AN ABSTRACT OF THE THESIS OF

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Title: IDENTIFICATION OF POLYCHLORINATED BIPHENYLS BY GAS-LIQUID CHROMATOGRAPHY AND ULTRAVIOLET DEGRADATION

Abstract approved: Dr. D. D. Bills

In this study the use of gas-liquid chromatography (GLC) in combination with degradation by ultraviolet light was investigated as a means of identifying polychlorinated biphenyls (PCBs). A commercial mixture of PCBs (Aroclor 1254), which contains an average chlorine content of 54 percent, was separated using four different gas chromatographic columns. Thirteen components were observed using a column packed with 2 % SE-30 and 2 % QF-1, 35 were observed using a column packed with 5 % Dexsil 300 GS, and 71 were observed using a capillary column coated with Apiezon L. While the resolution was best on the capillary column, the 2 % SE-30 and 2 % QF-1 column was selected for use in qualitative studies on the basis of a shorter time of analysis. It was recognized that the chromato-

graphic peaks obtained with this column represent more than a single compound.

Combined gas-liquid chromatography-mass spectrometry was used to confirm the presence of mono- through hexachlorobiphenyls in the mixture.

The complete mixture was irradiated with the laboratory uv light in hexane, water and benzene. While the PCBs were degraded in all three solvents, the rate of decomposition was dependent on the solvent with the fastest degradation occurring in hexane.

The individual components of the Aroclor 1254 mixture were then trapped in 7 cm lengths of dry ice-cooled Teflon tubing using a specially constructed Teflon stream splitter. Hexane was added to each tube, and the tube was sealed and irradiated for varying lengths of time. Upon reinjection of the contents of each tube into the gas chromatograph, each trapped component yielded a unique and reproducible degradation pattern. Dechlorination and rearrangement reactions appeared to be involved in the decomposition mechanism.

The possible interference by chlorinated pesticides was investigated by irradiating the individual PCB component along with the pesticide of corresponding GLC retention time. The presence of the pesticide had no effect on the PCB degradation pattern. The pesticides used were aldrin, dieldrin, p, p'-DDE and p, p'-DDT.

The utility of the technique for the identification of PCB residues from environmental samples was demonstrated with herring oil and salmon oil. PCB compounds were isolated and identified in both samples by their uv degradation patterns.

It was concluded that gas-liquid chromatography and uv degradation provide a relatively simple and inexpensive means of identifying PCBs in organochlorine residue extracts.

Identification of Polychlorinated Biphenyls by Gas-Liquid Chromatography and Ultraviolet Degradation

by

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INTRODUCTION

The analysis of organochlorine residues at extremely low concentrations has been made possible largely by advances in gas chromatography. The use of the halogen-sensitive electron capture detector has allowed detection at the ppb level. In the analysis of polychlorinated biphenyls (PCBs) by gas chromatography, consideration must be given to other chlorinated substances, such as chlorinated insecticides, which behave similarly to the PCBs. For this reason, the use of gas-liquid chromatography (GLC) retention time can be used as only a tentative identification tool.

For qualitative analysis, then, other techniques along with GLC analysis must be employed. One of the most popular techniques is mass spectrometry. Others include retention on two or more columns of different polarity, selective adsorption and chemical derivatization.

A relatively new field of study is the photolysis of PCBs by sunlight and laboratory ultraviolet (uv) light. The purpose of this study was to investigate the use of laboratory uv light to degrade PCBs and the use of the degradation products as a means of

identifying the parent compound. Such a procedure has been developed for the identification of certain chlorinated insecticides; but, no application of the procedure to PCBs has been reported.

REVIEW OF LITERATURE

Photolysis of Chlorinated Aromatic Compounds

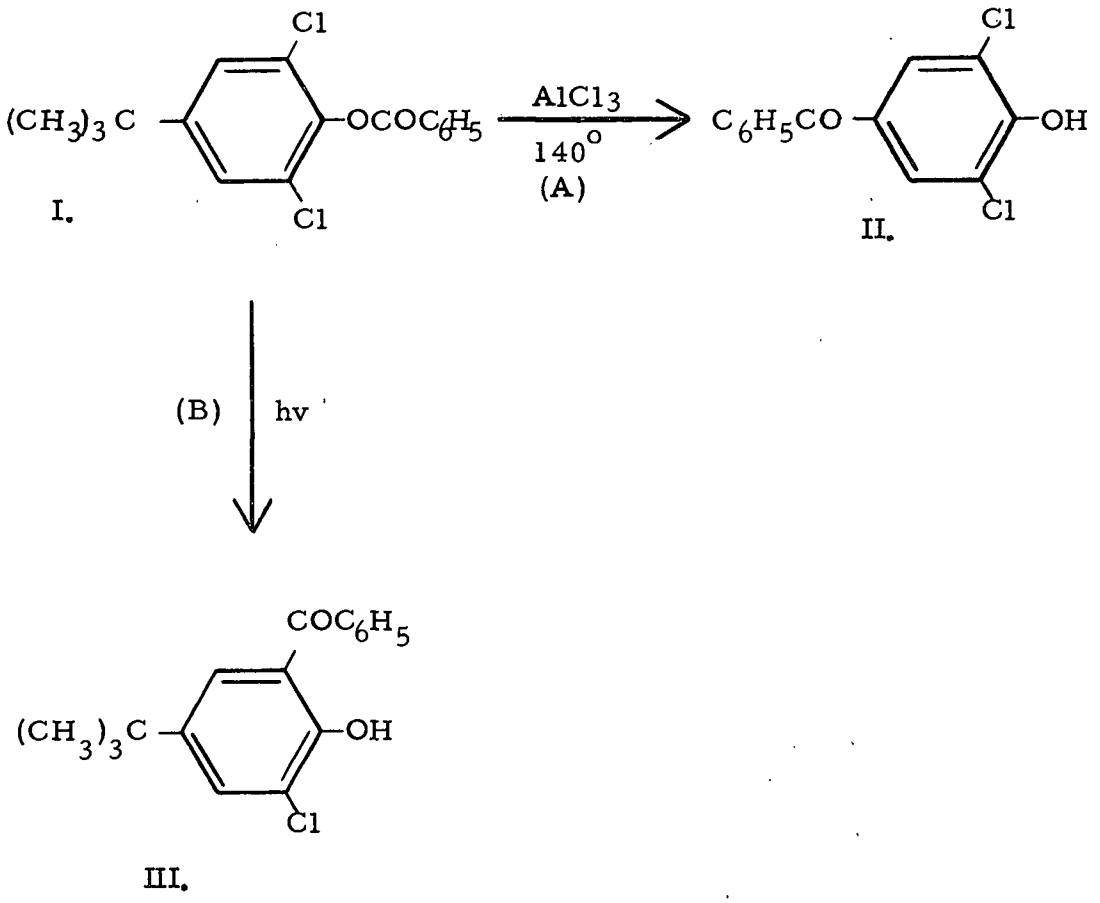
It has been generally held that there is little photo-induced cleavage of the C-Cl bond in aromatic compounds. Stenberg (1967) stated that chlorobenzenes are not photochemically active as are iodobenzenes. Sharma and Kharasch (1968) stated that there is little significant photochemical cleavage of C-Cl and C-F bonds in aryl halides. According to Kharasch, Sharma and Lewis (1966), the lability of the halide is proportional to the strength of the carbon-halide bond. They concluded that the 4-halogen biphenyls are increasingly resistant to photolysis in the order of the increasing bond strengths of the corresponding halogens. As a result of such statements, much of the work with halo aromatics has been done with bromo and iodo compounds. (Wolf and Kharasch, 1961, 1965; Matsuura and Omurak, 1966; Sharma and Kharasch, 1968).

