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THE FATE OF HAZARDOUS POLLUTING SUBSTANCES
IN AN AQUEOUS ENVIRONMENT

BY

ROBERT PAUL CASANI

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

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AT

NEWARK COLLEGE OF ENGINEERING

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1972

ABSTRACT

The fate of Hazardous Polluting Substances (HPS) in an aqueous environment has been investigated using ultraviolet light. Chlorobenzene, *o*-cresol and nitrobenzene were used as model HPS for this study. The kinetics were followed and good first order plots were obtained for all compounds. The temperature of the reaction was shown to effect the rate. Solid insoluble and soluble non-volatile products were formed in the photolytic reaction of the three model systems.

APPROVAL OF THESIS
THE FATE OF HAZARDOUS POLLUTING SUBSTANCES
IN AN AQUEOUS ENVIRONMENT
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DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY
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BY
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APPROVED: _____

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INTRODUCTION

I. Hazardous Polluting Substances:

Hazardous Polluting Substances (HPS) have been defined in the United States by the Department of Transportation (8) as "those materials that reach the aquatic system as a result of the...deliberate or accidental discharge of any materials 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."

The growth in the production and use of synthetic organic and inorganic chemicals in the last decade has produced a unique pollution problem. Effluent from the chemical industries has increased to environmentally significant quantities the amount of these chemicals in natural waters. Previously, the chemical industry has not given much attention to the make up of their discharges and the effect of these discharges on the environment. This is particularly true of industries whose discharges contain quantities of so-called insoluble chemicals. Although pretreatment of the discharges (i.e. usually by means of phase separators) removes most of these chemicals, quantities in the parts-per-million (ppm) are still present and are discharged into the receiving waters. While the toxic effect of the chemicals may be minimal, the products of their interaction with the environment may not.

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Investigations into the control and treatment of water has "led to the realization that the multiple chemical and biological species present in the aquatic environment interact with pollutants in complex manners. Determination of the ultimate results of these interactions is the only feasible way in which predictions can be made as to the effect the pollutant will have on the aquatic environment, and the fate of the pollutant once spilled...environmental testing will rely heavily on a thorough understanding of probable physical, chemical, and biological interactions so that the proper system parameters can be designed into the testing program. Unfortunately, the required information cannot readily be obtained from mathematical formulations or theoretical hypothesis. Rather it must come as the result of direct investigation into the intricate relationship between chemical and biological processes in the aquatic environment."(7) Also, any investigation must treat the subject "systematically and comprehensively if any useful information is to be obtained."(32)

Figure 1 shows the interactions of pollutants with the aquatic environment(7).

II. Current Research on Photochemical Treatment:

In this investigation we studied the ultraviolet light induced "chemical transformations" of selected organic chemicals in an aqueous environment. Previous research on the application of photomodification of organic compounds in aqueous media has been limited.

Schorr, et al(34) and Smith(36) used ultraviolet light as a

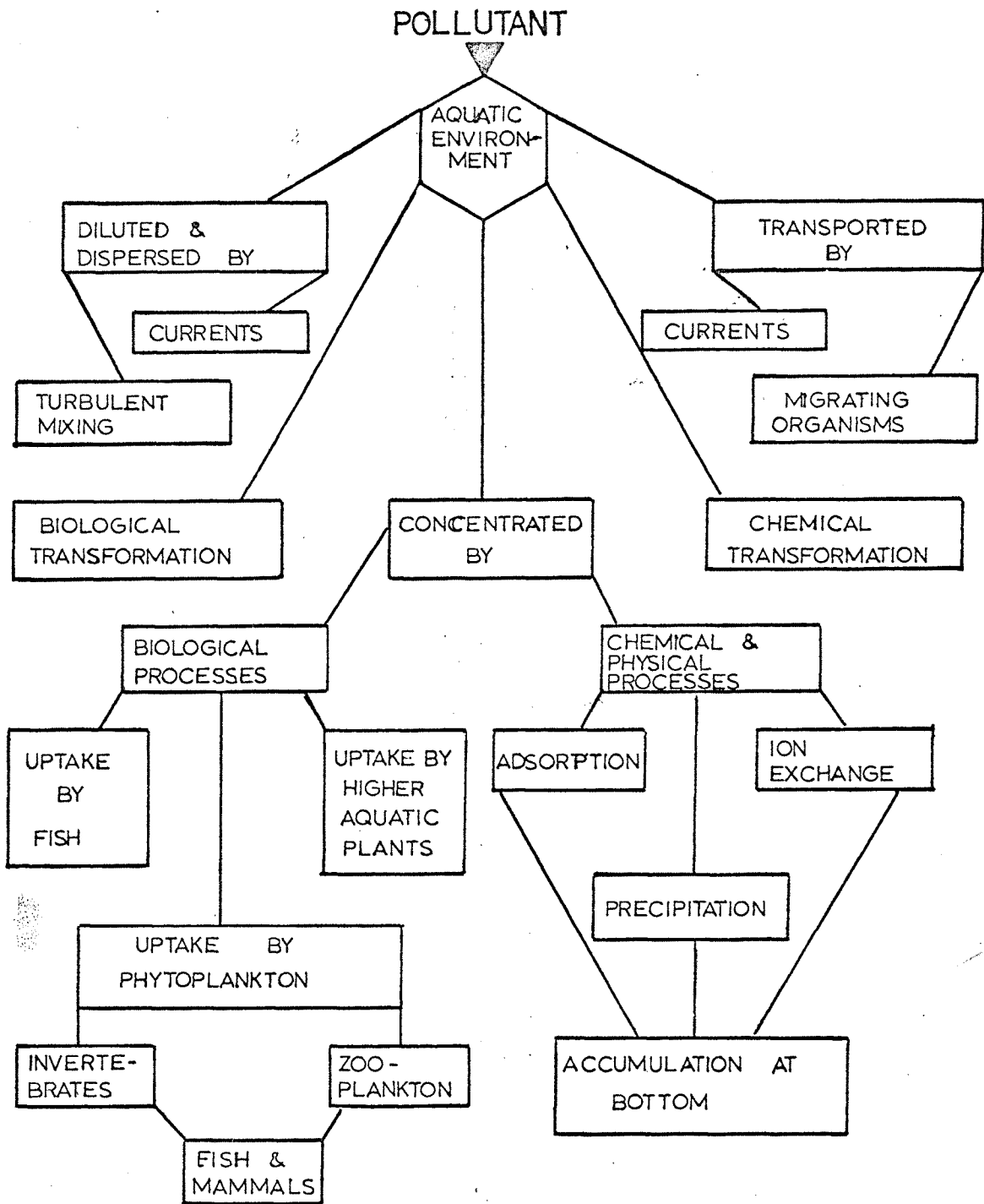


FIGURE 1
THE FATE OF POLLUTANTS IN THE AQUATIC ENVIRONMENT(7)

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tertiary treatment for secondary effluent of municipal wastewater treatment facilities. Schorr and his coworkers(34) found that the rate of reaction was first order in light radiation absorbed. They also studied the effect of oxygen on the rate expression. At low oxygen concentrations the rate was proportional to the oxygen concentration and at high concentrations the rate was independent of oxygen concentration. Smith(36) in his research found that the reaction rate was independent of the concentration of pollutants. He postulated that this was due to the partially oxidized state of the pollutants in secondary effluent.

The use of chlorine as a photosensitizer in the degradation of municipal wastewater has been studied by Hancil and Smith(10) and Meiners(25). The addition of chlorine was shown by Hancil and Smith(10) to increase the rate by one order of magnitude. They also found that, as with oxygen, the rate was proportional to the concentration of chlorine at low chlorine concentrations and independent of concentration at high chlorine concentrations. It was noted that the effect of the chlorine was independent of the oxygen concentration. Meiners(25) in his work on highly nitrified effluents from biological treatment plants also found a significant increase in the rate of degradation with the addition of chlorine. The optimum pH for the reactions was determined to be between 5.0-6.5.

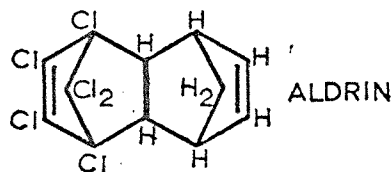
The effect of chlorine on the photooxidation of starch was also studied by Meiners(24). It was shown that the reaction is both pH and temperature dependent. The rate was found to triple with a pH

change from 0.5 to 4.0 (at 0°C) and to decrease with a change in temperature from 0°C to 25°C at both a pH of 0.5 and 4.0.

The rate of removal of dodecyl benzene sulfonates(IBM) from an aqueous solution by ultraviolet light was shown by Smith(36) to be proportional to the DBS concentration to the $\frac{1}{2}$ power and the intensity to the $\frac{1}{2}$ power. This result yielded a rate too low to be of practical use and he reports that the addition of ferric perchlorate increases the rate by two orders of magnitude. The addition of the ferric perchlorate complicates the rate expression to such an extent so as to reduce the study to empiricism. Smith concluded that the effective oxygen concentration is less than the concentration of oxygen in air at saturation.

The use of ultraviolet light to modify lignins and lignin sulfonates has been studied and it has been shown by Klein(17) that these products of the pulp and paper industry could be made more acceptable for conventional biological treatment. He found that light of wavelength 180-210nm, in the presence of oxygen, effectively modified lignins and lignin sulfonates so that they could be attacked by conventional organisms.

Bulla(3), and Bulla and Edgerly(4) showed that the persistent pesticide aldrin (below) can be removed from receiving waters with ultra violet light.



Although they found that the removal of aldrin could be accomplished photochemically, the products of the reaction were equal in toxicity to the reactant. The kinetics of the reaction were first order and independent of temperature over the range 20-40°C. Plimmer, et al (28) reported similar results for DDT and DDE.

Meallier(23) studied the effect of light intensity, temperature, and oxygen concentration on the photooxidation of aniline, toluidine, and 2,3-2,4-2,5-and 2,6-dimethylaniline. The effect of oxygen on the rate is the same as previously mentioned (34). Specifically, the rate is proportional to the oxygen concentration at low concentrations and independent at high concentrations. The temperature effect is reflected in the low values of activation energies found. For aniline, 2,4- and 2,5-xylidine a value of 3000 calories/mole was found. A value of 1000 calories/mole was reported for o-toluidine. Although Meallier was not interested in waste treatment, he is included here because of the obvious applicability.

It is obvious that most of the previous work is directed towards the treatment of municipal waste. What we concern ourselves with here is both the interactions and possible treatment of organic pollutants, from industrial sources, in an aqueous environment.

