DEVELOPMENT OF A DYE SENSITIZED PHOTOCHEMICAL REDUCTION PROCESS FOR THE DEGRADATION OF POLYCHLORINATED BIPHENYLS

by

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EXECUTIVE SUMMARY

The purpose of this study was to develop a photochemical dehalogenation process for the treatment of polychlorinated biphenyls. The photochemical dehalogenation process which was developed is a heterogeneous process. Typically three phases are present: a) solid alkali metal hydroxide, b) polar aprotic solvent, and c) hydrocarbon gas. However, the reaction will proceed quite rapidly with polychlorinated biphenyls in the absence of solid strong base until the more resistant monohalogenated isomers are remaining. The ease of dehalogenation (i.e., reactivity) increases with the number of chlorine substitutions. This reaction does not occur at a perceptible rate in the absence of visible light at room temperature.

The reaction assembly typically used for laboratory experiments is shown as a simplified schematic in Figure 1. The actual reflux condenser contains a helical glass coil. The glass is Pyrex which effectively attenuates wavelengths of light $\lambda > 300$ nm. Typical experiments would use one milliliter aliquots of N, N-dimethylformamide, DMF, each saturated with KOH and containing a solid pellet of KOH immersed in each of the solutions. The solutions would contain 0-350 mg/l methylene blue, and a fritted glass diffuser would deliver 0-140 ml/min of commercial grade propane. The substrate concentrations would range from 1-100 mg/l of Aroclor 1221, Aroclor 1254, transformer oil extract or 4-chlorobiphenyl. Solution temperatures were maintained at 30°, 40°, or 50° C $\pm$ 1°C.

The principal molecular species involved in the photochemical reactions are displayed in Figure 2. Obviously, several solvents, sensitizers, bases, and hydrogen sources can be substituted in this procedure. This reaction at a minimum requires a strong source of visible light, a sensitizer, a polar aprotic solvent, a hydrocarbon gas, and finally a PCB substrate.

The sensitizer typically used in these experiments, is methylene blue, a common dye frequently used in photooxidation processes. The excited state energy of methylene blue (i.e. the "triplet state") is about 40 kcal/mol. The absorbtion spectrum of methylene blue is compared to sunlight in Figure 3 (13). The maximum absorbtion of methylene blue is approximately 660 nm. Sunlight under certain circumstances could be used to excite the photochemical dehalogenation of PCB.

The monohalogenated isomers of biphenyl are somewhat resistant to this photochemical technique. Results of experiments with 4-chlorobiphenyl are displayed in Figure 4. This Figure demonstrates the rather rigorous requirement of solid strong base to attain acceptable kinetics. In the presence of solid strong base approximately 97% destruction of 100 mg/l 4-chlorobiphenyl solutions can be consistently achieved in 60 minutes illumination at 30° C. It is interesting to note that methylene blue sensitizer becomes a bright red in DMF upon the addition of strong base. This red form of methylene blue, has an absorbtion maximum at about 550 nm. The

reaction is practically complete when the red color of the dye finally becomes a light amber hue. The red hue returns upon exposure to oxygen.

The major reaction product and the initial substrate 4-chlorobiphenyl are shown as peaks on a gas chromatogram after being resolved by a 20 m capillary column as shown in Figure 5. The highest peak to the left is a major reaction product and the peak to the right is 4-chlorobiphenyl. A V.G. mass spectrograph was used to identify the major reaction product. A computer library function automtically identified the compound as 1, 1'-Biphenyl. This analysis result is displayed in Figure 6.

Heavily substituted biphenyls such as Aroclor 1254 do not require the presence of base to react in this photochemical procedure. In the complete absence of strong base Aroclor 1254 will undergo dehalogenation at a rapid rate until the resistant monohalogenated isomers are formed. Progress of the reaction is shown in Figures 7-11. These Figures are chromatograms obtained by a polar 2 m packed column and an electron capture detector. Note the peaks on the right in the chromotograms are more rapidly attenuated. These are the more heavily substituted isomers, while product peaks on the left increase. These are the less heavily substituted isomers.

Figures 12-14 show the results of photochemical experiments with Aroclor 1254 under various conditions. These results were obtained by integration of all the areas of the isomer peaks from the first to the

last of the initial solution and comparing this total area to the total area resulting after a predetermined illumination time. This method cannot be considered an accurate determination of the absolute amount of Aroclor 1254 remaining, but instead should be used as a relative guide to follow the extent of the dehalogenation of the PCB, since the electron capture response to the more heavily substituted isomers of PCB is far greater than the less heavily substituted isomers.

A possible mechanism is suggested in Figure 15. This mechanism is free radical in nature. This concept is supported by the complete inhibition of the reaction by the addition of iodine, a free radical scavenger. The low boiling liquids N-propyl and isopropyl chlorides, with B.P. 45° C and 37° C respectively, if formed have not been detected by the methods utilized, though preliminary results indicate the presence of chloride ions. Potassium chloride is only very sparingly soluble in DMF and would rapidly precipitate from the solution. The data contained in Figures 4-16 and Tables 1-22 were used to formulate this proposed mechanism. Extract from transformer oil (50 mg/l PCB) and 100 mg/l Aroclor 1221 solutions have been successfully treated by this photochemical method. Dimethyl sulfoxide, DMSO, can be substituted for DMF, toluidine blue-o can be substituted for methylene blue, and many metal hydroxides will substitute for KOH without a great difference in the rate of the reaction.

The potential engineering applications of this photochemical procedure are shown in Figures 17-19. Transformer oil processing shows considerable promise as an area for the application of the photoreduction method previously described. Leachate and soil processing also shows commercial potential.

CHAPTER I

INTRODUCTION

For more than fifty years, polychlorinated biphenyls (PCB) have been used industrially. Vast quantities of PCB are present in public buildings, landfills, industrial plants, and in the environment. They have been used as dielectric liquids in transformers and capacitors; as industrial liquids in hydraulic equipment, gas turbines, and vacuum pumps; as a plasticizing agent in adhesives; in textiles, copy paper, sealants, and surface coatings; and as heat transfer liquids, fire retardants, and fruit preservants (1).

PCB's are one of the most wide-spread hazardous wastes found in the environment. They are quite resistant to the ordinary mechanisms of environmental degradation. Vast quantities of this chemical have been manufactured and sold; perhaps 1.1 billion pounds were sold domestically from 1930-1970. An estimated 270,000 metric tons are currently in dumps and landfills, 54,000 metric tons in water, and 27,000 metric tons in the air (1).

PCB, even though it expresses low acute toxicity, has been demonstrated to be carcinogenic in humans. It also causes fetal resorption, birth defects, high offspring mortality, reproductive failure, reduced weight gain, increased mortality, and enlargement of the liver, kidneys, and heart in test animals (1).

The manufacture of PCB is now prohibited in the United States and the Environmental Protection Agency, (EPA), has issued a final order requiring the removal of PCB liquids or the transformers which contain them, from all commercial buildings by October 1, 1990.

The current practices of indefinite storage or incineration of PCB, even though widely utilized, are unacceptable from an environmental standpoint. First of all, no containment system will maintain its integrity for an infinite period of time and so leakage and contamination of the ecosystem is certain to eventually occur. Secondly, incineration is a very efficient process but 100 percent conversion to safe products is not possible with the best available technology. Incineration if not properly controlled can yield products which are far more toxic than the substrate PCB.

The objectives of this research were to develop a new photochemical procedure for the processing of PCB. Once a method was developed, it was necessary to determine the essential characteristics of the reaction, such as mechanism, kinetic order, and etc. to optimize the parameters of the process to obtain the best possible reaction kinetics.

CHAPTER II

REVIEW OF LITERATURE

In this section, a review of the literature pertinent to the photolysis of PCB is presented. Particular emphasis is placed on the indirect or sensitized methods which are related to the photodegradation process which was developed in this photoreduction research. The efforts directed towards the creation of an efficient photolytic process which operates with visible wavelength light are also outlined.

Direct photolysis of PCB by ultraviolet (U.V.) radiation has been studied for some time (1-4). However, the generation of ultraviolet radiation required for the reaction is quite expensive and the reactions yield a myriad of decomposition and rearrangement products.

Several investigators have examined the photochemical dehalogenation of aryl chlorides in the presence of amines. Ohashi, et al. in 1973 first demonstrated the sensitized dechlorination of 4-chlorobiphenyl in the presence of aliphatic amines (5). Irradiation with U.V., $\lambda > 300$ nm light for 70 hours of a 4-chlorobiphenyl/ triethylamine/ acetonitrile system yielded a 71% biphenyl product. The rate of 4-chlorobiphenyl decomposition was very low in the absence of amines. Butylamine and dipropylamine had a lower sensitizer efficiency than triethylamine (5).

Nordblom, et al. in 1974 studied the sensitized photoreduction of 4, 4' dichlorobiphenyl using near ultraviolet light (λ = 310 nm) (6). Aromatic amines, tryptophan, and diethylaniline were found to be effective sensitizers in the presence of nitrogen or air. Oxygen was shown to slow the photoreduction reaction considerably. In 2-propanol or methanol the reaction exclusively yielded hydrochloric acid and 4-chlorobiphenyl in degassed solution. The 4-chlorobiphenyl product proved to be stable under these reaction conditions. The photoreduction reaction did not proceed in the solvents diethyl ether, cyclohexane, or acetonitrile (6).

Ultraviolet radiation of a 3-chlorobiphenyl/triethylamine system was shown to yield a nuclear reduction product in addition to the expected biphenyl product by Tsujimoto et al. in 1975 (7). This indicates reduction of aryl ring systems is possible by sensitized photochemical methods.

Occhiucci, et al. in 1982 found that PCB adsorbed on silica gel and montmorillonite will undergo photoreduction with irradiation at λ = 254nm sensitized by triethylamine. The main products were less heavily substituted chlorobiphenyls, but as expected, decomposition products also occurred (8).

Bunce, et al. in 1982 demonstrated indirect or sensitized photolysis of arylchlorides with aromatic amines in the presence of ultraviolet radiation. Their attempts to extend the reaction to longer wavelengths were unsuccessful (9).

Direct photolysis of Aroclor 1242 (a PCB mixture manufactured by Monsanto) was demonstrated in 1984 by Baxter, et al. to occur with radiation of visible wavelengths. This reaction apparently did not proceed at an appreciable rate. The process was not presented as a commercial detoxification process, but instead as a method for the eventual environmental degradation of PCB in combination with microbial degradation (10).

Chaudhary et al. in 1984 found a sensitizer, hydroquinone, which in alcoholic solution promoted dechlorination of PCB at wavelengths greater than 300 nm (visible wavelengths). However, less than 60% dechlorination of Aroclor 1254 occurred after 7 hours of irradiation with 450 watts in their best experiment (11).

An examination of the literature indicates that no commercially viable visible light sensitized PCB degradation processes have been developed. The previously described processes occur at rates too slow to be economically applied as an industrial process.

CHAPTER III

METHODS AND MATERIALS

This chapter contains detailed descriptions of the equipment, chemicals, and procedures used during the research performed on the development of a dye sensitized photochemical reduction process for biphenyl chlorides. Methods of experimental anlaysis by gas chromatography and mass spectrography are also detailed.

MATERIALS

This section contains a discussion of the materials which were utilized in this investigation. A list of chemicals and equipment is given in the Appendix in Tables 23 and 24.

Photochemical Reaction Assembly

The photoreduction reactions were carried out in the custom made Pyrex glass reaction assembly shown in Figure 1. The reflux condenser contained a helical glass coil. This assembly was suspended in a reflective foil lined box which had a ventilating fan on the side. These reactions were carried out in a ventilating fume hood, and the propane gas to waste was carefully vented from the reaction assembly and exhausted from the fume hood. The experiments were carried out with two 200 w incandescent light bulbs taped so that the bulbs

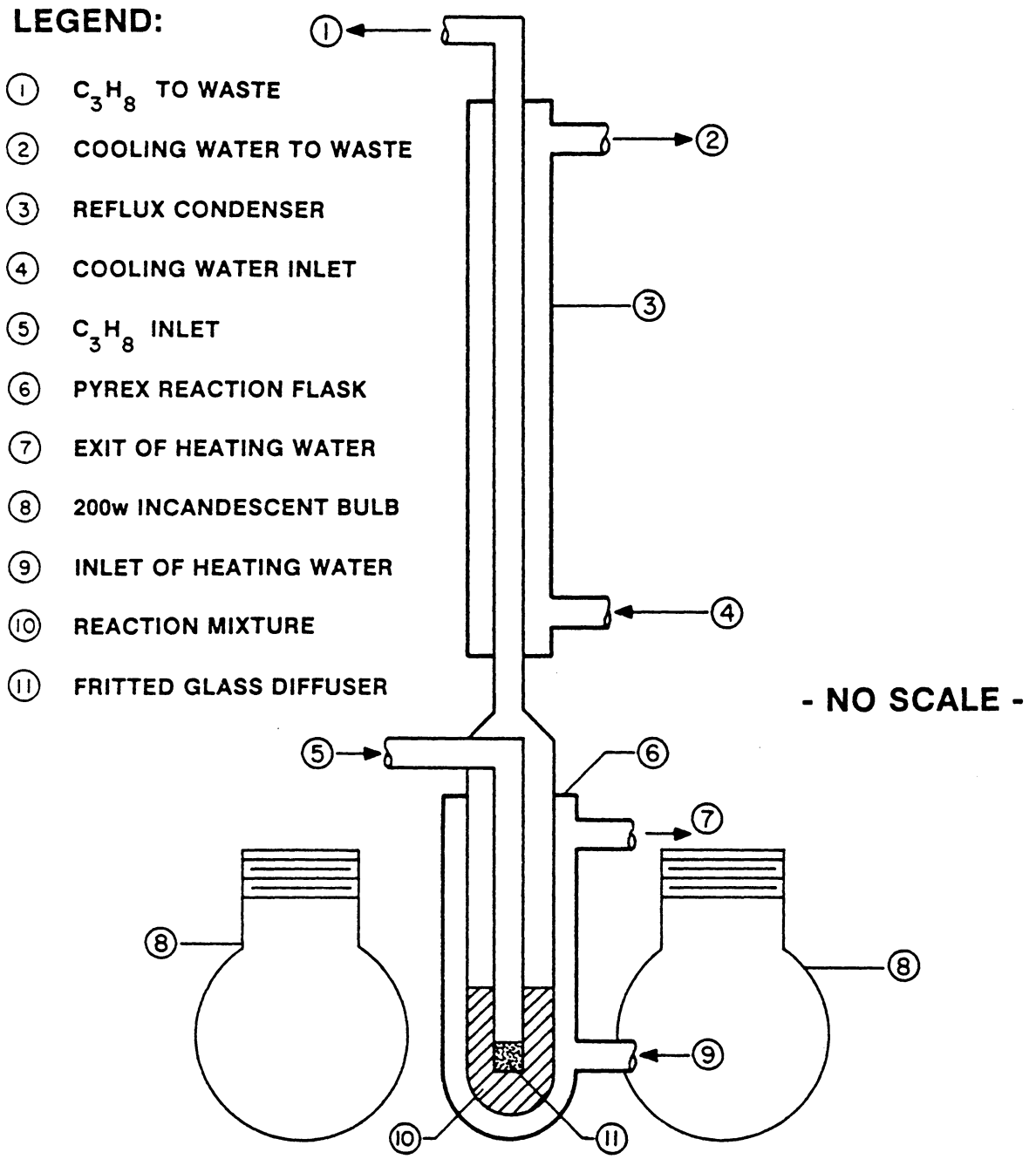


FIGURE 1. SIMPLIFIED SCHEMATIC OF THE LABORATORY PHOTOCHEMICAL REACTION ASSEMBLY.

actually touched the water jacket of the Pyrex reaction flask. The temperature was maintained constant (to $\pm$ 1°C.) by circulation of water from a thermostatically controlled Buchi water bath. Volatilized solvent was returned to the reaction flask by the reflux condensor which was cooled by tap water and this water was wasted.

Aroclor 1254 Stock Solution

Aroclor 1254 is a complex mixture of PCB isomers manufactured by Monsanto. Aroclor 1254 is 54% chlorine by weight, contains an average of 4.96 chlorine atoms per molecule, and has an average atomic weight of 327 (2). The material used for this research was a 1 mg/ml Aroclor 1254 in iso-octane solution distributed by the U.S. Environmental Protection Agency (EPA) for use as a standard.

