THE PHOTOLYSIS OF CHLOROBENZENE

IN AN AQUEOUS ENVIRONMENT

BY

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ABSTRACT

Chlorobenzene was chosen as a model system for the study of photochemically induced reactions in an aqueous environment. It was the goal of this research to achieve a reaction system which best approximates conditions existing in the environment. To do this, a basic model system was established, and then the effect on the rate by various parameters was studied. These parameters, which included the presence of oxygen and such inorganic compounds as might be present in receiving waters, (e.g. nitrate, sulfate, and phosphate), were chosen so as to meet the goal of this research.

Kinetic data was obtained for seven different systems. A value of 0.0319 min.$^{-1}$ was found when chlorobenzene was irradiated in the basic model system of helium and water. When oxygen was substituted for helium, the rate decreased to 0.0224 min.$^{-1}$. The presence of inorganic compounds resulted in both increases and decreases from the basic model system. When chlorobenzene was irradiated in solutions of $0.1M$ $NaNO_3$ and $0.01M$ Na_3PO_4, the rates decreased to 0.0193 min.$^{-1}$ and 0.0225 min.$^{-1}$ respectively. The increase in the rate to 0.0440 min.$^{-1}$ when chlorobenzene was photolyzed in a $0.00328M$ $Fe_2(SO_4)_3$ solution prompted us to look for a possible explanation for this increase. The systems of $0.1M$ $NaNO_3$ and $0.00328M$ $Fe_2(SO_4)_3$ were rerun using a pyrex filter which would insure that the energy absorbed by the chlorobenzene was through energy transfer from the inorganic compounds rather than by direct absorption of light. It was found that chlorobenzene did react in these systems which would indicate photosensitized reactions.

APPROVAL OF THESIS

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FOR THE

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INTRODUCTION

I. HAZARDOUS POLLUTING SUBSTANCES:

The Department of Transportation has defined Hazardous Polluting Substances as "those materials that reach the aquatic system as a result of the...deliberate or accidental discharge of any material in excess of continuous discharge levels permitted by water quality standards existing...that, upon reaching the aquatic system, present or have the potential of presenting an imminent and substantial danger to the public health and welfare, including but not limited to human health, fish, shellfish, wildlife, shorelines and beaches."(12)

There is little experimental data describing the intereaction of specific pollutants with chemical and biological species. Therefore, only generalizations can be made at this time on the intereaction the pollutants have with their environment.

Figure 1 shows the possible intereactions of pollutants with the aquatic environment.(10)

Industrial pollution has increased tremendously in the past decade. The variety of uses of synthetic chemicals is partly responsible for this increased pollution. The production of these synthetic chemicals has led to a more complicated waste containing Hazardous Polluting Substances which are being dumped into the waterways. Standard water quality methods of analysis yield only an indirect measure of the oxygen-demanding potential of these wastes. No concern is
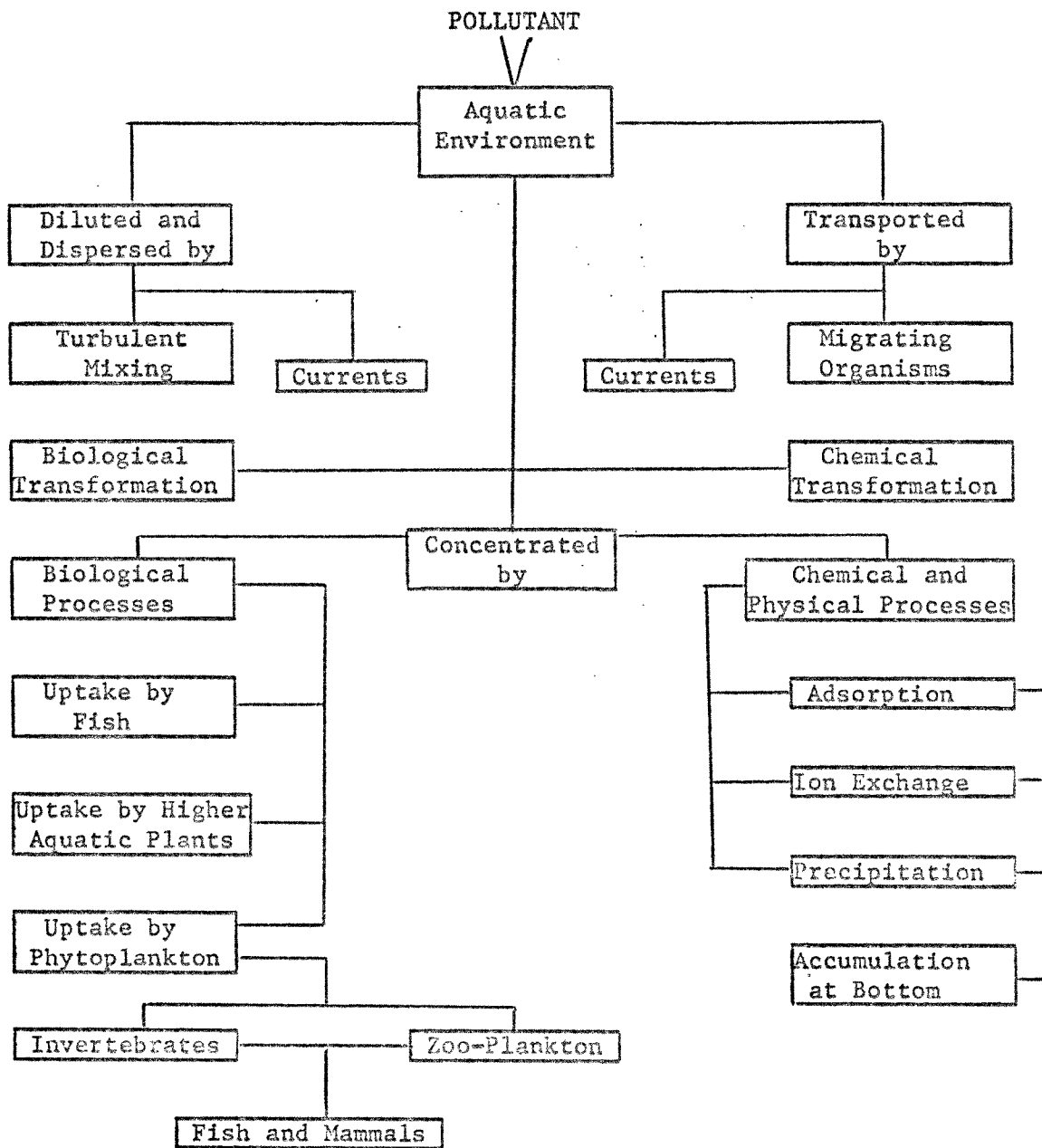
Figure 1- The Fate of Pollutants in the Aquatic Environment (10)

usually given to the quantity and identity of any specific component
of the waste stream (other than phenols) nor is any given to the pro-
ducts formed once these trace amounts of organic wastes have been
released into the hydrosphere and undergo reaction with other environ-
mental elements. Further, it is possible that the photoproducts of
certain pollutants are more toxic than the pollutants themselves and
would increase the danger to the public health and welfare. It is
to this concern that this research is directed. Specifically, we have
concerned ourselves with the possible intereaction of such a Hazardous
Polluting Substance with sunlight.

Chlorobenzene has been chosen as a model system for the study
of photochemically induced reaction in an aqueous environment from a
priority listing of Hazardous Polluting Substances by the Department
of Transportation.(12) The parameters used in ranking each pollutant
in terms of its potential threat to water quality includes "the low-
est range at which a substance impairs one of the beneficial uses of
water, and the quantity annually shipped by each mode of transport...."(12)
In addition, chlorobenzene is sufficiently uneffected by conventional
biological treatment and exhibits a finite solubility which well
exceeds the toxicity critical concentration (See Table 1). Therefore,
a possible alternative to such conventional treatment is a tertiary
treatment process using ultraviolet light.

Previous work has been done by Casani (8) showing that chloro-
benzene, when irradiated by ultraviolet light in an aqueous environment,
undergoes photolysis. It was our goal to achieve a reaction system

TABLE 1

Physical and Biological Constants of Chlorobenzene

Molecular Weight (gm.) (23)	112.56
Boiling Point (^{o}C) (23)	132.0
Specific Gravity (23)	1.1058
Refractive Index (23)	1.5241
BOD_5 (gm./gm.) (17)	0.03
Human Toxicity Critical Concentration (mg./l.) (10)	0.35f
Solubility (mg./l.) (41)	488.0

f-fish toxicity

which best approximates conditions existing in the environment. To do this, it was necessary to establish a basic model system and then study the effect on the rate by various parameters. These parameters which were chosen to meet our goal included oxygen concentration and the presence of inorganic compounds.

II. CURRENT RESEARCH ON PHOTOCHEMICAL TREATMENT:

Photochemical research on chlorobenzene in an aqueous environment is very limited. Much of the research which has been done is concerned with the treatment of municipal waste.

In studies carried out by Schorr, Boval, Hancil, and Smith (38), the rate of photooxidation of secondary effluent organic pollutants was found to be directly proportional to the oxygen concentration at low concentrations, while at high oxygen concentrations, the rate was independent of the concentration.

Klein (22) showed the photolysis of ligno-sulfonate, a by-product in the production of paper materials, is dependent on the presence of oxygen as a free radical acceptor. This was important because, while the ligno-sulfonates could not be treated biologically, the photo-products of these ligno-sulfonates could be treated.

Meallier (30) found in his studies of the photooxidation of aniline, toluidine, and 2,3-2,4-2,5-, and 2,6-dimethylaniline, that oxygen had the same effect on the rate as mentioned previously in the work done by Schorr, Boval, Hancil, and Smith (38).

Meiners (31) studied the effect of chlorine on the photooxidation of starch and found that the rate tripled when the pH is changed from 0.5 to 4.0 (at 0°C).

Meiners (31) also reported a temperature dependency of the rate of photooxidation. A decrease in the rate with a change in temperature from 0°C to 25°C at a constant pH was the result. This, however, is not always the case. Bulla (5), and Bulla and Edgerly (6) found the photoreaction of aldrin to be independent of temperature over the range from $20-40^\circ$C.

Schorr found that the rate of photooxidation of organic pollutants was first order with respect to light radiation absorbed. This differs from the study of the rate of removal of dodecyl benzene sulfonates from an aqueous solution by photoreaction done by Smith (40) who found it to be proportional to the intensity to the 1/2 power.

Since chlorine is usually present in treated wastewater, its use as a potential photosensitizer has been studied by Hancil and Smith(15) and Meiners (31). Hancil and Smith showed the addition of chlorine increased the photochemical oxidation of soluable organics twenty times at low chlorine concentrations ($\leqslant$2 mg/1). The rate is independent of chlorine concentration at higher concentrations. Meiners also reported an increase in the rate of photodegradation of nitrified effluents with the addition of chlorine.

To understand why the rate of photodegradation is a function of

pH, temperature, light intensity, oxygen concentration, and inorganic photosensitizers, a basic understanding of photochemistry is necessary.

III. PHOTOCHEMISTRY

Photochemistry deals with reactions that are dependent on the action of visible or ultraviolet light. The near ultraviolet (2100-3000Å) region of the electro-magnetic spectrum will be of interest to us. The wavelength given by the symbol, λ, is most often expressed in angstroms ($1\text{Å}=10^{-8}$ cm.).

Energy can be related to wavelength by $E=hc/\lambda$. This relationship was obtained by knowing the frequency $v=c/\lambda$, where c is equal to the velocity of light. Since $E=hv$, where h is Planck's constant (6.67×10^{-27} erg-sec), it follows that $E=hc/\lambda$.

There are three types of electronic orbitals of most interest in photochemistry. Each is characterized by their spatial properties. The π orbitals are represented by the sidewise overlap of the atomic p orbitals and are not symmetric to the nodal plane. In the σ orbitals, overlap occurs along the axis joining the atoms. The third type is the n orbital which contains the non-bonding electron pair and are localized on those atoms.