We initially chose five compounds for our study: aniline, toluene, chlorobenzene, nitrobenzene and o-cresol. These compounds were chosen as model HPS because they are among those chemicals produced in the largest amounts in the United States (6) and would most likely be found in the effluents of industries producing or utilizing them.

Although it can be said that some of these compounds are classified as being insoluble in water (specifically toluene, chlorobenzene and nitrobenzene), all exhibit a finite solubility which well exceeds the toxicity critical concentration (see Table I). Another characteristic that these compounds possess is that they are sufficiently, and in some cases totally, recalcitrant so as to be unaffected by conventional biological treatment. This recalcitrance is reflected in the biochemical oxygen demand (BOD) value (see Table I) which is the amount of oxygen used to biologically oxidize the compound.

Since we are following the guidelines of systematic and comprehensive investigation, our system initially consisted of reactant, water and ultraviolet light. This simple system allowed us to establish baseline values for rates of reaction, so that the effect of parameters such as light intensity, temperature and oxygen concentration, as well as the effect of the presence of inorganic compounds (photosensitizers) could be determined.

The reactions under study were assumed to follow first order kinetics, where

$$-dc/dt=kIC \quad (I)$$

where C is the concentration of reactant, k is the rate constant, I is the light intensity and t is the time.

Equation I can be integrated in the normal fashion to yield

$$\ln C/C_0 = -ktI \quad (II)$$

where C_0 is the concentration of reactant at $t=0$.

TABLE 1

Physical and Biological Constants of Selected Organics

<u>Compound</u>	<u>Molecular Weight (18)</u>	<u>Boiling Point(18)</u>	<u>Specific Gravity(18)</u>	<u>Refractive Index (18)</u>	<u>GLC Retention Time(min.) @ (°C)</u>	<u>BOD₅ (12) (gm./gm.)</u>	<u>Human Toxicity Critical Conc.(7) (mg./l.)</u>	<u>Solubility (7,37) (mg./l.)</u>
Aniline	93.13	184.13	1.02173	1.5863	10.75(230)	1.49	5	34000
Chlorobenzene	112.56	132	1.1058	1.5241	14.73(190)	0.03	35f	488
o-Cresol	108.15	190.95	1.02734	1.5361	36.29(180)	1.64	30f	31000
Nitrobenzene	123.11	210.8	1.2037	1.5562	18.63(230)	0	20f	1900
Toluena	92.15	110.6	0.8669	1.4961	6.40(200)	0	50	470
Diglyme	-	161- 163	-	-	23.40(190)	-	-	-

f-fish toxicity

III. Photochemistry:

Photochemistry concerns itself with the interaction of light and molecules. Specifically, it deals with the absorption of ultraviolet light (2000-4000Å) and/or visible light (4000-7000Å) by atoms or molecules and the subsequent deactivation processes. The two processes mentioned above, absorption and deactivation, are referred to as the primary photochemical process. The so-called "dark" or thermal reactions are called the secondary photochemical process. Not all light incident on a molecule is absorbed. Some is transmitted or reflected.

Quantum theory tells us that a molecule has a minimum energy content at any temperature. It also tells us that the molecule can only increase its energy by allowable discrete amounts. This increase in energy places the molecule into what is called an excited state. Only light which has an energy content equal to the difference between the excited state and the ground state will be absorbed. This energy is related to the frequency of the light by the equation $E=h\nu$, where h is Planck's constant (6.6×10^{-27} erg-sec) and ν is the frequency of the light.

The amount of light absorbed was shown to be a function of the concentration and is expressed by the Beer-Lambert law,

$$\log I_0/I = ecl \quad (III)$$

where I_0 and I are the intensities of the incident and transmitted light respectively, c is the concentration in moles/liter, l is the

optical path length in cms. and ϵ is the molar extinction coefficient, and is a measure of the intensity of absorption at a particular wavelength.

It is important at this point to understand what ground and excited states can exist. The singlet states(S) are distinguished from the triplet states(T), as shown in Figure 2, by the fact that all the electrons are spin paired (spin is indicated by the direction of the arrows) in the singlet states, while in the triplet states they are not. In Figure 2 the ground state is represented by a singlet state, and in most cases this is true. The oxygen molecule is an example of a compound which has a triplet ground state(27). The triplet ground state imparts to the molecule the property of paramagnetism.

The formation of the triplet excited state is a low probability transition and appears as a weak absorption in the ultraviolet spectrum. However, it is exactly this transition that is important in the photochemical mechanism.

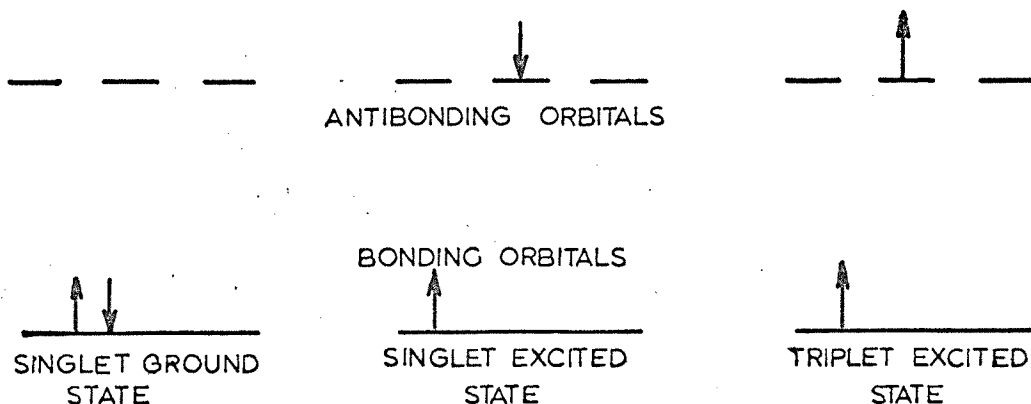


FIGURE 2 SINGLET AND TRIPLET ELECTRONIC STATES

Once in the excited state the molecule can undergo deactivation by one of many pathways:

(1)-fluorescence-emission of light during transition from S_1 to S_0 .

(2)-internal conversion-formation of heat during transition from S_1 to S_0 .

(3)-intersystem crossing-low probability transition from singlet excited state to triplet excited state, or from triplet excited state to singlet ground state.

(4)-energy transfer to an acceptor molecule-the loss of energy by the excited molecule raises the acceptor to an excited state.

(5)-Phosphorescence-emission of light during transition from triplet excited state to singlet ground state.

(6)-photochemical reaction-as many different types of photochemical reactions can take place as can occur in the ground state.

Figure 3 schematically summarizes the photochemical processes. For a more indepth explanation of the photochemical processes books by Calvert and Pitts(5), Kan(13), Neckers(26), Wayne(39) and the article by Owen(27) are recommended.

It is the possible photochemical reactions that can occur which interest us in this study, Particularly the reactions of those compounds (or those with similar structure) chosen as model HPS.

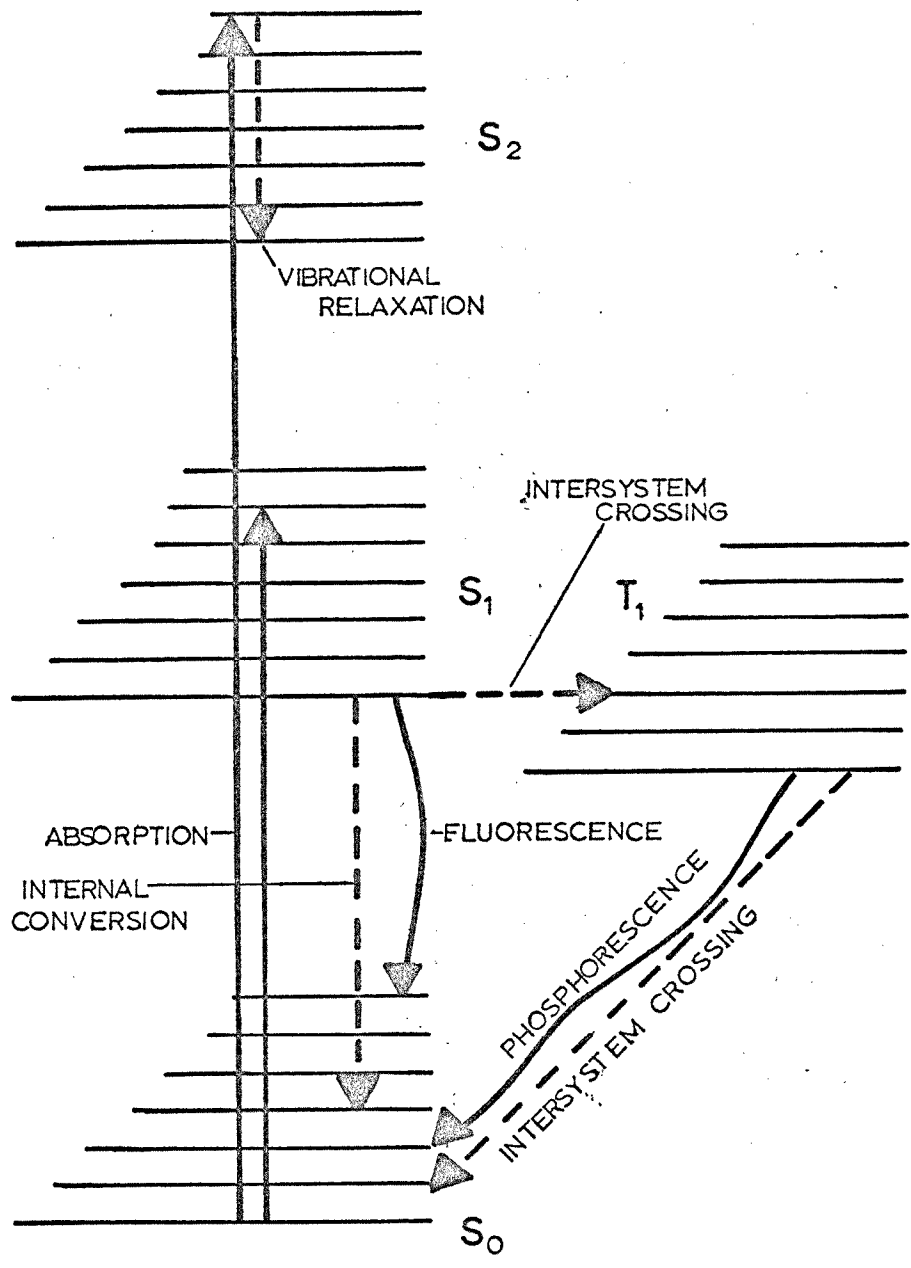
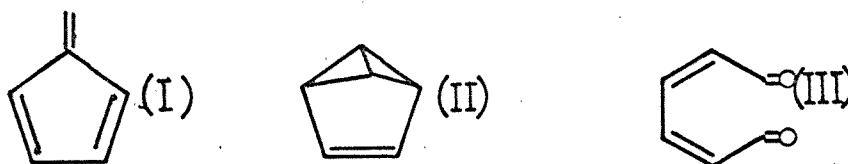


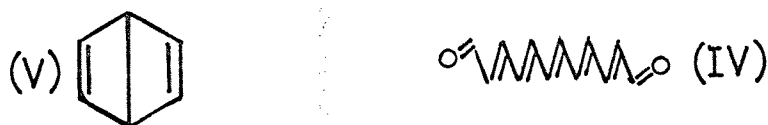
FIGURE 3-JABLONSKI DIAGRAM

Since all of the model HPS are benzenoid aromatics, the reactions of benzene are of interest here. Although we are especially concerned with reactions which take place in the aqueous phase, those which occur in the other phases, vapor and pure liquid, give us some insight into the products we can expect.