Aroclor 1221 Stock Solution

Aroclor 1221 is a complex mixture of PCB isomers manufactured by Monsanto Co. Aroclor 1221 is 20.5-21.5 percent chlorine by weight, contains 1.15 chlorine atoms per molecule, and has an average atomic weight of 192 (2). The material used for this research was a 1 mg/ml Aroclor 1221 in iso-octane solution distributed by the EPA for use as a standard.

METHODS

This section describes the experimental methods used in this research. Specific experimental operating parameters are indicated on pertinent Figures and Tables.

A Typical 4-Chlorobiphenyl Photoreduction Experiment

A potassium hydroxide saturated solution of DMF was prepared by stirring KOH pellets in a Voltex-Genie. The solution was set quiescently for a half an hour and then the clear liquid was drawn off. A sufficient quantity of 4-chlorobiphenyl was then added to the KOH saturated DMF solution to yield a 100 mg/l 4-chlorobiphenyl solution. A 1 ml aliquot was withdrawn and placed in a small test tube. A sufficient quantity of a previously prepared stock solution of methylene blue in DMF solution (0.2 gm/25 ml DMF) was added to the 1 ml aliquot. A single pellet of KOH was added to the reaction vessel in such a way that the light from the two light bulbs would not be blocked. The 1 ml aliquot containing a DMF saturated with KOH, 100 mg/l 4-chlorobiphenyl, and 350 mg/l methylene blue was then introduced into the reaction vessel. Next, 70 ml/min of propane was diffused into the 1 ml aliquot in the reaction vessel. The lights were switched on and timing began simultaneously. The volumetric delivery of propane was maintained constant by a rotameter which had been calibrated by timing the displacement of water from a graduated cylinder inverted in a vessel of water. Temperature in the reaction vessel was maintained $\pm$ 1°C by pumping water, from a thermostatically

controlled water bath, through the jacket. Evaporated solvent was returned to the reaction vessel by circulating cold water through the condenser (see Figure 1).

At the end of the prescribed period of illumination time, the lights and propane were shut off, and the pellet of KOH and the 1 ml aliquot was placed in a 7 ml glass extraction vial. 1 ml of iso-octane was then added to the extraction vial and mixed at the #3 setting on a Vortex-Genie. A 2 µl sample of the iso-octane extract was then introduced into the injection port of the 5880A gas chromatograph. Each of these steps were done without delay to minimize changes due to shifts in equilibrium or continuing reactions.

A 1 ml aliquot prepared exactly as previously prescribed but without propane diffusion and illumination was extracted and a sample injected into the chromatograph using the electron capture detector. The control solution was used to calibrate the integrator. The peak resulting from the control solution was compared on an area basis to the peak areas resulting from solutions which had been sparged with propane and illuminated for prescribed time periods. The syringe was cleaned with iso-octane several times before each new injection.

The 5880A chromatograph was operated using the following conditions:

Oven temperature - 200°C Isothermal

Carrier gas - N_2 at 60 ml/min

Detector temperature - 250°C

Injector temperature - 225°C

Column - 2 m, 4mm I.D., packed glass column
(1.5% OV - 17 + 1.95% QF-1 Chromasorb W-HP 100/200)

Detector - electron capture

The reaction solution peak area was compared to a control solution peak area using the external standard method.

A Typical Aroclor 1254 Photoreduction Experiment

An aliquot of stock EPA standard Aroclor 1254 in iso-octane (1 mg/ml) solution was introduced into a test tube and the solvent evaporated under a stream of nitrogen at room temperature. The PCB residual was dissolved in a predetermined amount of DMF, to yield a solution strength of 10 mg/l Aroclor 1254 in DMF. A 1 ml aliquot of

this solution was introduced into another test tube and a sufficient quantity of a previously prepared methylene blue in DMF solution was added to make a 350 mg/l methylene blue concentration. This resulting aliquot containing 10 mg/l Aroclor 1254, DMF, and 350 mg/l methylene blue was then introduced into the reaction vessel. Propane gas was diffused into the solution, then illumination and timing were started simultaneously. After a predetermined illumination time period the propane diffusion and illumination were discontinued, the aliquot removed and placed in an extraction vial with 1 ml iso-octane, extracted on a Vortex-Genie 1 minute at the #3 setting and 2 µl of the iso-octane extract was introduced into the chromatograph injection port.

A 1 ml aliquot prepared exactly as previously described but without propane diffusion and illumination was extracted and injected into the chromatograph using the electron capture detector. This control solution calibrated the integrator. The peaks which eluted from 3-40 minutes were summed together and the resulting area was compared with the area resulting from the summed peak areas (3-40 minutes) of solutions which had been propane diffused and illuminated. A linear relationship was assumed to exist between the total area under the curve, from 3-40 minutes, and the amount of Aroclor 1254 remaining. This method should only be considered a relative guide to follow the extend of the dehalogenation of the Aroclor 1254, rather than the absolute amount of Aroclor 1254 remaining, since the electron capture detector sensitivity to the more heavily substituted isomers of PCB is far greater than the less heavily substituted isomers.

The chromatograph was operated under the identical condition previously described in the "Typical 4-Chlorobiphenyl Photoreduction Procedure" section, with the exception of the differences in integrator function already discussed.

Method of Detection of the Biphenyl Reaction Product

A 1 mg/ml Aroclor 1254 in iso-octane solution showed no detectable biphenyl when examined on a Tracor 560 gas chromatograph using a flame ionizing detector. Samples of 2 µl from iso-octane extracts of Aroclor 1254 reaction mixtures (containing KOH) were introduced into the chromatograph after illumination and propane sparging.

The Tracor 560 chromatograph was operated under the following conditions:

Oven temperature - 130° C isothermal

Carrier gas - N_2 @ 1.5 setting

Detector Temperature - 250°C

Injector temperature - 225°C

Column - 2 m, 4mm I.D., packed glass column
(5% SP - 2100 100/120 Supelcoport)
Detector - Flame ionization with air at
300 ml/min and hydrogen at 30 ml/min

Standard solutions of biphenyl were injected to determine the retention time of this compound.

Identification of the Major Reaction Product by Gas Chromatography/ Mass Spectrography

A 100 mg/l 4-chlorobiphenyl in DMF solution was photoreduced for 1 hr.,as described in the section - "Description of a Typical 4-Chlorobiphenyl Photoreduction Experiment." The iso-octane extract was removed and concentrated under a stream of nitrogen. The concentrated iso-octane extract was then introduced into a Hewlett-Packard Gas Chromatograph/V.G. Mass Spectrograph assembly in the Virginia Tech Biochemistry Department. The major reaction product was automatically identified by the associated computer by comparison with its library of mass spectrographs in its data bank. These anlayses were performed by Kim Harich, Mass Spectrograph Technician.

Detection of Chloride Concentrations in a Reaction Mixture

A solution was prepared and photoreduced for one hour as previously described in the description of "A Typical 4-Chlorobiphenyl Photoreduction Experiment." The photoreduced aliquot, KOH pellet and

distilled water washings of the reaction vessel were placed in a small flask and heated under a stream of air until dry. The resulting residue was then redissolved in a small amount of water. This aqueous solution was then heated while illuminating with light and sparging with oxygen. After a time, evaporation of a considerable amount of the water and a precipitation of most of the dye occured. This procedure was also carried out on a reagent blank or control solution, identical in composition but which had not been diffused with propane or illuminated.

The application of light and oxygen was not necessary to achieve dye precipitation but appeared to promote it. The precipitated dye was removed by vacuum filtration on a 2.1cm grade 934 AH Reeve Angel glass fiber filter. The resulting filtrates were then diluted with distilled water to obtain 1 ml volumes. Diphenylcarbazone indicator, weighing 0.0759 gr, was added to each aliquot and titration proceeded with either 0.000705 N or 0.0001763 N mercuric nitrate solution to the prescribed endpoint (12).

Determination of the Saturation Concentration of KOH in DMF

A supersaturated solution was prepared by heating pellets of KOH in DMF. The resulting solution was withdrawn from the container leaving the pellets behind. Phenolphthalein was added to a 1 ml aliquot. The resulting solution was titrated with 0.01 N H_2SO_4. This procedure indicated a saturated DMF solution contained about 41 mg/l KOH at 25°C.

Transformer Oil Processing Method

Transformer oil manufactured in the past frequently contained PCB. This oil is non-polar and is immiscible with DMF. A 50 mg/l PCB transformer oil was obtained from the Virginia Tech Safety Office, and extracted with DMF. The resulting DMF extract was saturated with strong base, methylene blue was added, and the solution was sparged with propane and illuminated. An extraction ratio of one part transformer oil to ten parts DMF was used to minimize inferences from color and foaming, since low extraction ratios yielded an uptake of a large amount of a yellowish coloring matter and a great deal of foaming upon propane diffusion.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter the results of the experiments performed and discussion of the results will be presented. Each experimental subject will be examined in a separate subdivision.

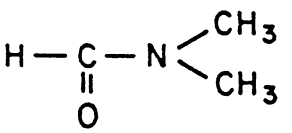
GENERAL OBSERVATIONS

Major Molecular Species

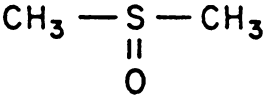
The major molecular species involved in the photoreduction process are displayed in Figure 2. The solvents involved were of the polar aprotic type, and the solvent most commonly used in these experiments was N, N-dimethylformamide (DMF), though dimethyl sulfoxide (DMSO) was also found to be useful. This process required the presence of light and a dye sensitizer to achieve acceptable rates of aryl chloride reduction. The dyes found to be most effective were thiazine derivatives, principally methylene blue, but toluidine blue-o was also very effective. Strong bases such as the alkali metal hydroxides were found to be useful for general acceleration of the photoreduction reaction. Potassium hydroxide was most often employed. The main source of hydrogen for the photoreduction of aryl chlorides was a hydrocarbon gas, propane. The substrates for these reactions were either commercial mixtures of PCB or the monohalogenated isomer, 4-chlorobiphenyl.

SOLVENTS:

N,N-DIMETHYLFORMAMIDE **DIMETHYL SULFOXIDE**



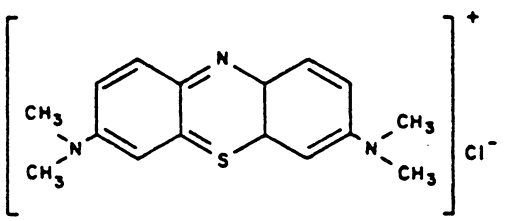
OR



OR OTHER POLAR APROTIC SOLVENTS

SENSITIZERS:

METHYLENE BLUE **TOLUIDINE BLUE - 0**



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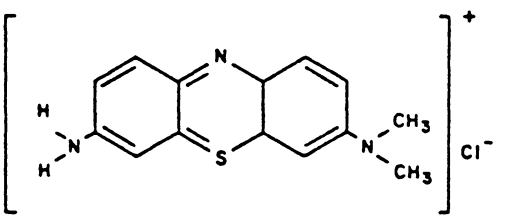
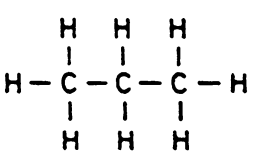


BASES:

LiOH **OR** $Ca(OH)_2$ **OR** NaOH **OR** KOH

OR OTHER STRONG BASES

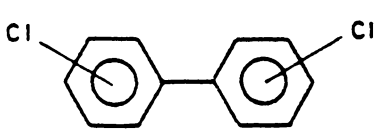
HYDROGEN SOURCE:



PROPANE

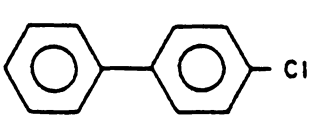
OR OTHER HYDROCARBON GASES

SUBSTRATE:



PCB

OR



4 - CHLORO BIPHENYL

FIGURE 2. PRINCIPAL MOLECULAR SPECIES OF THE PCB PHOTOCHEMICAL DEGRADATION PROCESS.

Sensitizer Absorption Spectrum

The photochemical process uses visible wavelength light to drive the reaction. Figure 3 shows the emission spectrum of the sun compared to the absorbtion spectrum of methylene blue (13). Sunlight could be used for the photoreduction of aryl chlorides under certain conditions. In near zero pOH solutions the absorbance maximum of methylene blue in DMF or DMSO is at about 660 nm, but if a strong base is added the color changes to a bright red and the absorption maximum is shifted to the left at about 550 nm.

PROCESS DEVELOPMENT AND OPTIMIZATION

Photoreduction of 4-Chlorobiphenyl

The monochlorinated isomers of biphenyl are very chemically stable. Figure 4 shows the progress of the photoreduction in DMF solution with a methylene blue sensitizer present. Note that KOH accelerates the reaction, and that a saturated KOH solution with a solid pellet of KOH present is required to achieve acceptable reaction kinetics. The presence of a solid pellet of KOH does not perceptibly reduce the concentration of a 4-chlorobiphenyl in DMF solution when stored in the dark for twenty four hours. When all the reaction conditions described in Figure 4 are maintained with the exception of illumination, the 4-chlorobiphenyl reduction reaction does not proceed by a thermal mechanism in one hour of propane diffusion time.