The general order of orbital energies is shown in Figure 2 from which it is apparent that $n\rightarrow\pi^{*}$ transitions lie at the longest wavelength with $\pi\rightarrow\pi^{*}$ at intermediate, and $\sigma\rightarrow\sigma^{*}$ transitions at the shortest wavelengths. These transitions occur when the absorption

of electronic energy cause the transition of an electron from either

a bonding or non-bonding orbital to an anti-bonding orbital.

Only two half-vacant orbitals are associated with a molecule in

the excited state in most photochemical reactions. They are the orbital

from which the transition takes place and the antibonding orbital to

which the electron is promoted. Consequently, two values for mul-

tiplicity are obtained: one and three. The first, called the singlet

state, has had its spin preserved, while the spins for the second value

for multiplicity, called the triplet state, are now parallel.

Deactivation of these excited states to the ground state can take

place in many ways. Florescence or internal conversion can cause trans-

ition from a singlet excited state to a singlet ground state. Inter-

system crossing and phosphorescence can cause transition from the triplet

excited state to the singlet ground state. It is important to note

Energy

σ^*

π^*

n

π

σ
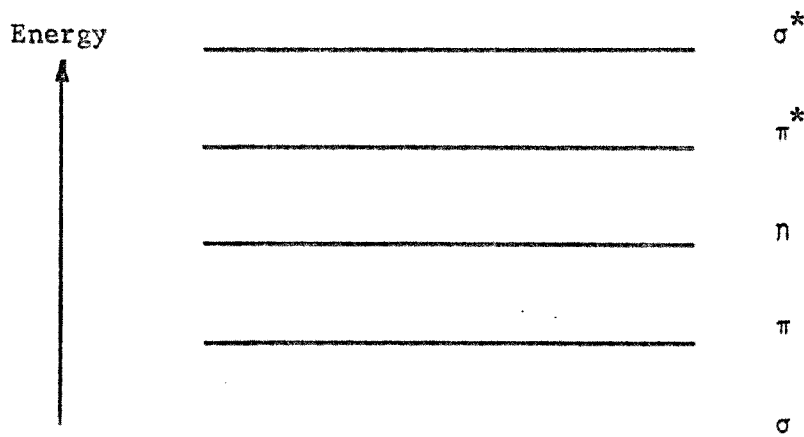
Figure 2 - General Order of Orbital Energies

that the only way to get to the triplet excited state is by inter-system crossing from singlet excited state. Figure 3 schematically summarizes the photochemical processes.

Photochemical reactions and sensitization are the other means of deactivation from excited states. Sensitization, which utilizes the energy from deactivation of excited states to excite other species electronically, must meet some conditions before it can occur. The first condition is that the excited state must not deactivate before it can transfer energy to an acceptor. The second condition is that the spin be conserved. The important feature in sensitized reactions is that the incident light need only be of the wavelenght absorbed by the sensitizer.

The photosensitization occurs as follows:

$$D \xrightarrow{h\nu} D^* \ (S_1)$$
$$D^* \ (S_1) \longrightarrow D^* \ (T_1)$$
$$D^* \ (T_1) + A \longrightarrow D + A^* \ (T_1)$$
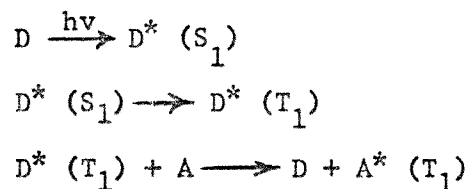
where D is the photosensitizer and A is the acceptor.

Although there has been little work done on the photochemical reactions of chlorobenzene, the photochemical reactions of other halogenated aromatics and benzene may lend much insight into the reactions which may take place.

In work done by Angus, Blair, and Bryce-Smith (2), liquid chloro-benzene has been reported to undergo decomposition to complex products
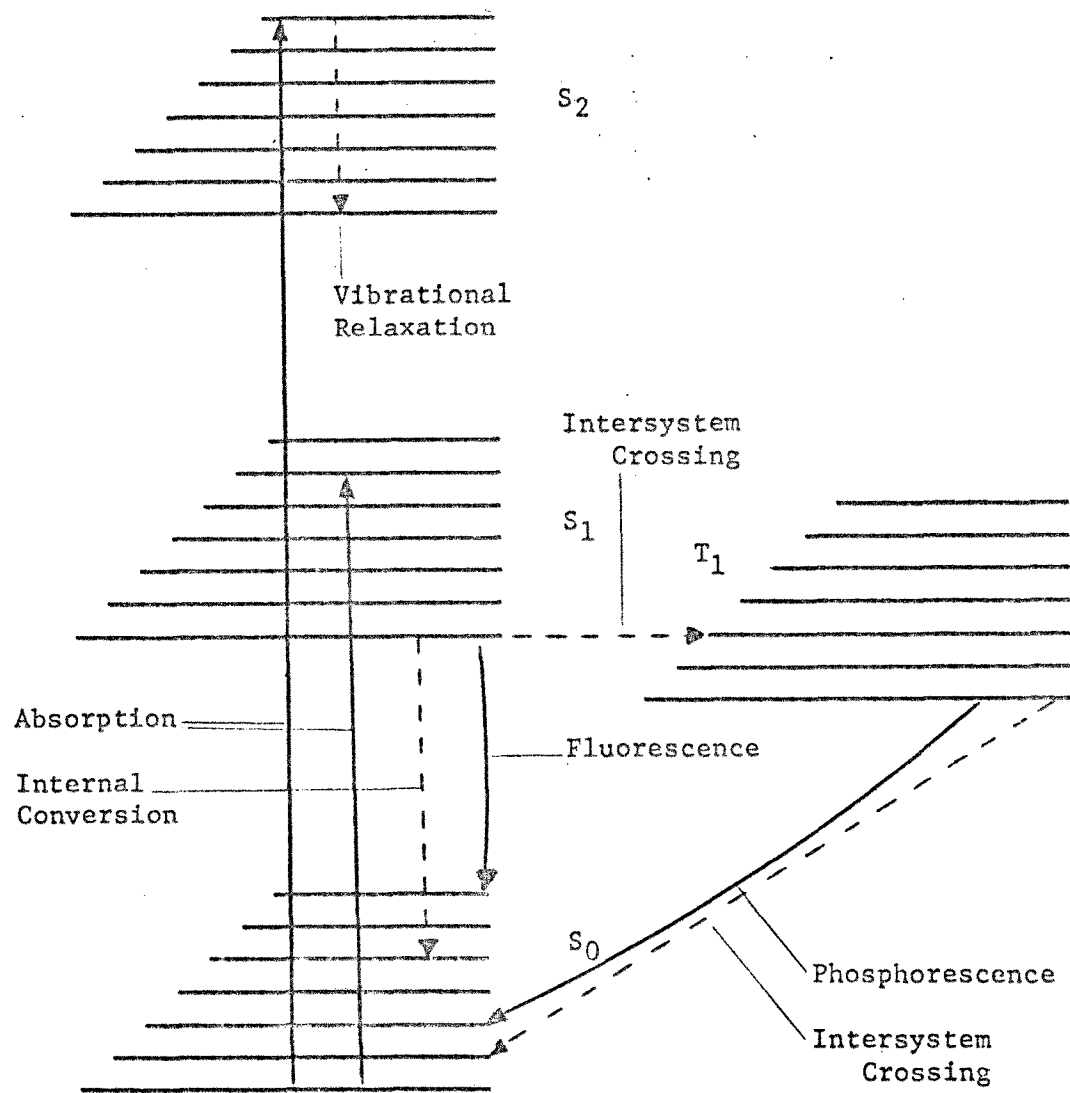
Figure 3 - Jablonski Diagram

not yet identified. Irradiation was done at 2537 Å under an atmosphere of nitrogen.

Pinhey and Rigby (34) reported the formation of a phenyl radical (I) when chlorobenzene was irradiated under nitrogen using a mercury arc in a water-cooled quartz well. Four grams of chlorobenzene were dissolved in 670 ml of ethanol. Similar results were reported by Porter and Ward (35) when liquid bromo- and chlorobenzene were irradiated using a mercury lamp under a nitrogen atmosphere.
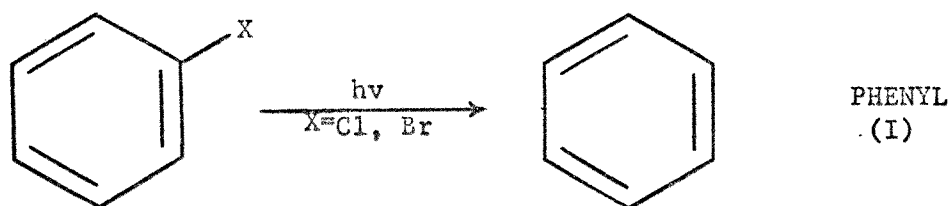
Robinson and Vernon (36) reported the formation of biphenyls (II) upon irradiation of chlorobenzene using a mercury arc lamp under nitrogen.
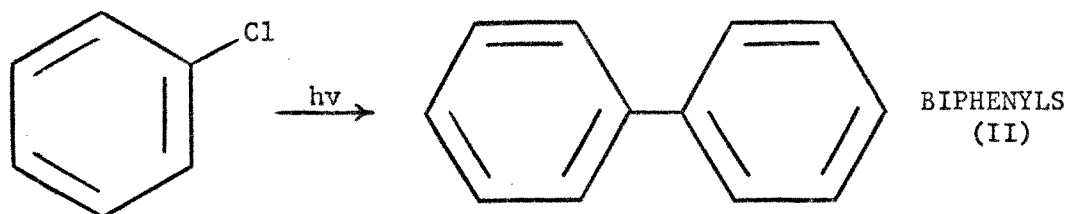
Barltrop, Bunce, and Thomson (3) while studying the photonucleophilic substitution reactions of mono-substituted benzene found that chlorobenzene photopolymerrized readily in the presence of good nucleo-

philes when irradiated at 2800 Å. The Traceable products of this

reaction were benzene, a small amount of white solids of biphenyls (II),

and ortho-, meta-, and para-chlorobiphenyls (III). Similarly, Blair

CHLOROBIPHENYLS
(III)
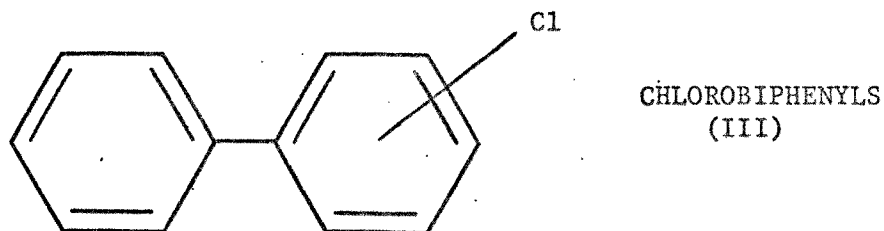
and Bryce-Smith (29) have reported that upon the irradiation of liquid

iodobenzene under nitrogen, benzene, biphenyls, and iodobiphenyls to

be the main products.

These photoproducts presumably arise from the initial photolysis

of monohalogenated benzene to halogen atoms and phenyl radicals.

These radicals may then either abstract hydrogen to give benzene or

substitute ground state monohalogenated benzene to give halogenated

biphenyls. In turn, these may undergo a secondary photolysis giving

rise to biphenyls.

Since phenyl radicals may be important intermediates in our

reactions, the photochemistry of benzene is of great interest to us.

Ward and Wishnok (44) reported that liquid benzene upon irrad-

iation between 2000-1650 Å under nitrogen give only three volatile

products: benzvalene (IV), fulvene (V), and Dewar benzene (VI).