Contrary to these statements about the stability of the C-Cl bond, there have been a number of reports of photo-induced reactions involving chlorinated aromatic compounds over the last ten years. In 1962, Kobsa described a reaction similar to the aluminum chloride-catalyzed Fries reaction which is later referred to by Stenberg

(1967) as the "photo" - Fries reaction. In the Fries reaction, 2, 6-dichloro-4-t-butylphenylbenzoate and 2-chloro-4-t-butylphenylbenzoate rearrange via migration of the acyl group into the para position and elimination of the t-butyl group to give the corresponding p-hydroxybenzophenones. In the "photo" - Fries reaction with the same two compounds, the chlorine substituents are easily eliminated forming the corresponding ortho-hydroxybenzophenones (Figure 1).

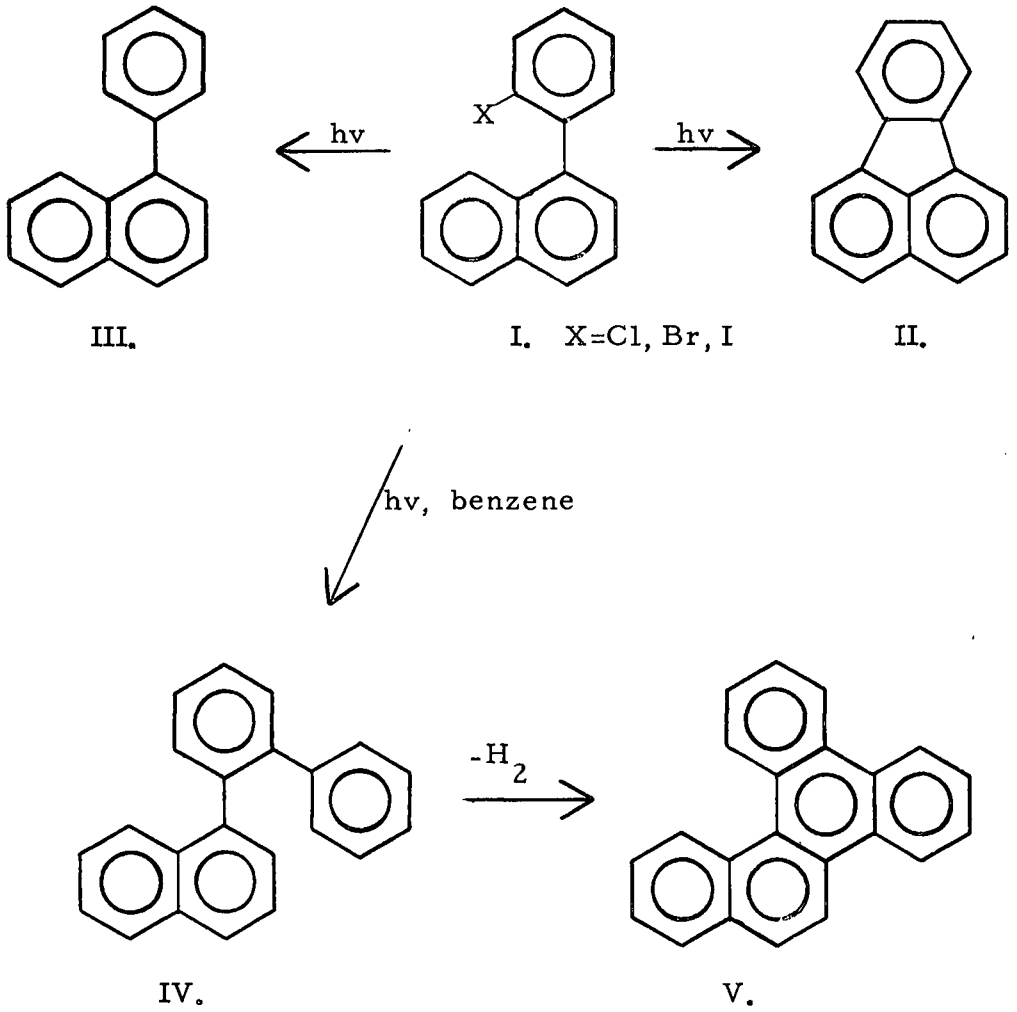
Nijhoff and Havinga (1965) described the photoreaction of 2-chloro-4-nitroanisole in alkaline solution. The products reported were 5-nitroquaicol (48% isolated), a small amount of 2-chloro-4-nitrophenol and a tarry product. They concluded from their investigation of other similar reactions that the substitution of the halogen by OH is a rather specific reaction.

Henderson and Zweig (1967) studied the photocyclization of 1-o-halophenylnaphthalenes. When irradiated at 3130 Å in deoxygenated benzene, the iodo compound decomposed rapidly but gave practically no fluoranthene while the chloro compound reacted slowly but gave 44-59% fluoranthene, with the bromo compound being intermediate in behavior. Other products formed from the chloro compound were 17-28% 1-phenylnaphthalene and 24-31% 2-α-naphthylbiphenyl plus benzo(g)chrysene (Figure 2). Possible explanations for the differences in reactivity of the three compounds were given as



I. 2, 6-dichloro-4-t-butylphenylbenzoate
II. 3, 5-dichloro-p-hydroxybenzophenone
III. 3-chloro-5-t-butyl-o-hydroxybenzophenone

Figure 1. Fries (A) and "photo"-Fries (B) reaction of 2, 6-dichloro-4-t-butylphenylbenzoate.



III. I. X=Cl, Br, I II.

IV. V.

I. 1-o-halophenylnaphtahlene
II. fluoranthene
III. 1-phenylnaphthalene
IV. 2-∝-naphthylbiphenyl
V. benzo(g)chrysene

Figure 2. Photocyclization of 1-o-halophenylnaphthalenes.

differences in the lifetimes of the excited singlets produced on irradiation due to the heavy atom effect, or the differences in electronegativity of the halogen atoms which would impart different degrees of carbonium ion character to the aryl radical.

Pinhey and Rigby (1969a) reported the photoreduction of chlorobenzene, bromobenzene and some simple derivatives. Some iodoaromatics were also studied for comparative purposes. They found using chloro-, bromo-, and iodobenzene; p-chloro-, p-bromo-, and p-iodophenol; and o-chloro-, o-bromo-, and o-iodophenol that the chloro, bromo, and iodo compounds were reduced at comparable rates with good yields in all cases. This appears to be contradictory to the findings of Kharasch et al. (1966). Also, the reactions proceeded faster and with higher yields with isopropanol as the solvent than with ethanol.

A free radical mechanism was proposed by Pinhey and Rigby (1969a) as indicated by the formation of pinacol in the reactions in isopropanol (Figure 3). After the adsorption of light, the excited haloaromatic undergoes carbon-halogen bond homolysis, producing radicals which abstract hydrogen from the solvent. Hydrogen halides were also detected in the photolysis mixture.