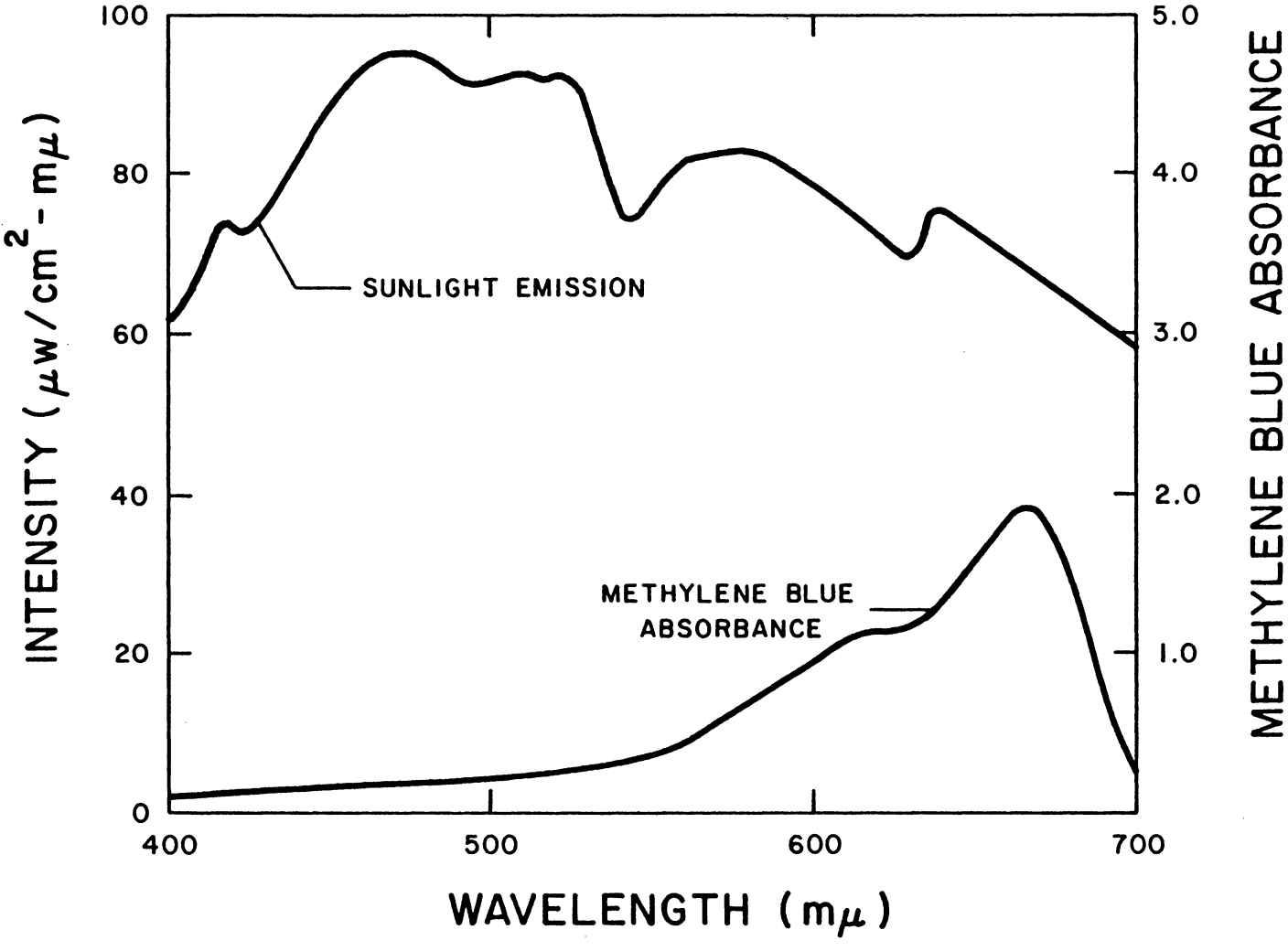
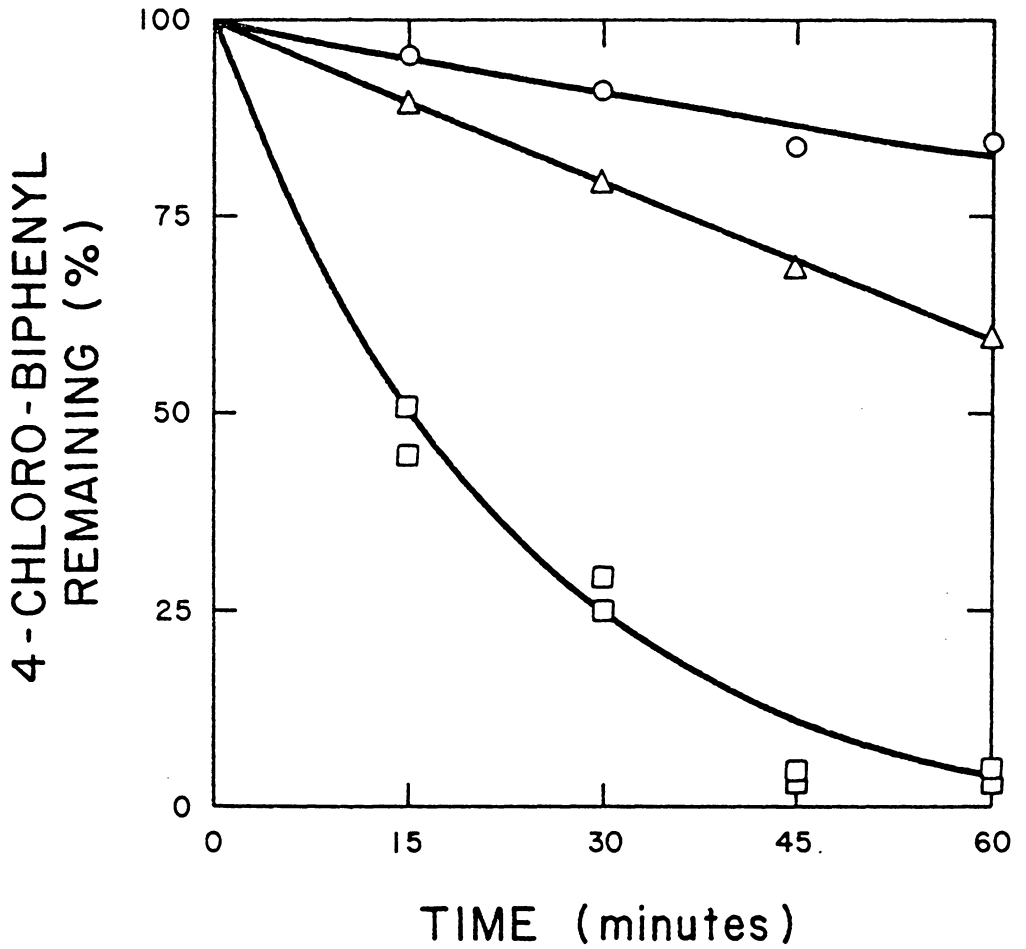


FIGURE 3. COMPARISON OF THE ABSORBANCE SPECTRUM OF METHYLENE BLUE AND SUNLIGHT EMISSION.



LEGEND:

- ○ **NO KOH**
- △ **SATURATED WITH KOH**
- □ **WITH SOLID KOH PRESENT, SOLUTION PREVIOUSLY SATURATED WITH KOH**

FIGURE 4. PHOTOCHEMICAL DESTRUCTION OF A 100mg/ℓ 4 - CHLORO BIPHENYL IN DMF SOLUTION, SPARGED WITH 70mℓ/ MINUTE PROPANE, AND IRRADIATED IN A PYREX REACTION VESSEL WITH TWO 200w INCANDESCENT LIGHT BULBS. SOLUTION TEMPERATURE WAS MAINTAINED AT 30°C ± 1°C, APPROXIMATELY 350mg/ℓ METHYLENE BLUE WAS USED AS THE SENSITIZER.

Identification of the Major Photoreduction of 4-Chlorobiphenyl Reaction Product

A gas chromatogram obtained from a 20 m capillary column is shown in Figure 5. This chromatogram shows the initial susbtrate at 217 seconds and the major reaction product at 147 seconds of the 4-chlorobiphenyl photoreduction reaction. Figure 6 shows the mass spectrograph of the major reaction product, compared to the library spectrograph of biphenyl. The V.G. mass spectrograph's associated computer automatically identified the major reaction product as biphenyl.

Determination of the Final Residence Form of the Chlorine Involved in the 4-Chlorobiphenyl Photoreduction Reaction

A 100 mg/l 4-chlorobiphenyl solution was photoreduced and analyzed by the procedure outlined in the Materials and Methods section called "Method Used to Detect Chloride Concentrations in a Reaction Mixture." The titrations to the diphenylcarbazone endpoint with 0.000705 N mercuric nitrate indicated 0.197 mg/l Cl^- dissolved in a reagent blank (control) while the reaction mixture contained 0.263 mg/l Cl^- a titration with 0.0001763 N mercuric nitrate indicated that 0.148 mg/l Cl^- was dissolved in a reagent blank (control), while 0.312 mg/l Cl^- was contained in a reaction mixture. These results indicate significantly more chloride ion was to be found dissolved in a reaction mixture. This implies chloride ion is a major reaction product in this photoreduction process.

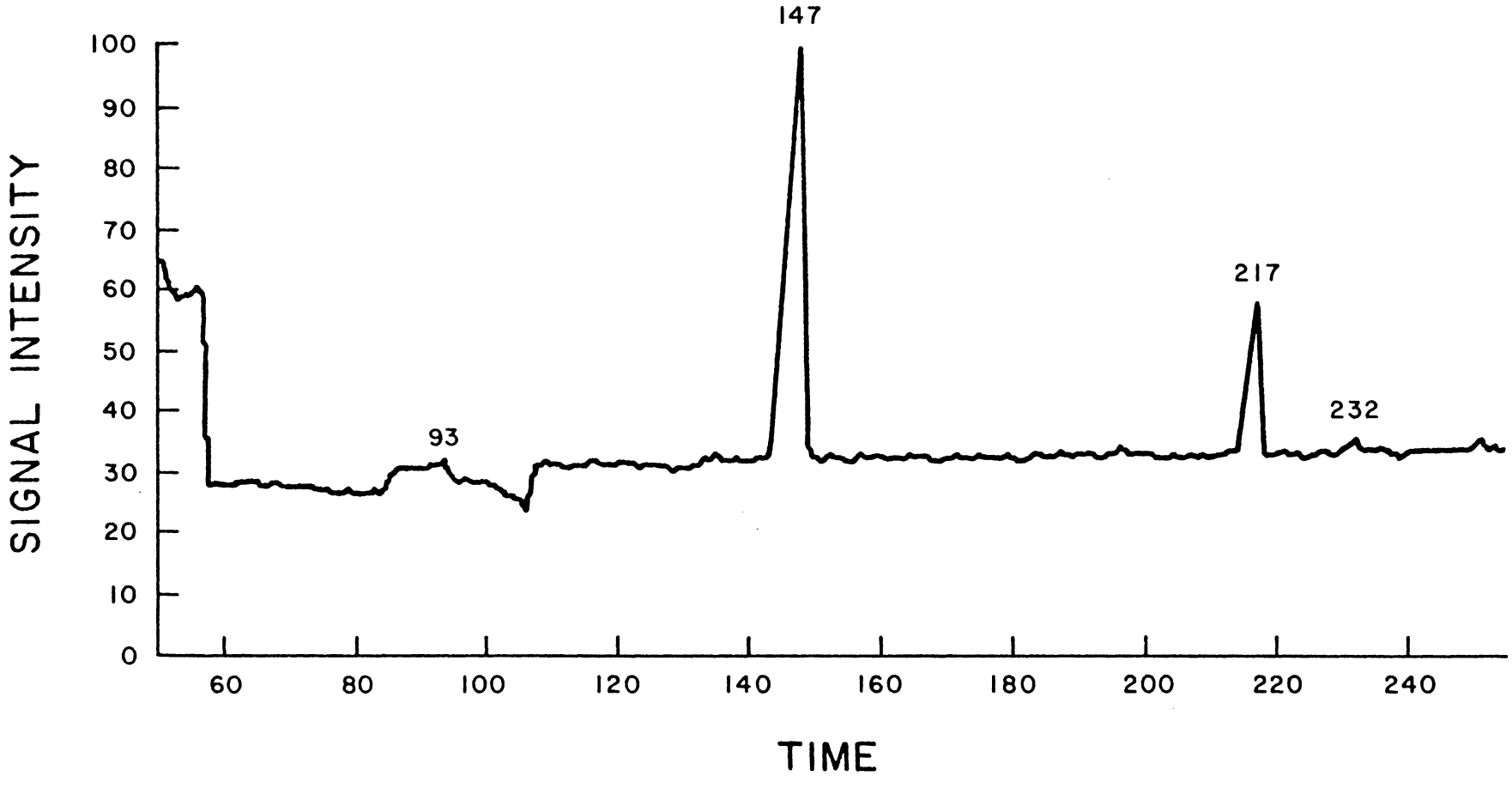


FIGURE 5 - CHROMATOGRAM OF A CONCENTRATED ISO-OCTANE EXTRACT FROM A 100mg/ℓ 4 - CHLORO BIPHENYL IN DMF SOLUTION (CONTAINING 350mg/ℓ METHYLENE BLUE, SOLID KOH, AND SPARGING WITH 70mℓ/min $C_3 H_8$) AFTER IRRADIATION (400w, $\lambda > 300$ nm). THE PEAK AT 147 IS THE MAJOR REACTION PRODUCT, AND THE PEAK AT 217 IS 4 - CHLORO BIPHENYL.

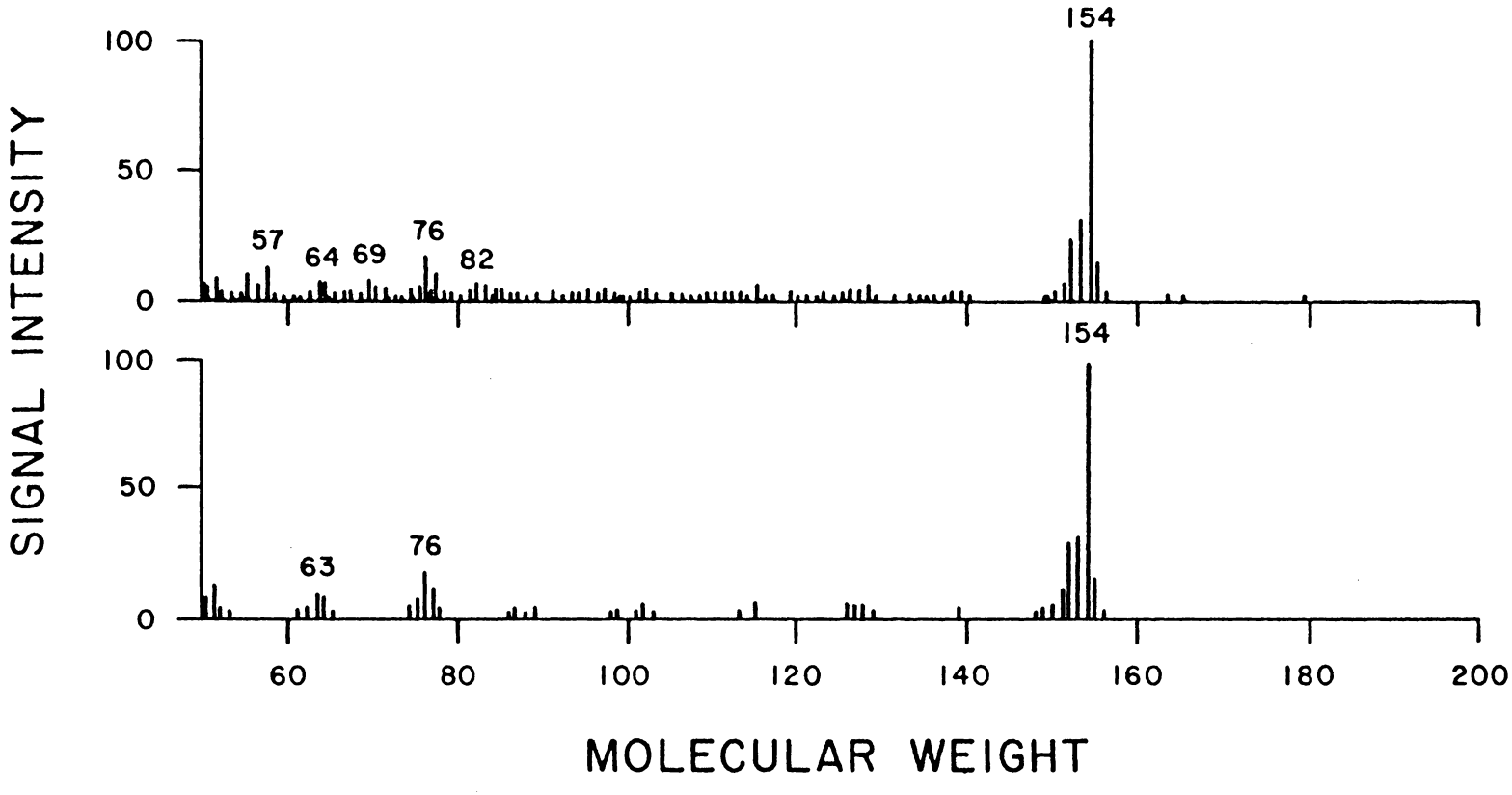


FIGURE 6. COMPUTER IDENTIFICATION OF THE MASS SPECTROGRAPH OF THE MAJOR REACTION PRODUCT. THE UPPER GRAPH IS THE MAJOR REACTION PRODUCT SPECTROGRAPH, THE LOWER GRAPH IS THE COMPUTER LIBRARY SPECTROGRAPH OF 1,1' BIPHENYL,WHICH WAS THE COMPUTER GENERATED IDENTIFICATION OF THE MAJOR REACTION PRODUCT.

Potassium chloride is only very sparingly soluble in DMF. Therefore it would quickly precipitate from the reaction mixture as it is formed. Diffuser function is impaired as a function of illumination time during a photoreduction reaction in the presence of strong base, i.e. volumetric delivery of propane is reduced and this restriction of flow is quickly restored by washing with distilled water; this flow restriction may be due to the precipitation KCl in the diffuser.

Kinetic Evaluation of the 4-Chlorobiphenyl Photoreduction Reaction

The 4-chlorobiphenyl photoreduction reaction data, as presented in Figure 4, were plotted to determine the reaction order with respect to the disappearance of the 4-chlorobiphenyl substrate. The possibilities of 0, 0.5, 1, 1.5, 2, 3, 4 order reactions were evaluated. The plot with the 1st order assumption showed the highest linear correlation coefficient (0.9695) for the reaction in the presence of solid strong base, with a rate constant of 0.0586 $min.^{-1}$ in the reaction with a KOH saturated solution. The 1st order assumption with respect to 4-chlorobiphenyl demonstrated the best linear correlation coefficient (0.9946), with a rate constant of 8.075×10^{-3} min^{-1}.