Kaplan and Wilzbach (21) found only benzvalene (IV) formation

for vacuum ultraviolet photolysis at 2537 Å of liquid benzene.
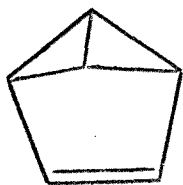
_(IV)
BENZVALENE
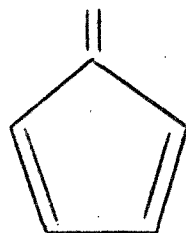
(V)
FULVENE
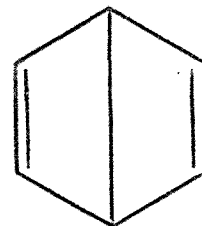
(VI)
DEWAR BENZENE

When benzene was irradiated in the vapor phase, Kaplan and
Wilzbach (19) & (20) reported that in the range of 2000-1650 Å
benzvalene (IV) was present in a small amount.

Wei, Mani, and Pitts (46) showed that the photooxidation of
liquid benzene gace mucondialdehyde (VII) and 2,4,6,8,10 dodecapenta-
enedial (VIII). The irradiation was carried out at 2537 Å.
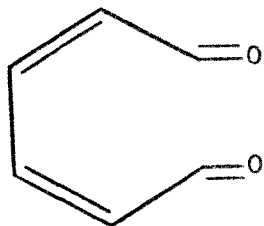
(VII)
MUCONDIALDEHYDE

(VIII)
2, 4, 6, 8, 10 DODECAPENTAENEDIAL

In the presence of water, the photooxidation of benzene was
reported by Farenhorst (14) and then by Luria and Stein (25) to give
2-formyl-4H-pyran (IX) which forms a cyclopentadienyl isomer (X)
upon stabilization. All irradiations were done at a wavelength of
2537 Å.

In order to hypothesize a resonable mechanism for photochemical

(IX)
2-FORMYL-4H-PYRAN

(X)
CYCLOPENTADIENYL ISOMER
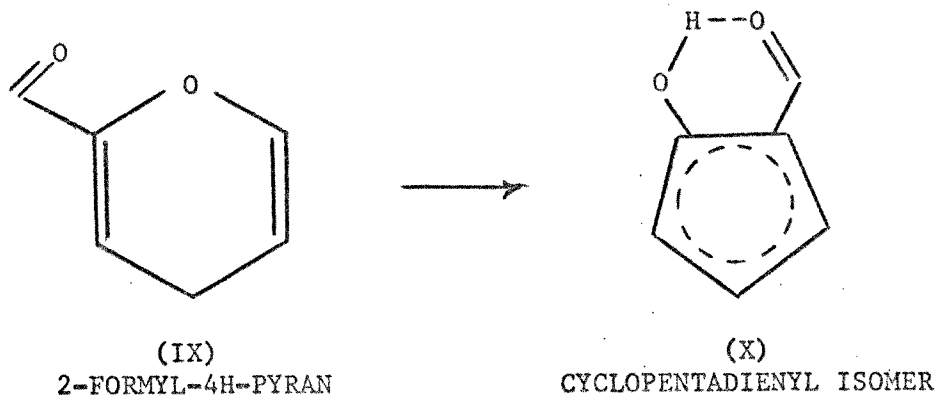
organic reactions, the electronic structure of the excited state must be known. This knowledge provides the organic chemist with an opportunity for studying structure-reactivity relationships. Zimmerman and Sandel (49) have studied the first electronic state LCAO (linear combination of atomic orbitals) molecular orbital distribution of monosubstituted benzene containing electron withdrawing groups and electron donating groups. In the case of the former, $\pi \rightarrow \pi^*$ excitation involved the removal of an electron from a molecular orbital where it can appear meta and was promoted to a non-bonding level in which the electron could not appear meta. In the case of the latter, excitation enhances the meta electron density by removing an electron from a level in which it could not appear meta.

This ortho-meta transmission and withdrawal in the first excited state chemistry is contrasted by the long established ortho-para transmission and withdrawal of ground state chemistry.

Chlorobenzene, being an electron withdrawing group, would exhibit ortho-meta elctron withdrawal. Once the products of the photoreaction are identified, it will be possible to find a mechanical description for experimental reality.

EXPERIMENTAL

I. REAGENTS

The chlorobenzene used was of ACS reagent grade and was used without further purification.

The 1,2 dimethoxyethane used as the internal standard for gas-liquid chromatography was 99+ % pure and needed no further purification.

The water used for the reactions was treated to remove ions by passing tap water through a Barnsted Mixed Resin Red Dot Cartridge. When the resistance of this specially treated water was measured, it was found to be greater than 2.5×10^6 ohms.

The inorganic compounds used as possible photosensitizers in our studies, namely $NaNO_3$, Na_3PO_4, and $Fe_2(SO_4)_3$ were all of ACS reagent quality.

II. EQUIPMENT

The internal irradiation of the solution was accomplished using a high pressure mercury arc lamp (#6515-34 Hanovia 450 watt), protected by a water cooled quartz immersion well.

Figure 4 shows the experimental set-up of equipment.

The reaction vessel was placed in an oil bath whose temperature was temperature was kept constant by using a Bronwill circulating constant temperature unit. The oil used was Fischer paraffin oil.
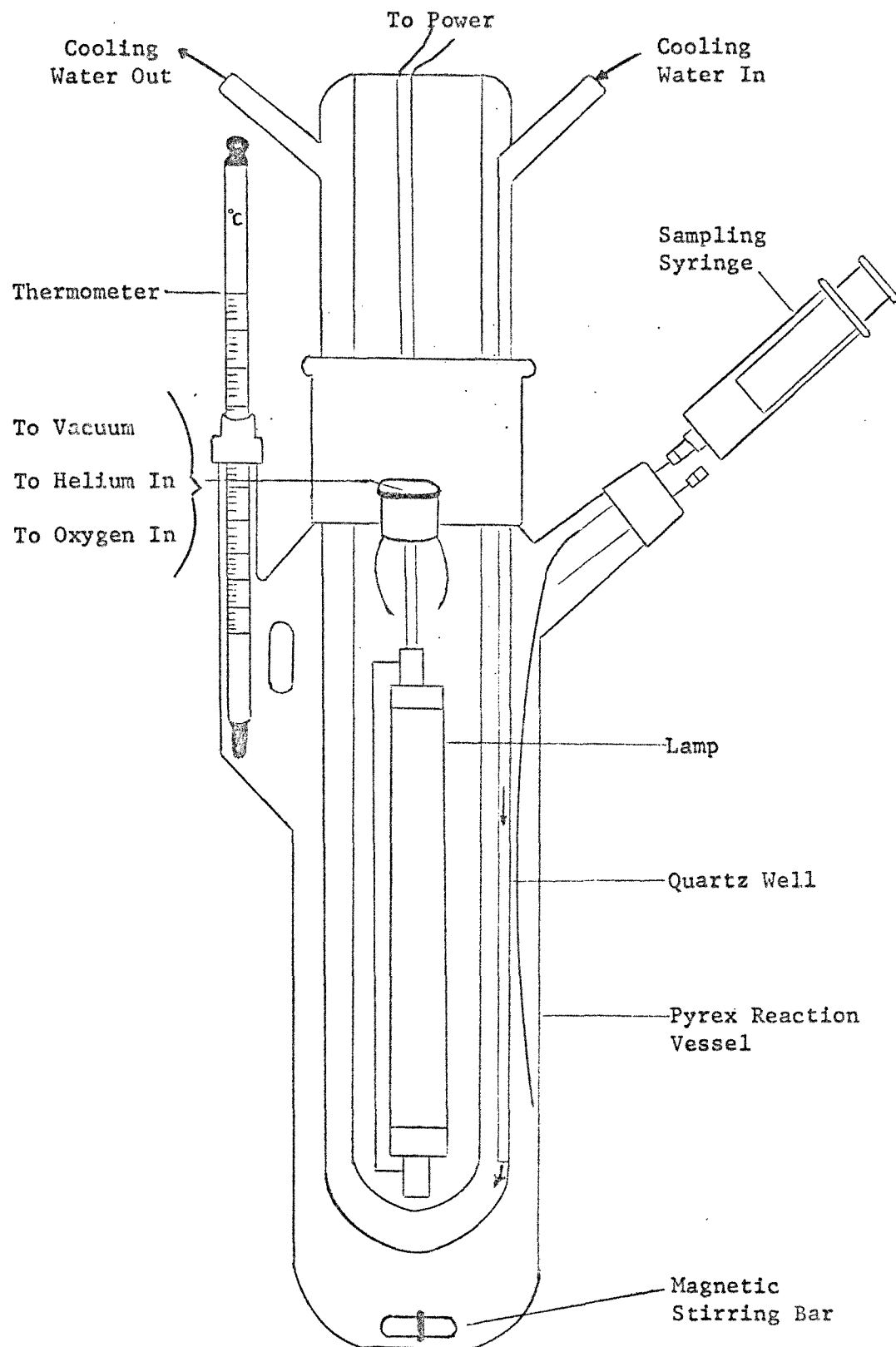
Figure 4- Quartz Immersion Well Photoreactor

Analysis to obtain kinetic data was done on a F&M Model 810 GLC equipped with dual flame detectors. Various length columns (2, 4, and 6 feet) 1/8 of an inch in diameter were made of stainless steel and packed with 60/80 mesh Porapak QS. An oven temperature of 205°C was found to give good peak separation.

A Beckman DB-G UV-Visible Spectrophotometer was used to obtain ultraviolet spectra of chlorobenzene and the inorganic compounds in water.

III. PROCEDURE

Approximately 0.2 grams of chlorobenzene and 0.15 grams of standard were carefully weighed out and dissolved in 750 ml of either specially treated water (vide supra), or a solution containing a specific amount of the inorganic compound of interest in treated water, depending on whatever system was being investigated. Of this 750 ml of solution, 600 ml was placed in the reaction vessel and the vessel was immersed in an oil bath at 29°C. The system was then evacuated with a water aspirator and flushed with either helium or oxygen, depending again on the system being studied. The procedure of alternately evacuating and then flushing was done four times while stirring.

Depending upon the reaction, either a steel mesh screen, or a pyrex filter was placed between the light source and the reaction solution. The steel mesh screen was used to decrease the intensity of the light by allowing only 26.9% transmission.* This was done so

*The value is from specifications of the Newark Wire Cloth Company, the manufacturer.

that the reaction would be slowed down sufficiently to obtain useful

data. The pyrex filter was used to cut out incident light below 2800 Å.

Figure 5 shows the per cent of light transmitted by the pyrex

filter at different wavelengths.

A 5 cc. sample of solution was taken and the mercury lamp was turned

on along with the cooling water. Then, between four and five samples

were taken at selected intervals, the time of these intervals again

depending on the system under investigation. The samples were removed

by means of a 5 cc. syringe and a teflon sampling tube. After sam-

ples had been taken, the solution was subjected to irradiation for the

remainder of a two hour period.

A 25 ul. aliquot of each sample was analysed by GLC. The cut

and weigh method was used to measure the areas of the GLC peaks. The

area ratios were calculated by dividing the area of chlorobenzene

peaks by the areas of the standard peaks. A plot was made of AR/AR_o

versus time, where AR is the area ratio at any time, and AR_o is the

area ratio at t=0. The rate constant could then be calculated since

it can be shown that AR/AR_o equals C/C_o.

Upon irradiation of chlorobenzene in a 0.1M $NaNO_3$ solution using

a pyrex filter, it was found that the standard began to disappear.