Kaplan and Wilzbach(14) and Wilzbach, Ritscher and Kaplan(42) studied the photolysis of benzene vapor at 1849 and 2537Å. The reported products were the isomers fulvene(I) and benzvalene(II) respectively.



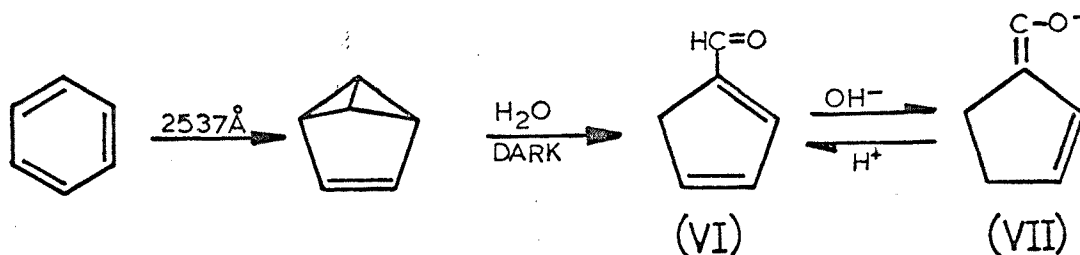
Wei, Mani and Pitts(40) reported that the photolysis of dry liquid benzene yielded two dialdehydes, mucondialdehyde(III) and 2,4,6,8,10 dodecapentaenedial(IV).



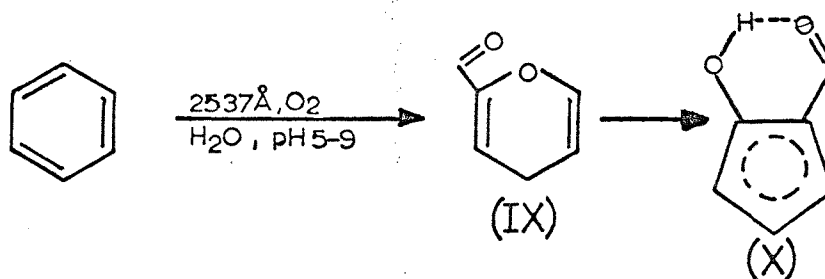
However, when liquid benzene is photolyzed under a vacuum (O_2 eliminated), Ward and Wishnok(38) reported that Dewar benzene(V), (I) and (II) are formed in the ratio 1:2:5: respectively.

The importance of the benzvalene structure(II) was shown by Kaplan, Wendling and Wilzbach(15,16) in the photolysis of aqueous benzene at 2537Å in the presence of oxygen. They isolated both the

cyclopentadienyl carboxaldehyde(VI) and its anion(VII) which are believed to be formed thru a benzvalene intermediate as follows,

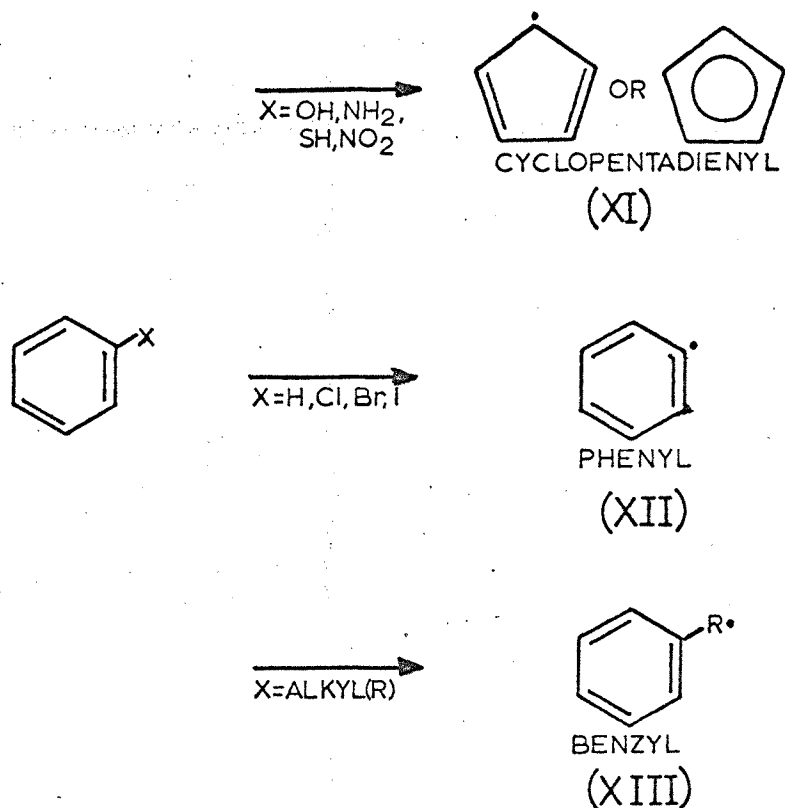


There is some disagreement as to the final product of the aqueous photolysis of benzene. Loeff and Stein(19) originally reported that the photolysis of aqueous benzene at 2537 Å, neutral pH and in the presence of oxygen yielded not (VI) or (VII), but what seemed to be the dialdehyde(IV). However, both Farenhorst(9) and Luria and Stein(20,21) identified this product as 2-formyl-4H-pyran(IX) which undergoes stabilization to (X).

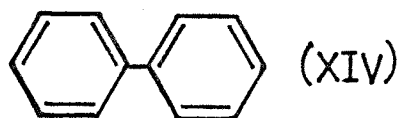


Obviously, the reactions of substituted benzenes, if known, are of greater importance. The literature contains reactions of substituted benzenes of identical or similar structure as our model HPS. Again, although the phase may not be aqueous the information available offers assistance in our work.

Porter and Ward(29) reported the formation of three radicals (XI, XII, and XIII) besides the anilino($\phi\text{NH}\cdot$) and phenoxy($\phi\text{O}\cdot$) previously reported(30) as products of the vapor phase flash photolysis of the monosubstituted benzenes shown below.

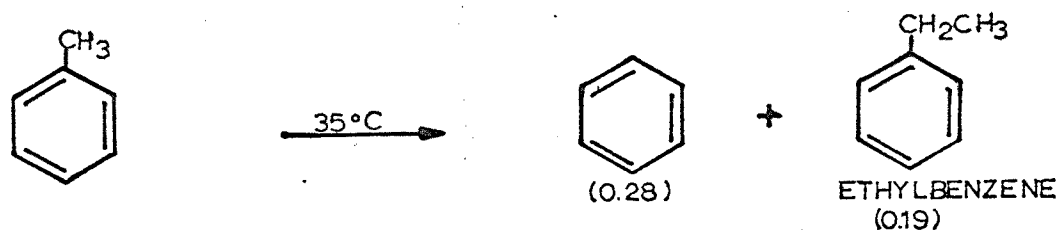
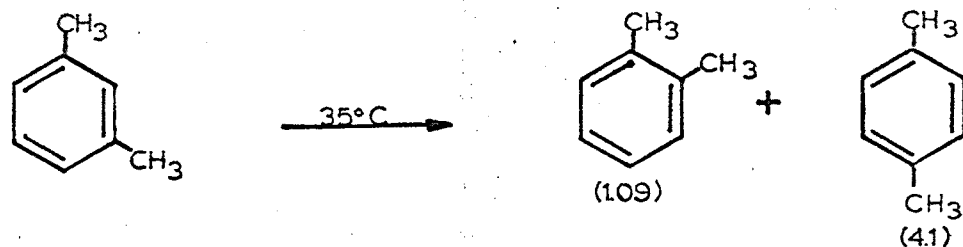
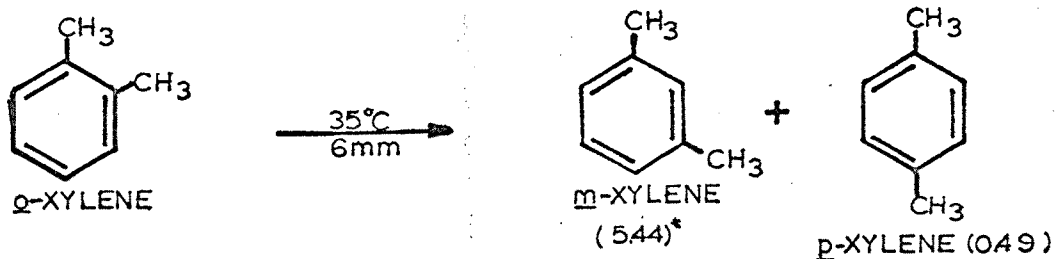


Robinson and Vernon(31) reported the formation of biphenyl(XIV) as the product of the photolysis of chlorobenzene.

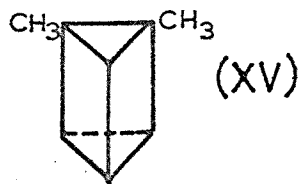


This would lend support to the findings of Porter and Ward above, as to the formation of the phenyl radical which then couples with another phenyl radical to give rise to (XIV).

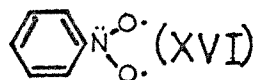
Wilzbach and Kaplan(41) not only reported the previously isolated gaseous and polymerization products(11,35), but also important isomerization products of the vapor phase photolysis of *o*-xylene, *m*-xylene and toluene.



The intermediate responsible for the isomerization has been shown to be the Ladenberg type benzene structure(XV).



Scheinbaum(33) reports that the diradical(XVI) is the intermediate in the photochemical reactions of nitrobenzene.



*numbers in parenthesis are the yields in mole%

EXPERIMENTAL

I. Reagents:

The reactants(aniline, toluene, chlorobenzene, nitrobenzene and *o*-cresol) were ACS reagent grade and were used without further purification.