Photoreduction of Aroclor 1254 at 30°C in the Absence of Metal Hydroxide

A chromatogram of Aroclor 1254 is shown in Figure 7. This chromatogram is an iso-octane extract of a reaction mixture containing Aroclor 1254 and methylene blue in DMF. The more heavily substituted isomers of PCB elute at longer retention times, while the less heavily substituted isomers elute first. Figures 7-11 show the progress of photoreduction reactions with Aroclor 1254 solutions as a function of time. Note the signal originating from the more heavily substituted isomers is attenuated first, with corresponding new signals originating at low retention times beginning at 15 minutes illumination time, which indicates the formation of less substituted reaction products.

With increasing illumination time the signal from the more heavily substituted isomers is completely attenuated while a resistant product peak prominently remains at 60 minutes illumination. This resistant product has a short retention time and is probably a mono-halogenated isomer. These monochlorinated biphenyls are very chemically stable and require the presence of solid strong base to react at a significant rate, as was demonstrated by the experiments with 4-chlorobiphenyl. These results are shown in Figure 12. Nearly 99% removal of Aroclor 1254 occured in 60 minutes illumination at 30°C.

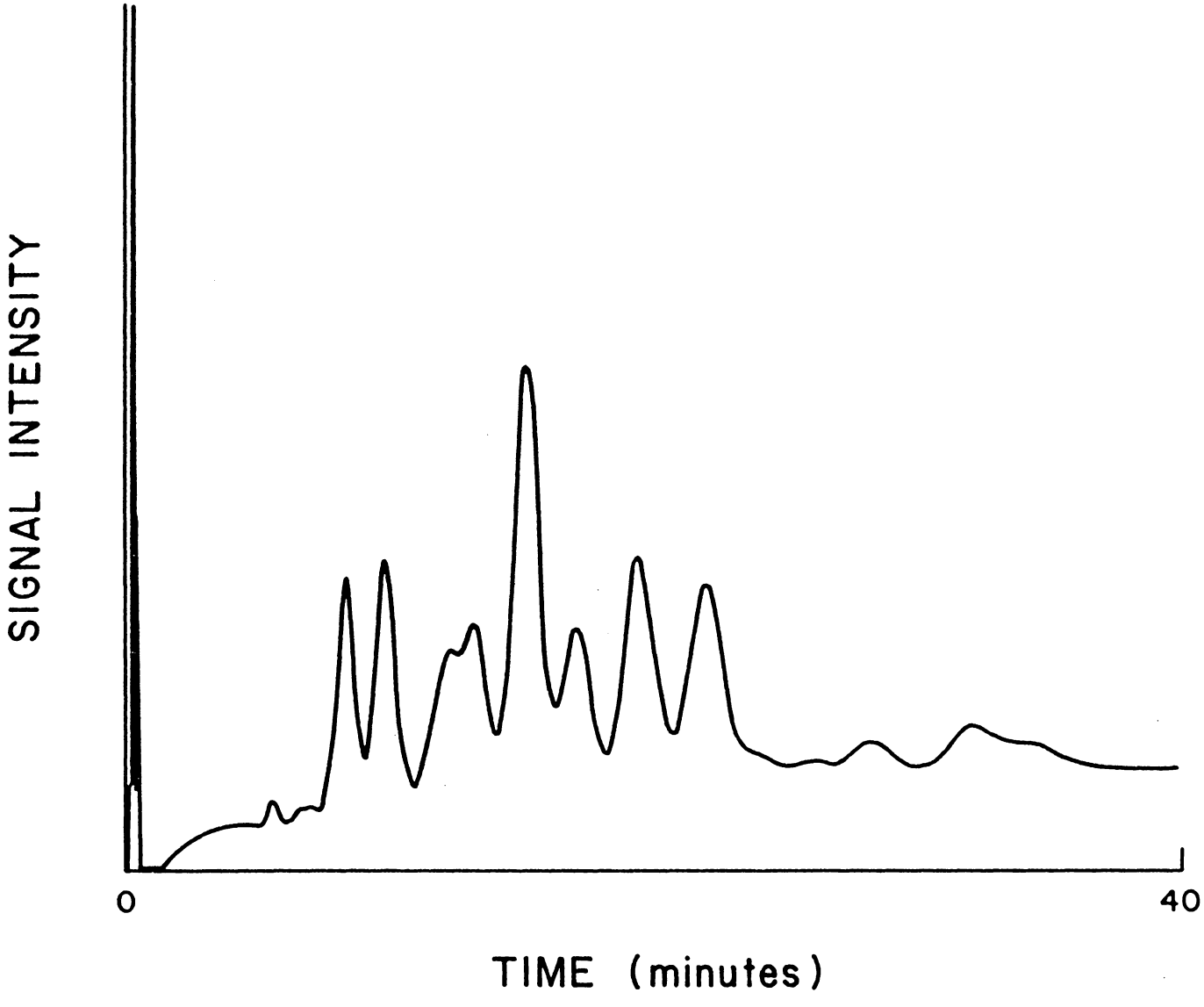


FIGURE 7. CHROMATOGRAM OF A 10mg/ℓ AROCLOR 1254 IN DMF SOLUTION, 350mg/ℓ METHYLENE BLUE, WHICH WAS EXTRACTED WITH ISO-OCTANE BEFORE IRRADIATION AND SPARGING WITH PROPANE.

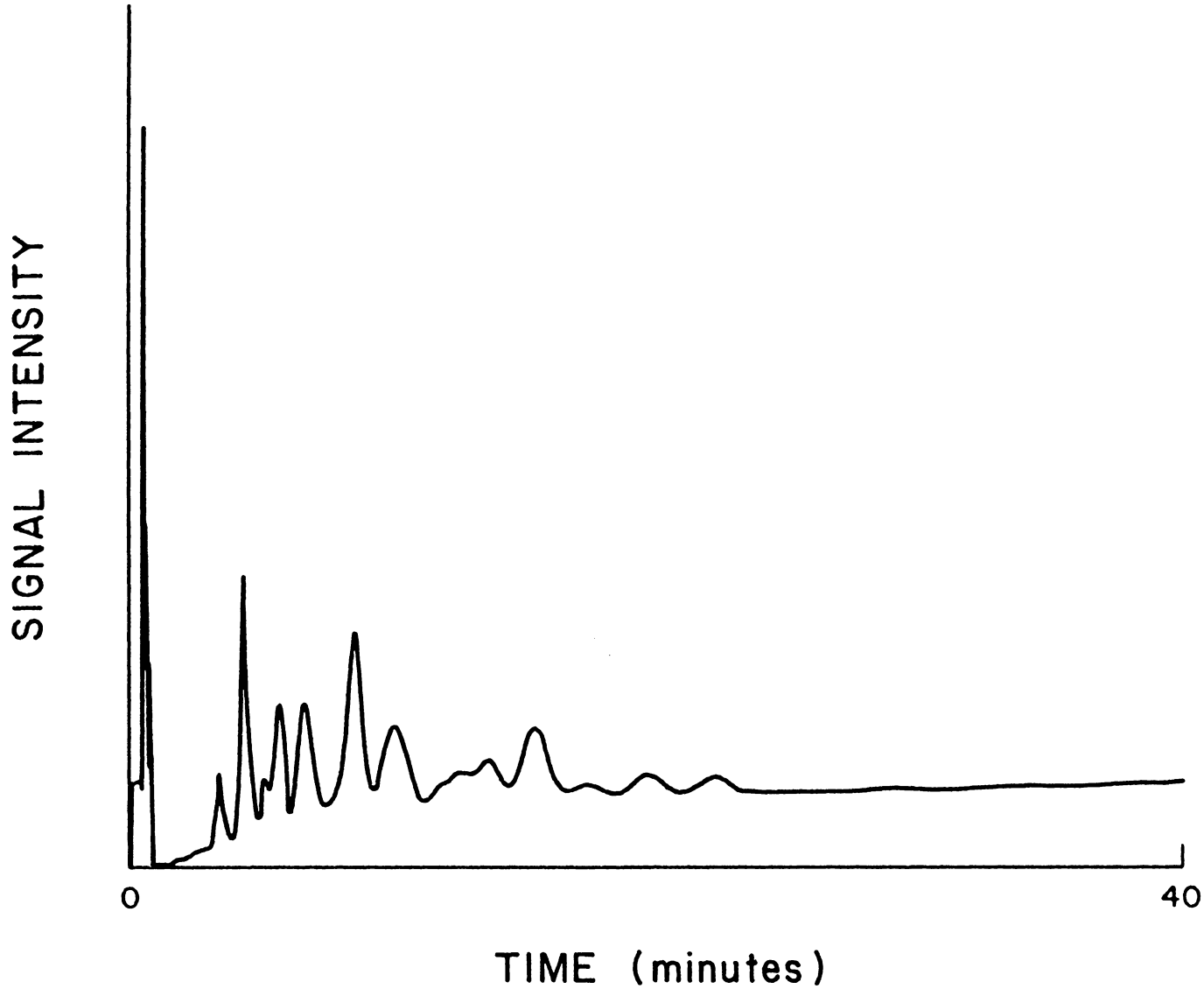


FIGURE 8. CHROMATOGRAM OF A 10mg/ℓ AROCLOR 1254 IN DMF SOLUTION, 350mg/ℓ METHYLENE BLUE, WHICH WAS EXTRACTED WITH ISO-OCTANE AFTER 15 MINUTES OF IRRADIATION (400w, $\lambda > 300$ nm) AND SPARGING WITH 70mℓ/min PROPANE AT A SOLUTION TEMPERATURE OF 30°C ± 1°C.

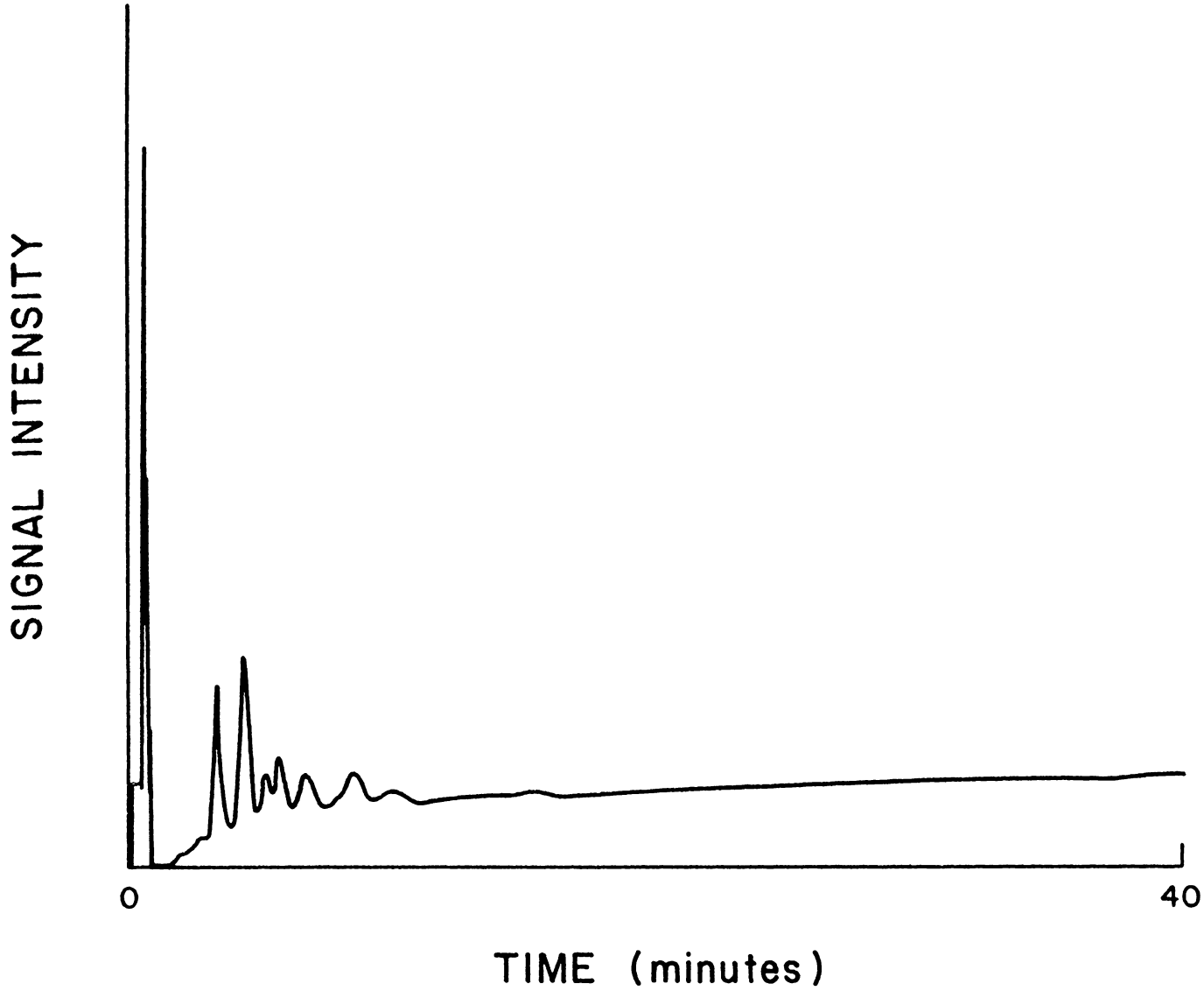


FIGURE 9. CHROMATOGRAM OF A 10mg/ℓ AROCLOR 1254 IN DMF SOLUTION, 350mg/ℓ METHYLENE BLUE, WHICH WAS EXTRACTED WITH ISO-OCTANE AFTER 30 MINUTES OF IRRADIATION (400w, $\lambda > 300$ nm) AND SPARGING WITH 70mℓ/min PROPANE AT A SOLUTION TEMPERATURE OF 30°C ± 1°C.

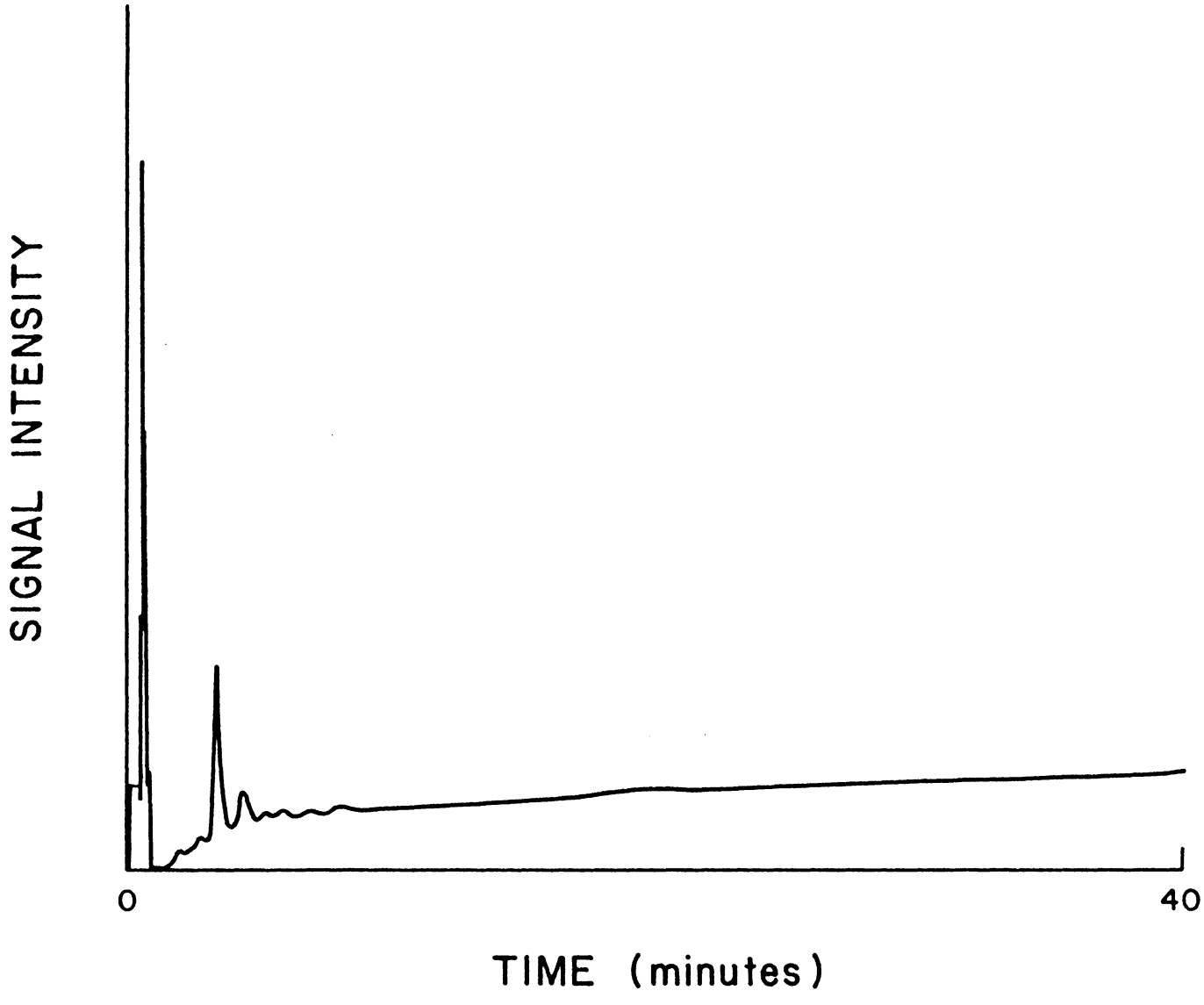


FIGURE 10. CHROMATOGRAM OF A 10mg/ℓ AROCLOR 1254 IN DMF SOLUTION, 350mg/ℓ METHYLENE BLUE, WHICH WAS EXTRACTED WITH ISO-OCTANE AFTER 45 MINUTES OF IRRADIATION (400w, $\lambda > 300$ nm) AND SPARGING WITH 70mℓ/min PROPANE AT A SOLUTION TEMPERATURE OF 30°C ± 1°C.