The standard was not added in subsequent reactions, and the rate

constant was calculated by just using the chlorobenzene peaks.
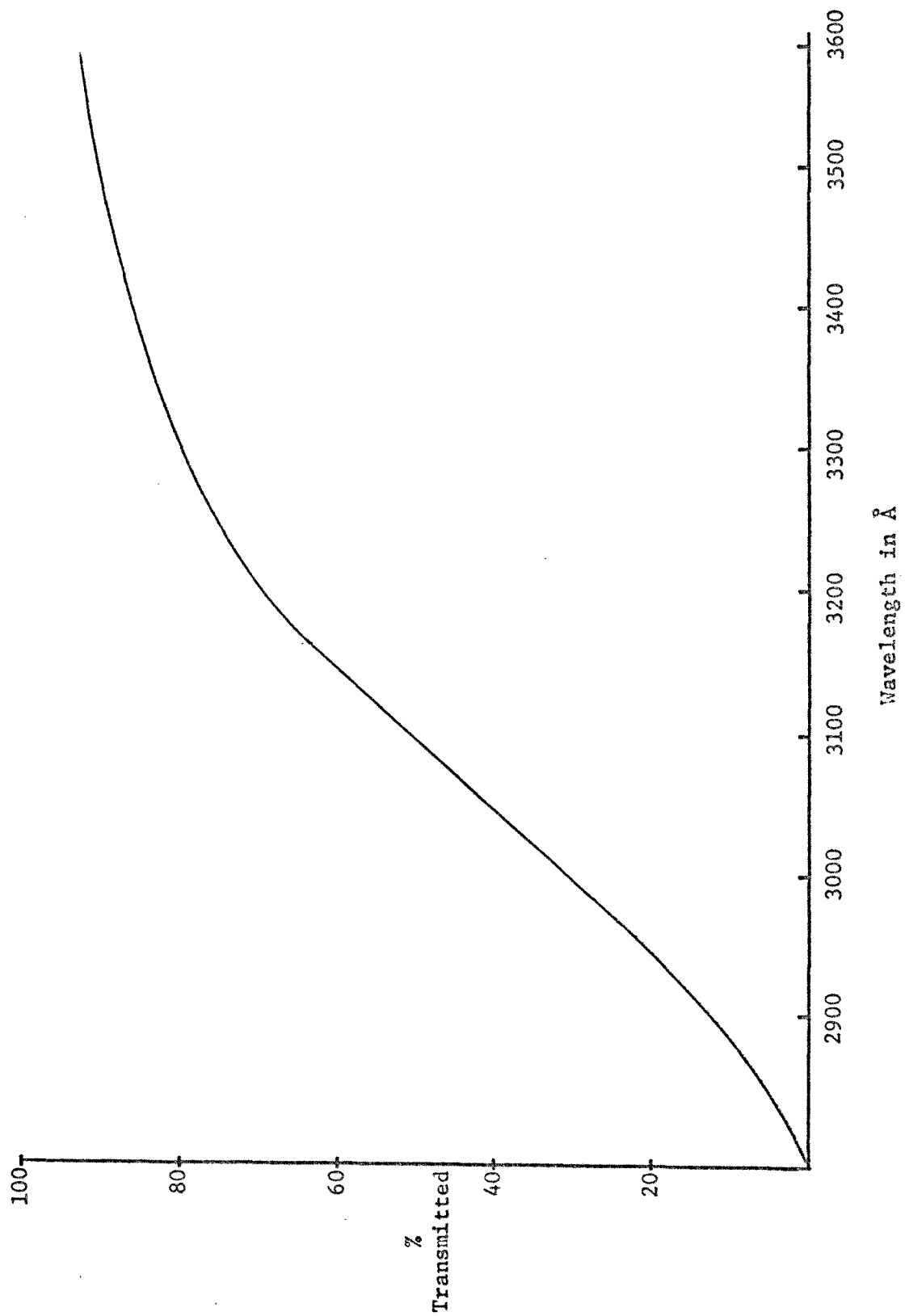
Figure 5- Per Cent of Light Transmitted by a Pyrex Filter vs. Wavelength

<u>RESULTS</u>

Kinetic data was obtained for the photoreaction of chlorobenzene in seven different systems. The rate constants were found for each system by taking the negative slope of a first order plot of log C/C_o versus time. These plots are shown in Figures 6-12. The data used to make these plots may be found in Tables 5-11.

The rate constant for the helium-water system using screen A was found to be 0.0319 min.$^{-1}$. Corresponding data and a first order plot can be found in Table 5 and Figure 6 respectively. The rate decreased to 0.0224 min.$^{-1}$ when oxygen was substituted for helium (refer to Figure 7 and Table 6). When chlorobenzene was photolysed in a $0.1M$ $NaNO_3$ solution under helium with screen A, the rate was found to decrease to 0.0193 min.$^{-1}$ (see Figure 8 and Table 7). Two other inorganic solutions of chlorobenzene were also irradiated under helium with screen A. When $0.00328M$ $Fe_2(SO_4)_3$ was irradiated, a rate of 0.044 min.$^{-1}$ was found (refer to Figure 10 and Table 9). Finally, when a $0.01M$ Na_3PO_4 solution of chlorobenzene was irradiated, the rate was found to be 0.0225 (see Figure 12 and Table 11).

A ferric sulfate-helium system and a sodium sulfate-helium system were also irradiated using a pyrex filter in place of screen A. The $0.1M$ $NaNO_3$-helium system gave a rate of 0.0046 min.$^{-1}$ (refer to Figure 9 and Table 8). The rate for the $0.00328M$ $Fe_2(SO_4)_3$-helium system was found to be 0.0255 min.$^{-1}$ (see Figure 11 and Table 10).