The irradiation of p-chlorophenoxyacetic acid was also reported by Pinhey and Rigby (1969a). The products after

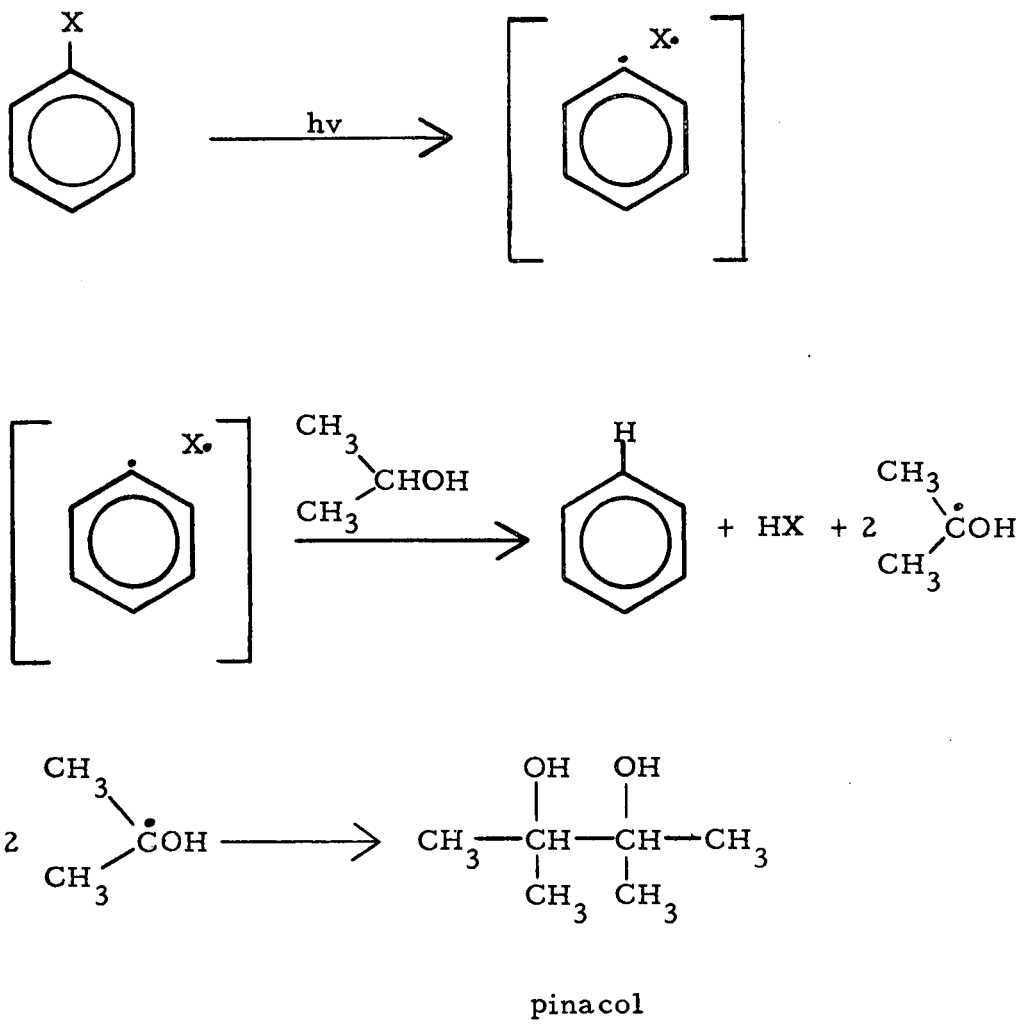


Figure 3. Formation of pinacol upon irradiation of aryl halide in isopropanol via free radical mechanism (Pinhey and Rigby, 1969a).

distillation were the same as those obtained from phenoxyacetic acid: 2-coumarone, phenol, and phenoxyacetic acid. The presence of phenoxyacetic acid indicates that the loss of chlorine occurs prior to the homolysis of the O-CH_2COOH bond. This might be expected due to the greater energy of the C-O bond compared to the C-Cl bond.

In a second study by Pinhey and Rigby (1969b) they irradiated several meta substituted haloaromatics. Unlike the o- and p- substituted chlorophenols which are largely dechlorinated in isopropanol (Pinhey and Rigby, 1969a), m-chlorophenol gives phenol as only a minor product while the major product was m- isopropoxyphenol. It is suggested that the reaction involved two competing pathways; one a free radical mechanism leading to the subsequent reduction of the compound and the second an aromatic nucleophilic photo-substitution (Figure 4). A second explanation of the substitution pathway was given as fission to form the aryl cation plus chloride ion.

Crosby and Hamadmad (1971) reported the irradiation at 2537 Å in organic solvents of the fungicides pentachloronitrobenzene, pentachlorobenzene, and pentachlorophenol; and Munakata and Kuwahara (1969) have studied the sunlight irradiation of pentachlorophenol in water. In organic solvents, reductive dechlorination was

