can be integrated to give:

$$- \ln (C/C_o) = kt$$

where C_o is the reactant concentration at t=0, and k is the rate constant.

EXPERIMENTAL

I. Reagents

Eastman Kodak reagent grade *p*-xylene was used without further purfication.

The sodium nitrate, ferric sulfate, sulfuric acid and sodium phosphate tribasic were 'Baker Analyzed' reagents and were used without further purification.

The compressed gases used were purchased from Liquid Carbonic. The helium had a purity of 99.995% and the oxygen was 99.9% pure.

Tap water was purfied by passing it through a Barnstead Mixed Resin Cartridge (#D8902).

II. Equipment

Photolysis was carried out in a 750 ml glass reaction vessel equipped with a double-walled quartz immersion well, a teflon coated magnetic stirring bar and a 20 cm teflon sampling tube. The reaction vessel is shown in Figure 3.

During the irradiation period the reaction vessel was placed in a thermostated oil bath. The temperature of the Fischer paraffin oil was held constant by a Bronwill circulating constant temperature unit.

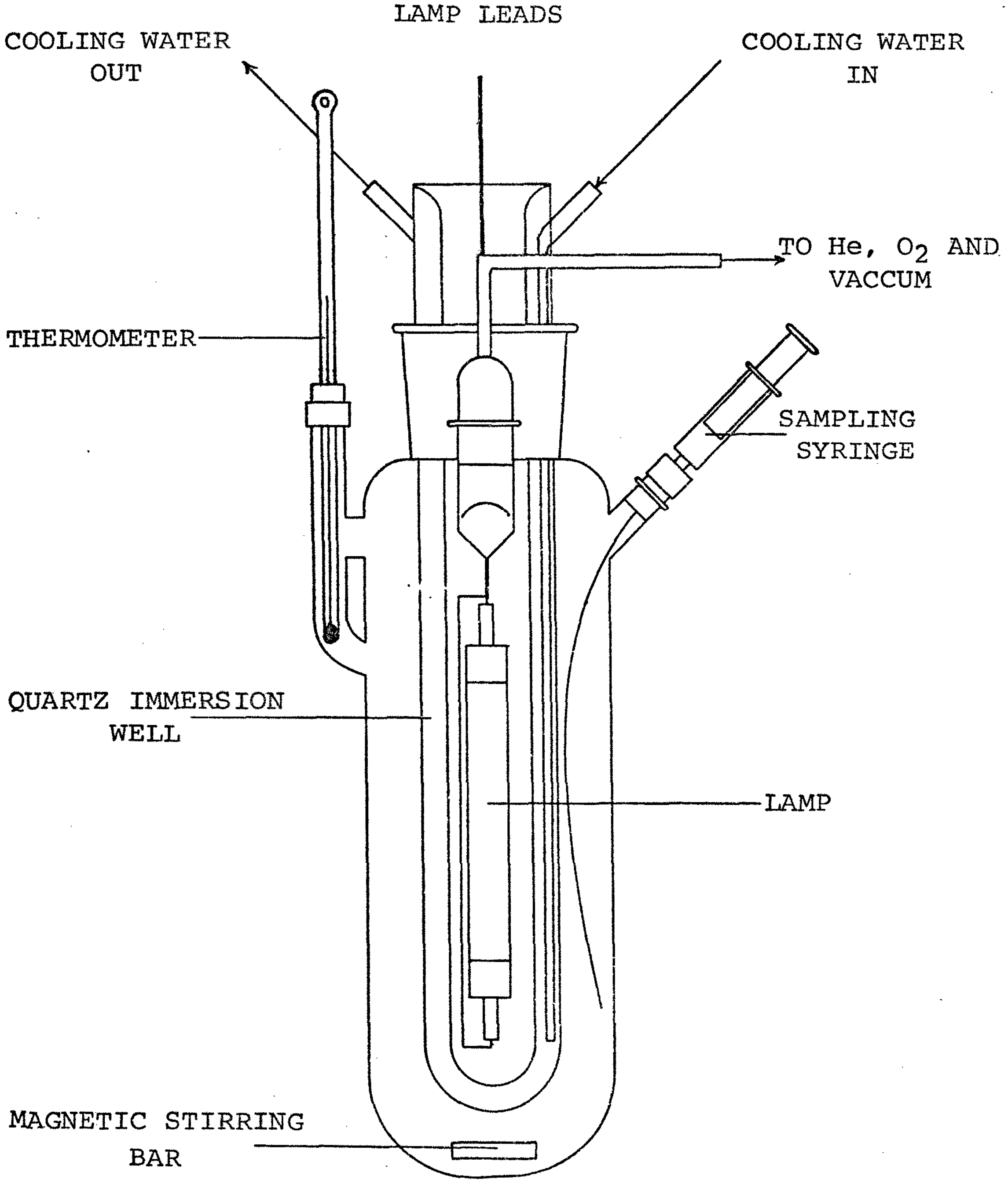


Figure 3. Quartz Immersion Well Reactor

A Hanovia (679A36,450-watt) high pressure, quartz, mercury-vapor lamp was the source of radiation. The spectrum of the energy output, as supplied by the manufacturer (14), is given in Table 2.

A sleeve of steel screen was used to lower the intensity of the light reaching the reaction mixture. The screen transmitted 26.9*% of the incident radiation.

A sleeve made of pyrex 7740 was used to block out radiation below 280 mμ. The absorption spectrum of the sleeve, as supplied by the manufacturer (15), is shown in Figure 4.

A F & M model 810-19 analytical gas chromatograph was used to analyze the reaction mixture. It was equipped with dual columns (4' x 1/8" SS) and dual flame ionization detectors. The columns were packed with 80-100 mesh Porapak Type Q-S packing. The oven was kept at about 220°C. Helium was used as a carrier gas.

The ultraviolet spectra of the reagents were obtained on a Beckman DB-G UV-Visible spectrophotometer.

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* specification of the manufacturer, Newark Wire Cloth Co.

Table 2.

Spectral Energy Distribution of Hanovia 679A36 High Pressure Mercury Vapor Lamp

Lamp watts	450
Lamp volts	135
Current (amps)	3.6
Arc length (inches)	4.5

Wavelength (Å)	Radiated energy (watts)
13673 (infrared)	2.6
11287	3.3
10140	10.5
5780 (yellow)	20.0
5461 (green)	24.5
4358 (blue)	20.2
4045 (violet)	11.0
3660 (U-V)	25.6
3341	2.4
3130	13.2
3025	7.2
2967	4.3
2894	1.6
2804	2.4

Table 2. (continued)

Wavelength (Å)	Radiated energy (watts)
2753	0.7
2700	1.0
2652	4.0
2571	1.5
2537	5.8
2482	2.3
2400	1.9
2380	2.3
2360	2.3
2320	1.5
2224	3.7
Total watts	175.8