A comprehensive list of these rates can be found in Table 2.
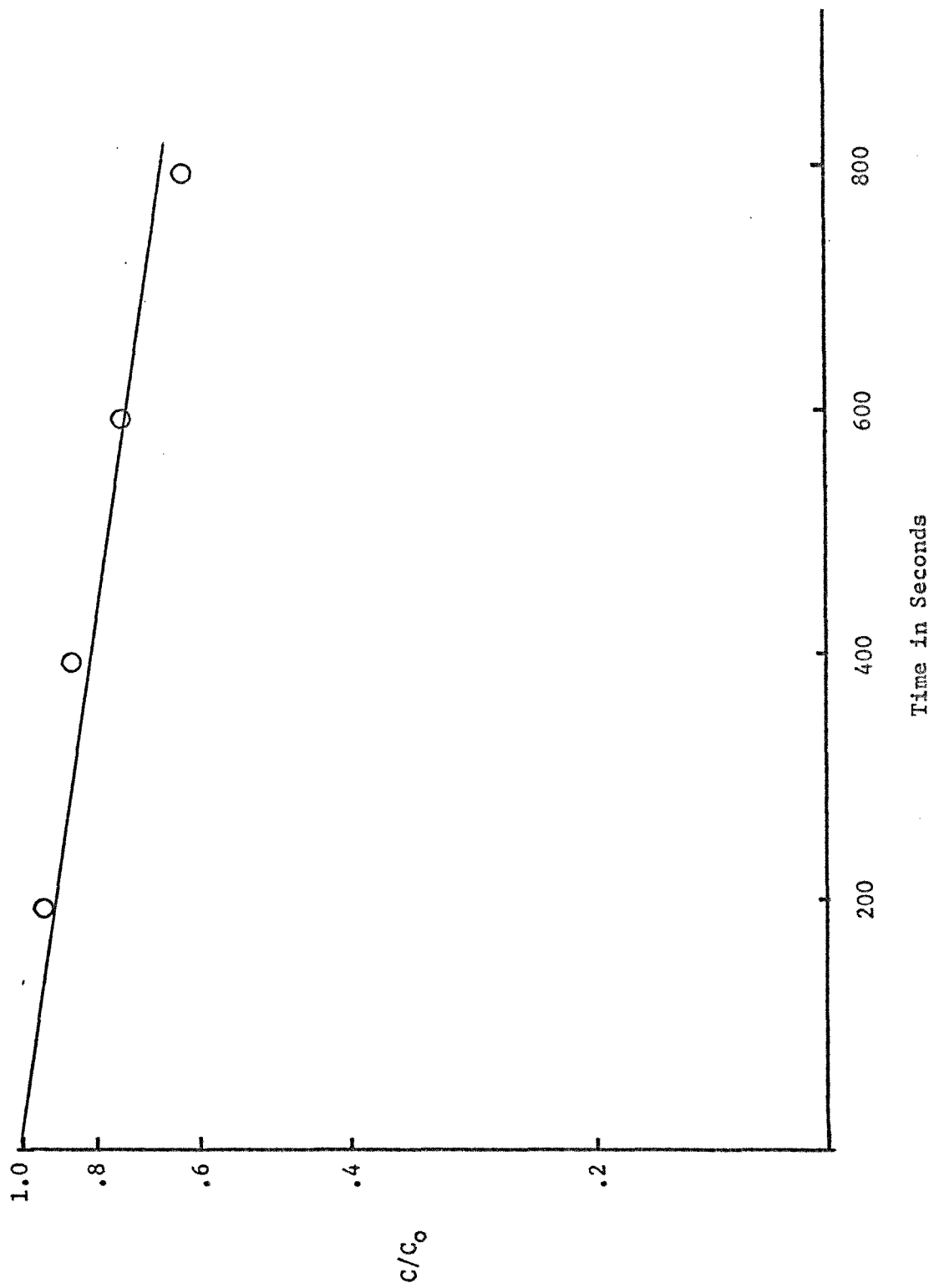
Figure 6- Photolysis of Chlorobenzene in Water Under Helium
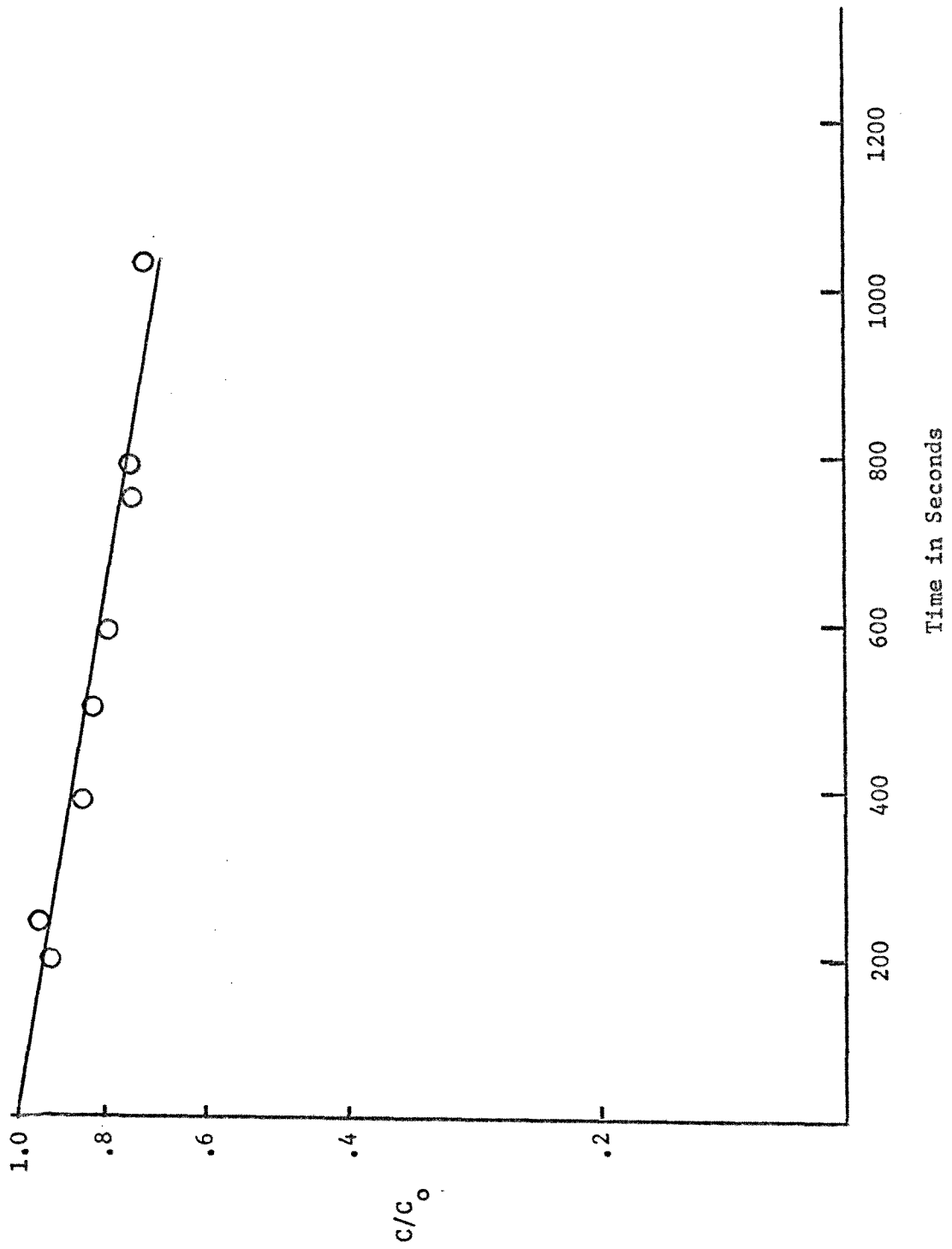
Figure 7- Photolysis of Chlorobenzene in Water Under Oxygen
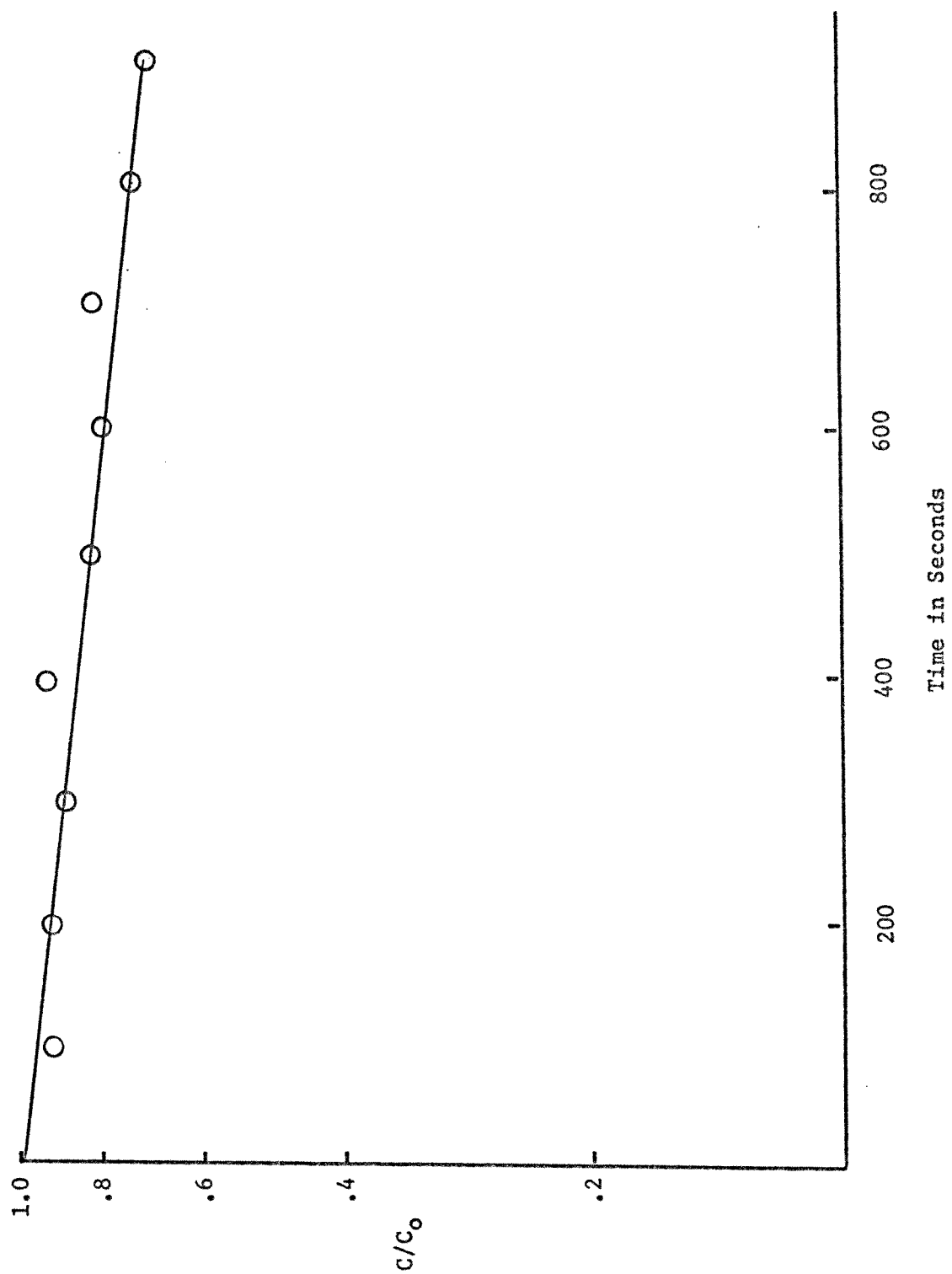
Figure 8- Photolysis of Chlorobenzene in 0.1M NaNO₃ Under Helium
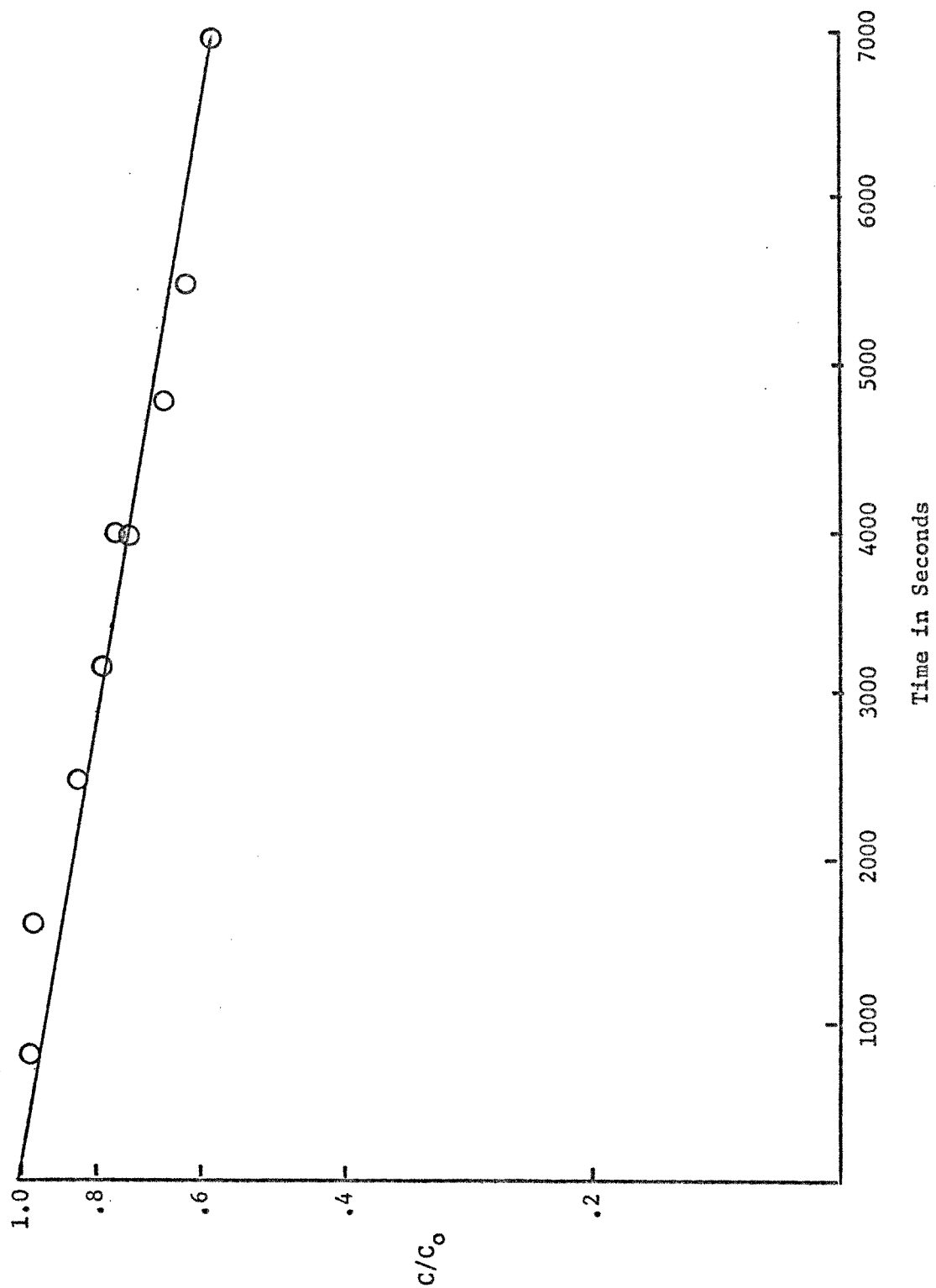
Figure 9- Photolysis of Chlorobenzene in 0.1M NaNO$_3$ Under Helium With a Pyrex Filter
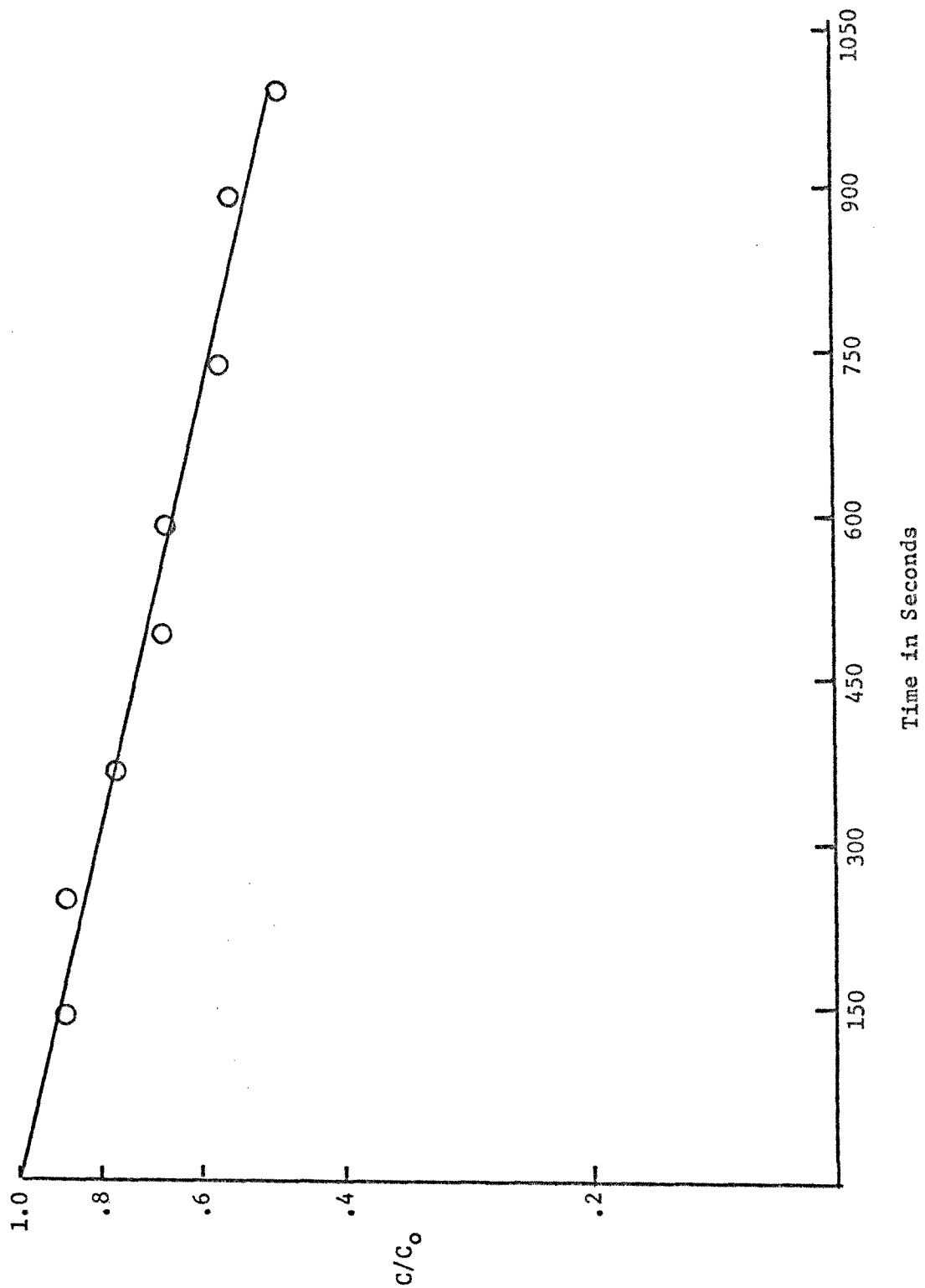
Figure 10- Photolysis of Chlorobenzene in 0.00328M $Fe_2(SO_4)_3$ Under Helium
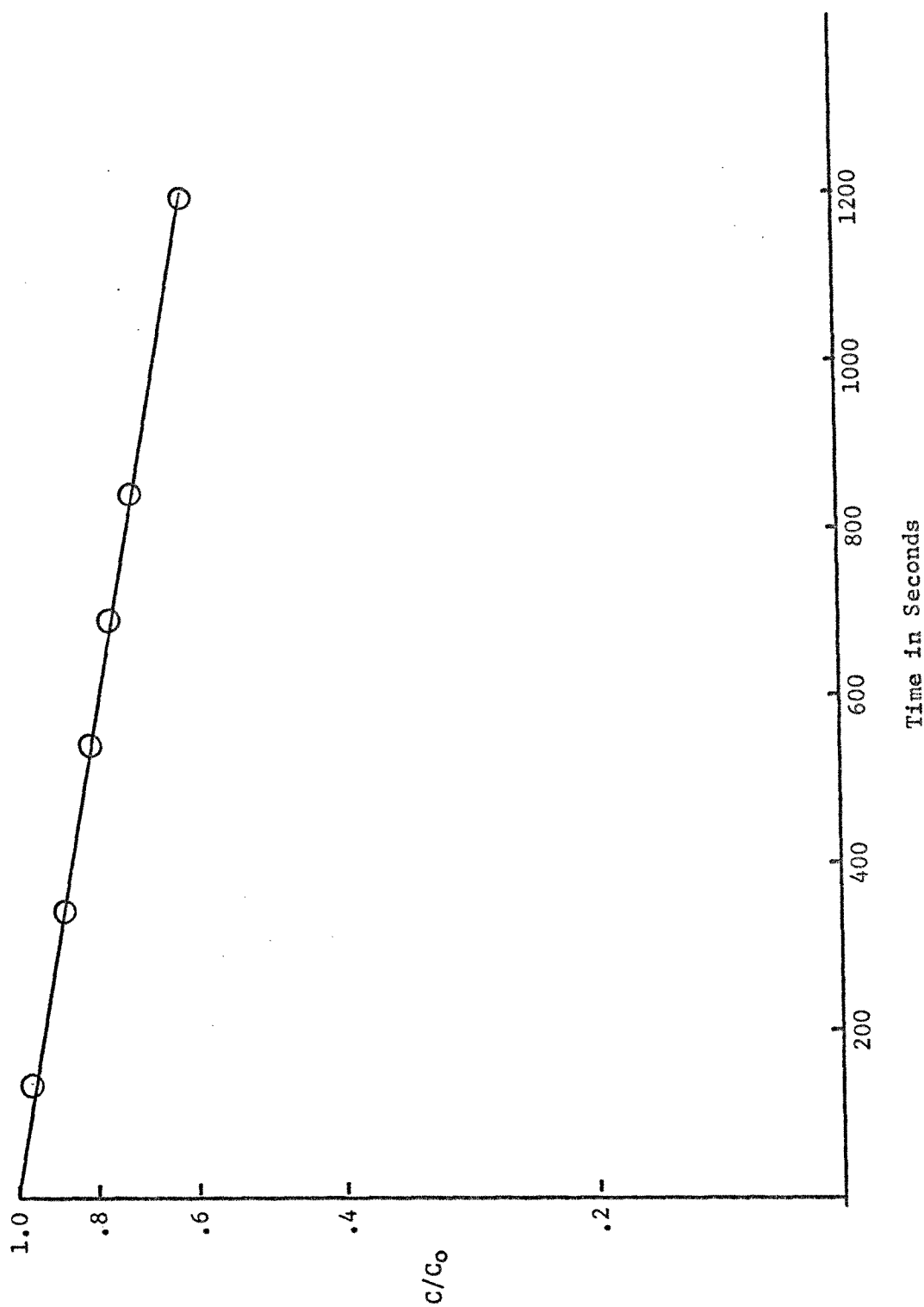
Figure 11- Photolysis of Chlorobenzene in 0.00328M $Fe_2(SO_4)_3$ Under Helium with a Pyrex Filter
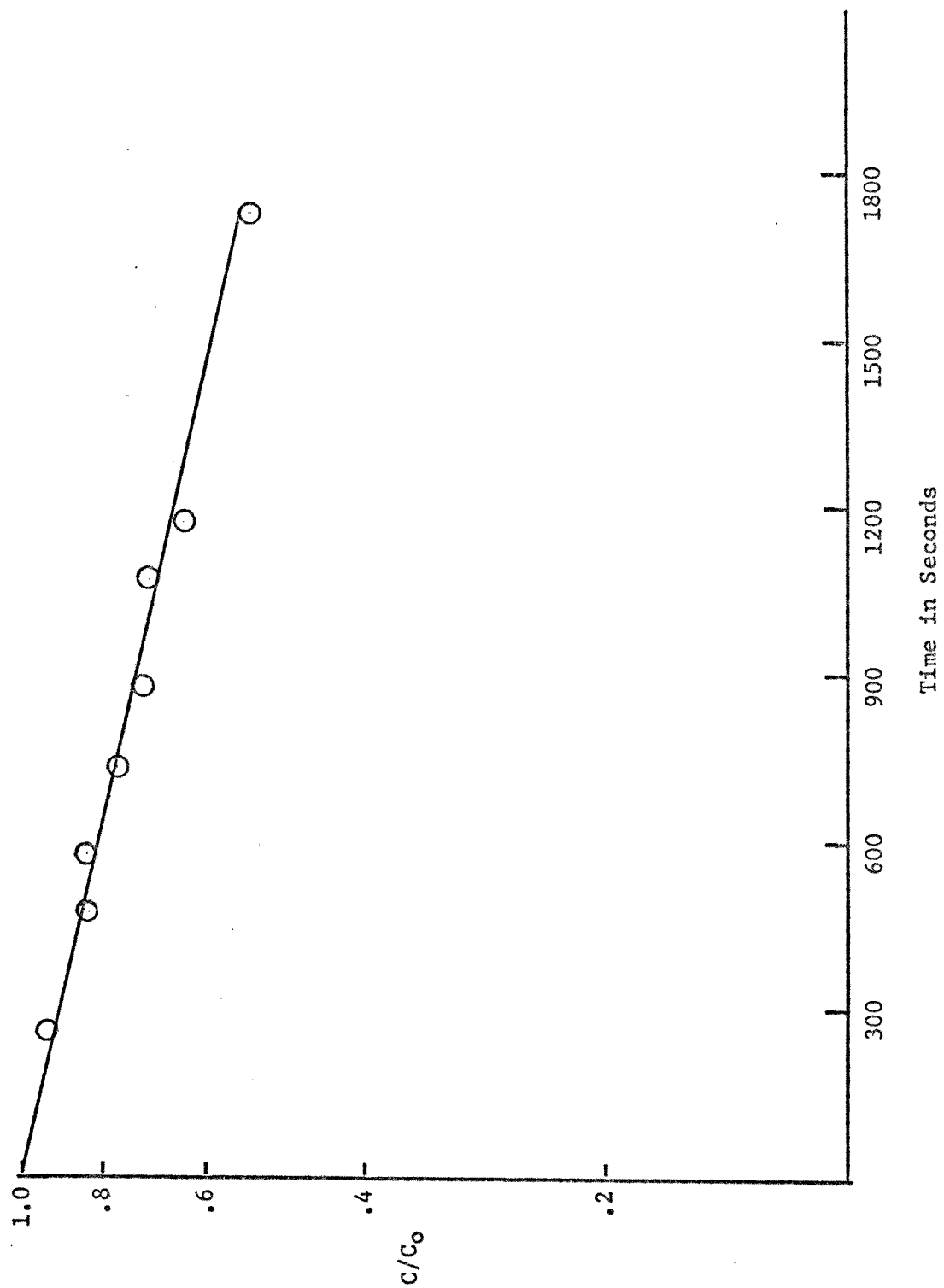
Figure 12- Photolysis of Chlorobenzene in 0.01M Na₃PO₄ Under Helium