The diethylene glycol dimethyl ether(diglyme) used as the gas-liquid chromatography(GLC) internal standard (2) was purified by atmospheric distillation over sodium.

The water used in the reactions was prepared by passing tap water through a Bantam Mixed Resin Cartridge to remove ions. The measured resistance of the purified water was greater than 2.5×10^6 ohms.

II. Equipment:

Kinetic analysis was done on an F&M model 810 GLC equipped with dual flame ionization detectors. A 6 foot by 1/8 inch stainless steel column packed with 60/80 mes Porapak QS was employed. An oven temperature of 190°C was found to give good separation of components.

Infrared spectra were obtained on a Perkin Elmer model 457 infrared spectrophotometer.

Ultraviolet spectra were obtained on a Beckman DB-G UV-Visible spectrophotometer.

The photolysis was carried out using a quartz immersion well reactor and a Hanovia high pressure mercury vapor lamp (#6515-34 450 watts). Figure 4 shows the experimental setup.

The temperature was maintained by placing the reaction vessel in a thermostated oil bath. The oil used was Fischer paraffin oil and the temperature was kept constant by a Bronwill circulating constant temperature unit.

III. Kinetics:

Weighed amounts of reactant(ca. 0.1000 gms.) and standard(ca. 0.2000 gms.) were brought up to a volume of 750 ml. with the purified water. A known volume(ca. 600 ml.) of this reaction mixture was placed into the reactor flask, which was equipped with a teflon coated magnetic stirring bar and teflon sampling tube. The flask was then placed into the oil bath.

The reaction vessel was alternately evacuated with a water aspirator and flushed with helium at least five times. This was done to remove dissolved oxygen. The photoreactions were conducted at temperatures of approximately 30, 40 and 50°C.

The reaction mixture was then subjected to ultraviolet light for at least two hours. At selected intervals (time of sampling varied depending on the speed of reaction and was determined empirically) samples were removed by means of a 1 cc syringe. A 25ul. aliquot of this 1 cc sample was then analyzed via GLC.

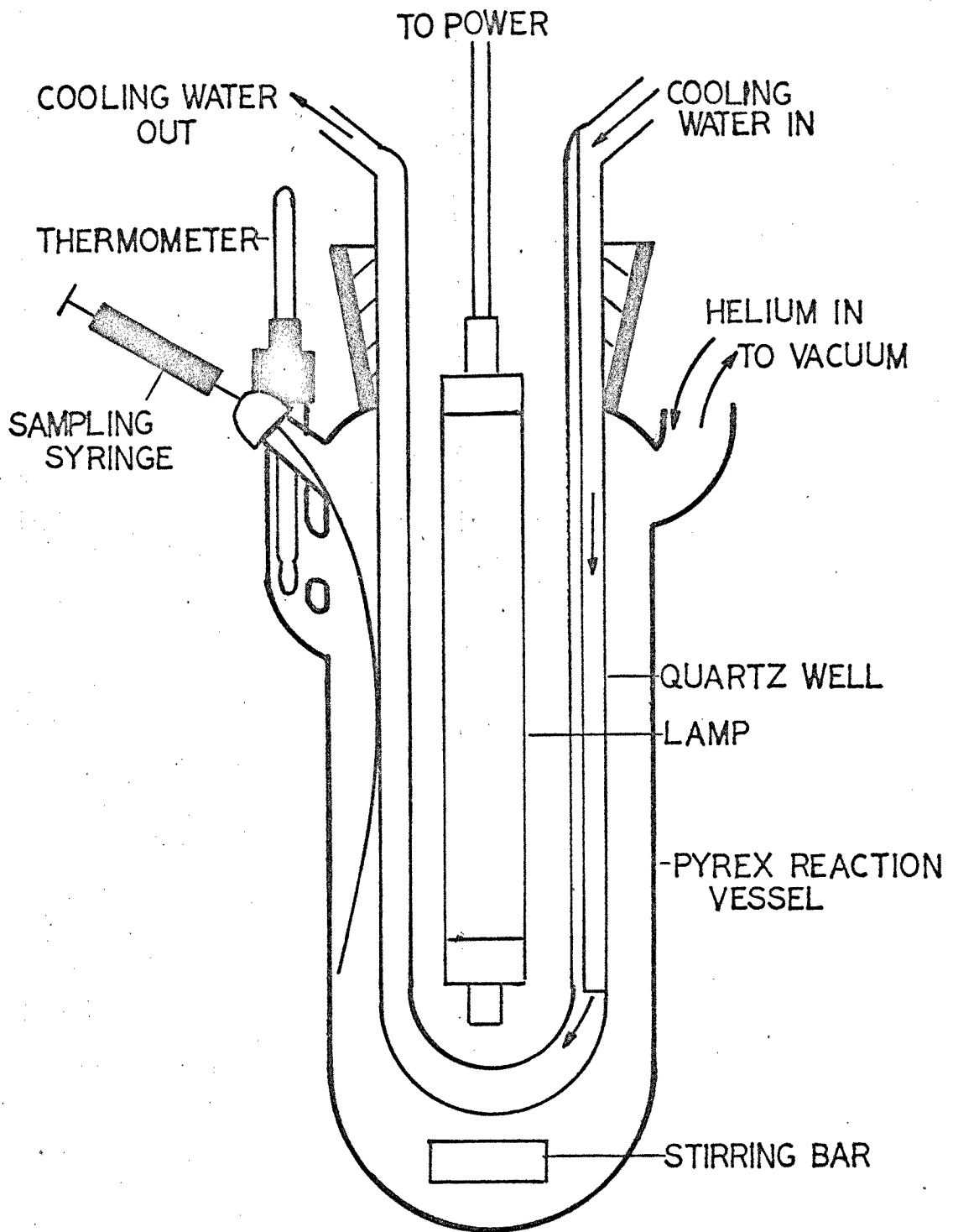


FIGURE 4-QUARTZ IMMERSION WELL PHOTOREACTOR

The areas of the GLC peaks were measured by the cut and weigh method (2) and the area ratios (AR) were calculated, AR area of reactant peak/area of standard peak. A plot was made of AR/AR₀ versus t was made and the rate constants calculated*.

IV. Isolation of Photoproducts:

The photoproducts were isolated by extraction of the photolyzed reaction mixture with ether in a one liter continuous extractor for a period 72 hours. The resultant ether layer was then subjected to consecutive extractions with aqueous 2N NaOH and aqueous 2N HCl. The aqueous layers of each extraction were neutralized and extracted with ether. The three ether layers thus contained, in order, the neutral, the acidic and the basic products. (Figure 5 represents this scheme graphically.) The ether layers were then placed into a rotary evaporator and the ether removed under reduced pressure by means of a water aspirator.

The non-volatile compounds remaining were chromatographed on Eastman thin layer chromatography plates(TLC) (silica gel on polyethylene, a 99% benzene-1% methanol mixture was used as a solvent to develop the plates) to determine number and purity of compounds present.

The final products were separated by adsorption chromatography (80-200 mesh, activated alumina, Matheson, Coleman and Bell) by eluting with petroleum ether, followed by a 99% benzene-1% methanol mixture.

* it can be shown that AR/AR₀ equals C/C₀

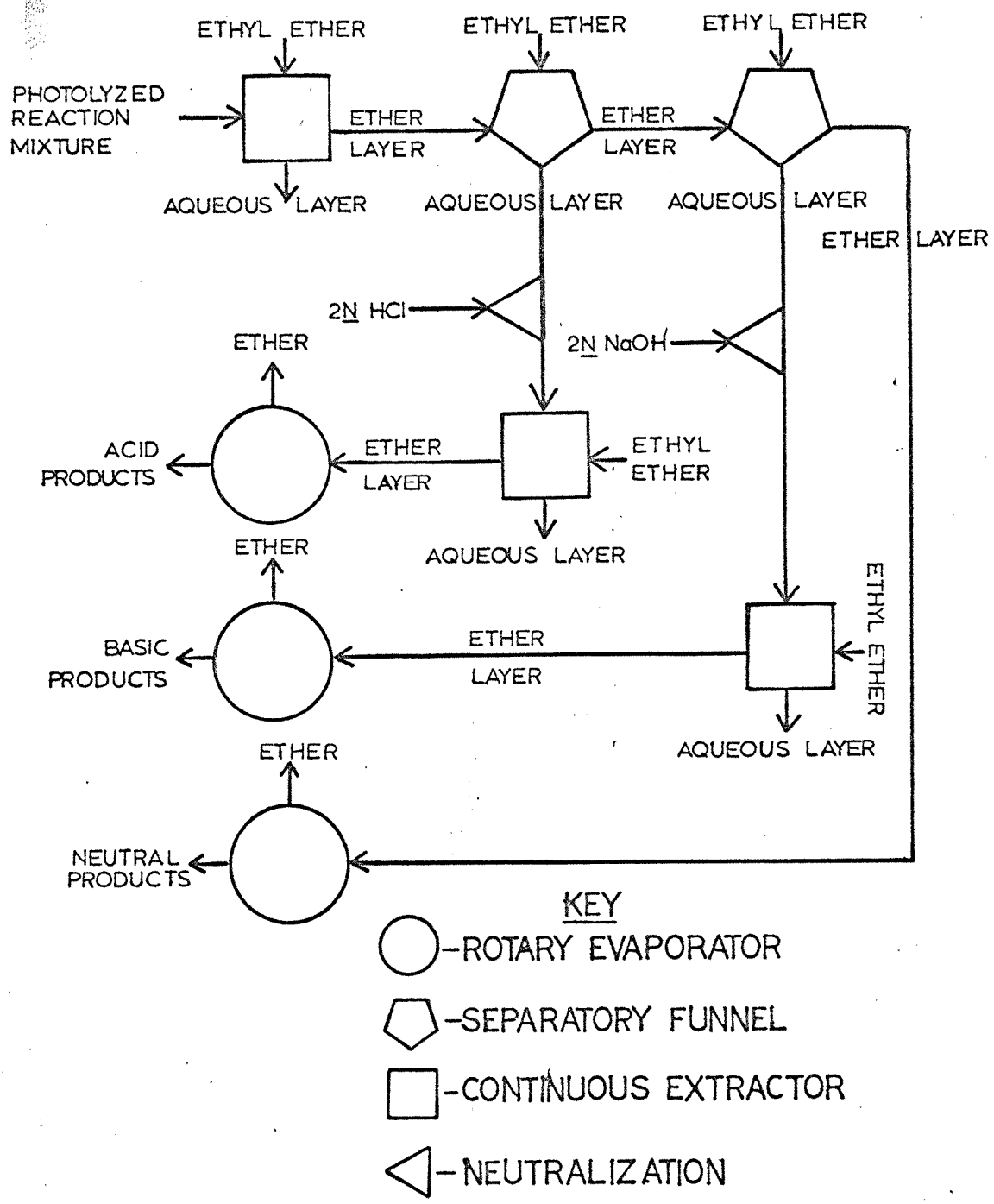


FIGURE 5
PHOTOPRODUCT EXTRACTION FLOW DIAGRAM

RESULTS

I. Kinetics:

All selected reactants (i.e. chlorobenzene, *o*-cresol and nitrobenzene)* were found to photoreact in an aqueous medium.