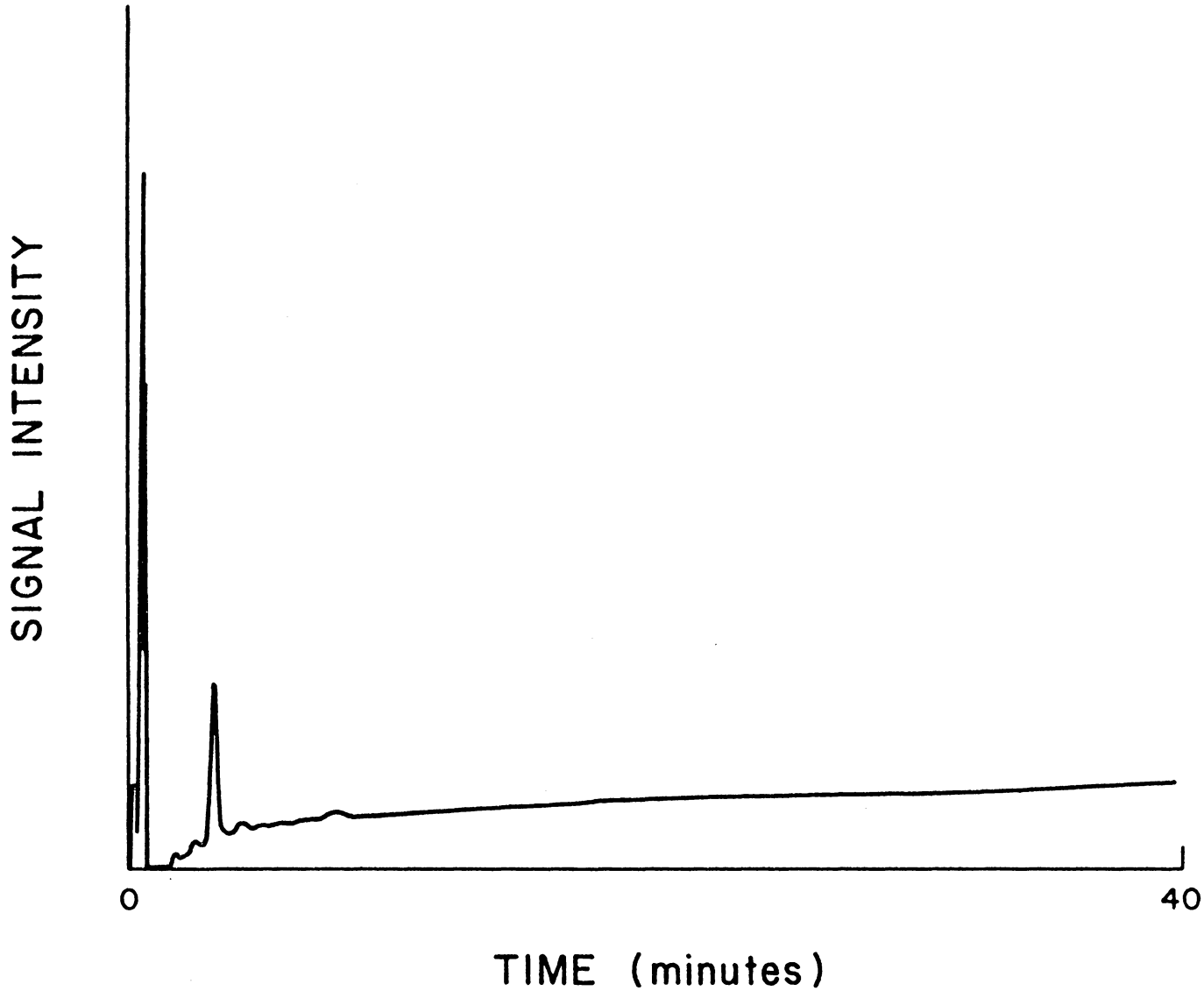


FIGURE 11. CHROMATOGRAM OF A 10mg/ℓ AROCLOR 1254 IN DMF SOLUTION, 350mg/ℓ METHYLENE BLUE, WHICH WAS EXTRACTED WITH ISO-OCTANE AFTER 60 MINUTES OF IRRADIATION (400w, λ > 300 nm) AND SPARGING WITH 70mℓ/min PROPANE AT A SOLUTION TEMPERATURE OF 30°C ± 1°C.

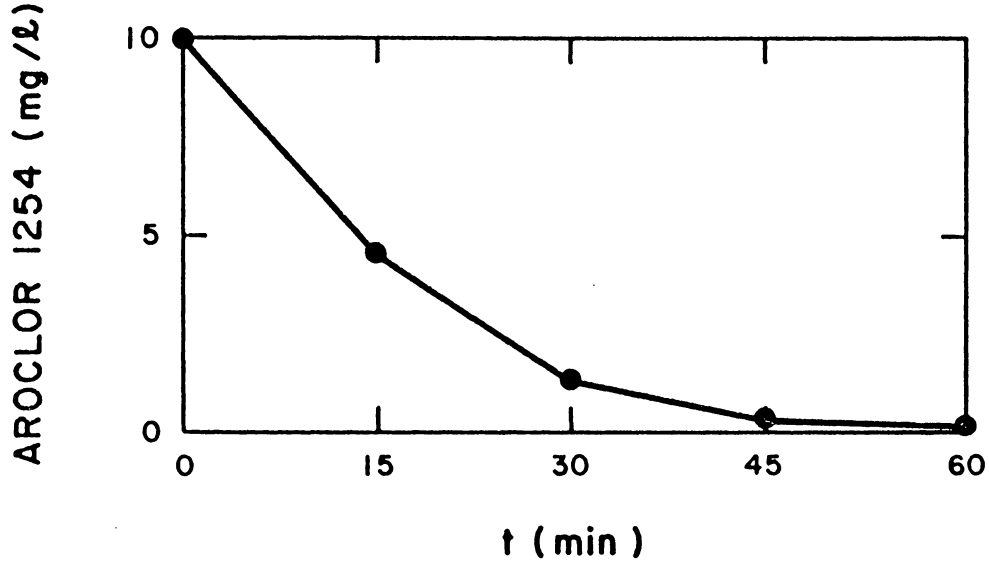


FIGURE 12. PHOTOCHEMICAL DEHALOGENATION OF AROCLOR 1254 IN DMF, 350 mg/ℓ METHYLENE BLUE, IRRADIATED 400 WATTS h.ν., SPARGED WITH PROPANE (70mℓ/min) AT 30° C.

Photochemical Reduction of Aroclor 1254 in the Presence of Potassium Hydroxide

The rate of photoreduction of Aroclor 1254 is enhanced by saturating the reaction mixture with potassium hydroxide at 30° C as demonstrated in Figure 13. The rate can be further increased by increasing the temperature to 40°C as indicated in Figure 14. As the Aroclor 1254 signal attenuates with increasing illumination time, a product signal appears and increases (upon examination with a flame ionization detector) which has been identified to be biphenyl.

Photoreduction of Aroclor 1254 in the Absence of Sensitizer

Examination of Table 1 shows the progress of photoreduction of a Aroclor 1254 in DMF solution without any dissolved sensitizer. The reaction proceeds, but only very slowly. Perhaps 13% dehalogenation of Aroclor 1254 occurs after 60 minutes of irradiation. Direct excitation of the PCB molecule may be occurring. Most PCB's show at least some absorption at λ >280 nm (2), and this may be enough energy input to weakly drive the photoreduction reaction.

Photoreduction of a 100 mg/l Aroclor 1221 Solution

Table 2 shows data from a photochemical reduction experiment carried out at 50° C with a solid pellet of potassium hydroxide immersed in the solution. Approximately 88% destruction was obtained after 30 minutes of illumination. Since Aroclor 1221 is less heavily

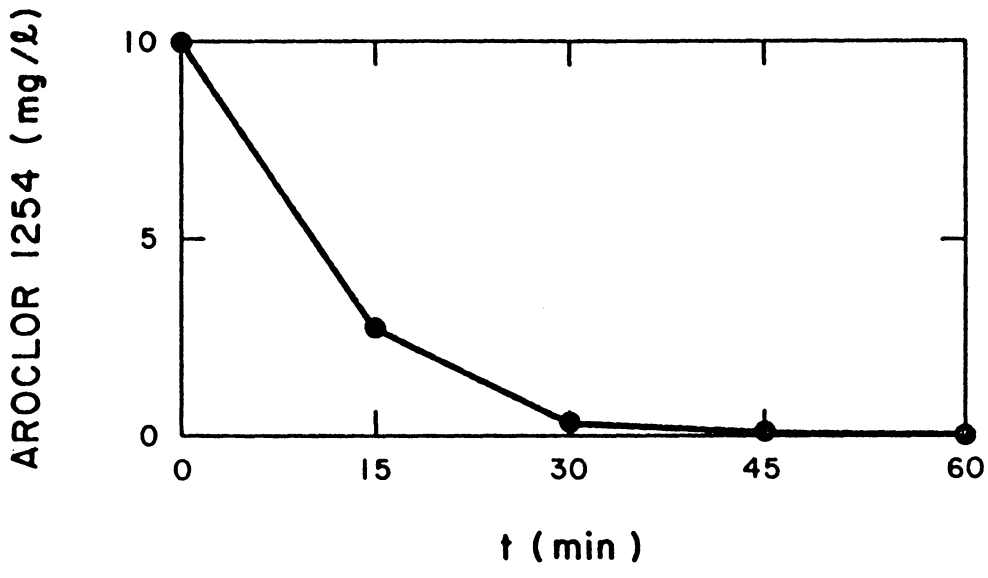


FIGURE 13. PHOTOCHEMICAL DEHALOGENATION OF AROCLOR 1254 IN DMF, SATURATED WITH KOH, 350mg/ℓ METHYLENE BLUE, 400 WATTS h.ν., SPARGED WITH PROPANE (70mℓ/min), AT 30°C.

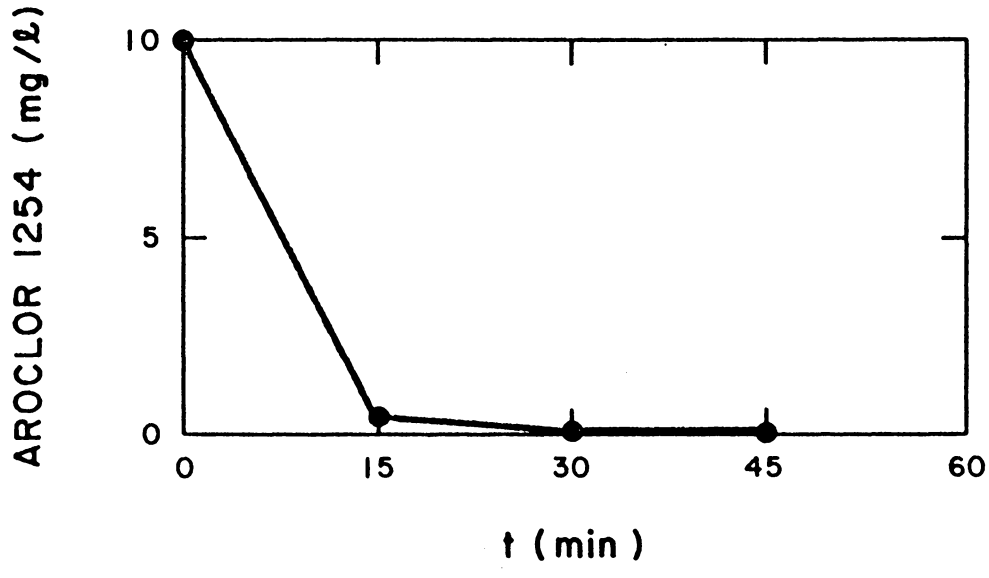


FIGURE 14. PHOTOCHEMICAL DEHALOGENATION OF AROCLOR 1254 IN DMF, SATURATED WITH KOH, 350 mg/ℓ METHYLENE BLUE, 400 WATTS h.ν. ,SPARGED WITH PROPANE (70mℓ/min), AT 40°C.

TABLE 1. REACTION OF AROCLOR 1254 IN THE ABSENCE OF SENSITIZING DYE*

ILLUMINATION TIME (MIN)	CONCENTRATION OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
15	10.105
30	8.422
45	8.758
60	8.711

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions. The solutions were sparged with 70 ml/min propane and the solution temperature was maintained at 30°C $\pm$ 1°C. Illumination was with 400 w $h.\nu.$, λ>300 nm.

TABLE 2. AROCLOR 1221 DEGRADATION REACTION*

ILLUMINATION TIME (MIN)	CONCENTRATION OF AROCLOR 1221 REMAINING (MG/L)
0	100,000
30	11,734

*Photochemical dehalogenation of a 100 mg/l Aroclor 1221 in DMF solution, 700 mg/l methylene blue, sparged with 140 ml/min propane, a solid pellet of KOH was present, and the solution temperature was maintained at 50° C ± 1° C. Illumination was with 400 w $h.\nu.$, $\lambda > 300$ nm.

substituted than Aroclor 1254, Aroclor 1221 would be expected to dehalogenate at a far lower rate, yet acceptable kinetic rates were achieved.

Photoreduction of Aroclor 1254 in the Presence of Nitrogen

Aroclor 1254 in DMF solutions were illuminated for 60 minutes with and without methylene blue. The results of these experiments are displayed in Table 3. It is interesting to note that limited reduction of this low concentration of Aroclor 1254 solution (i.e. 1 mg/l) will occur in the absence of methylene blue. This may be due to the direct excitation of the PCB molecule by light absorbtion and hydrogen abstraction occurring between PCB molecules, and also between PCB molecules and solvent molecules. More photoreduction occurs in the solution containing methylene blue. This is most likely due to a larger population of excited PCB molecules, which are indirectly excited by an energy transfer from the strongly absorbing dye molecules. The dye molecules also provide another potential source of hydrogen for abstraction.