TABLE 2

Rate Constants of the Photolysis of Chlorobenzene

Atmosphere	Solution	Filter	K (min.$^{-1}$)
Helium	Water	Screen A	0.0319
Oxygen	Water	Screen A	0.0224
Helium	0.1M $NaNO_3$	Screen A	0.0193
Helium	0.1M $NaNO_3$	Pyrex	0.0046
Helium	0.00328M $Fe_2(SO_4)_3$	Screen A	0.0440
Helium	0.00328M $Fe_2(SO_4)_3$	Pyrex	0.0255
Helium	0.01M Na_3PO_4	Screen A	0.0225

Visible insoluable material was present after the solutions in all seven systems were irradiated.

DISCUSSION

Chlorobenzene has been shown to react at different rates when ir-
radiated in different systems. To see what effect the system had on
the reaction rate, it was necessary to establish a basic model system
and then study the effect on the rate of various added parameters.
Our aim in choosing the parameters was to achieve a reaction system
which best approximates conditions existing in the environment. Our
basic system consisted of chlorobenzene dissolved in specially treated
water (vide supra). Photoreaction of this basic system was conducted
under an inert atmosphere of helium so as to preclude the influence
of oxygen. In order to more conviently discuss reactions run under
comparable conditions, a listing of relative rates is presented in
Table 3.

The mechanisms of our reactions were assumed to be dependent on
the collision of the molecule and a quantum of energy. Because the
radiation source emits a constant supply of energy, from theory it
follows that the rate of degradation is proportional to the amount
of compound present, and that the reaction should follow first order
kinetics (40).

The relationship between fraction remaining and time is give by:

$$C/C_o = e^{-K(TIME)}$$

where K is the rate constant, C_o is the concentration of reactant
initially, and C is the concentration of the reactant at any time.

TABLE 3

Relative Rate Constants of the Photolysis of Chlorobenzene

Atmosphere	Solution	Filter	Relative Rate
Helium	Water	Screen A	1.000
Oxygen	Water	Screen A	0.702
Helium	0.1M NaNO$_3$	Screen A	0.605
Helium	0.00328M Fe$_2$(SO$_4$)$_3$	Screen A	1.380
Helium	0.01M Na$_3$PO$_4$	Screen A	0.706

It was found that upon the introduction of oxygen into the reaction, a rate decrease of 29.8% was exhibited. This quenching effect by oxygen has been reported by Leonard and Hammond (43). Oxygen, being a ground state triplet, can quench triplets to So*, a vibrationally excited ground state, by a spin allowed pseudo-annihilation process. Oxygen can also enhance intersystem crossing by magnetic intereaction by serving as a paramagnetic impurity. Therefore, because oxygen does effectively quench excited triplet states, the rate decrease when oxygen was present is strongly suggestive of a triplet intermediate.