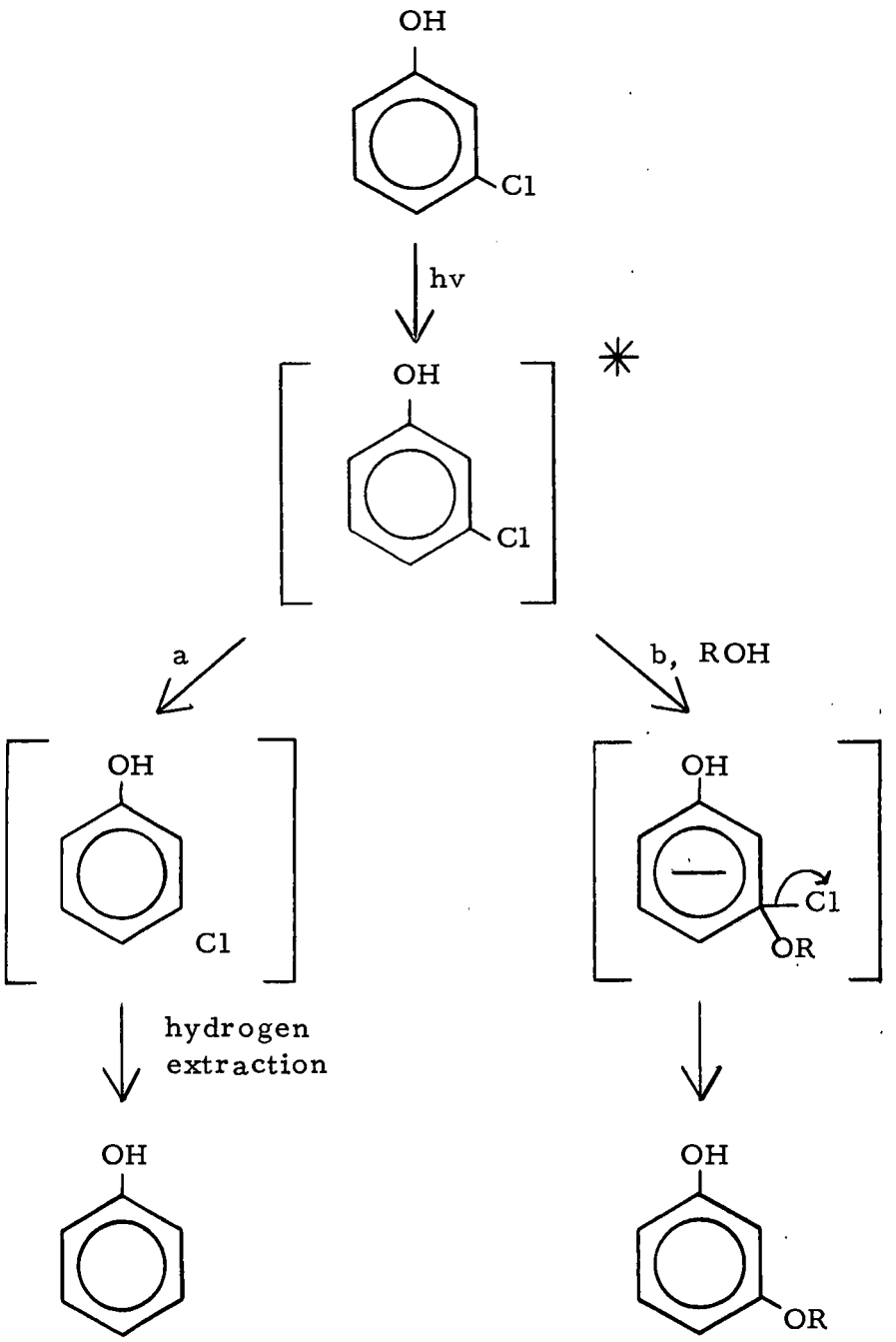


Figure 4. Proposed pathways for degradation of m-chlorophenol in nucleophilic solvent (Pinhey and Rigby, 1969b).

the main reaction noted with reduction occurring ortho and meta to the electron withdrawing substituent, para to the electron releasing group and meta and para when the substituent was hydrogen (Figure 5). Crosby and Hamadmad (1971) concluded this is indicative of a free radical or hydride transfer mechanism. Six products were isolated and identified by Munakata and Kuwahara (1969) from the irradiation of pentachlorophenol in water. They consisted of oxidized monomers, dimers and a trimer and are listed in Table I. These authors also proposed a free radical mechanism for the formation of these materials.

The irradiation of several of the chlorinated herbicides have been reported in the literature. Crosby and Tutass (1966) irradiated 2, 4-dichlorophenoxyacetic acid (2, 4-D) in aqueous solution and reported rapid decomposition using both laboratory uv light and sunlight. Products formed were 2, 4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1, 2, 4-benzenetriol, and polymeric humic acids. The proposed scheme for the degradation of 2, 4-D is shown in Figure 6.

Crosby and Leitis (1969a) studied the photolysis of three sodium monochlorophenylacetates and a herbicide mixture of predominantly 2, 3, 6-trichlorophenylacetic acid known as Fenac. Upon irradiation in aqueous solution, the three monochloro isomers