The chlorobenzene reacted too fast under the full intensity of the light to obtain useful data. Therefore a steel mesh was employed to physically diminish the intensity of the light without changing the spectrum. Three cylindrically shaped attenuators were constructed out of steel screen to fit around the lamp. The three filters had the following per-cent transmissions: 26.9, 37.1 and 44.8 (these values are the specifications of the manufacturer Newark Wire Cloth Co.). The filter with 26.9 per-cent transmission was used for the chlorobenzene reaction to give maximum reaction time. The use of this filter means that the rate constant values for chlorobenzene are .269 the value of the constant at full intensity.

The photolysis of chlorobenzene is shown in Figure 6 as a first order plot of $\log C/C_0$ versus time (t) at 28.9, 38.5 and 46.7°C. The initial concentrations for the three reactions were the same (see Table 3, Appendix). The rate constant (k), as determined by taking the negative slope, at 28.9°C was found to be 0.0221 min.⁻¹. The rate decreased as the temperature was increased to 38.5°C (k 0.0148 min.⁻¹),

* Aniline and toluene which were initially included in the study has to be eliminated due to problems of volatility and GLC analysis.

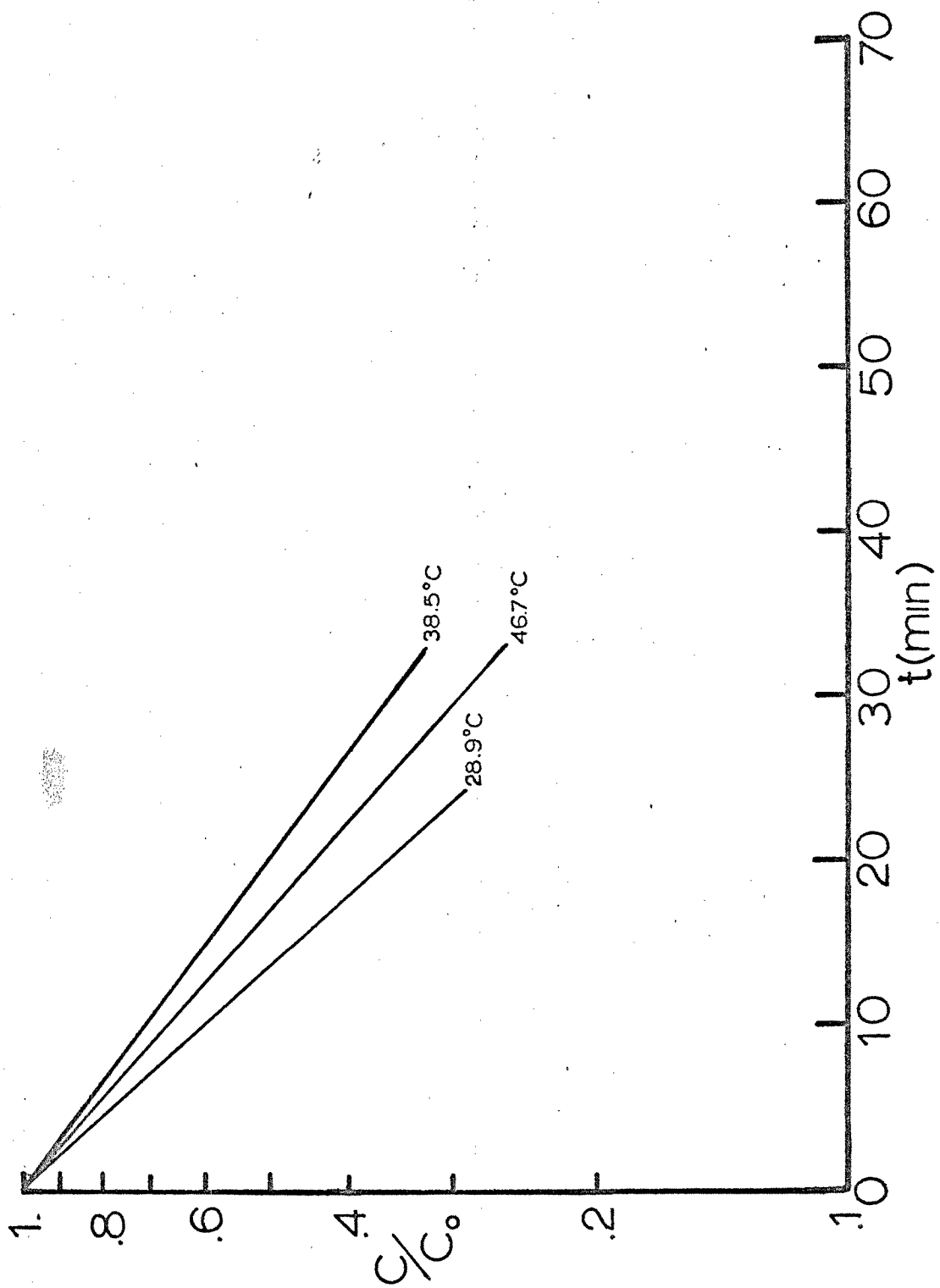


FIGURE 6-AQUEOUS PHOTOLYSIS OF CHLOROBENZENE

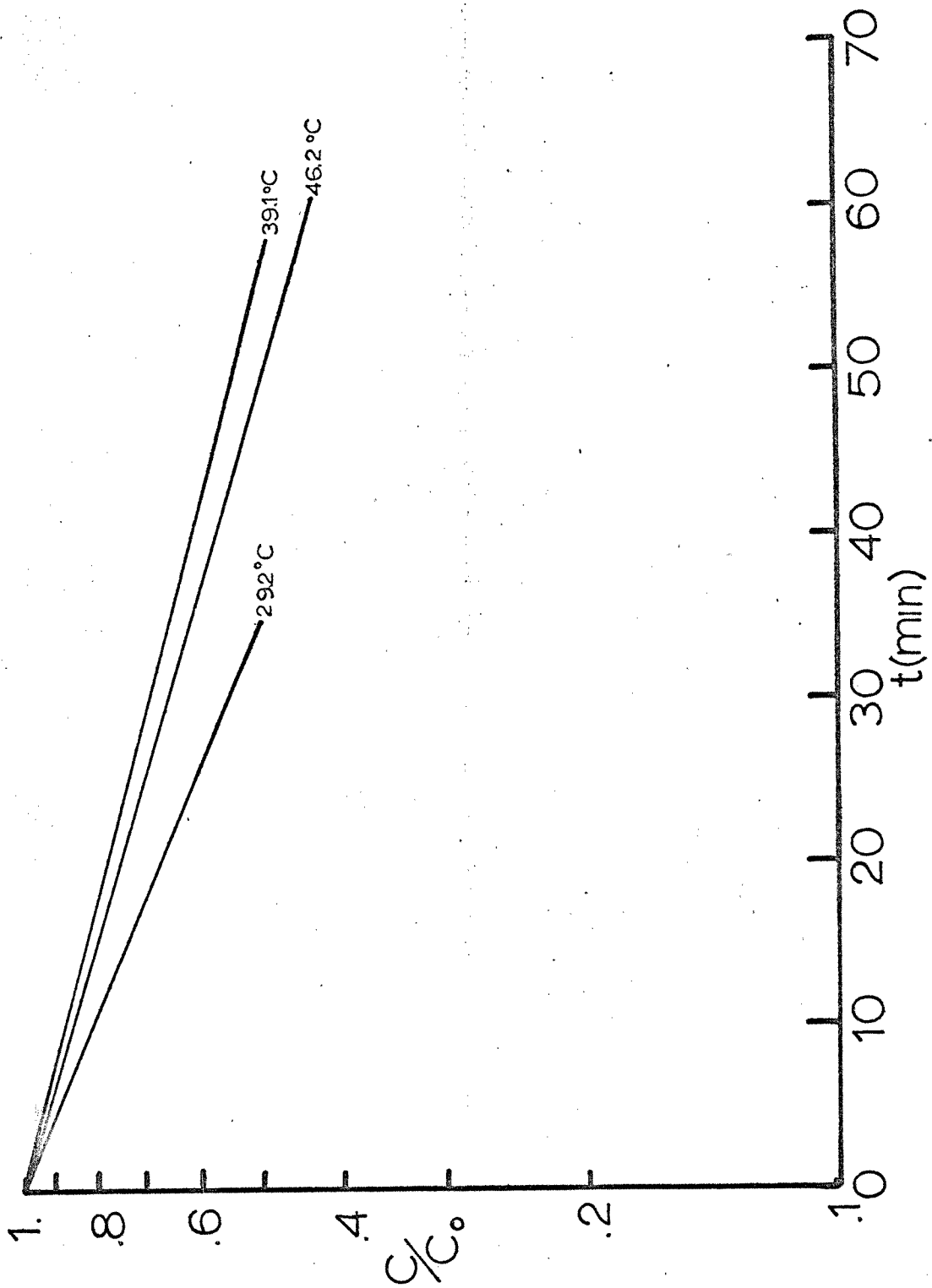


FIGURE 7-AQUEOUS PHOTOLYSIS OF *o*-CRESOL

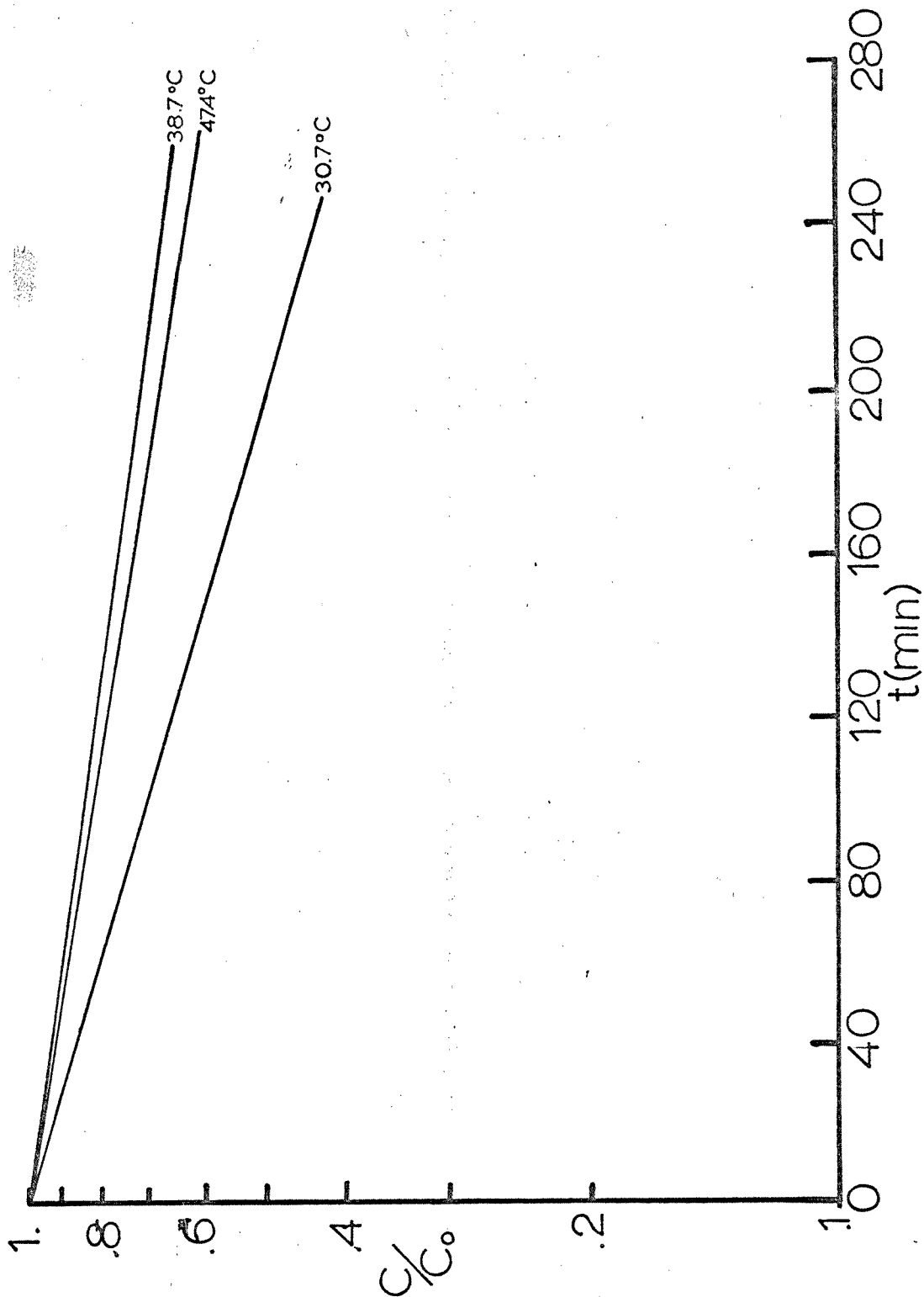


FIGURE 8—AQUEOUS PHOTOLYSIS OF NITROBENZENE

but remained constant when the temperature was raised to 46.7°C (k 0.0147 min.⁻¹).

The same trend in the rate was found in the photoreactions of o-cresol (Figure 7) and nitrobenzene (Figure 8). The rate constant for o-cresol at 29.2, 39.1 and 46.2°C were 0.0085, 0.0054 and 0.0059 min.⁻¹ respectively. For nitrobenzene at 30.7, 38.7 and 47.4°C the constants found were 0.0015, 0.0009 and 0.0007 min.⁻¹ respectively.

Figures 9 and 10 show the temperature effect more clearly as t at C/C_0 equal to 0.5 versus temperature is plotted for the three compounds.

II. Photoproducts:

In all photoreactions, the formation of solid non-volatile products was observed. No volatile photoproducts were detected by GLC.

The ether extract of the photolyzed chlorobenzene solution, on extraction with 2N NaOH, exhibited a strong color change from clear to bright yellow. No color change in the aqueous layer was observed when extraction with 2N HCl was carried out. White particles were observed between the layers of water and ether.

A similar strong color change was observed (orange yellow to blood red) for the photolyzed nitrobenzene solution upon base extraction. Again no color change took place upon acid extraction. A brown solid precipitated out of the photolyzed solution.