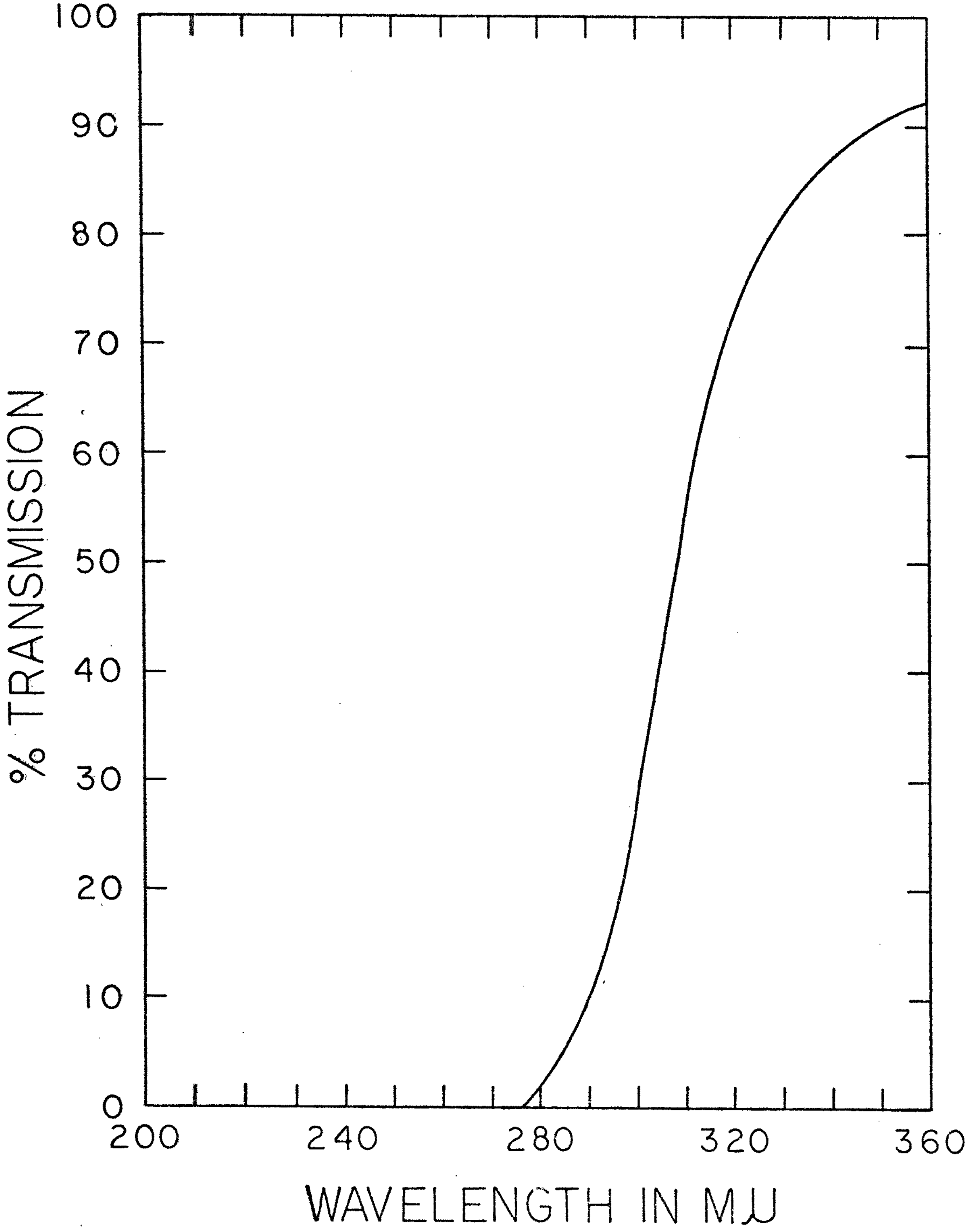

Figure 4. Transmission of Pyrex 7740 Filter

III. Procedure

Reaction mixtures were prepared by dissolving about 100 mg of p-xylene in 750 ml of the purified tap water (vide supra), 0.05M sodium phosphate tribasic, 0.1M sodium nitrate or $3.28\text{X}10^{-4}$ ferric sulfate. Five drops of concentrated sulfuric acid per liter of solution were added to the ferric sulfate solution to prevent the formation of a precipitate. About 600 ml of the reaction mixture were placed into the reaction vessel. In order to achieve an oxygen free solution, the reaction vessel was alternately evacuated to about 20 mm Hg, and flushed with helium, four times. When the photolysis was to be carried out on an oxygenated aqueous solution the water was first saturated with oxygen and then the p- xylene was added. The water was saturated with oxygen by bubbling pure oxygen through it for about fifteen minutes. The oxygenated solution was then placed in the reaction vessel and the system was flushed with oxygen. A slight positive pressure was maintained in the reaction vessel with either oxygen or helium during the irradiation period.

An initial sample was taken from the reaction vessel and the lamp was turned on. Four other samples were collected at selected intervals. The samples were removed with a 10 cc glass syringe and stored in 9 cc pyrex tubes with teflon lined screwcaps. The sample tubes were covered with aluminum foil to prevent exposure of the solution to light.

Photolysis by exposure to sunlight was carried out in pyrex sample tubes. Dissolved oxygen was removed from the reaction mixture by evacuating and flushing with helium. Then the tubes were filled with a 10 cc glass syringe with a 6 inch 18 gauge needle to prevent reaeration. Some of the tubes were wrapped with aluminum foil and were used as controls. All tubes were then exposed to sunlight for two days, smaples being withdrawn at selected intervals.

All samples were analyzed by injecting 25 µl aliquots into the chromatograph. The areas of the peaks were measured by the cut and weigh method (2).

RESULTS

I. Kinetics

The effect of dissolved oxygen and several inorganics on the photolysis of aqueous p-xylene was investigated by measuring the rate of disappearance of the p-xylene. in most cases the reaction rate was found to be too fast for accurate measurement when the solution was exposed to the full radiation of the lamp, so the steel screen was used to lower the amount of radiation reaching the solution.

The photolysis of the p-xylene was found to follow first order kinetics in every case. The rate constant was determined by measuring the slope of the line on a plot of $- \ln (C/C_o)$ versus time. A Hewlett-Packard calculation (model 9100A) programed for least-squares analysis was used for these calculations.

Each photolysis was run in duplicate, and the rate constants were averaged. Loss of p-xylene by thermal reaction or by evaporation was determined by making dark runs (lamp turned off). In all cases the loss was found to be negligible.

The photolysis of aqueous p-xylene in the absence of oxygen was found to have a rate constant of 0.0169 min^{-1}. This rate is the rate of the basic system to which all other rates were compared. A semi-log plot of C/C_o versus time is shown in Figure 5.

The rate constant for the photolysis of p-xylene in water saturated with oxygen was found to be 0.0207 min^{-1}. The oxygen increased the rate by a factor of 1.22. A semi-log plot of C/C_o versus time for this reaction is shown in Figure 6.

The effect of phosphate on the reaction rate was investigated by carrying out the photolysis in a 0.05M solution of sodium phosphate tribasic. The rate constant was found to be 0.0126 min^{-1}. The phosphate lowered the reaction rate, as compared to the basic system, by a factor of 0.747. Figure 7. shows the reaction rate.

The photolysis of p-xylene in solutions of sodium nitrate and ferric sulfate was conducted using the full spectral output of the lamp, and with part of it blocked. The steel screen was used during photolyses with the full spectrum and the pyrex filter was substituted for the screen when radiation below 280 mμ was to be blocked out.