When the photolysis of chlorobenzene in a 0.1M NaNO$_3$ solution under helium employing screen A was performed, a rate decrease of 39.5% was observed. The decrease was similar to the decrease described when oxygen was introduced into the system. To explain this rate decrease, one must examine the photochemistry of NaNO$_3$ in an aqueous solution along with its ultraviolet spectrum (see Figure 14). Daniels, Meyers, and Belardo (11) reported that upon irradiation of NO$_3^-$ at 3000 Å, oxygen was one of the photoproducts. Therefore, the oxygen quenching effect would partially explain the rate decrease. From the ultraviolet spectra of 0.1M NaNO$_3$ and chlorobenzene (see Figures 14 and 13 respectively), one can see that there would be a competition for the light since each absorbed at the same wavelength. This competition would also explain the rate decrease since there would be less energy available for the photoreaction.

In the case of the 0.01M Na$_3$PO$_4$ solution which was irradiated
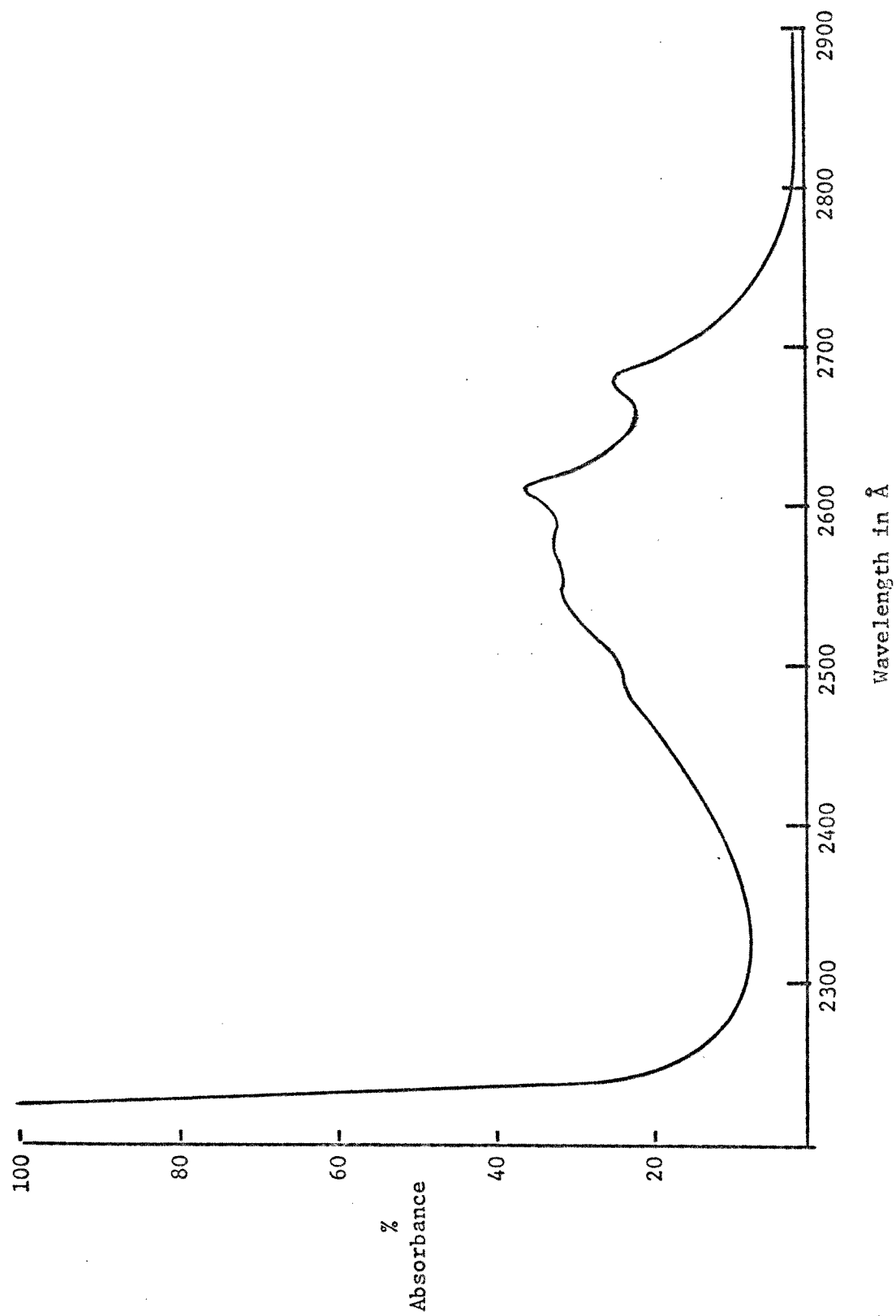
Figure 13— Ultraviolet Spectrum of 300 mg./l. of Chlorobenzene in Water
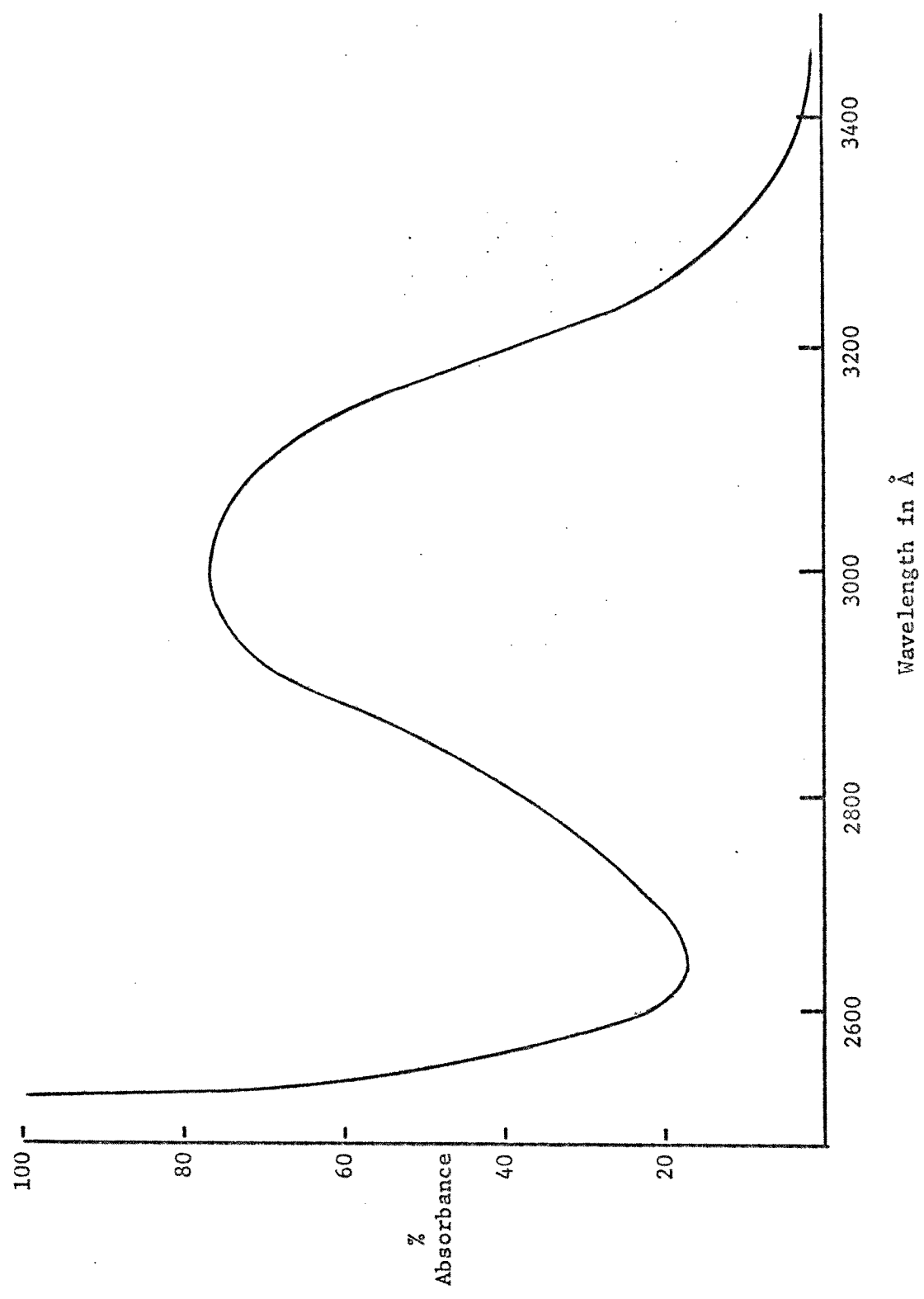
Figure 14- Ultraviolet Spectrum of 0.1M NaNO₃
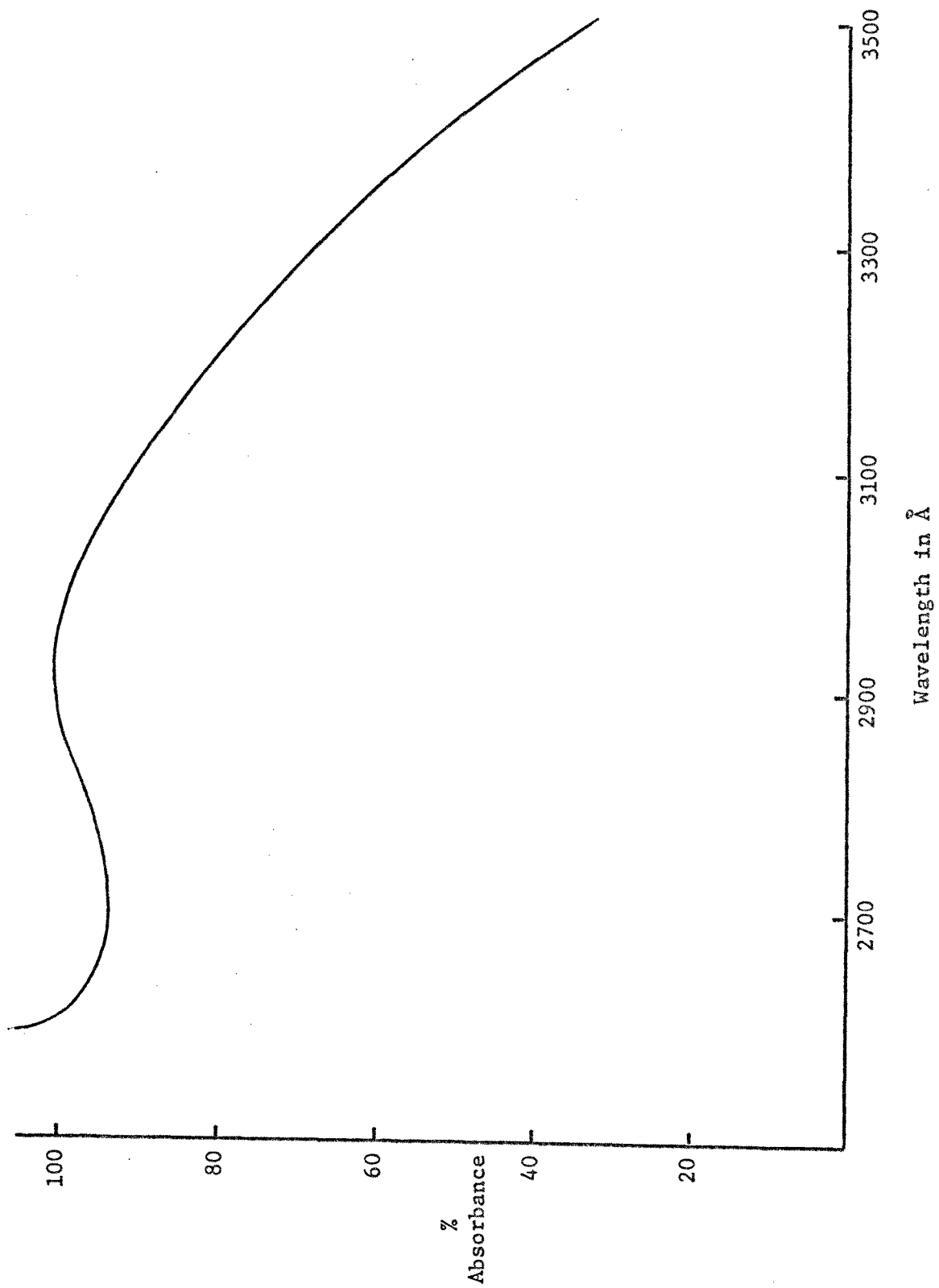
Figure 15- Ultraviolet Spectrum of 0.00328M $Fe_2(SO_4)_3$
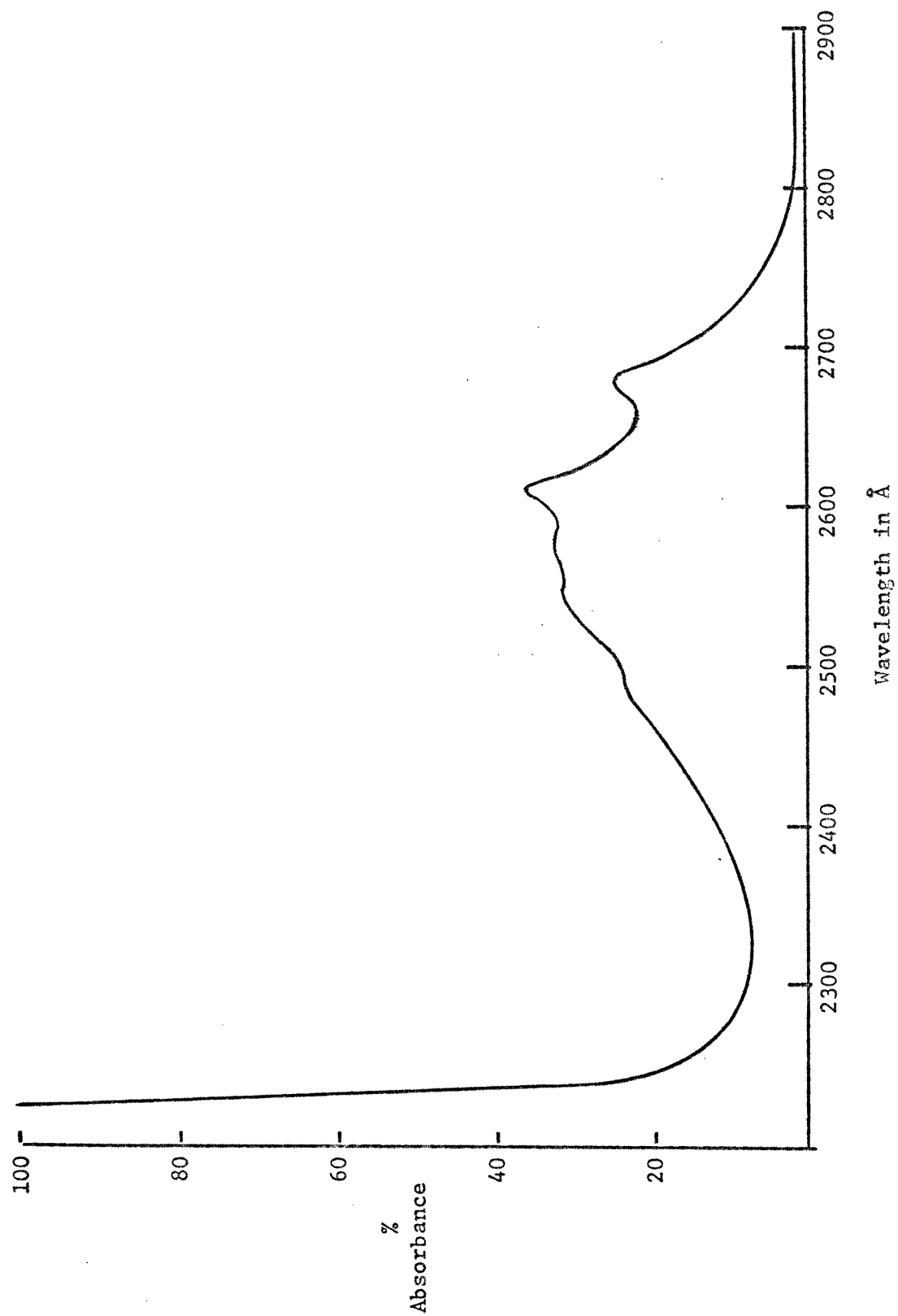
Figure 13- Ultraviolet Spectrum of 300 mg./l. of Chlorobenzene in Water