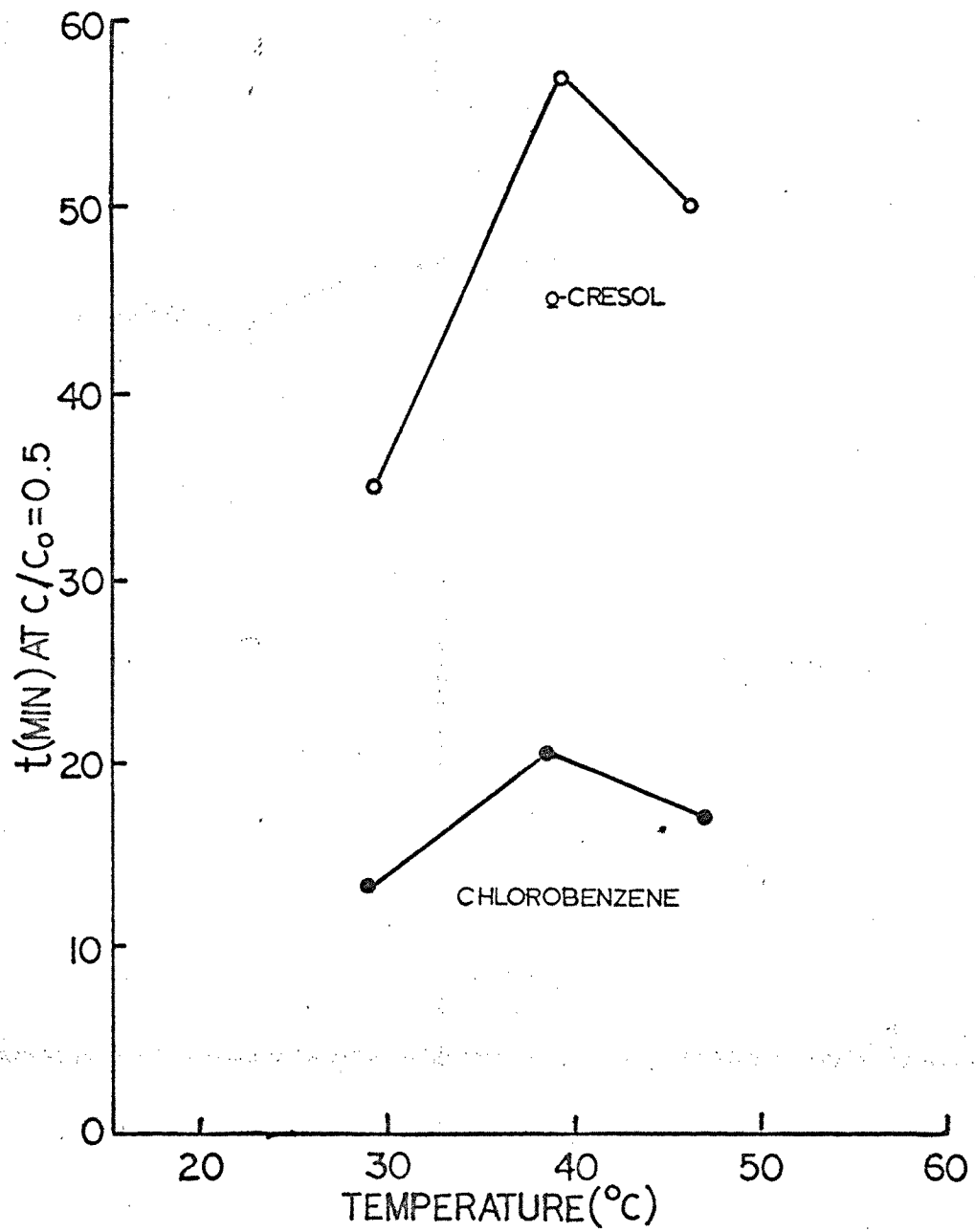


FIGURE 9—THE EFFECT OF TEMPERATURE ON THE PHOTOREACTIONS OF CHLOROBENZENE AND *o*-CRESOL

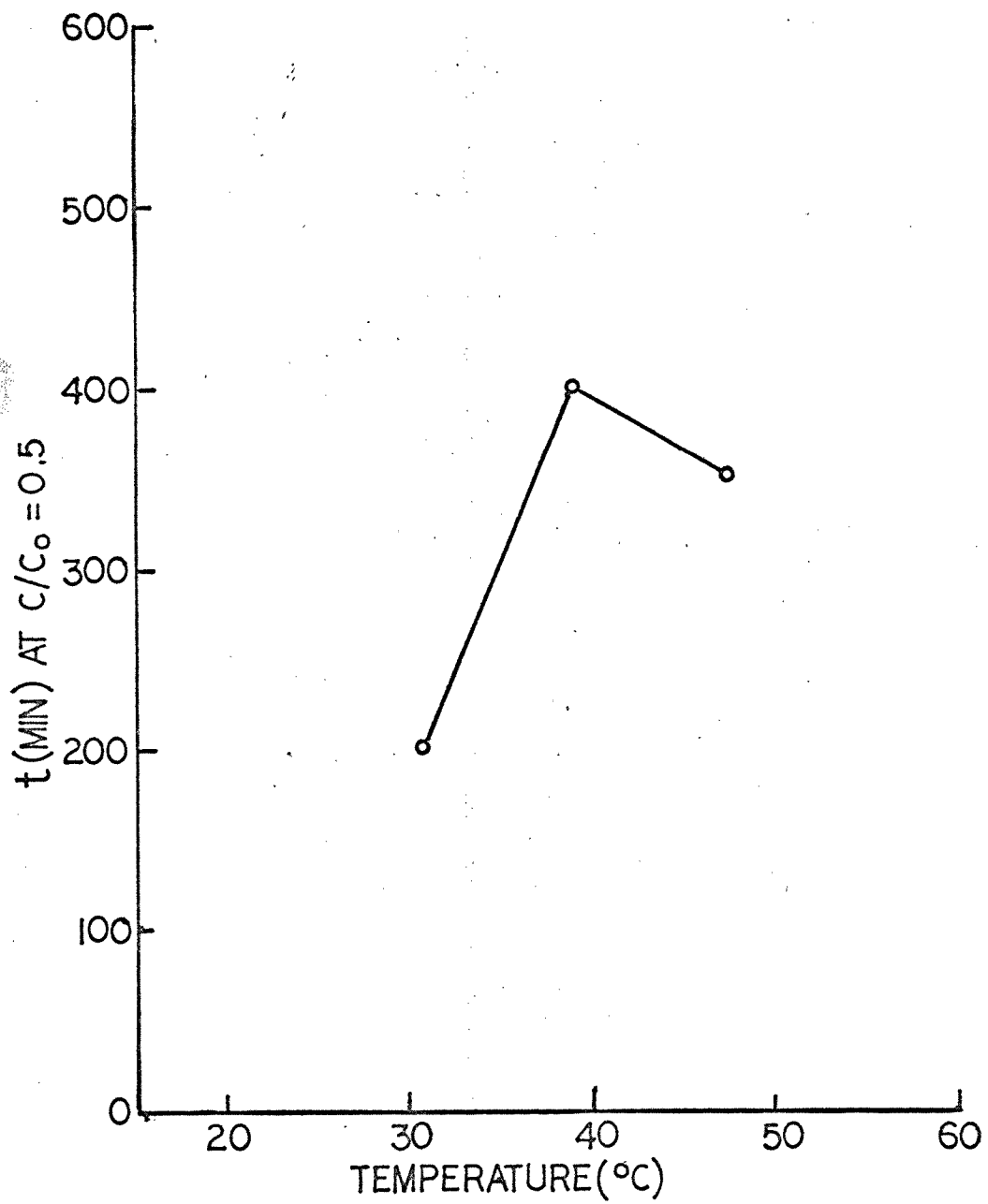


FIGURE 10-THE EFFECT OF TEMPERATURE ON THE PHOTOREACTIONS OF NITROBENZENE

The o-cresol mixture was a milky white and immediately turned dark on addition of base and back to milky white on neutralization of the basic aqueous layer. Acid extraction produced no color change and a solid product again was visible.

Incomplete infrared data yielded strong absorption for all base extracted products in the 5.8-6.0 μm range in carbon tetrachloride solution.

DISCUSSION

I. Kinetics:

Chlorobenzene, *o*-cresol and nitrobenzene are shown to undergo photochemical reaction in an aqueous medium. The ultraviolet spectra for these compounds are illustrated in Figures 11, 12 and 13. Since these compounds exhibit strong absorption above 2200Å and since the high pressure mercury arc lamp emits a significant amount of light above 2200Å (Table 2), the photoreaction of these compounds was not unexpected.

Water, the photolytic medium, shows an absorption spectrum below 2000Å (5) and therefore would not be expected to interfere with the photoreactions. This would eliminate the possible formation of ozone or hydrogen peroxide from the water.

The reactions show good agreement with first order kinetics, also as expected. What wasn't expected was the temperature dependence exhibited by the photoreactions of all three compounds.

Based on the literature previously cited, there exists the possibility of two effects of temperature on the rates: Meiners(24) found that the rate of photooxidation of starch decreased as the temperature increased from 0 to 25°; Bulla(3), Bulla and Edgerly(4) and Matsuura and Smith(22) found that the rate was independent of temperature in the photolysis of aldrin and formic acid, respectively. Meallier(23) also found little temperature dependence, which is reflected in the low