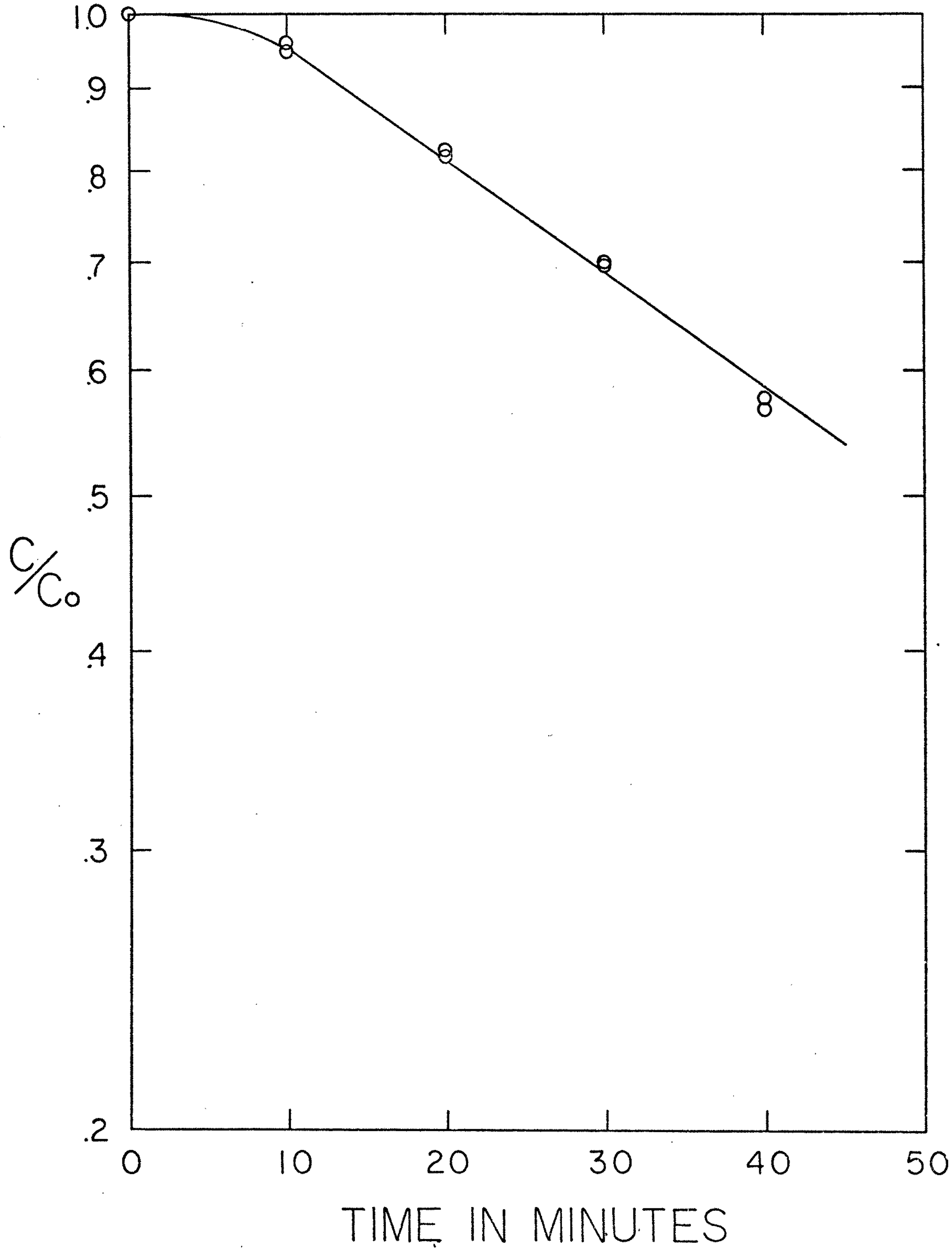

Figure 5. Photolysis of p-Xylene in Deaerated Water

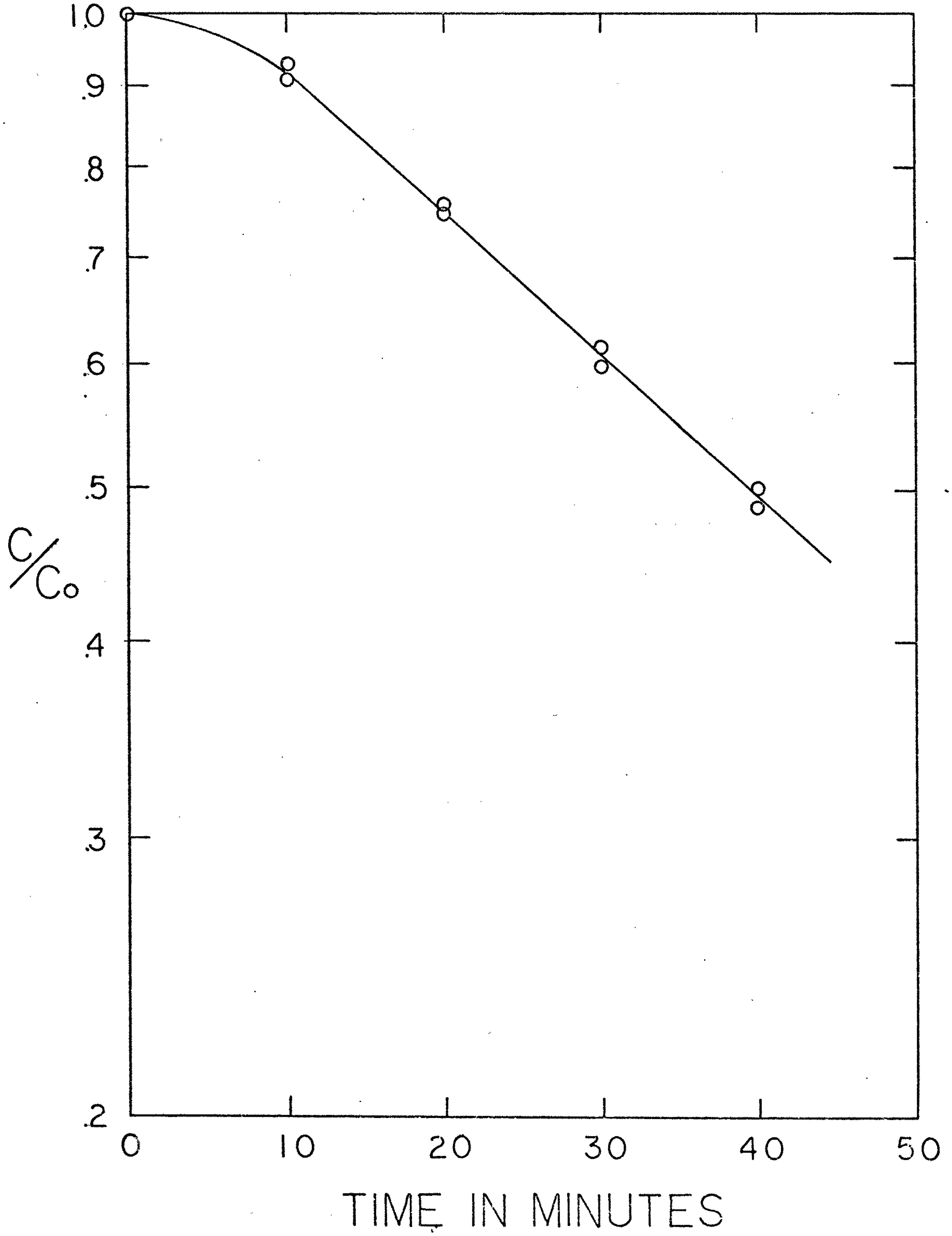

Figure 6. Photolysis of p-Xylene in Water Saturated with Oxygen

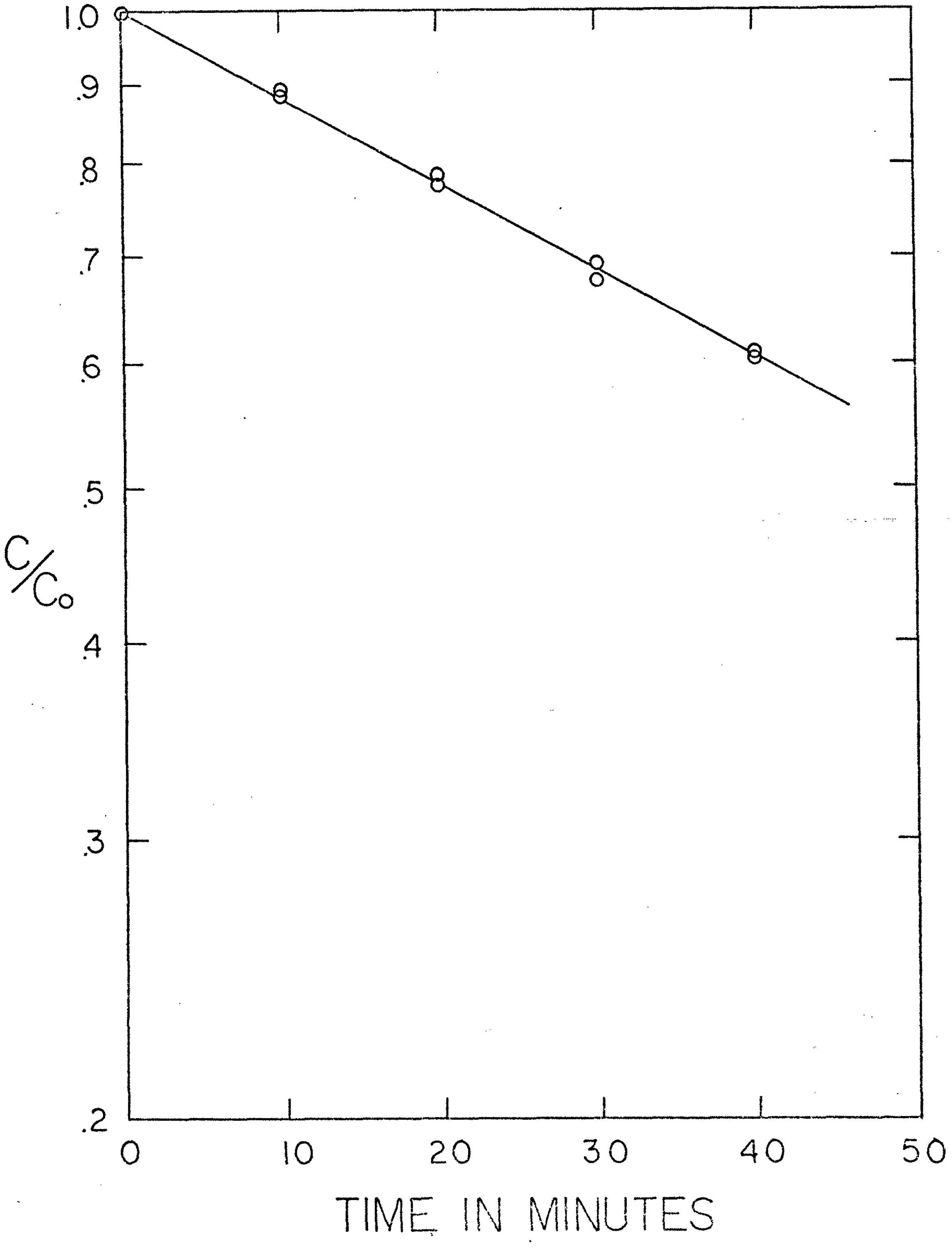

Figure 7. Photolysis of p-Xylene in 0.05M Na_3PO_4

The unfiltered photolysis of p-xylene in a 0.1M sodium nitrate solution was found to have a rate constant of 0.0138 min^{-1}, while the filtered photolysis had a rate constant of 0.00311 min^{-1}. The nitrate lowered the rate, as compared to the basic system, by a factor of 0.816. The reaction rates are shown in Figures 8. and 9.