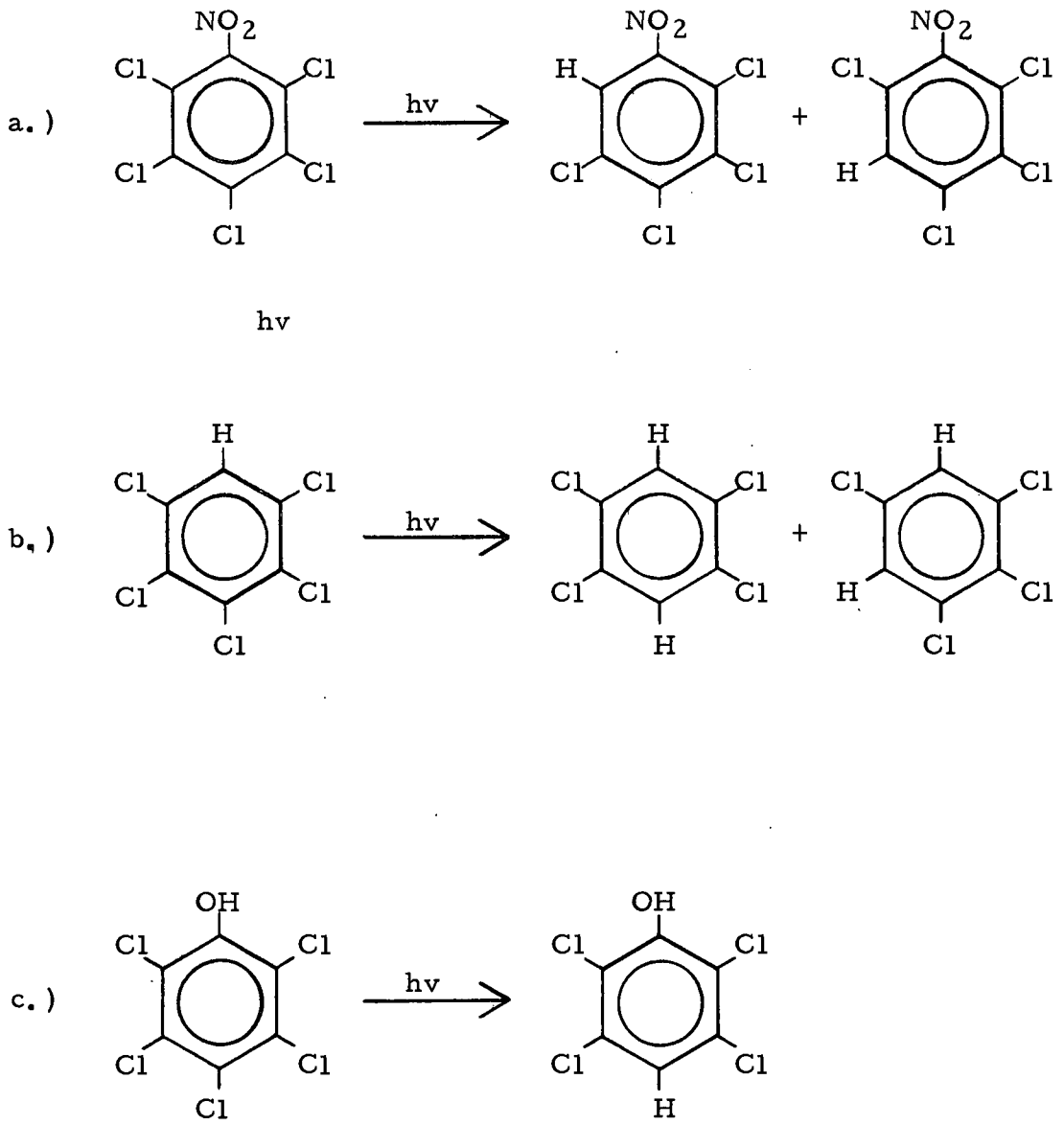
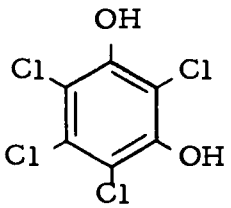
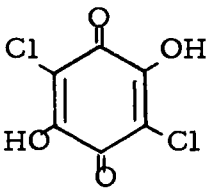
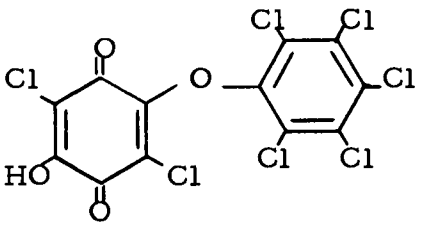
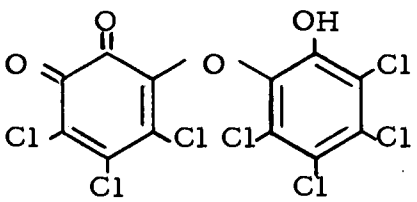
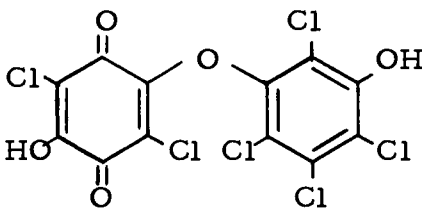
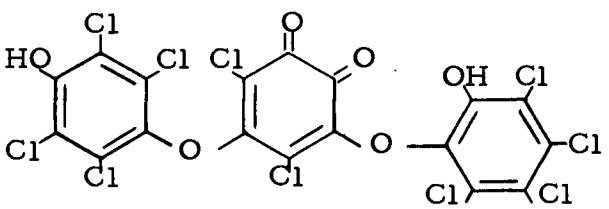
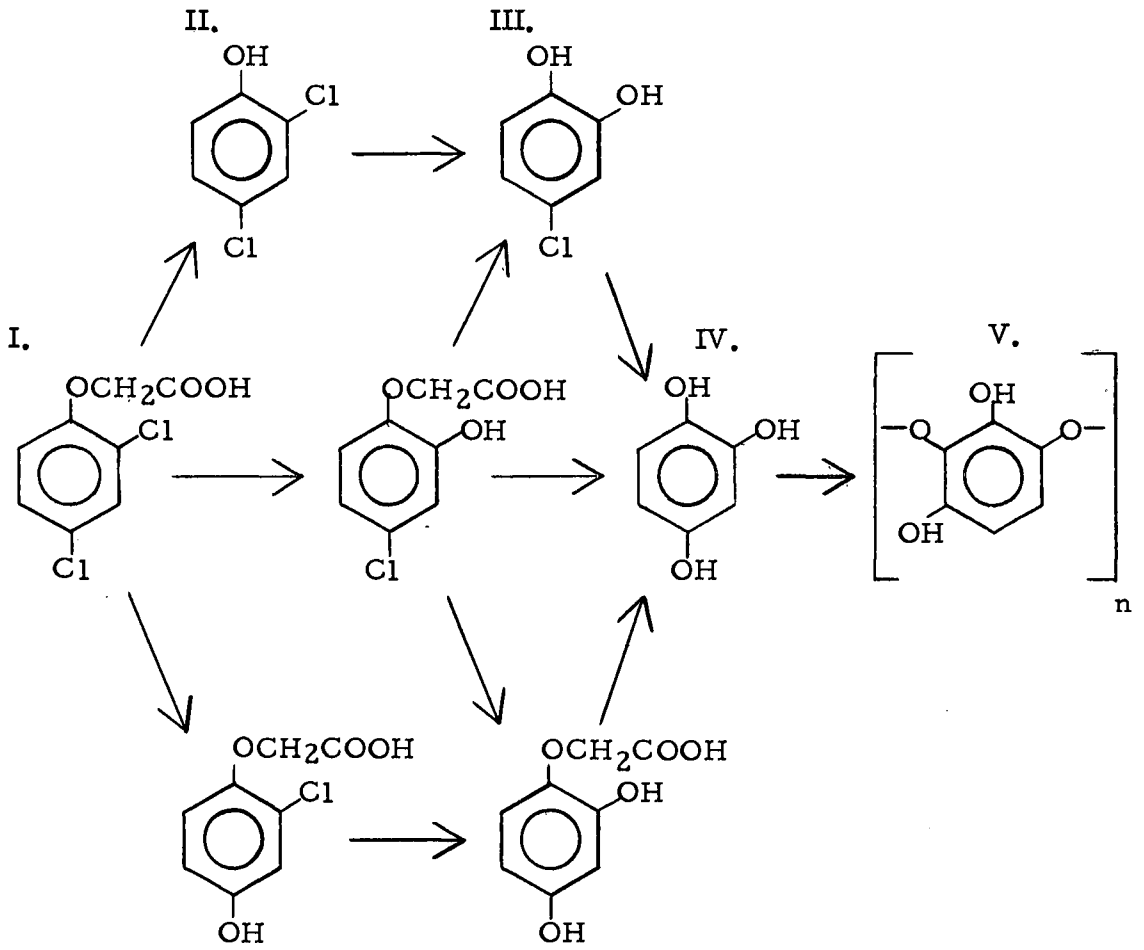


Figure 5. Photo-reduction of pentachloronitrobenzene (a.), pentachlorobenzene (b.), and pentachlorophenol (c.) in organic solvents (Crosby, Hamadmad, 1971).

Table 1. Products of sunlight irradiation of Na-pentachlorophenol in water (Munakata and Kuwahara, 1969).

	Proposed Structure	Name or Formula
I.		Tetrachloro-resorcinol
II.		Chloranilic acid
III.		$C_{12}HO_4Cl_7$
IV.		$C_{12}HO_4Cl_7$
V.		$C_{12}H_2O_5Cl_6$
VI.		$C_{18}H_2O_6Cl_{10}$



I. 2, 4-D
II. 2, 4-dichlorophenol
III. 4-chlorocatechol
IV. benzenetriol
V. polymeric humic acid

Figure 6. Photo-degradation of 2, 4-dichlorophenoxy-acetic acid (2, 4-D) in aqueous solution (Crosby and Tutass, 1966).

yielded phenylacetic acid, benzyl alcohol, benzaldehyde, benzoic acid, hydroxyphenylacetic acids, hydroxybenzyl alcohols, and humic acid. The herbicide mixture produced oxidized, reduced, and hydroxylated compounds including dichlorobenzaldehyde, dichlorobenzyl alcohol, and trichloro benzaldehyde. The replacement of chlorine by hydroxyl groups was felt to be a key reaction in the photochemical fate of these compounds.

The replacement of chlorine by hydroxyl groups as well as hydrogen also occurs upon irradiation of chlorobenzoic acids with laboratory uv light to give the corresponding hydroxybenzoic acids and benzoic acid (Crosby and Leitis, 1969b). In sunlight, monochlorobenzoic acids were unaffected while 3-amino-2,5-dichlorobenzoic acid decomposed rapidly.