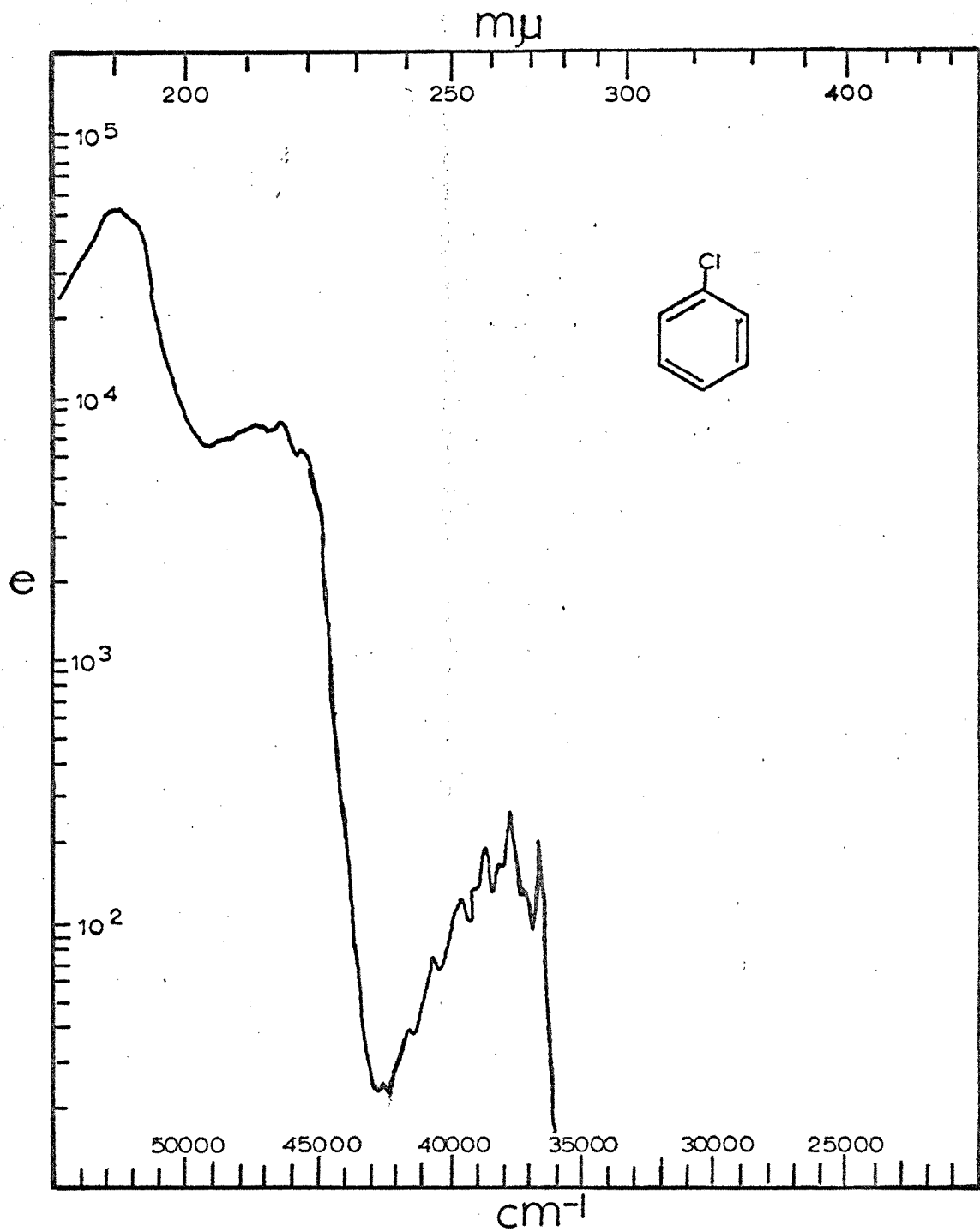


FIGURE II
ULTRAVIOLET SPECTRA OF CHLOROBENZENE IN HEPTANE

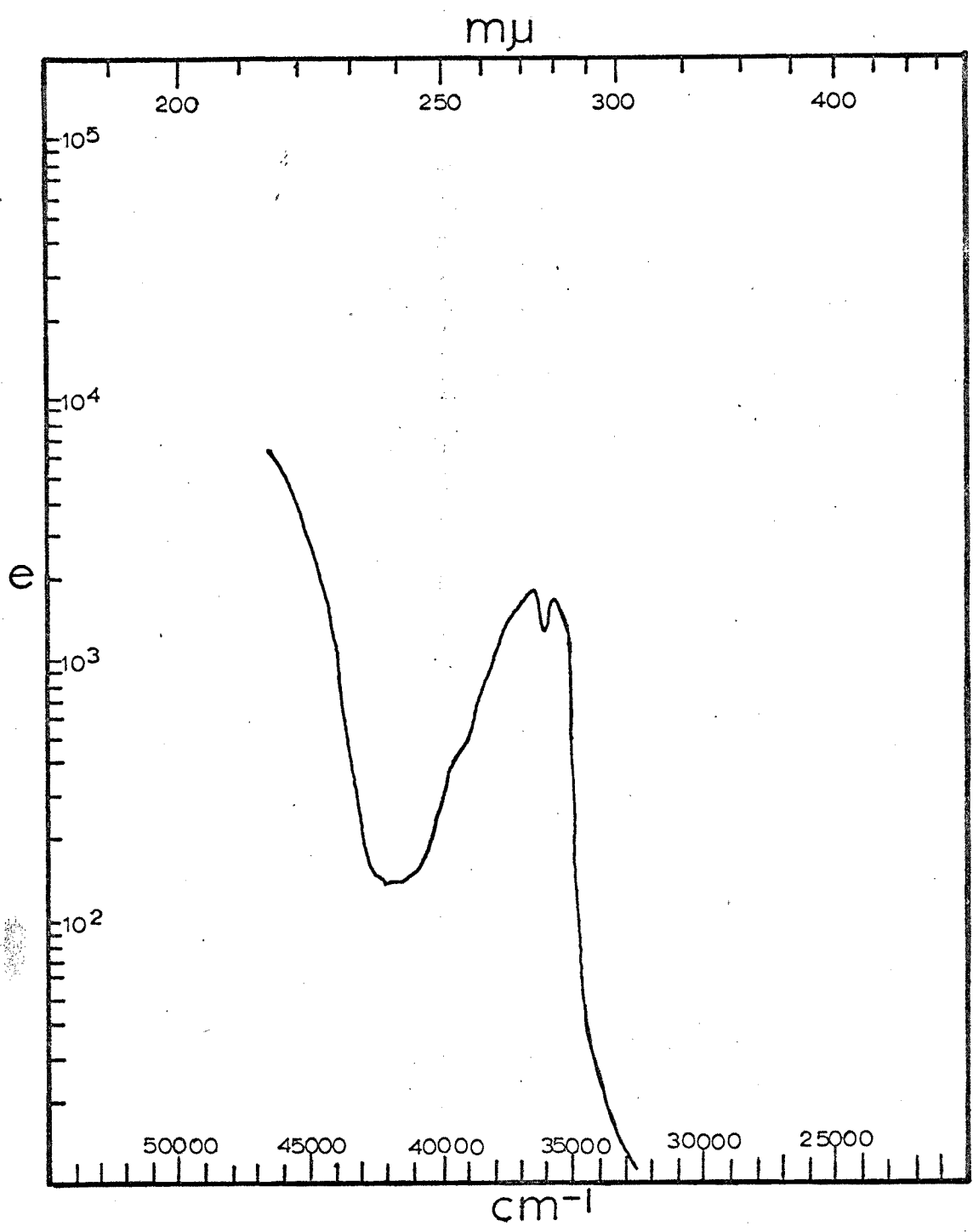


FIGURE 12
ULTRAVIOLET SPECTRA OF *o*-CRESOL IN ISO-OCTANE

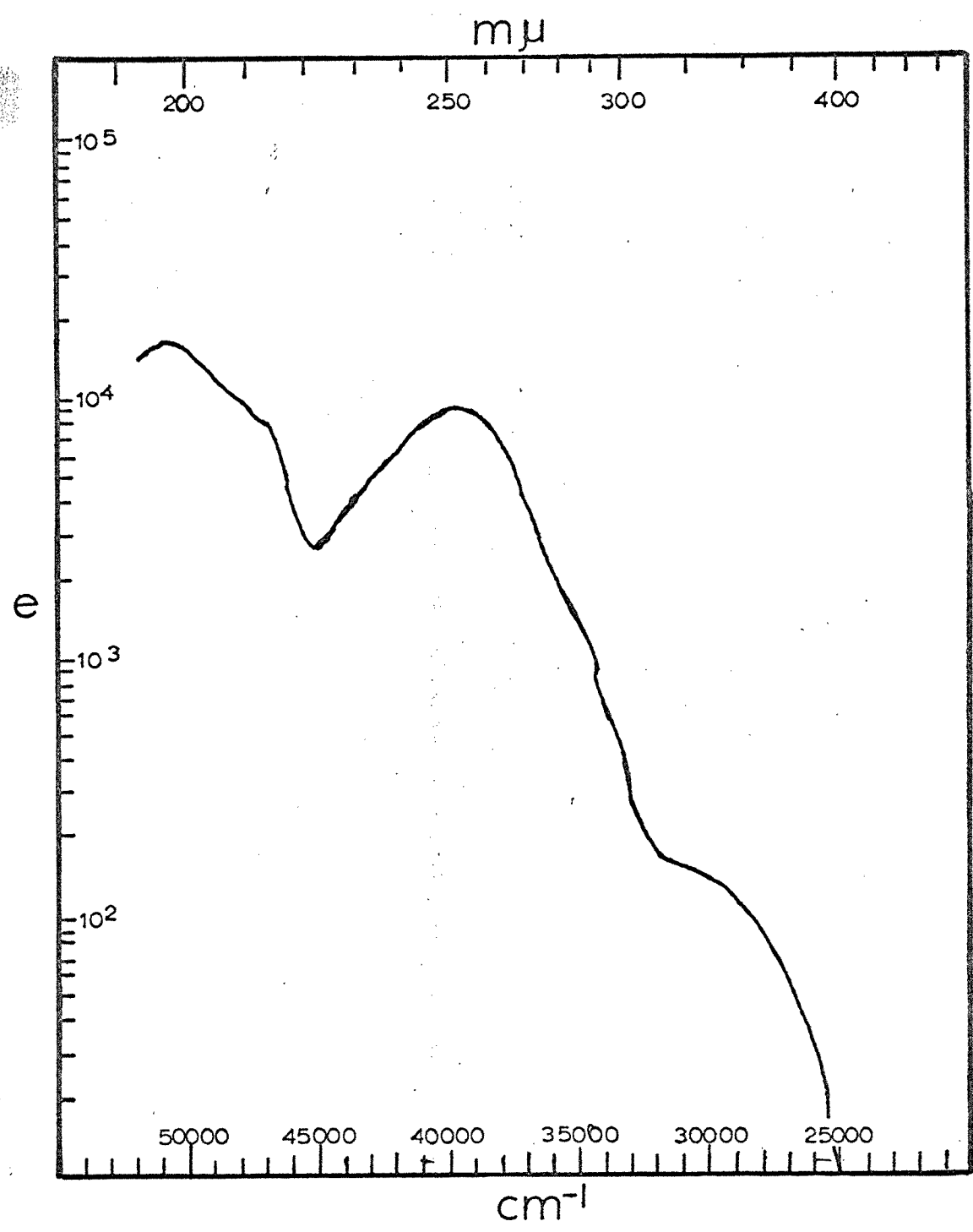


FIGURE 13
ULTRAVIOLET SPECTRA OF NITROBENZENE IN
LIGHT PETROLEUM

Table 2Spectral Energy DistributionHanovia 6515-34 High Pressure Quartz Mercury Vapor Lamp

Lamp Watts	450
Lamp Volts	135
Current	3.6
Arc Length	4.5"
<u>Wavelength (Å)</u>	<u>Radiated Energy (Watts)</u>
13673	2.6
11287	3.3
10140	10.5
5780	20.0
5461	24.5
4358	20.2
4045	11.0
3660	25.6
3341	2.4
3130	13.2
3025	7.2
2967	4.3
2894	1.6
2804	2.4
2753	0.7
2700	1.0

Table 2 (cont'd)

<u>Wavelength (Å)</u>	<u>Radiated Energy (Watts)</u>
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	3.5
Total Watts	175.8

activation energies reported in his work on amines.

As can be seen in Figures 9 and 10 our reactions behave as "hybrids" of the systems mentioned above. There is an initial decrease in rate with the initial increase in temperature and then a relatively constant rate over the next increase in temperature. Trying to explain this on the basis of the reported effects is difficult since only the amines are of structure similar to our reactants. Starch, aldrin and formic acid bear little structural similarity to chlorobenzene, o-cresol and nitrobenzene. Another dissimilarity is that Matsuura and Smith(22) measured their reaction rates from the formation of gaseous products, namely CO and CO₂, in the photolysis of formic acid. These gases are formed as products of the secondary photochemical process involved in the overall photolysis of formic acid. In our experiments we are looking at the primary photochemical process (i.e. the disappearance of reactant), which would exhibit different temperature effects.

One possibility for explaining this apparent anomaly is the effect of temperature on the geometry of the transition state. The geometry of the ground state and the geometry of the excited are not necessarily identical. In fact, they are very rarely identical, because what is an allowable geometry in the ground state may not be allowable in the excited state, or vice versa (13).

Once the molecule has been excited it seeks a geometry which reduces the interaction between unpaired electrons. This is done by

distortion of the bonds and as much as 90° is possible. In other words, the molecule tends towards the lowest energy geometry. The lowest energy geometry depends upon the temperature and therefore what is a favorable geometry at a high temperature may not be favorable at low temperature. The fact that transition state geometry effects the possibility of reaction and, hence, the rate of reaction is well known.

Only mechanistic studies can resolve this problem (see Future Work Section), however they are beyond the scope of this work.

II. Photoproducts:

It is not possible at this point to say what products were obtained as a result of the aqueous photolysis of our model HPS. However, it is possible to say what products one might expect to find based on the reactions reported in the literature and on what little data we have collected in this respect.

The color change exhibited by the acid products in basic solutions is of the type associated with highly conjugated anions. Structures similar to cyclopentadiene carboxaldehyde(VII) are a possibility. The appearance of an infrared absorption at $5.8-6.0 \mu\text{m}$, which is associated with the carbonyl ($\text{C}=\text{O}$) group, lends support to this type of structure.