The rate constant for the photolysis of p-xylene in a $3.28\text{X}10^{-4}$M solution of ferric sulfate was 0.142 min^{-1} for the unfiltered run, and 0.0435 min^{-1} for the filtered run. The ferric sulfate increased the reaction rate to 8.38 times the rate of the basic system. The reaction rates are shown in Figures 10. and 11. All of the results are given in Table 3.

Solutions of p-xylene in $3.28\text{X}10^{-4}$M ferric sulfate showed a 49.4% reduction in the p-xylene concentration over a two day exposure to sunlight passing through ordinary window glass. Analysis of the wrapped sample tubes showed no appreciable thermal reaction.

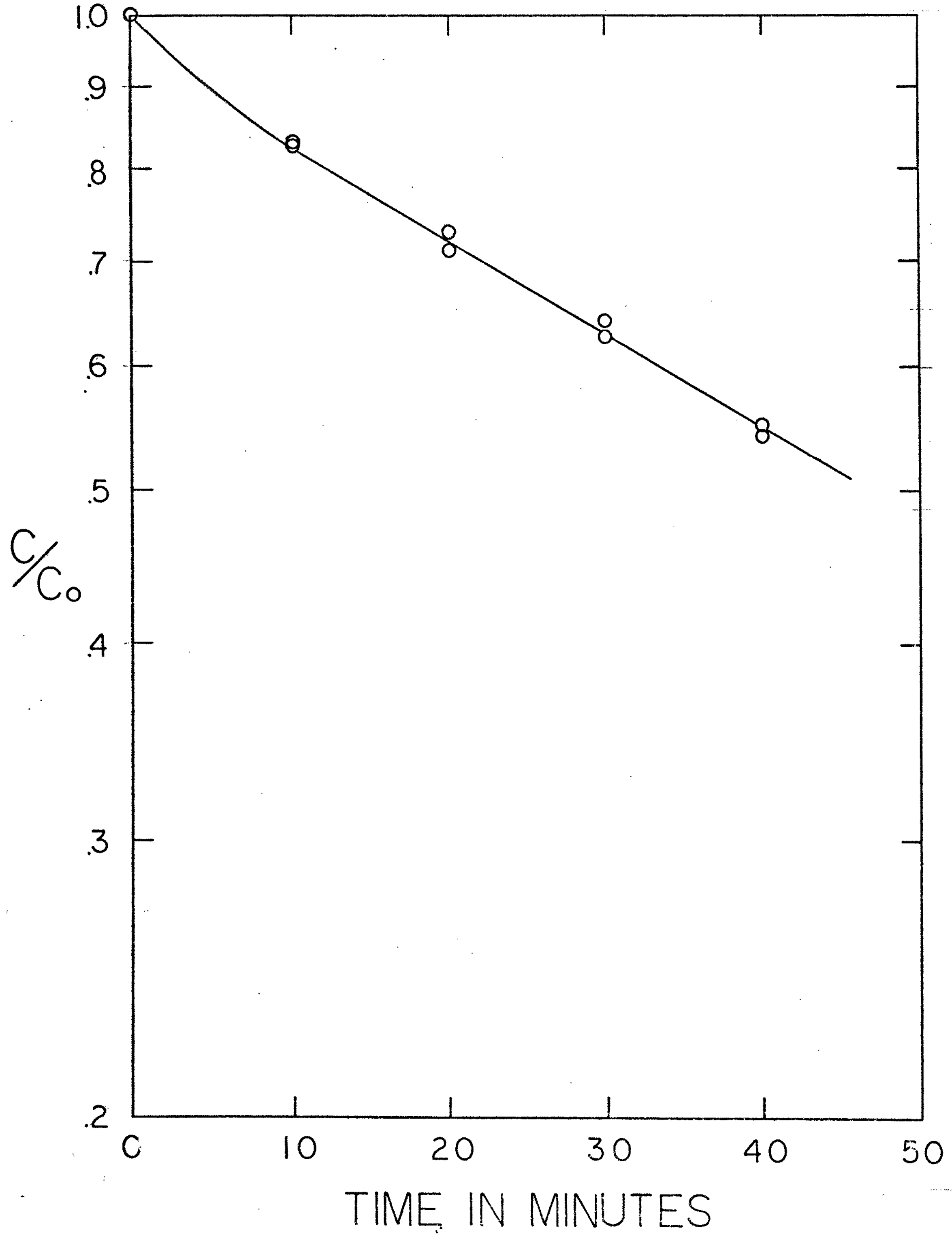

Figure 8. Photolysis of p-Xylene in 0.1M $NaNO_3$

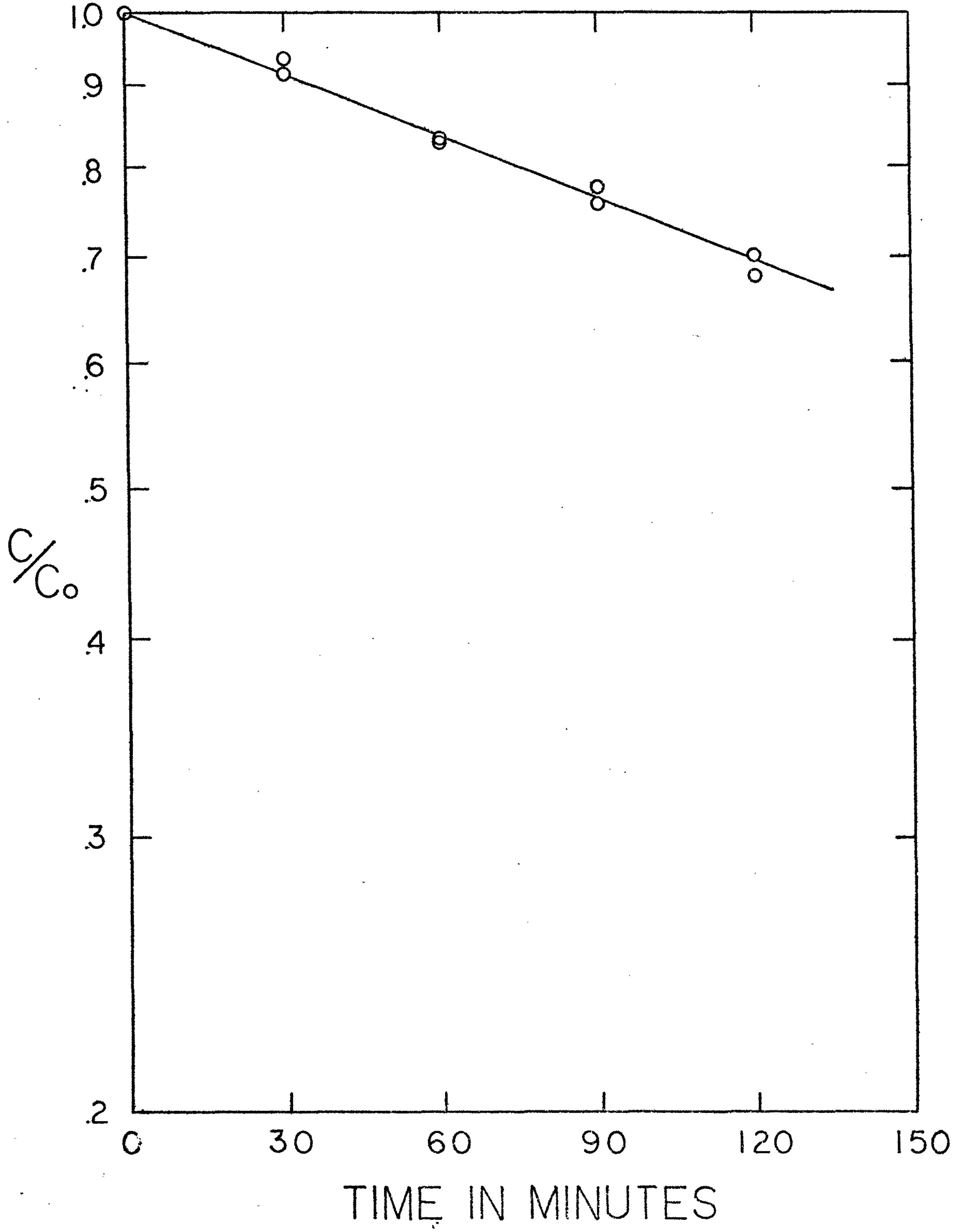

Figure 9. Photolysis of p-Xylene in 0.1M $NaNO_3$ with Pyrex 7740 Filter

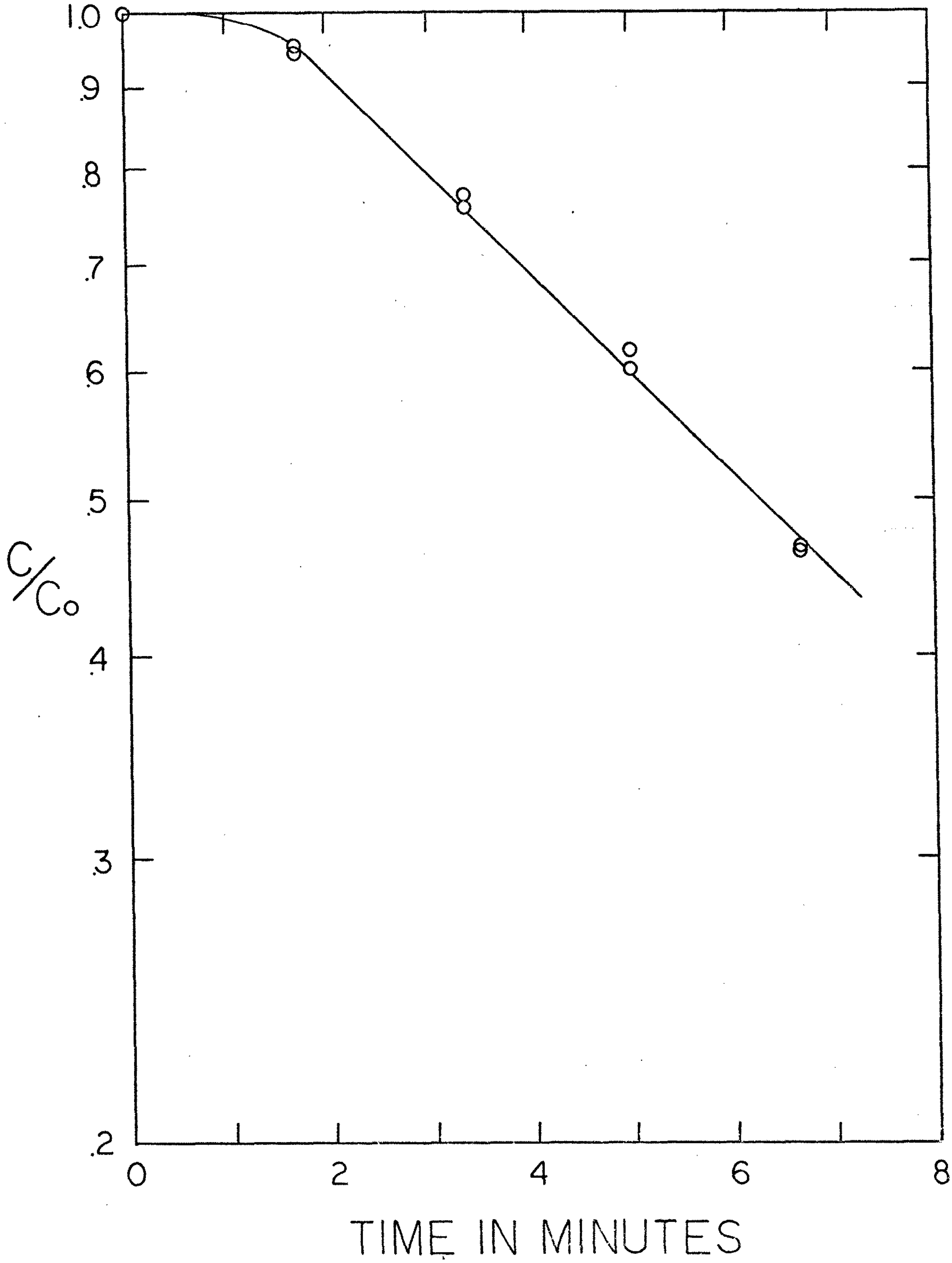

Figure 10. Photolysis of p-Xylene in $3.28\text{X}10^{-4}$M $Fe_2(SO_4)_3$

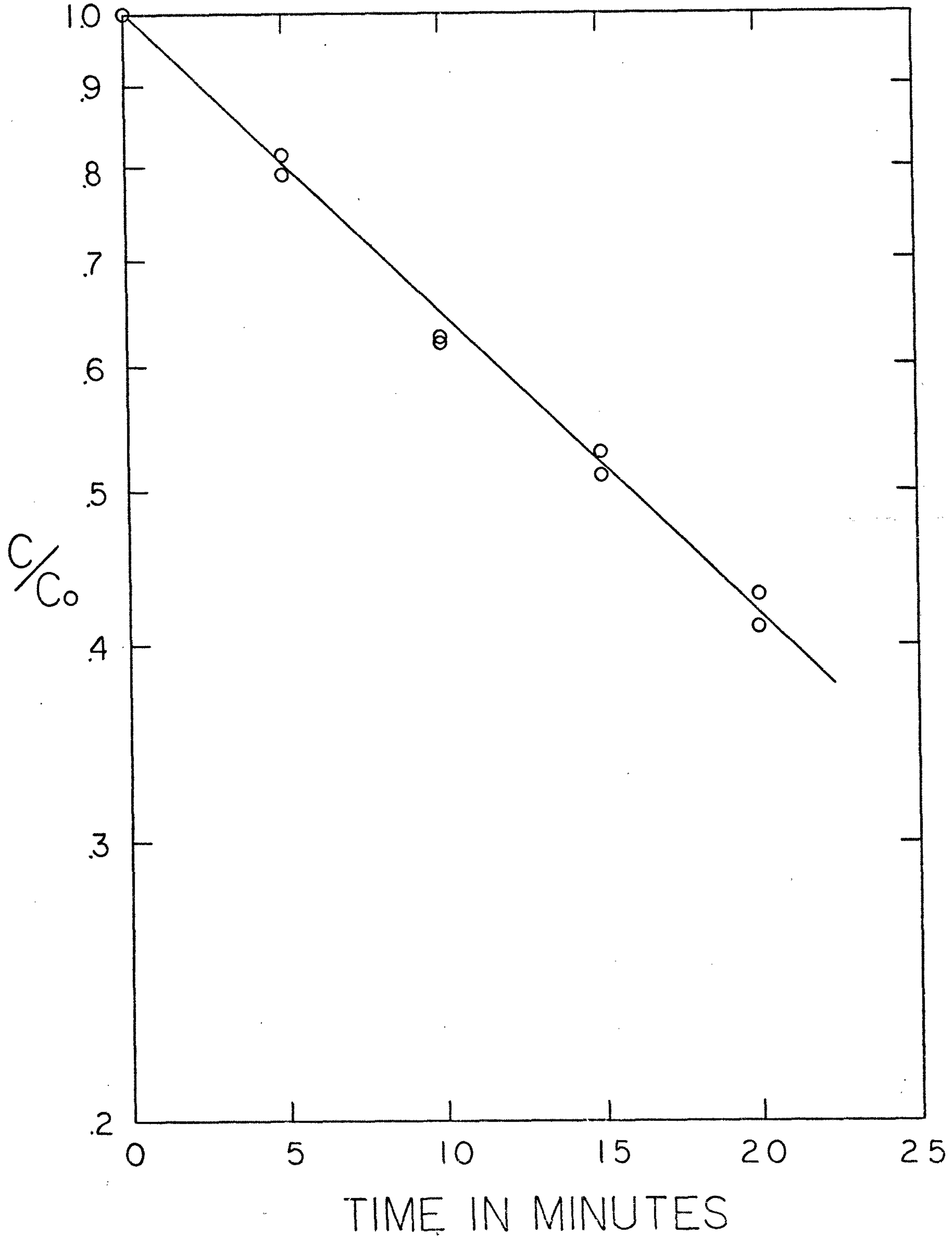

Figure 11. Photolysis of p-Xylene in $3.28X10^4M$ $Fe_2(SO_4)_3$ with Pyrex 7740 Filter

Table 3.

Experimental Results