under helium using screen A, a rate decrease of 29.4% from the basic model system was observed. To explain this decrease in the rate, it is necessary to again look at the ultraviolet spectrum of the compound (see Figure 16). As in the case of the 0.1M $NaNO_3$, both chlorobenzene and Na_3PO_4 absorb light in the same region. Therefore, a portion of the energy used to photo-excite chlorobenzene could be absorbed by the 0.01M Na_3PO_4 solution resulting in an apparent rate decrease. It has been reported that there is no photoreaction of PO_4^- in an aqueous solution when irradiated at 1850 Å (43).

A 0.00328M $Fe_2(SO_4)_3$ solution of chlorobenzene was also irradiated under helium using screen A. This reaction gave the only rate which was greater than that of the basic system. As was the case with the phosphate ion, the sulfate ion does not photoreact when irradiated at 1850 Å in an aqueous solution (43). However, the absence of oxygen does not explain the 38% rate increase. A possible explanation may be the role photosensitization plays in transferring energy to the chlorobenzene. Therefore, the reaction was rerun and a pyrex filter was substituted for screen A to see if photosensitization took place.

For the photoreaction in which the pyrex filter was used, it was important to find inorganic compounds which would absorb light above 2800 Å. From the ultraviolet spectrum of chlorobenzene, one can see that it does not absorb light above 2800 Å. Therefore, since all light below 2800 Å is cut off by the pyrex filter, any energy trans-

ferred to the chlorobenzene is solely through photosensitization.
From the ultraviolet spectra of 0.00328M $Fe_2(SO_4)_3$, 0.1M $NaNO_3$, and
0.01M Na_3PO_4 (see Figures 14,15, and 16), only the ferric sulfate
and sodium nitrate solutions absorb light above 2800 Å.

It was found that when a 0.1M $NaNO_3$ solution was irradiated
under an atmosphere of helium with a pyrex filter, the chlorobenzene
photoreacted. A blank reaction was run so as to insure that the only
way to explain this photoreaction was by a photosensitized reaction.
Chlorobenzene also was found to photoreact in a 0.00328M $Fe_2(SO_4)_3$
solution which would indicate a photosensitized reaction.

Blanks were run to insure photoreactions for the pyrex filtered
systems were due to photosensitization. This was done by running the
reaction without an inorganic present. An oxygen blank was also
performed to insure that there was no reaction of chlorobenzene or
standard with oxygen when the light was off.

Water which absorbs below 2000 Å would not be expected to decom-
pose to ozone and hydrogen peroxide which might effect the reactions
since the mercury arc lamp only emits a significant amount of light
above 2200 Å (see Table 4).

TABLE 4

Spectral Energy Distribution

Hanovia 6515-34 High Pressure Quartz Mercury Vapor Lamp

Lamp Watts	450
Lamp Volts	135
Current	3.6
Arc Length	4.5"

Wavelength (Å)	Radiated Energy (watts)
13673	2.60
11287	3.30
10140	10.5
5780	20.0
5461	24.5
4358	20.2
4045	11.0
3660	25.6
3341	2.40
2652	4.00
2571	1.50
2537	5.80
2482	2.30
2400	1.90
2380	2.30

TABLE 4 (cont'd)

Wavelength (Å)	Radiated Energy (watts)
2360	2.3
2320	1.5
2224	3.5
Total Watts	175.8

CONCLUSION

Chlorobenzene has been found to photoreact when irradiated by a mercury arc lamp at different rates depending upon the presence of certain parameters. The parameters were chosen to best approximate conditions existing in the environment. Oxygen was found to decrease the reaction rate. Sodium nitrate and sodium phosphate also decrease the rate, while ferric sulfate, on the other hand, enhanced the rate. Sodium nitrate and ferric sulfate were also found to act as photosensitizers.

Visible insoluable materials were found to form upon photolysis which would lead one to consider the possibility of having photolysis as a tertiary treatment process.

FUTURE WORK

Now that the kinetics have been established for the systems chosen, and we have found that photosensitization takes place in certain systems, future work would include the identification of photoproducts and an investigation into the mechanisms of these reactions. Ultimately, using sunlight as the energy source and having all parameters present, it might be possible to relate our findings in the lab to what actually happens in the waterways. This may be done by identifying the photoproducts and by using our knowledge of the mechanisms, we can then postulate possible intereactions

APPENDIX

Complete kinetic data of the aqueous photolysis of chlorobenzene.

TABLE 5

Kinetic Data of the Photolysis of Chlorobenzene

Helium-Water System with Screen A

Temperature (°C)

28.7		28.9	
t (sec)	C/C_0	t (sec)	C/C_0
0	1.000	0	1.000
200	0.952	200	0.917
400	0.840	400	0.849
600	0.744	600	0.726
800	0.591	800	0.617

TABLE 6

Kinetic Data of the Photolysis of Chlorobenzene

Oxygen-Water System with Screen A

Temperature (°C)

28.9			28.7	
t (sec)	C/C_0		t (sec)	C/C_0
0	1.000		0	1.000
200	0.927		250	0.951
400	0.839		510	0.802
600	0.784		760	0.730
800	0.734		1040	0.718

TABLE 7

Kinetic Data of the Photolysis of Chlorobenzene

Helium-0.1M NaNO$_3$ System with Screen A

Temperature (°C)

28.5		28.7	
t (sec)	C/C$_o$	t (sec)	C/C$_o$
0	1.000	0	1.000
200	0.946	100	0.956
400	0.893	300	0.911
600	0.827	500	0.842
800	0.753	700	0.815
		900	0.744

TABLE 8

Kinetic Data of the Photolysis of Chlorobenzene

Helium-0.1M NaNO₃ System with the Pyrex Filter

Temperature (°C)

	29.6			28.8	
t (sec)	C/C_0		t (sec)	C/C_0	
0	1.000		0	1.000	
2500	0.847		800	0.988	
4000	0.754		1600	0.959	
5500	0.615		3200	0.794	
7000	0.575		4000	0.728	
			4800	0.658	

TABLE 9

Kinetic Data of the Photolysis of Chlorobenzene

Helium-0.00328M $Fe_2(SO_4)_3$ System with Screen A

Temperature (°C)

26.3		26.8	
t (sec)	C/C_0	t (sec)	C/C_0
0	1.000	0	1.000
375	0.759	100	0.885
505	0.656	300	0.839
750	0.556	600	0.654
1000	0.469	900	0.539

TABLE 10

Kinetic Data of the Photolysis of Chlorobenzene

Helium-0.00328M $Fe_2(SO_4)_3$ System with the Pyrex Filter

Temperature (°C)

	27.6		27.4
t (sec)	C/C_o	t (sec)	C/C_o
0	1.000	0	1.000
200	0.917	150	0.949
350	0.863	350	0.854
700	0.750	550	0.792
1200	0.604	850	0.701

TABLE 11

Kinetic Data of the Photolysis of Chlorobenzene

Helium-0.01M Na_3PO_4 System with Screen A

Temperature (°C)

26.9		27.0	
t (sec)	C/C_0	t (sec)	C/C_0
0	1.000	0	1.000
250	0.988	300	0.922
500	0.826	600	0.817
750	0.756	900	0.700
1000	0.692	1200	0.633
1750	0.518		

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