The formation of biphenyls and/or phenols is also a possibility, especially in the photoreactions of chlorobenzene, since Porter and Ward(29) reported the formation of phenyl radicals in the vapor phase photolysis of chlorobenzene. The biphenyl would result from an attack

of another molecule of chlorobenzene or phenyl radical by a phenyl radical. The phenol would result from an attack of a water molecule by a phenyl radical. Since water molecules would predominate over molecule of chlorobenzene in our system, the phenol would be the most probable result.

Again based on the findings of Porter and Ward(29), nitrobenzene and *o*-cresol would yield a product with a five membered ring. This would result from the formation of the cyclopentadienyl radical. However, this would not yield a carbonyl compound like that which resulted from the benzvalene intermediate, but perhaps some kind alcohol.

Another product which is mentioned and is a possibility for all the reactants is polymer. The formation of polymer has been noted in the reactions of alkyl benzenes(41) and would most likely be found here.

The myriad of possibilities leads one to recommend that preparative reactions be run, eliminating the complicating factor of the standard, to determine what the actual products are.

FUTURE WORK

In the introduction it was stated that this work was to establish baseline kinetic values for the model systems chosen. Future work would investigate the effect of oxygen and the effect of inorganic (i.e. mercury) and organic (i.e. acetone) photosensitizers on the rates of reaction.

Since this work was basically limited to kinetics, further investigation into the mechanism and products of the reactions is planned.

Aniline was eliminated from this study because of problems in analysis by GLC. It is recommended that different columns be tried to resolve this problem, as we feel aniline should be considered as a model HPS. Toluene was also eliminated because of its volatility and it is recommended that other alkyl benzenes, such as xylene or ethyl benzene, be considered.

Finally, to determine whether the photomodification is feasible as an advanced industrial waste water treatment process, characterization of the products as to toxicity and ease of removal from the aquatic environment is planned.

APPENDIX

Complete kinetic data for the aqueous photolysis of Chlorobenzene,
o-Cresol and Nitrobenzene.

Table 3

Kinetic Data for Photolysis of Chlorobenzene

<u>Temperature (°C)</u>					
28.9		38.5		46.7	
<u>C₀ (gm/l)</u>					
0.1452		0.1459		0.1420	
<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>
0	1.000	0	1.000	0	1.000
10	0.688	12.5	0.636	11.7	0.696
14	0.840	20	0.485	16.7	0.491
16.7	0.301	33.3	0.379	30	0.272

Table 4

Kinetic Data for Photolysis of o-Cresol

<u>Temperature (°C)</u>					
29.2		39.1		46.2	
<u>C₀ (gm/l)</u>					
0.1360		0.1462		0.1475	
<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>
0	1.000	0	1.000	0	1.000
10	0.736	11.7	0.767	18.3	0.802
18.3	0.573	12.5	0.719	20	0.754
20	0.785	21.7	0.877	30	0.466
22.8	0.646	33.3	0.752	46.7	0.537
33.8	0.664	43.3	0.838	60	0.443

Table 5

Kinetic Data For Photolysis Of Nitrobenzene

		<u>Temperature(°C)</u>					
		30.7		38.7		47.4	
		<u>C₀(gm/l)</u>		0.1456		0.1419	
<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>	<u>t(min)</u>	<u>C/C₀</u>
0	1.000	0	1.000	0	1.000		
15	0.888	60	0.947	60	0.879		
30	0.890	120	0.889	120	0.898		
60	0.742	180	0.773	180	0.690		
120	0.804	240	0.726	240	0.676		
180	0.652						
240	0.596						

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