Inhibition of the Photoreduction of Aroclor 1254 in the Presence of Air

A 10 mg/l Aroclor 1254 solution was sparged with air and illuminated for different time intervals. The results of these experiments are shown in Table 4. The reaction was for all practical purposes completely inhibited. Air contains a high concentration of

TABLE 3. NITROGEN DIFFUSION REACTION OF AROCLOR 1254*

CONCENTRATION OF METHYLENE BLUE (MG/L)	INITIAL CONCENTRATION OF AROCLOR 1254 (MG/L)	CONCENTRATION OF AROCLOR 1254 REMAINING AFTER 60 MINUTES OF ILLUMINATION (MG/L)
350	1.000	0.681
0	1.000	0.862

*Photochemical reduction of 1 mg/l Aroclor 1254 in DMF solutions while sparged with 70 ml/min of nitrogen. One solution contained 350 mg/l methylene blue the other solution did not contain methylene blue, solution temperature was maintained at 30°C $\pm$ 1°C. Illumination was 400 w $h.\upsilon.$, λ >300 nm.

TABLE 4. AIR DIFFUSION INHIBITION OF AROCLOR 1254 REACTION*

ILLUMINATION TIME (MINUTES)	AMOUNT OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
30	9.604
60	11.885

*Photochemical reaction of Aroclor 1254 in DMF solutions, 350 mg/l methylene blue, the solution was sparged with 70 ml/min of air. The solution temperature was maintained at 30°C $\pm$ 1°C . Illumination was with 400 w $h.\nu.$, λ>300 nm.

oxygen, which is a well known free radical scavenger (14). This evidence further supports the hypothesis of a free radical step being involved in the photochemical reduction process.

Iodine Inhibition of the Photoreduction of Aroclor 1254

Aliquots of a 10 mg/l Aroclor 1254 in DMF solution containing a one-tenth molar concentration of iodine were illuminated for different time intervals. The data from these experiments are listed in Table 5. The reaction was completely inhibited by the iodine. Iodine is a well known free radical scavenger (15). These results support the hypothesis of a free radical step involved in the photoreduction of aryl chlorides.

Sulfuric Acid Inhibition of the Photodehalogenation of Aroclor 1254

A 10 mg/l Aroclor 1254 in DMF solution was acidified with surfuric acid and illuminated for 15 minutes. The result of this experiment is displayed in Table 6. The addition of acid appears to strongly inhibit the progress of the photoreduction reaction. Under similar conditions, but without the addition of acid, a destruction of greater than 50% would be expected in 15 minutes illumination (see Table 20); but only 15% destruction occurred in the presence of sulfuric acid in 15 minutes of illumination time.

TABLE 5. IODINE INHIBITION OF AROCLOR 1254 REACTION*

ILLUMINATION TIME (MINUTES)	AMOUNT OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
30	10.219
60	10.435

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions with 1/10 mole I_2 added. Each solution contained 350 mg/l methylene blue, and was sparged at 70 ml/min. propane. The solution temperature was maintained at $30^{\circ}C \pm 1^{\circ}C$. Illumination was with 400 w $h.\nu.$, $\lambda > 300$ nm.

TABLE 6. SULFURIC ACID INHIBITION OF AROCLOR 1254 REACTION*

ILLUMINATION TIME (MINUTES)	CONCENTRATION OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
15	8.458

*Photochemical dehalogenation of a 10 mg/l Aroclor 1254 in DMF solution which was acidified with sulfuric acid. 0.03 ml of concentrated H_2SO_4 was added to a 1 ml aliquot containing 350 mg/l methylene blue, this solution was sparged with 70 ml/minute propane. Solution temperature was maintained $30^{\circ} \pm 1^{\circ}C$. Illumination with 400 w $h.\nu.$, $\lambda > 300$ nm.

Inhibition of the Reduction of Aroclor 1254 in the Absence of Light

Aroclor 1254 in DMF solutions were placed in the reaction assembly and sparged in the dark with sensitizer dye present. The data resulting from these experiments are found in Table 7. The reaction was completely inhibited in the absence of light. The data indicate an increase in Aroclor 1254 concentration as a function of propane diffusion time, this increase is due to an evaporation of solvent which is not returned by the reaction assembly reflux condenser and is lost with the wasted propane (see Figure 1).

Optimization of Potassium Hydroxide

The addition of alkali metal hydroxides have a pronounced effect upon the rate of photochemical reduction of Aroclor 1254 in DMF solutions. A saturated solution of DMF was prepared and then diluted to various base concentrations, to each of these solutions Aroclor 1254 and methylene blue were added, sparged with propane and simultaneously illuminated. The results of these experiments are displayed in Table 8.

Examination of the data indicates a rapid rate of reaction with no base added, a significant decrease of the rate with a 25% saturated solution of potassium hydroxide, and then increases in the rate of reaction with increasing base concentration until a 100% saturated solution shows a better performance than the absence of

TABLE 7. INHIBITION OF THE AROCLOR 1254 REACTION IN THE ABSENCE OF LIGHT*

ILLUMINATION TIME (MINUTES)	CONCENTRATION OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
30	10.548
60	12.521

*Reaction of Aroclor 1254 in DMF with 70 ml/minute sparging of propane in the dark. The solution contained 350 mg/l methylene blue, and solution temperature was maintained 30°C $\pm$ 1°C. Illumination with 400 w $h.\nu.$, $\lambda > 300$ nm.

TABLE 8. POTASSIUM HYDROXIDE OPTIMIZATION*

PERCENT OF SATURATION WITH KOH	INITIAL CONCENTRATION OF AROCLOR 1254 (MG/L)	AMOUNT OF AROCLOR 1254 REMAINING AFTER 15 MINUTES ILLUMINATION (MG/L)
0	10.000	4.132
25	10.000	6.279
50	10.000	4.515
75	10.000	5.536
100	10.000	3.853

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions with different amounts of dissolved KOH. A KOH saturated DMF solution was prepared and different base concentrations were prepared by dilution, Aroclor 1254 was added to each of these solutions to yield 10 mg/l Aroclor 1254, methylene blue was added to yield 350 mg/l, propane was sparged at 70 ml/minute, and the solution was maintained at 30°C $\pm$ 1°C. Illumination was with 400 w $h.\nu.$, λ>300 nm.

strong base. An explanation of these results is most likely to be found in the examination of the effects of strong base upon the sensitizer and upon side reactions involving the hydroxyl ion.

First, consider the effect of strong base upon the dye sensitizer, i.e. methylene blue. In DMF solution methylene blue displays a brilliant blue practically identical to that displayed in aqueous solution, but upon the addition of strong base in DMF a reaction occurs which yields a brilliant red; and this effect is not observed in water or methanol. In this red phase the absorption spectrum is shifted to shorter wavelengths and the maximum absorbance is not as great, i.e., in other words the optical density is decreased. Therefore, the dye does not appear to absorb as much light in the red phase as it does in the blue form and for that reason cannot transfer as much energy to drive the photoreduction reaction. This could explain the slowing of the rate of reaction in presence of low base concentrations.

Interestingly, as the photoreduction of aryl chlorides proceeds with methylene blue and strong base in DMF, the brilliant red color fades and becomes a light amber of very low optical density. The reaction appears to be virtually complete upon the development of this amber hue in the solution. The red color is returned upon exposure of the reaction mixture to air or pure oxygen. Also, the blue color can be returned to the solution by the addition of acid. In the absence of strong base, no color change is detected in the reaction mixture, no matter how long propane diffusion and illumination continues.

The rate of reaction begins to increase as the base concentration increases. This may be due to several effects. First, there may be a base catalysis occurring to improve reaction rates. Second, the base may be reacting with hydrogen chloride product to form water and a salt, thereby removing an inhibitory compound (sulfuric acid has been demonstrated to inhibit the reaction and hydrochloric acid may act in a similar fashion). These processes will be considered further in the "Proposed Mechanism of Photochemical Dehalogenation of 4-Chlorobiphenyl" section of this Chapter.

Photochemical Reduction on Aroclor 1254 With Pure Propane

Most of the photochemical reduction reactions performed in this research were done with commercial grade propane. Commercial grade propane contains hydrogen sulfide and trace amounts of other hydrocarbon gases. A doubt existed whether propane was actually involved in the reaction or whether some trace constituent was the hydrogen source. To demonstrate propane itself was the source of hydrogen for aryl chloride reduction, a highly purified instrument grade propane was obtained and used for the reaction. The results of these experiments are given in Table 9. Note that excellent performance is obtained with pure propane. Greater than 95% destruction of a 10 mg/l Aroclor 1254 solution occurred in 60 minutes illumination.

TABLE 9. PURE PROPANE DIFFUSION REACTION OF AROCLOR 1254*

ILLUMINATION TIME (MIN)	CONCENTRATION OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
30	0.812
60	0.416

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions, containing 350 mg/l methylene blue. Each solution was sparged with 70 ml/minute of instrument grade propane (highly purified, containing no H_2S). Solution temperature was maintained at 30° C $\pm$ 1° C. Illumination was with 400 w $h.\upsilon.$, λ>300 nm.

Optimization of Propane

Propane diffusion dramatically increased the rate of photoreduction of aryl chlorides. Experiments were performed with different volumetric delivery rates of propane. The data resulting from these experiments are shown in Table 10. Examination of the data indicates an improvement in reaction rate until a flow rate of 140 ml/min. was reached. At 140 ml/min. a dramatic decrease in reaction efficiency was observed. This phenomenon may be due to a reduction in the average retention time of the propane or a volatile reaction intermediate. Also, there may be effects due to reactions occurring in bubbles suspended in and on top of the reaction solution.

Hydrogen Diffusion Photoreduction of Aroclor 1254

Propane has been shown to improve the rate of photoreduction of aryl chlorides. To obtain a possibly "cleaner" reaction, hydrogen gas was diffused into a reaction mixture and illuminated. The results of this experiment are given in Table 11. Note the reaction scarcely proceeded with hydrogen gas sparging, i.e., on the order of the performance obtained with nitrogen gas (see Table 3). This indicates hydrogen gas is not a good source of hydrogen atoms for the photoreduction process. Considering the bond dissociation energies of hydrogen (104 kcal/mole) versus a bond dissociation energy for abstraction of a hydrogen atom from N- propane (98 kal/mole) (15), the difference of 6 kcal/mole may be the key. Only a limited amount of electromagnetic wave energy can be absorbed by the dye and then

TABLE 10. PROPANE OPTIMIZATION*

PROPANE FLOW RATE (ML/MIN)	INITIAL CONCENTRATION OF AROCLOR 1254 (MG/L)	AMOUNT OF AROCLOR 1254 REMAINING AFTER MINUTES ILLUMINATION (MG/L)
0	10.000	11.624
35	10.000	6.862
70	10.000	5.718
105	10.000	4.911
140	10.000	7.139

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions with different rates of propane sparging. Each reaction mixture contained 350 mg/l methylene blue and the solution temperature was maintained at 30°C ± 1°C. Illumination was with 400 w *h.υ.*, λ >300 nm.

TABLE 11. HYDROGEN DIFFUSION REACTION OF AROCLOR 1254*

ILLUMINATION TIME (MIN)	CONCENTRATION OF AROCLOR 1254 REMAINING AFTER ILLUMINATION (MG/L)
0	1.000
60	0.877

*Photochemical degradation of a 1 mg/l Aroclor 1254 in DMF solution, saturated with KOH, containing 350 mg/l methylene blue, and sparging with 70 ml/min H_2. Solution temperature was maintained at 30° C $\pm$ 1° C. Illumination was with 400 w $h.\upsilon.$, λ >300 nm.

transferred to the aryl chloride molecule. Therefore, if the energy of activation exceeds the energy which can be obtained from the dye and by direct absorption combined, the reaction will not proceed.

Optimization of the Dye Sensitizer

Photoreductions of Aroclor 1254 in DMF solutions were performed with various concentrations of methylene blue. The data resulting from these experiments are recorded in Table 12. Examination of these data shows a low rate of photoreduction in the absence of methylene blue, good reaction rates at 115.5 - 350 mg/l, and decreasing rates at concentrations above 350 mg/l. The low reaction rate in the absence of dye is due to the low rate of direct absorption of light by PCB molecules. The increase in photoreduction rates from 115.5 mg/l to 350.0 mg/l is most likely due to an increase in light absorbtion and resulting increasing energy transfer with increasing dye concentration. Using this line of reasoning, it might be expected that the rate of reaction would increase with increasing dye concentration ad infinitum, but as the dye concentration increases, the optical density of the solution increases until it becomes practically opaque. In this nearly opaque condition only the dye molecules at the periphery of the solution are able to absorb light and then transfer this energy to the PCB molecules. Conversely, at low concentrations, all the dye molecules in the solution could be excited almost simultaneously and transfer the absorbed energy to PCB molecules throughout the solution volume.

TABLE 12. METHYLENE BLUE OPTIMIZATION*

CONCENTRATION OF METHYLENE BLUE (MG/L)	CONCENTRATION OF AROCLOR 1254 REMAINING AFTER 15 MINUTES ILLUMINATION (MG/L)
0	9.600
115.5	2.726
350.0	2.097
583.0	5.243
816.6	5.080
1166.6	9.265

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions, each solution containing a different concentration of methylene blue, the solution was sparged with 70 ml/min propane. The solution temperature was maintained at 30°C $\pm$ 1°C. Illumination was with 400 w $h.\nu.$, $\lambda > 300$ nm.

Comparison of the Rates of Photoreduction of Aroclor 1254 in the Presence of Various Alkali And Alkaline Earth Metal Hydroxides

Saturated solutions of lithium, potassium, sodium and calcium hydroxides in DMF were separately prepared. Then Aroclor 1254 and methylene blue were added to each solution. These solutions were sparged with propane and illuminated for identical time periods at 30 C. The data which resulted from these procedures are listed in Table 13. Note the efficiency of the photoreduction reaction increases with decreasing metal ion size. This effect may be due to the increase in solubility of the base with a decrease in ionic size.

Solvent Comparison

Various solvents were tested for this photochemical reduction process. The results of these trials are recorded in Table 14. Note the polar aprotic solvents DMF and DMSO yield the most efficient reaction rates, and DMSO is apparently somewhat superior to DMF. Methanol and methanol-water mixtures were totally ineffective. Pure water solutions were not tried due to the virtual insolubility of PCB in aqueous solution. Hexamethyl phosphorous triamide proved to be ineffective due to the insolubility of the thiazine dyes in this solvent.

Obviously the solvent plays a very important role in this photochemical process. The solvent may be ordering the molecular reaction system in some way and thereby lowering the energy of

TABLE 13. ALKALI AND ALKALINE EARTH METAL HYDROXIDE COMPARISON*

ALKALI METAL HYDROXIDE	INITIAL CONC. OF AROCLOR 1254 (MG/L)	AMOUNT OF AROCLOR 1254 REMAINING AFTER 25 MINUTES ILLUMINATION (MG/L)
LiOH	10.000	1.638
KOH	10.000	2.971
NaOH	10.000	3.002
$Ca(OH)_2$	10.000	3.034

*Comparison of Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions with saturated solutions of various alkali and alkaline earth metal hydroxides. Each solution contained 350 mg/l methylene blue, was sparged with 70 ml/min propane, and solution temperature was maintained at 30°C $\pm$ 1°C. Illumination with 400 w $h.\nu.$, λ>300 nm.

TABLE 14. SOLVENT COMPARISON*

SOLVENT	INITIAL CONCENTRATION OF AROCLOR 1254 (MG/L)	AMOUNT REMAINING OF AROCLOR 1254 AFTER 15 MINUTES ILLUMINATION (MG/L)
DMSO	10.000	2.268
DMF	10.000	3.164
MeOH	10.000	10.899
MeOH-H_2O	10.000	11.086

*Illumination with 400 w $h.\nu.$, $\lambda > 300$ nm, at 30° C + 1°C.

activation or increasing the probability of collisions of the involved molecules in the appropriate orientation to cause the reaction to occur.

The effective solvents are polar aprotic. The polarity will yield a more ordered molecular system due to dipole-dipole interactions. Also, the absence of ionization of the solvent may be playing an important role, as the presence of hydrogen ions appears to strongly inhibit this photodehalogenation reaction.

Dye Sensitizer Comparisons

Seven different possible sensitizer dyes were evaluated for use in the photoreduction of aryl chlorides. The results of these experiments are listed in Table 15. Note only the thiazine derivatives, methylene blue and toluidine blue-o, show acceptable rates of reaction. Roseaniline, rose bengal, and methyl orange demonstrated a weak performance. Neutral red and rhodamine B appeared to completely inhibit the photoreduction process.

Transformer Oil Processing

The result of the transformer oil processing experiment is shown in Table 16. Approximately 75% destruction of the PCB was obtained in 30 minutes illumination.