Summary of Photolysis of Haloaromatic Compounds

From the recent reports in the literature, it would appear that there is actually considerable photochemical activity in haloaromatic compounds. A free radical mechanism appears to have been proposed most often leading to a number of possible reactions which may occur. Among these are reductive dechlorination, oxidation, hydroxylation and polymerization. Nucleophilic photo-substitution may also occur. The variables affecting which of the above

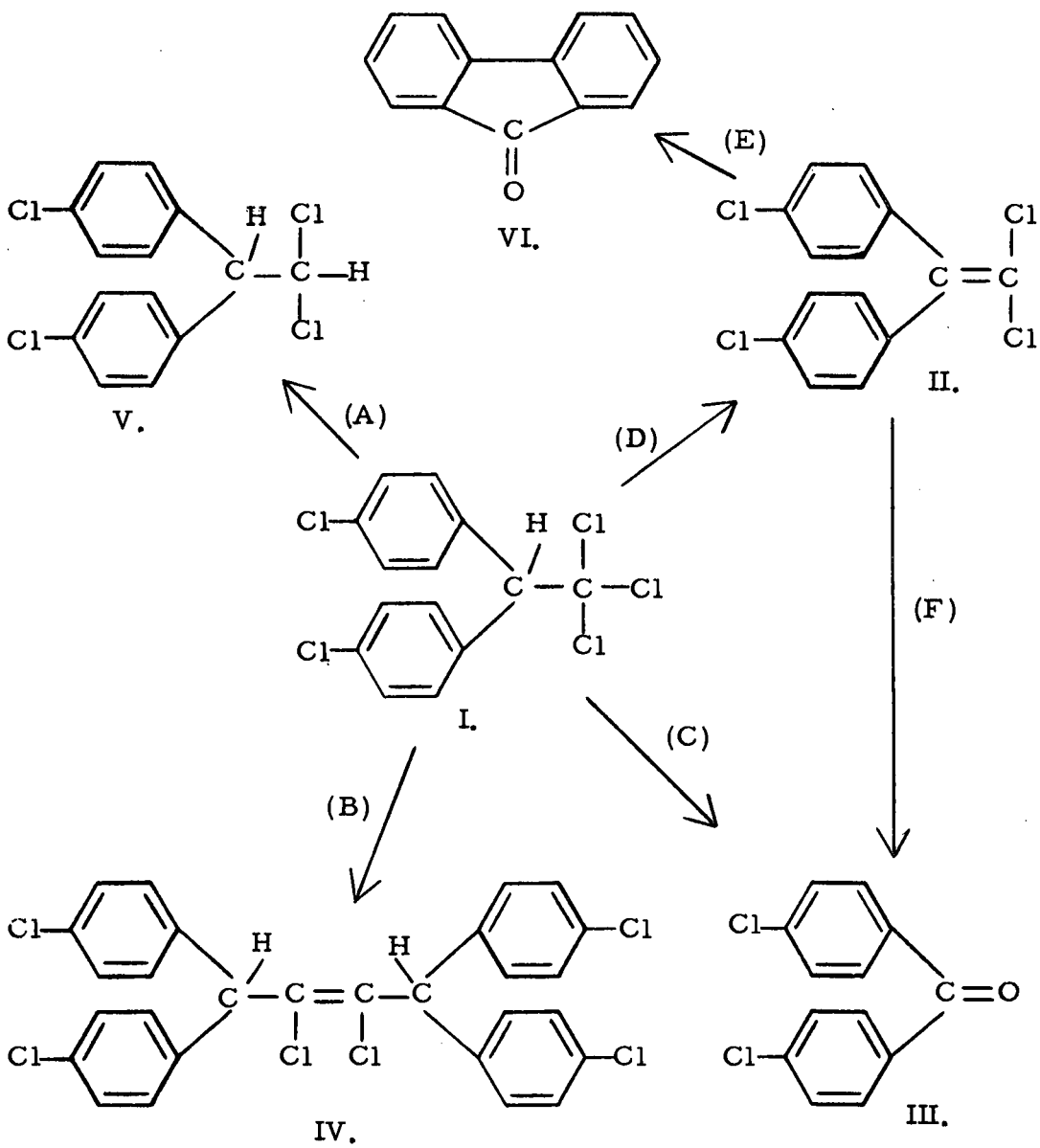
reactions predominate are substituent effects, nature of the solvent, and wavelength and intensity of light.

Photo Degradation of DDT and Its Analogs

Polychlorinated biphenyls have often been likened in structure and properties to certain organochlorine insecticides, in particular the DDT group (Reynolds, 1971; Edwards, 1971; Platonow, Saschenbrecker and Funnel, 1971; Keil, Priester and Sandifer, 1971). The photolysis of DDT and its analogs has been studied extensively, and it has been found that they are readily degraded by uv light.

The major uv degradation products of DDT can be summarized by the reaction scheme shown in Figure 7. Reaction (B) which requires the presence of a solvent that can act as a chlorine acceptor was proposed by Fleck (1949). Reaction (C) was reported by Wichman et al. (1946) and Fleck (1948) while Roburn (1963), Harrison et al. (1967) and Mosier, Guenzi and Miller (1969) observed reactions (A), (D), and (F). Plimmer and Klingebiel (1969) reported reaction (E). A free radical mechanism for the photodegradation of DDT has been proposed by Mosier et al. (1969) and Plimmer, Klingebiel and Hummer (1970).

It can be seen from Figure 7 that the site of action for most of the transformations of DDT is the ethane component connecting



I. DDT
II. DDE
III. DDC=O
IV. 2, 3-dichloro-1, 1, 4, 4-tetrakis -(p-chlorophenyl)-2-butene
V. DDD
VI. 3, 6-dichlorofluorenone

Figure 7. Degradation of DDT by ultraviolet light (Kaufman, 1971).

the aromatic rings. PCBs contain no such site, so it is likely that they will be more stable than DDT and its metabolites.(Peakall and Lincer, 1970; Jensen et al., 1969).

Photolysis of PCBs

There have been very few reports of any photolytic studies done on PCB compounds. The first was in 1966 by Kharasch, Sharma and Lewis who studied 4-chlorobiphenyl in conjunction with three other 4-halobiphenyls. The 4-chlorobiphenyl was found to give only 1% p-terphenyl after 24 hours irradiation at 2537 Å compared to 70-80% p-terphenyl plus biphenyl for 4-bromobiphenyl under the same conditions. A free radical mechanism was proposed and the difference in reactivity was accounted for by the difference in bond strengths.

The first report of photolysis of a PCB compound isolated from an environmental extract was by Risebrough et al. (1968). The PCB compound found in birds from the Gulf of California was readily degraded by uv irradiation in laboratory experiments.

Two extensive laboratory investigations of the photolysis of PCBs have been reported by Safe and Hutzinger (1971) and Hutzinger, Safe and Zitko (1972). In the earlier study 2, 4, 6, 2', 4', 6'-hexachlorobiphenyl was irradiated in hexane at 3100 Å and products

were analyzed by thin layer and gas chromatography and mass spectrometry. A number of products were isolated including oxygenated polychlorinated compounds and reduced PCBs.

The study by Hutzinger et al. (1972) included irradiation of several individual PCBs and a commercial mixture of PCBs under differing conditions. Irradiation in hexane resulted in GLC peaks with shorter retention times and lower chlorine content. A study of the comparative stability of chlorobiphenyl isomers showed no correlation between steric hindrance of ortho chlorine substitution or uv spectra and photochemical lability, but did show that the higher chlorinated compounds degraded more readily.