Atomosphere	Light	Temperature (°C)	Solution	Rate Constant (min^{-1})	Average Rate Constant (min^{-1})
helium	screen	29.7	water	0.0170	0.0169
helium	screen	25.9	water	0.0168	
oxygen	screen	24.7	water	0.0202	0.0207
oxygen	screen	25.1	water	0.0212	
helium	screen	25.1	0.05M Na_3PO_4	0.0124	0.0126
helium	screen	23.0	0.05M Na_3PO_4	0.0128	
helium	screen	21.1	0.1M $NaNO_3$	0.0139	0.0138
helium	screen	21.4	0.1M $NaNO_3$	0.0137	
helium	pyrex filter	29.4	0.1M $NaNO_3$	0.00320	0.00311
helium	pyrex filter	28.1	0.1M $NaNO_3$	0.00301	
helium	screen	22.4	$3.28X10^{-4}M$ $Fe_2(SO_4)_3$	0.143	0.142
helium	screen	26.1	$3.28X10^{-4}M$ $Fe_2(SO_4)_3$	0.141	
helium	pyrex filter	23.1	$3.28X10^{-4}M$ $Fe_2(SO_4)_3$	0.0430	0.0435
helium	pyrex filter	24.1	$3.28X10^{-4}M$ $Fe_2(SO_4)_3$	0.0439	

II. Photoproducts

The formation of insoluble products from the photolysis of p-xylene was observed in reactions occuring in water, both with and without dissolved oxygen, and in solutions of sodium phosphate tribasic and ferric sulfate. The product was milky-white and took several weeks to settle. The solutions of sodium nitrate and p-xylene turned a clear yellow during photolysis. No insoluble products were observed.