TABLE 15. DYE COMPARISON*

DYE	INITIAL CONCENTRATION OF AROCLOR 1254 (MG/L)	AMOUNT REMAINING OF AROCLOR 1254 AFTER 15 MINUTES ILLUMINATION (MG/L)
Toluidine blue-o	10.000	2.052
Methylene blue	10.000	2.097
Roseaniline	10.000	7.275
Rose bengal	10.000	7.560
Methyl orange	10.000	7.816
Neutral red	10.000	10.429
Rhodamine b	10.000	10.554

*Illumination with 400 w $h.\nu.$, $\lambda > 300$ nm, at $30^{\circ}C + 1^{\circ}C$.

TABLE 16. TRANSFORMER OIL PROCESSING*

ILLUMINATION TIME MINUTES	CONCENTRATION OF AROCLOR 1254 REMAINING AFTER ILLUMINATION (MG/L)
0	5.000
30	1.235

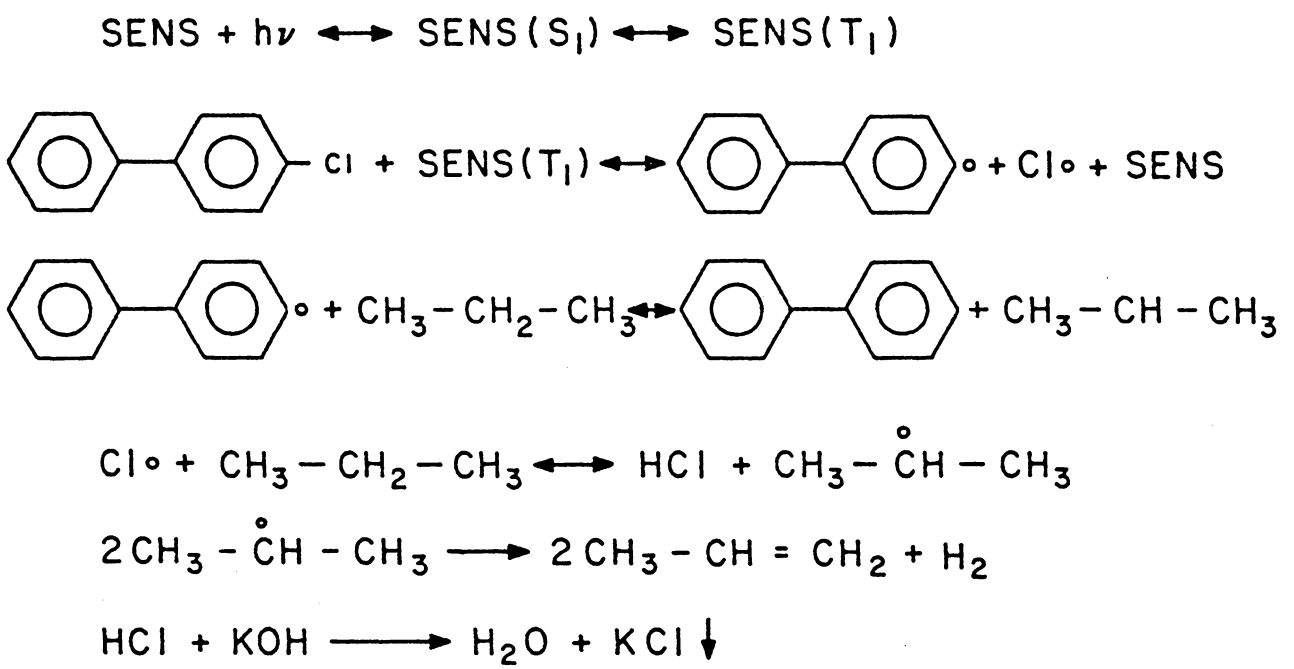
*Photochemical degradation of a DMF extract from a PCB contaminated transformer oil. 1ml of 50 mg/l PCB transformer oil was extracted into 10 ml of DMF. The DMF extract was then saturated with KOH and a 1 ml aliquot was taken, methylene blue was added to yield a 350 mg/l solution. This aliquot was sparged with 70 ml/min propane and solution temperature was maintained at 30°C $\pm$ 1°C. Illumination with 400 w $h.\nu.$, λ >300 nm.

Two interferences were noted in experiments with transformer oil. Firstly, coloring matter in this particular oil, which was strongly yellow in color, was taken up in the DMF thereby inhibiting the reaction. Secondly, at low transformer oil to DMF ratios of extraction severe foaming occurred upon the diffusion of the reaction mixture with propane. These problems were overcome by extracting a small amount of transformer oil with a large amount of DMF. These problems could possibly be overcome by the addition of antifoaming agents or prefiltration of the oil to remove coloring matter. These problems may not occur with all transformer oils since their composition and color may vary widely.

PROPOSED REACTION MECHANISM

A photoreduction reaction mechanism is proposed in Figure 15. This mechanism is free radical in nature which is supported by the complete inhibition of the reaction by the addition of iodine, a free radical scavenger.

In the proposed mechanism the dye sensitizer absorbs light which promotes electrons in the dye molecule yielding an excited triplet state from the singlet ground state. This excited dye molecule then transfers the energy to an aryl chloride molecule causing homolytic cleavage of the carbon-chlorine bond. This yields a biphenyl radical and a chlorine radical. These radicals attack propane molecules abstracting hydrogen atoms. Biphenyl, hydrogen chloride, and propyl



IF N-PROPYL AND ISOPROPYL CHLORIDES ARE FORMED

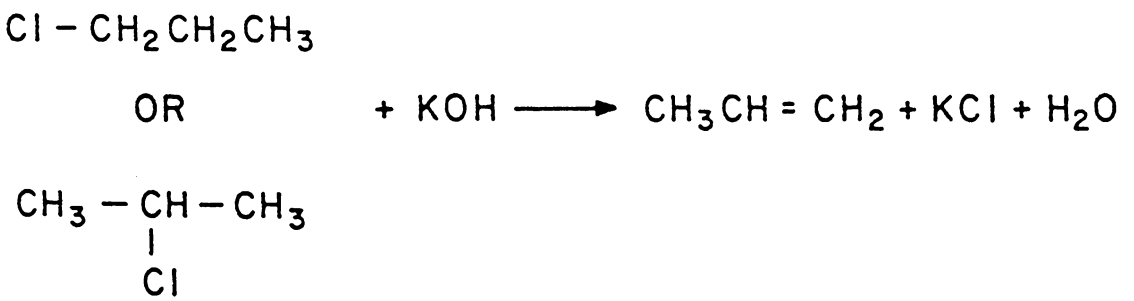


FIGURE 15. PROPOSED MECHANISM FOR THE PHOTOCHEMICAL DEHALOGENATION OF 4 - CHLORO BIPHENYL IN A POLAR APROTIC SOLVENT. THIS MECHANISM COULD BE EXTENDED TO PCB IN A STEPWISE FASHION.

radicals result. The propyl radicals may react with one another forming propene and hydrogen gas. The hydrogen chloride may react with potassium hydroxide to form water and a sparingly soluble potassium chloride salt which most likely precipitates from the solution.

Propyl chlorides, if formed may undergo dehydrohalogenation to yield propene, potassium chloride, and water. These propyl chloride products are low boiling liquids and have not been detected with the analytical methods utilized.

An alternate mechanism may also be suggested. In this variation of the previously proposed mechanism, the aryl chloride molecule is excited by interacting with the dye molecule but does not undergo immediate cleavage of the carbon-chlorine bond. Instead an excited aryl chloride molecule contacts a propane molecule, forms a short lived intermediary complex, and abstracts a hydrogen atom yielding biphenyl and a propyl chloride.

It is also conceivable that the triplet state of the dye is not involved. Instead, a ground state singlet to an excited singlet excitation may be occurring with a decay of the electron to an intermediate level with the emission of a photon. This is is a "lasing" process. The emitted electromagnetic radiation may be of the frequency which can be readily absorbed by the aryl chloride molecule exciting it and causing cleavage of the carbon-chlorine bond, and initiating the photoreduction reaction.

SUMMARY

There is a tremendous market for effective hazardous waste treatment. If one assumes a linear relationship, about 6 million pounds of PCB could be processed each year for the next 40 years or so. Hazardous waste processing is likely to become a high profit growth industry in the years to come, as indefinite storage will prove to be an environmentally unacceptable alternative when compared to responsible chemical processing and recycling of products. The dye sensitized photochemical reduction scheme which has been developed by this research may provide the means by which this type of environmentally acceptable processing and recycling can be achieved.

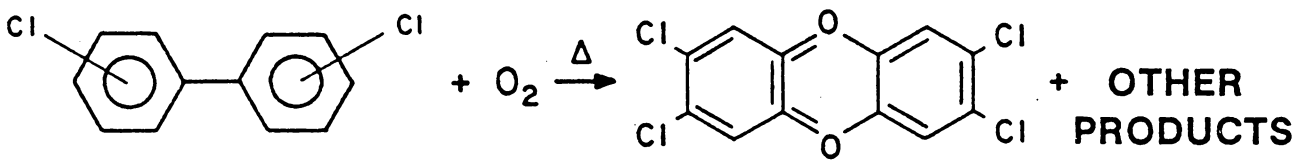
ENGINEERING APPLICATIONS

The typical method of PCB disposal is by incineration. This method can yield 2, 3, 7, 8 - tetrachloro-dibenzo-p-dioxin, TCDD, in trace amounts which is three orders of magnitude more toxic than the original PCB. This reaction is shown in Figure 16. The photochemical method previously outlined is very unlikely to produce this undesirable product.

Transformer oil which contains PCB could be processed by the method outlined on Figure 17. Mixer/settlers could be substituted for the extraction column. Preliminary cost estimated indicate that this new technique could perhaps be as low as 1/4 the current rate payed for the disposal of PCB contaminated transformer oils. This estimate does not include capital costs, labor costs, or management overhead costs. Some costs could be offset by the recovery of reaction products for reuse or sale.

PCB contaminated soils could be treated by the process train outlined in Figure 18. Many industrial sites have soils contaminated with PCB. This could prove to be a lucrative market for this type of process.

There are many landfills containing PCB. The leachate from these landfills could be detoxified by the approach outlined in Figure 19. Under certain circumstances sunlight could be used to run the reaction in remote locations to reduce operating expenses.



2,3,7,8 - TETRACHLORO-DIBENZO-P-DIOXIN [TCDD]

FIGURE 16. INCINERATION PRODUCTS OF PCB.

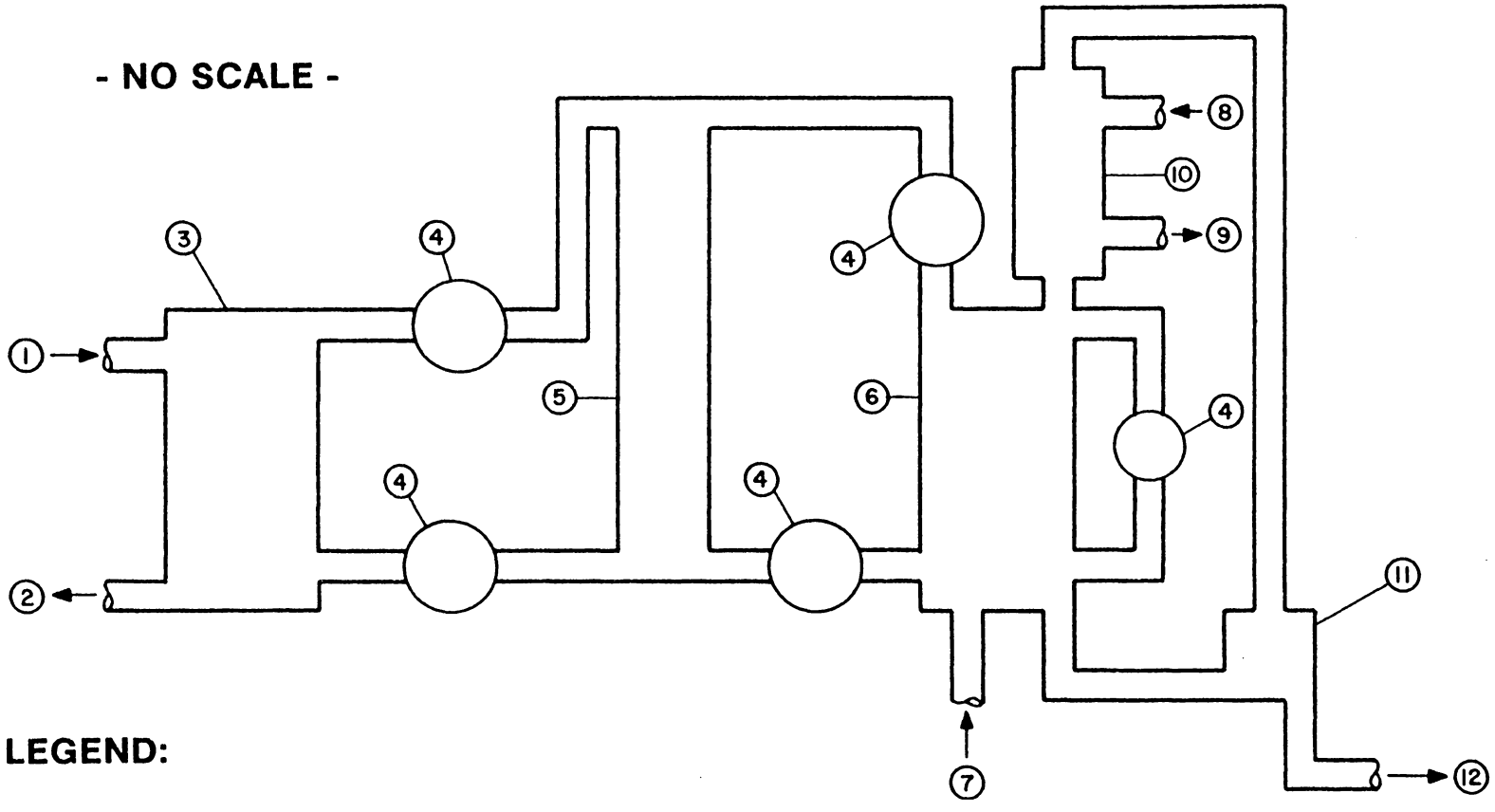


FIGURE 17. SIMPLIFIED SCHEMATIC OF A PCB CONTAMINATED TRANSFORMER OIL PROCESSING FACILITY.