Irradiation of PCBs in aqueous solvent systems resulted in production of "hydroxy" and "carboxy" polar compounds as well as non-polar compounds with longer and shorter retention times than the starting materials. Hutzinger et al. (1972) concluded from these results that dechlorination, formation of polymers and carboxylic products, and hydroxylation occur during irradiation.

From this work, it seems likely that the photolytic reactions of PCBs are very similar to those previously described for other chlorinated aromatic compounds.

Methods of Analysis

The major problems to overcome in the identification of PCBs from environmental samples are that they are present in very small quantities and that they closely resemble many organochlorine insecticides. To overcome the first problem, gas-liquid chromatography (GLC) coupled with the extremely sensitive electron capture (EC) detector has become practically the universal method for analysis of all types of organochlorine residues. Confirmation of the presence of PCBs once they have been tentatively identified by GLC has been accomplished by selective adsorption, chemical modification and spectrophotometric procedures. The following section describes some of these techniques as applied to PCB analysis.

Gas-Liquid Chromatography

Gas chromatographic retention data for PCBs is well documented in the literature (Weingarten et al., 1962; Zitko, Hutzinger and Safe, 1971; Sissons and Welti, 1971; and Cook, 1972). Identification of PCBs from environmental samples is usually based on both corresponding retention times and on matching the entire chromatographic pattern with that of a commercial mixture used as a

standard. These approaches can be misleading, however, since there are substances such as organochlorine insecticides and chlorinated naphthalenes which have similar retention times. The retention time of a component is not a specific criterion of chemical identity. Also, the pattern of peaks in a commercial mixture may be altered by environmental factors such as fractionation due to dissolving and vaporization, photolysis and chemical decomposition, and selective metabolism and excretion by organisms (Reynolds, 1969; Nisbet and Sarofim, 1972).

Retention times on two or more different stationary phases may also be used for identification. However, these cannot be regarded as independent parameters of identity (Robinson, 1967).

The most common gas chromatographic procedures involve the use of 1/8 and 1/4 inch O. D. packed columns with silicone rubber stationary phases such as OV-17, SE-30, QF-1, and DC-200 (Edwards, 1971; Zitko et al., 1971; Risebrough, Reiche and Olcott, 1969). Reynolds (1971) suggests the use of more polar stationary phases such as DEGA and DEGS to distinguish p, p'DDD and p, p'-DDT from PCBs. High column temperatures, near 200° C, are used due to the high boiling nature of the compounds. The use of open tubular capillary columns has been reported by Weingarten et al. (1962) and Sissons and Welti (1971) but they have not been used for analysis of environmental samples.

Specialized Chromatographic Detectors

There are several gas chromatographic detectors which are sensitive to halogenated compounds. The electron capture detector and the microcoulometric detector have found general application in the field of PCB analysis. The plasma chromatograph detector has been introduced only recently and has not been used extensively.

1. The electron capture (EC) detector responds only to those molecules which readily capture thermal electrons. Since the carbon-chlorine bond has a relatively high electron capture potential, this detector is very sensitive to PCBs and has been widely used for PCB analysis. The EC detector is among the most sensitive of all gas chromatographic detectors so it is suited for analysis of trace residues. One of the drawbacks is that the electron capture response is not linearly related to the number of chlorine atoms present, thus making quantitation difficult. Also, the detector is not specific for chlorinated compounds and is sensitive to some oxygen, nitrogen, and phosphorous containing compounds.

2. The microcoulometric detector has been employed for the specific analysis of chlorine in PCB analysis. The column eluate is reduced to the hydrochloride and allowed to react with silver ions in solution which changes the potential of the detector cell. This

detector is particularly useful for quantitation work since the response is proportional to the amount of silver ion removed from solution.

3. The plasma chromatograph detector utilizes a ^{63}Ni radioactive beta source to create ions for reaction with trace constituents in a gas. Ion-molecule complexes are produced which are then separated and detected. The instrument includes a positive and negative ion-molecule reactor coupled with an ion drift spectrometer that produces a plasmagram of separated ion-molecule peaks from a sample mixture (Cohen and Karasek, 1970). Karasek (1971) has applied the technique to the identification of PCBs and reported strong positive and negative plasmagram patterns for a series of PCB compounds containing one to ten chlorine atoms.

Pyrolysis Gas Chromatography

In this technique, the sample is pyrolyzed at high temperature and the reaction products are separated by GLC. The ensuing pyrogram can be compared with those of known standards as a means of tentative identification. One of the major problems is the lack of reproducibility. This procedure has not been applied to PCBs, possibly due to their heat resistance and fire retardant properties.

Carbon Skeleton Chromatography

This procedure resembles pyrolysis chromatography in that the sample is thermally degraded prior to being chromatographed. Here a catalyst is used, however. Asai et al. (1971) have applied this technique to PCBs using a NaCl-neutral palladium catalyst and shown that all PCBs are reduced to the same products: cyclohexylbenzene and/or bicyclohexane. A drawback for trace analysis is that the products must be detected by a less sensitive means than electron capture.

Photolysis Gas Chromatography

In this technique, the sample molecule is altered by ultraviolet light and the products are chromatographed to give a "fingerprint" pattern. It has been applied to the identification of organochlorine insecticides by Banks and Bills (1968), Kaufman (1971) and Kaufman, Bills and Hannan (1972) but has not been applied to PCBs.

Advantages of this method over pyrolysis include the relative ease with which reproducible results may be obtained and the simplicity of the apparatus. Photolytic degradation products are considerably fewer in number than observed in the more energetically severe pyrolytic cracking technique.

Selective Adsorption

Several liquid chromatographic techniques have been developed which are used in the cleanup of PCB residue extracts. These techniques provide separation of PCBs from interfering substances such as chlorinated insecticides prior to analysis. In addition, they may provide qualitative evidence of the presence of PCBs.

Reynolds (1969, 1971) has reported the use of activated Florisil to separate PCBs from p, p'-DDD, p, p'-DDT and other pesticides. When p, p'-DDD and p, p'-DDT peaks are used as the basis of identification, the presence of PCBs is indicated if apparent DDD and DDT peaks are present in the initial chromatogram and are not removed by elution from Florisil.

Snyder and Reinert (1971) describe a procedure for separating PCBs from DDT and its analogs on silica gel columns, while Armour and Burke (1970) used silicic acid-celite and reported the separation of PCBs and aldrin from lindane, heptachlor, heptachlor epoxide, dieldrin, endrin, p, p'-DDE, o, p-DDT, p, p'-DDD and p, p'-DDT. Berg, Diosady and Rees (1972) have recently reported a technique using activated charcoal which separates the PCBs from DDT and its analogs.

Chemical Modification

Another technique that has been employed to separate and differentiate PCBs from interfering substances is chemical derivatization. Because of the chemical inertness of the PCB molecule, it generally remains unchanged while the organochlorine insecticides are altered in such a manner to shift their chromatographic retention time so they no longer coincide. There may be other inert molecules present, however, such as polychlorinated terphenyls and polychlorinated naphthalenes, so identification by this procedure is tentative at best.