The formation of volatile products from the photolysis of solutions of p-xylene and ferric sulfate was observed. Two very close product peaks appeared in the chromatograms of the reaction mixture. The products had a much greater retention time in the gas chromatograph than the p-xylene.

DISCUSSION

I. Kinetics

The disappearance of the p-xylene in most of the photolysis was first order except during the first few minutes of the irradiation period. The reason for this was that during the first few minutes the lamp was warming up and the intensity of the light was changing.

The ultraviolet spectrum of p-xylene in water at the reaction concentration (about 120 $^{mg}/l$) is shown in Figure 12. p-Xylene absorbs radiation of wavelengths shorter than about 280 mμ. Since some of the output of the lamp is in the 220-280 mμ region of the spectrum, radiation is absorbed by the p-xylene and photochemical reaction does occur.

Water is transparent to the radiation put out by the mercury vapor lamp. For this reason the photochemical reaction of the p-xylene in deaerated water must be initiated by absorption of radiation by the p-xylene alone. When other compounds are added to the basic system they may complicate the reactions in the following ways:

(1)- they may absorb radiation themselves and thus lower the amount of radiation absorbed by the p-xylene,

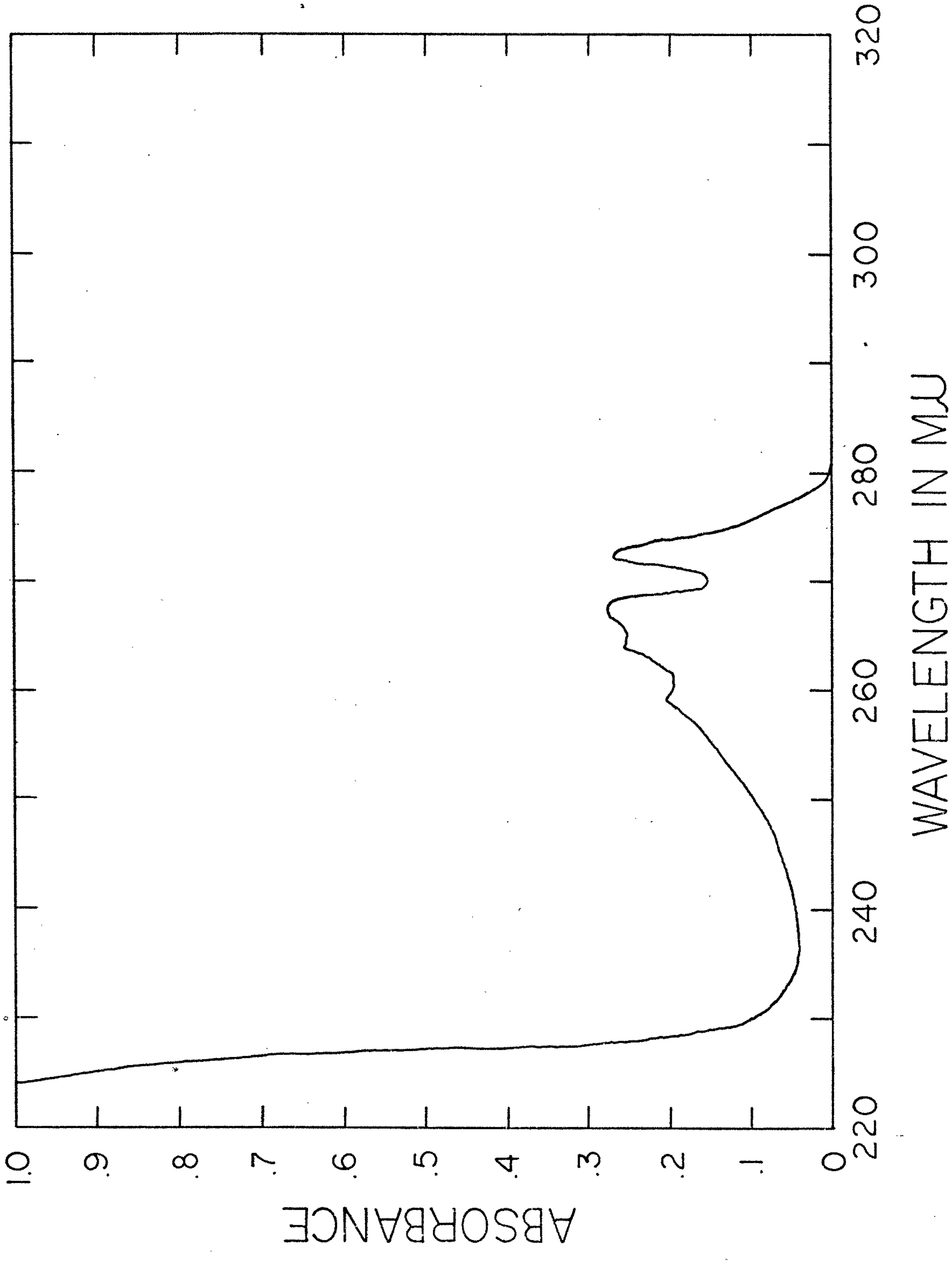

Figure 12. Ultraviolet Spectrum of p-Xylene in Water

(2)- they may react with excited p-xylene molecules and form new products,

(3)- they may absorb radiation and transfer the energy to p-xylene molecules (photosensitization),

(4)- they may undergo photochemical reactions themselves.

Oxygen absorbs radiation of wavelengths less than 240 mμ and can form ozone (5), but the formation of ozone in the reaction mixture was minimized by the fact that radiation from the lamp passed through an air space and the aerated cooling water before it entered the reaction vessel. The increase in reaction rate in the presence of oxygen may be due to reaction of excited p-xylene molecules with the oxygen.

The ultraviolet spectrum of sodium phosphate tribasic in water at the reaction concentration (0.05M) is shown in Figure 13. The sodium phosphate tribasic may absorb radiation and undergo photochemical reaction, but its contribution to the disappearance of the p-xylene is probably small. The lowering of the reaction rate is probably due to the fact that less radiation is absorbed by the p-xylene since the sodium phosphate tribasic also absorbs radiation.