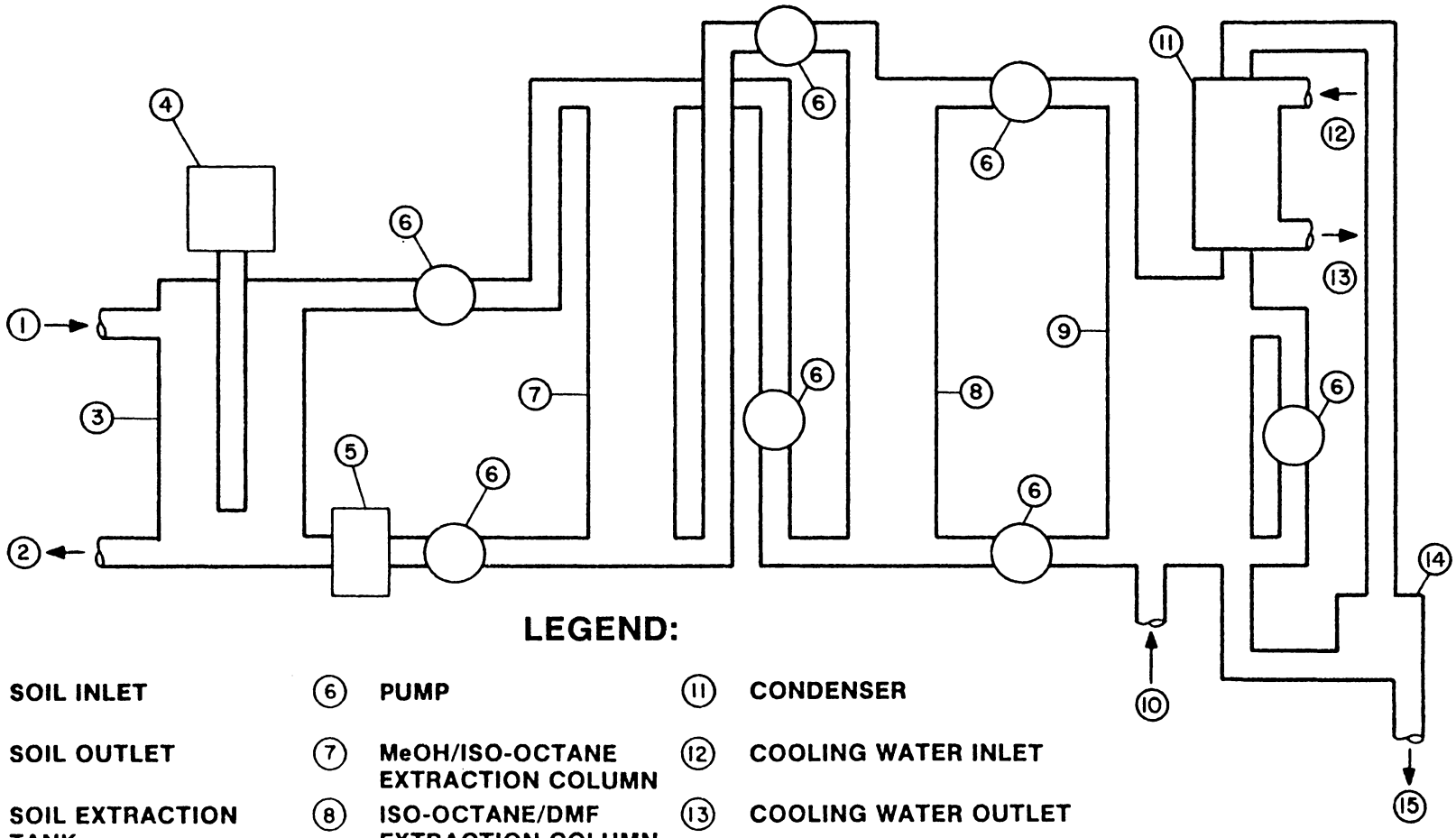


FIGURE 18. SIMPLIFIED SCHEMATIC OF A PCB CONTAMINATED SOIL PROCESSING FACILITY.

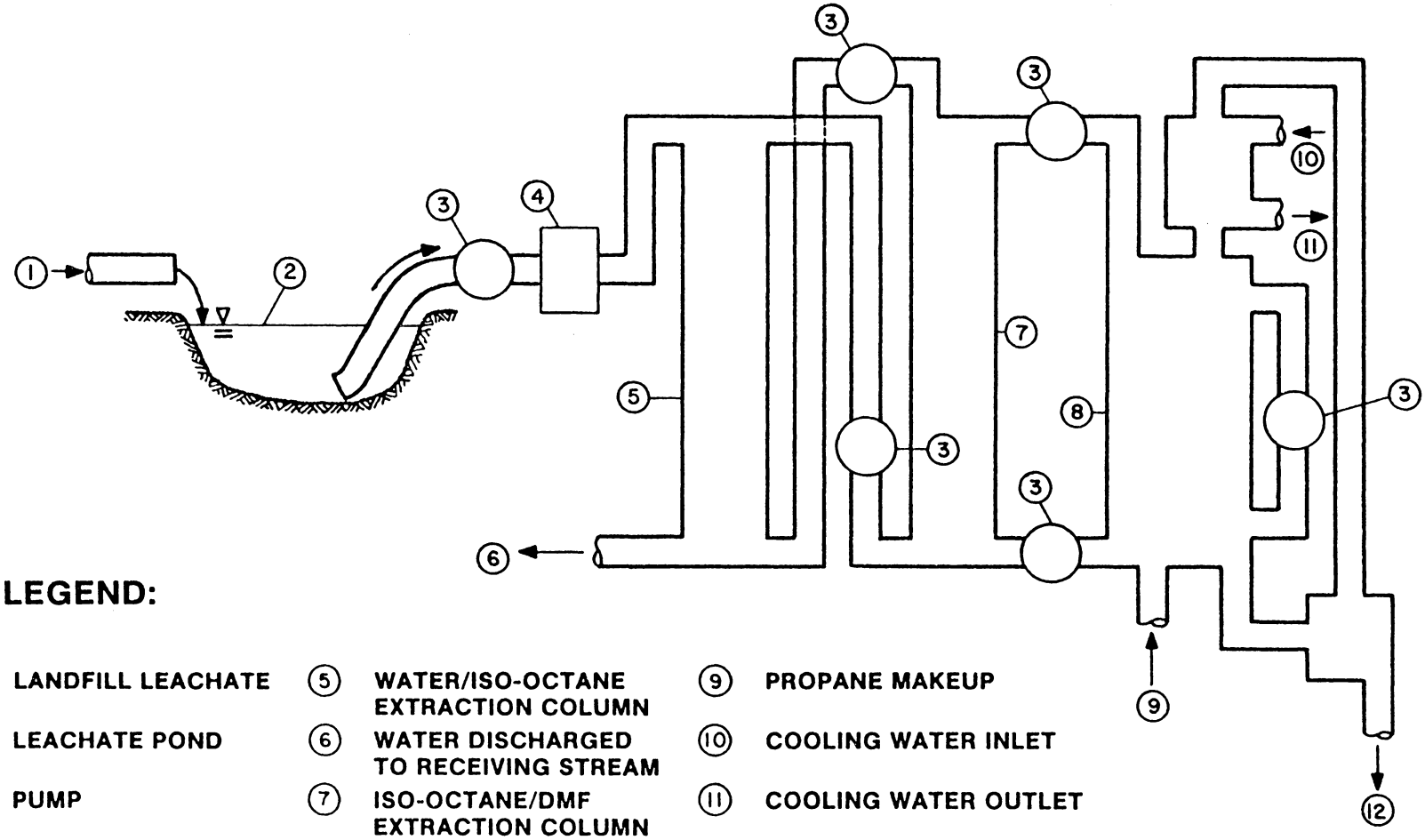


FIGURE 19. SIMPLIFIED SCHEMATIC OF A PCB CONTAMINATED LANDFILL LEACHATE PROCESSING FACILITY.

This photochemical reaction may prove to be effective for the processing of pesticides such as lindane and other related halogenated hydrocarbons. If so, other markets could be opened for this procedure.

CONCLUSIONS

Based on a thorough analysis of the results obtained in this study it may be concluded that:

1. Aryl chlorides can be photoreduced to biphenyl, by visible wavelength light, in a solution consisting of a polar aprotic solvent, aryl chloride, thiazine dye, and diffusion with a hydrocarbon gas.

2. Alkali metal hydroxides increase the rate of the photoreduction reaction.

3. Solid alkali metal hydroxide is required in the reaction mixture to achieve acceptable reaction kinetics with monohalogenated isomers of biphenyl.

4. The photoreduction process appears to include a free radical type reaction.

5. The photochemical process can be used to process PCB contaminated transformer oils.

SUGGESTIONS FOR FUTURE RESEARCH

Many areas of research could be profitably pursued in relation to this procedure. Some of these topics will be discussed in this section.

One interesting area would be to study the mechanism of energy transfer from the sensitizer to the substrate molecules. Conceivably a direct contact, short range radiative transfer, or long range radiative transfer could be occurring. The amine functional groups may be integrally involved in the energy transfer process and the preparation of amine, dimethyl amine, diethyl amine, and dipropyl amine thiazine derivatives may prove to be enlightening. The unshared pair of electrons on this amine group may be the energy transfer site, and the attachment of different groups will expand or contract the volume occupied by the unshared pair.

It may be possible to construct a dye laser, using methylene blue as the lasing dye. This dye laser could be pumped by a nitrogen laser. The resulting emission from the dye laser could possibly drive the photoreduction reaction. The absorption of the laser emission by the aryl chloride molecule in a remotely located solution may cause the cleavage of the carbon-chlorine bond.

Further kinetic studies could be performed. This area could provide important evidence for the derivation of a more certain reaction mechanism.

Many halogenated compounds now exist in the environment. This photochemical process may be effective for many classes of compounds. Of particular interest would be an investigation of halogenated pesticides which exhibit aromaticity.

It may be possible to find solvents or solvent mixtures, hydrogen sources, light sources, and etc. which would vastly improve the rate of this photochemical reduction reaction. This area of research could be inexpensively pursued and may improve the commercial potential of this procedure.

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APPENDIX

TABLE 17. REACTION OF 4-CHLOROBIPHENYL IN DMF AT 30°C*

ILLUMINATION TIME (MIN)	CONCENTRATION OF 4-CHLOROBIPHENYL REMAINING (MG/L)
0	100.0
15	95.8
30	90.9
45	83.5
60	83.7

*Photochemical dehalogenation of a 100 mg/l 4-chlorobiphenyl in DMF solution containing 350 mg/l methylene blue, and sparging at 70 ml/min of propane. The solution temperature was maintained at 30°C ± 1°C. Illumination was with 400 w *h.v.*, λ>300 nm.

TABLE 18. REACTION OF 4-CHLOROBIPHENYL IN DMF, SATURATED WITH KOH, AT 30°C*

ILLUMINATION TIME (MIN)	CONCENTRATION OF 4-CHLOROBIPHENYL REMAINING (MG/L)
0	100.0
15	89.4
30	78.6
45	67.3
60	62.9

*Photochemical dehalogenation of a 100 mg/l 4-chlorobiphenyl in DMF solution, saturated with potassium hydroxide, containing 350 mg/l methylene blue, and sparged with 70 ml/min propane. Illumination was with 400 w $h.\nu.$, $\lambda > 300$ nm.

TABLE 19. REACTION OF 4-CHLOROBIPHENYL IN DMF, SATURATED WITH POTASSIUM HYDROXIDE AND SOLID POTASSIUM HYDROXIDE PRESENT, AT 30°C*

ILLUMINATION TIME (MIN)	CONCENTRATION OF 4-CHLOROBIPHENYL REMAINING (MG/L)
0	100.00
15	50.51, 44.82
30	29.21, 25.18
45	4.89, 4.12, 4.47
60	3.12, 4.94

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions containing 350 mg/l methylene blue, andd sparged by 70 ml/min propane. Solution temperature was maintained at 30° C $\pm$ 1° C. Illumination was with 400 w *h.v.*, λ>300 nm.

TABLE 20. REACTION OF AROCLOR 1254 IN THE ABSENCE OF STRONG BASE*

ILLUMINATION TIME (MIN)	CONCENTRATION OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
15	4.672
30	1.477
45	0.392
60	0.231

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions containing 350 mg/l methylene blue, and sparged by 70 ml/min propane. Solution temperature was maintained at $30^{\circ}C \pm 1^{\circ}C$. Illumination was by 400 w $h.\nu.$, $\lambda > 300$ nm.

TABLE 21. REACTION OF AROCLOR 1254 IN SOLUTION SATURATED WITH POTASSIUM HYDROXIDE AT 30°C*

ILLUMINATION TIME (MIN)	CONCENTRATED OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
15	2.871
30	0.313
45	0.168
60	8664 EE -02

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solution, saturated with potassium hydroxide, containing 350 mg/l methylene blue, and sparged by 70 ml/min propane. The solution temperature was maintained at 30°C ± 1°C. Illumination was with 400 w *h*. υ., λ>300 nm.

TABLE 22. REACTION OF AROCLOR 1254 IN POTASSIUM HYDROXIDE SATURATED DMF SOLUTION AT 40°C*

ILLUMINATION TIME (MIN)	CONCENTRATION OF AROCLOR 1254 REMAINING (MG/L)
0	10.000
15	0.446
30	0.106
45	2.796 EE -02

*Photochemical dehalogenation of 10 mg/l Aroclor 1254 in DMF solutions saturated with potassium hydroxide, containing 350 mg/l methylene blue, sparged with 70 ml/min propane. Solution temperature was maintained at 40°C $\pm$ 1°C. Illumination was by 400 w $h.\nu.$, λ>300 nm.

TABLE 23. CHEMICALS USED IN THE PHOTOREDUCTION REACTION RESEARCH AND THEIR SOURCE

CHEMICAL	GRADE	SOURCE
Methylene blue	-	Fisher Scientific Co.
Rose bengal	92%	Aldrich Chemical Co.
Neutral red	76%	Aldrich Chemical Co.
Toluidine blue o	57%	Aldrich Chemical Co.,
Flourescein	Practical	Eastman Kodak Co.
Methyl orange	Reagent	-
4-chlorobiphenyl		Alfa Products
Biphenyl	Reagent	Fisher Scientific Co.
Iodine	Certified A.C.S.	Fisher Scientific Co.
Potassium hydroxide pellets	Certified A.C.S.	Fisher Scientific Co.
Rosaniline chloride	Practical	Eastman Kodak Co.
N,N-dimethylformamide	Certified A.C.S.	Fisher Scientific Co.
Methanol	Certified A.C.S.	Fisher Scientific Co.
Dimethylsulfoxide	Certified A.C.S.	Fisher Scientific Co.
Iso-octane	Pesticide Grade	Fisher Scientific Co.
Diphenylcarbazone indicator	-	Hach Chem.
Mercuric nitrate solution	0.0141 N	Hach Chem.
Rhodamine B	-	-
Phenolphthalein	-	-
Sulfuric acid	Reagent A.C.S.	Fisher Scientific Co.
Aroclor 1221	1 mg/ml in iso-octane	E.P.A. Standard
Aroclor 1254	1 mg/ml in iso-octane	E.P.A. Standard
Transformer oil	50 mg/l PCB	Va Tech Safety Office
Propane	Commercial	Industrial Gas and Supply Co.
Propane	Instrument	Air Products
Nitrogen	5.0	AIRCO
Hydrogen	5.0	AIRCO

TABLE 24. PRINCIPAL EQUIPMENT USED IN PHOTOCHEMICAL REDUCTION RESEARCH

EQUIPMENT

Pump
Manostat, varistalic pump, solid state model

Rotameter
Brooks Inst. Div., Size 1.65A

Water Bath
Buchi Co., 30 - 110 range thermostat

Thermometer
Fisher, #14-983-10B

Gas Chromatography Column (PCB Analysis)
1.5% OV -17 + 1.95% QF 1
Chromasorb W-HP 100/120
2m length, 4nm I.D.

Gas Chromatography Column (Biphenyl Analysis)
5% SP-2100
100/120 Supelcoport
2m length, 4nm I.D.

Chromatographs
Hewlett-Packard, Model 5880A with 588A Series GC Terminal/Integrator and Electron Capture Detector
Tracor 560 with Hewlett-Packard 3390A Integrator and
Flame Ionization Detector Air: 300ml/min, H_2:30 ml/min

Syringe
Hamilton Co., #701, 10

Reaction Assembly
Va Tech Glass Shop, custom made, see Figure 3.

Extraction Vials
7 ml volume glass vials with teflon septum type liners in lid.

Extraction Mixer
Vortex-Genie, Fisher Scientific Co.

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DEVELOPMENT OF A DYE SENSITIZED PHOTOCHEMICAL REDUCTION PROCESS FOR THE DEGRADATION OF POLYCHLORINATED BIPHENYLS

by

Michael Lee Stallard

Committee Co-Chairman: J.H. Sherrard

Civil Engineering

Committee Co-Chairman: M.A. Ogliaruso

Chemistry

(ABSTRACT)

A method has been developed that can photoreduce polychlorinated biphenyl (PCB) to biphenyl with great speed and efficiency as well as at relatively low cost. This process uses visible light, generated by ordinary incandescent light bulbs, which is absorbed by a common dye sensitizer. The dye molecules, when excited by the absorption of light, can promote a chemical reaction between polychlorinated biphenyls and a hydrocarbon gas such as propane. In this chemical reaction, hydrogen is abstracted from the hydrocarbon gas molecule and is substituted for chlorine on the PCB molecule in a stepwise fashion, which ultimately yields the major reaction product biphenyl. This reaction occurs in a polar aprotic solvent at room temperature and is accelerated by the presence of an alkali metal hydroxide.

The final residence of the chlorine appears to be a salt which precipitates from the reaction mixture. This procedure could be applied to the treatment of PCB contaminated transformer oils, soils, and landfill leachates.