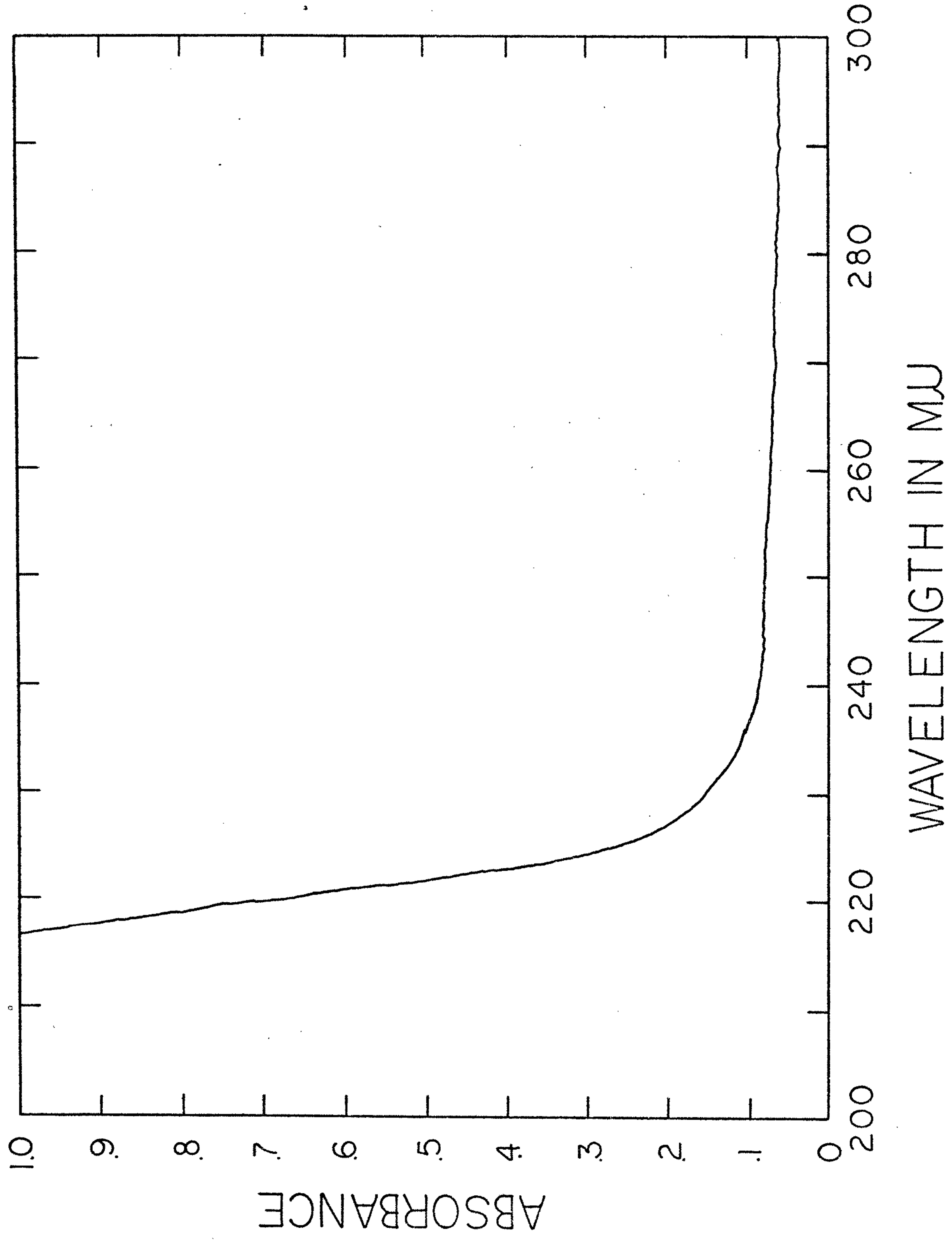

Figure 13. Ultraviolet Spectrum of Na_3PO_4 in Water

When the pyrex filter is used to block out radiation of wavelengths shorter than 280 mμ the disappearance of the p-xylene must be initiated by the absorption of light by other compounds present in the system. The ultraviolet spectra of sodium nitrate and ferric sulfate in water at the reaction concentrations (0.1M $NaNO_3$, $3.28X10^{-4}M$ $Fe_2(SO_4)_3$) are shown in Figures 14. and 15. Both of these compounds exhibit significant absorption of light at wavelengths longer than 280 mμ. Also both of these compounds are known to undergo photochemical reactions.

Gori, Petriconi and Papée (12) studied the photolysis of sodium nitrate in aqueous solution by sunlight. They found that when the solution is exposed to sunlight it undergoes photolysis. Daniela, Meyers and Belardo (6) studied the photolysis of aqueous sodium nitrate at 3000 Å and proposed the following mechanism:

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O$$

$$O + NO_3^- \longrightarrow O_2 + NO_2^-$$

$$O + NO_2^- \longrightarrow NO_3^-$$

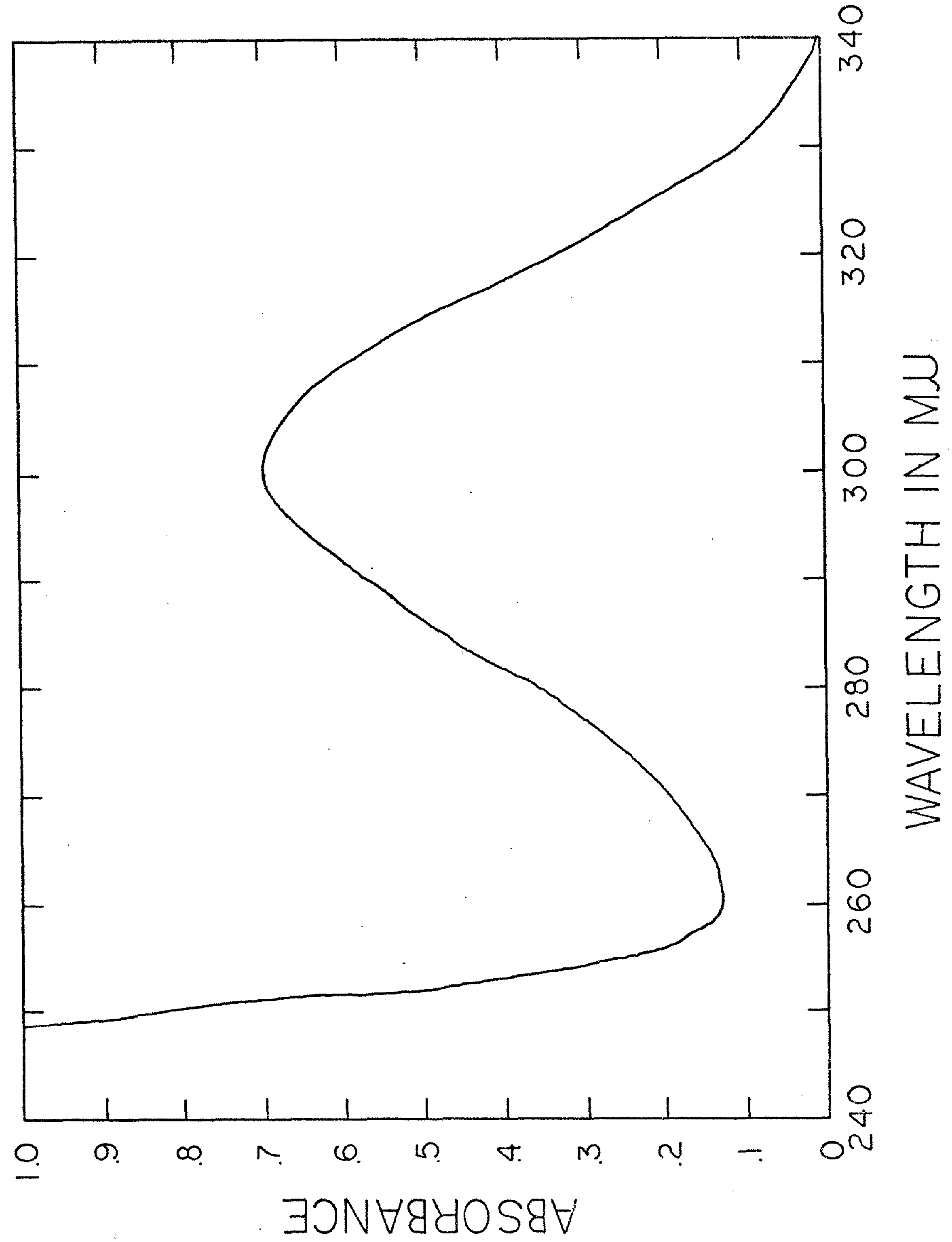

Figure 14. Ultraviolet Spectrum of $NaNO_3$ in Water

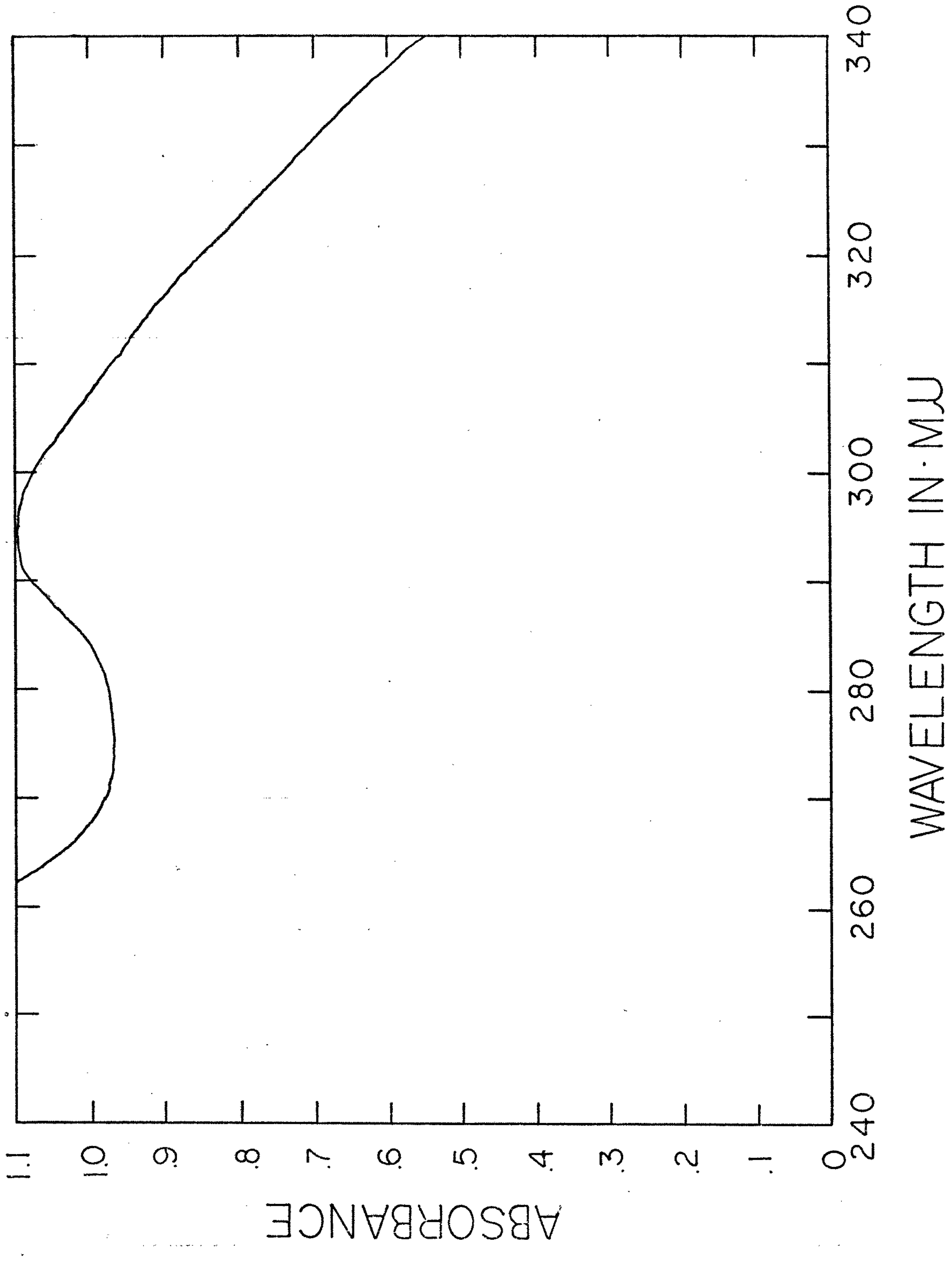

Figure 15. Ultraviolet Spectrum of $Fe_2(SO_4)_3$ in Water

They also proposed that in the presence of radical scavengers such as benzene a second primary process takes place:

$$NO_3^- \xrightarrow{h\nu} NO_2 + O^-$$

Electrons can be transferred from one molecule or ion to another by the action of ultraviolet and visible light. The charge transfer in aqueous solutions of ferrous sulfate occurs as follows (16,35):

$$Fe^{2+}H_2O \xrightarrow{h\nu} Fe^{3+}H_2O^-$$

$$Fe^{3+}H_2O^- \rightleftharpoons Fe^{3+} + OH^- + H$$

or in acid solution,

$$Fe^{3+}H_2O^- + H^+ \rightleftharpoons Fe^{3+}H_2O + H$$

Charge transfer for the ferric ion occurs as follows (42):

$$Fe^{3+}H_2O \xrightarrow{h\nu} Fe^{2+}H_2O^+$$

$$Fe^{2+}H_2O^+ \rightleftharpoons Fe^{2+} + OH + H^+$$

Thus irradiation of aqueous ferric ions leads to the formation of ferrous ions which are also photochemically reactive.

The wavelength at which charge transfer occurs can be increased by the presence of anions with which the cation can form a complex.

Exposure of the p-xylene - sodium nitrate system to light of wavelengths greater than 280 mμ (using the pyrex filter) resulted in a disappearance of the p-xylene. Since products obtained from the photolysis appear to be different from those obtained in the basic system, it is probable that the p-xylene undergoes different reactions from those in the basic system. Even when the mixture is exposed to the full spectral output of the lamp (using the screen) these new reactions appear to be predominant. The observed decrease in reaction rate, as compared to the basic system, was due to the fact that the p-xylene was undergoing different, slower reactions.

The p-xylene - ferric sulfate system underwent photochemical reaction when exposed to light of wavelengths greater than 280 mμ. The products of the reactions appeared to be similar to those obtained in the basic system. Exposure of the system to the full spectral output of the lamp resulted in a reaction rate which was much faster than the reaction rate of the basic system. This increase in reaction rate may be due to the fact that the products of the photolysis of the ferric sulfate may react with p-xylene in the ground state. Thus absorption of light by either the p-xylene or the ferric sulfate would result in the disappearance of the p-xylene.

The fact that the p-xylene - ferric sulfate system underwent photochemical reaction when exposed to sunlight shows that it is possible for refractory organics to undergo photochemical reaction in the environment. Since the photochemical reactions of a compound are influenced by the presence of other compounds, it is necessary to know what a pollutant will come into contact with before the products of the photochemical reactions can be predicted.

II. Photoproducts

The major product from the photolysis of p-xylene in deaerated water, water saturated with oxygen, sodium phosphate tribasic solution and ferric sulfate solution was insoluble in water. This product may be the previously mentioned polymer (1,44). The fact that the product was insoluble in water suggest that photochemical treatment of waste streams may be useful in the removal of some pollutants. The pollutants could be converted to insoluble products which could easily be removed by conventional methods such as filtration or clarification. In the past photochemical treatment of waste streams was not used commercially because of the high cost of quartz reaction vessels and mercury arc lamps. It may be possible to eliminate the need for this expensive equipment by adding other compounds to the waste stream which would initiate photochemical reaction at higher wavelengths. Ferric sulfate has been shown to initiate the photochemical reaction of p-xylene by absorbing light passing through pyrex and ordinary window glass. Thus photochemical treatment may be feasible in some applications.

FUTURE WORK

This research was directed mainly towards the study of the photochemical reactions of one hazardous polluting substance in the laboratory. The photochemical reactions of other hazardous polluting substances, both in the laboratory and in the environment, should be investigated. Exposure of the various solutions of the hazardous polluting substances to sunlight would give an indication of reaction rates in the environment.

The products of the photochemical reactions should be identified and their toxicity should be ascertained so that their effect on the environment can be determined.

The economic feasibility of photochemical treatment as a means of removing pollutants from waste streams should be investigated. The effect of adding sensitizers to the waste stream before exposure of the stream to light should also be investigated. This study should be conducted by setting up a continuous process. The effectiveness of such a process on waste streams which contain many different compounds could be measured by monitoring the reduction in total organic carbon (TOC).

APPENDIX

Complete Kinetic Data for the Photolysis of p-Xylene in Deaerated Water, Water Saturated with Oxygen, 0.05M Na_3PO_4, 0.1M $NaNO_3$ and $3.28X10^{-4}$M $Fe_2(SO_4)_3$

Table 4.

Kinetic Data for the Photolysis of p-Xylene in Deaerated Water

Temperature (°C):	29.7	25.9
Time (min)	C/C_o	C/C_o
0	1.000	1.000
10	0.946	0.957
20	0.820	0.813
30	0.698	0.696
40	0.566	0.515

Table 5.

Kinetic Data for the Photolysis of p-Xylene in Water Saturated with Oxygen

Temperature (°C):	24.7	25.1
Time (min)	C/C_o	C/C_o
0	1.000	1.000
10	0.906	0.927
20	0.746	0.757
30	0.597	0.614
40	0.498	0.491

Table 6.

Kinetic Data for the Photolysis of p-Xylene in $0.05M\ Na_3PO_4$

Temperature ($^{\circ}$C):	25.1	23.0
Time (min)	C/C_o	C/C_o
0	1.000	1.000
10	0.892	0.884
20	0.189	0.777
30	0.692	0.675
40	0.610	0.602

Table 7.

Kinetic Data for the Photolysis of p-Xylene in $0.1M\ NaNO_3$

Temperature ($^{\circ}$C):	21.1	21.4
Time (min)	C/C_o	C/C_o
0	1.000	1.000
10	0.826	0.830
20	0.710	0.730
30	0.626	0.641
40	0.542	0.550

Table 7. (continued)

With Pyrex 7740 Filter

Temperature (^oC):	29.4	28.1
Time (min)	C/C_o	C/C_o
0	1.000	1.000
30	0.933	0.913
60	0.830	0.829
90	0.774	0.754
120	0.680	0.700

Table 8.

Kinetic Data for the Photolysis of p-Xylene in $3.28X10^{-4}M$ $Fe_2(SO_4)_3$

Temperature (^oC):	22.4	26.1
Time (sec)	C/C_o	C/C_o
0	1.000	1.000
100	0.951	0.942
200	0.755	0.770
300	0.601	0.617
400	0.465	0.464

Table 8. (continued)

With Pyrex 7740 Filter

Temperature (°C):	23.1	24.1
Time (min)	C/C_o	C/C_o
0	1.000	1.000
5	0.814	0.790
10	0.623	0.621
15	0.511	0.529
20	0.431	0.409

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