The most popular of the procedures which leave the PCB molecule intact are saponification with alcoholic NaOH or KOH (Archer and Crosby, 1966; Reynolds, 1971), nitration with sulfuric acid: nitric acid mixture (Reynolds, 1969; Peakall and Lincer, 1970) and reaction with hydrogen bromide/acetic anhydride reagent to give bromohydrin or bromacetoxy derivatives (Reynolds, 1971). Some workers have reported negative results using nitration arising from reactions with the more volatile PCBs and more complex chromatograms (Reynolds, 1969; Armour and Burke, 1969).

A method which alters the PCB molecule has been developed by Berg et al. (1972). The PCBs may be either catalytically de-

chlorinated to bicyclohexyl using a Pt or Pd catalyst, or they may be perchlorinated with antimony pentachloride to form decachlorobiphenyl. The latter procedure was preferred because the derivative could be analyzed by GLC - EC. This procedure is particularly useful in that the PCBs may be quantitated in terms of a specific derivative.

Mass Spectrometry

The use of the mass spectrometer is perhaps the best technique for identifying PCBs from environmental samples. Desirable features are the small sample size required and short scan time which make mass spectrometry compatible with gas chromatography. The high cost of the apparatus is a limiting factor, however.

The primary ion spectra of most isomeric PCB compounds are similar, with successive loss of Cl from the molecular ion (Safe and Hutzinger, 1972). It is therefore possible to confirm the identity and the number of chlorines per molecule from the molecular ion and fragmentation pattern but it is difficult to distinguish positional isomers. The mass spectra of many of the PCB compounds are found in the literature (Bagely, Reichel and Cromartie, 1970; Hutzinger, Jamieson and Zitko, 1970; Bonelli, 1972; Safe and Hutzinger, 1972).

Bonelli (1972) reported the use of a mass selector and computor data storage to identify and quantitate PCBs in the presence of chlorinated insecticides and other interfering substances.

Nuclear Magnetic Resonance (NMR)

NMR has been used to identify the structure of individual PCB isomers separated from commercial mixture and of synthesized standards (Tas and deVos, 1971; Sissons and Welti, 1971). Information relating to the positions of the chlorines on the molecule is available by this method which is not available from mass spectrometry. However, due to the low inherent sensitivity of the instrument (10-20 mg of sample are required) it is not readily applicable to routine analyses of environmental samples.

Infrared Spectroscopy (IR)

Infrared Spectroscopy has been used in identifying individual PCB compounds (Tas and deVos, 1971) and showing structural characteristics of ultraviolet degradation products of PCBs (Safe and Hutzinger, 1971). Like NMR, however, the utility of IR spectroscopy in trace analysis is limited by the sample size requirement.

Thin Layer Chromatography (TLC)

TLC is a useful tool for the isolation and separation of PCBs from interfering substances (Westoo and Noren, 1970; Fehringer and Westfall, 1971; deVos and Peet, 1971; Mulhern et al., 1971). As an identification tool, however, it is relatively poor. Compared to GLC the sample size required is large and the resolution is poor.

Summary of Analysis Techniques

The two most valuable and widely used techniques in the identification of PCB residues are gas-liquid chromatography with the electron-capture detector and mass spectrometry. Confirmatory information can also be obtained using liquid chromatography as well as chemical and physical modification of the PCB molecule and of suspected interfering compounds. The technique of photolysis gas chromatography had not been applied to PCB analysis but seemed promising because of the apparent lability of the molecules to uv light and the simplicity and comparative low cost of the procedure and apparatus.

EXPERIMENTAL

Sources of PCBs and Insecticides

The commercial mixture of PCBs (Aroclor 1254) used throughout this investigation was supplied by the Monsanto Chemical Co., St. Louis, Missouri. This particular mixture is composed of a number of biphenyl molecules with varying degrees of chlorination and has an average chlorine content of 54 percent.

The analytical grade pesticides used in this work were obtained from the following sources: p, p'-DDT and p, p'-DDE - Geigy Chemical Corp., Ardsley, N. Y.; aldrin and dieldrin - Shell Chemical Co., Modesto, California.

Equipment and Supplies

The following three gas chromatographic instruments were used during the course of this work: an F and M Model 810 equipped with a tritium electron capture (EC) detector; F and M Scientific Corp., Avondale, Pa., connected to a Speed Servo strip chart recorder, Esterline Angus Instrument Co., Inc., Indianapolis, Ind.; a Varian Aerograph Series 1200 equipped with a flame ionization detector (FID), Varian Aerograph Instruments, Inc., Walnut Creek,

Calif., connected to a Speed Servo strip chart recorder; and a Varian Aerograph Model 90P3, Varian Aerograph Instruments, Inc., equipped with a Carle 100 Microdetector, Carle Instruments, Inc., Fullerton, Calif., connected to a Speedomax H strip chart recorder, Leeds and Northrup Co., Philadelphia, Pa.

Combined gas-liquid chromatography-mass spectrometry was done on an F and M Model 810 gas chromatograph coupled to a Varian-MAT Atlas CH-4 single focusing mass spectrometer, Varian Aerograph Instruments, Inc., equipped with a Llewellyn single stage molecular separator and a double ion source - 20 eV source to obtain a chromatogram and 70 eV source for the mass spectra. A Carle Valve, Carle Instruments, Inc., was used to vent the solvent to the atmosphere to prevent flooding of the ion source. The mass spectra were recorded on a Honeywell Visicorder Model 1508.

The uv light used for irradiation of the samples was a Hanovia Utility Model Quartz Lamp, #616A, manufactured by the Hanovia Lamp Div., Englehard-Hanovia, Inc., Newark, N. J. This medium-pressure mercury lamp emitts a discrete line spectrum that includes 253.7 nm along with many other lines in the far and near ultraviolet. Table 2 indicates the energy distribution and spectrum from information given by the company.

Table 2. Spectral Energy Distribution for the Hanovia Mercury Lamp #616A.

Wavelength, nm	Watts	Einstein $sec^{-1} \times 10^{11}$
366.0	1.82	55.6
334.1	0.18	5.03
313.0	1.30	34.0
302.5	0.57	14.4
296.7	0.30	7.44
289.4	0.19	4.59
280.4	0.19	4.45
275.3	0.08	1.84
270.0	0.09	2.03
265.2	0.47	10.4
257.1	0.19	4.09
253.7	0.37	7.86
248.2	0.19	3.92
240.0	0.12	2.41
238.0	0.09	1.78
236.0	0.06	1.18
232.0	0.02	0.39
222.4	0.02	0.37

The teflon tubing used for trapping and irradiating the samples was #16 thin-walled Teflon tubing made by Trimflex, Inc., Dover, N. J. The quartz cuvettes used for irradiating samples were Beckman Standard 1 mm adsorption cells, Beckman Instruments, Inc., Fullerton, Calif.

For sample cleanup a Florisil Column was packed in a Kontes glass column, 2. 2 cm in diameter and 50 cm long. The Florisil, 100-200 mesh, is produced by the Floridin Co. and was purchased from Fisher Scientific Co., Fairlawn, N. J.

The two types of syringes used were a 10 µl Hamilton syringe made by the Hamilton Co., Inc., Whittier, Calif., and a 100 µl Pressure-Lok syringe made by Precision Sampling Corp., Baton Rouge, La.

The solvents used were of "Nanograde" quality obtained from Mallinkrodt Chemical Works, St. Louis, Mo.

GLC Separations of Aroclor 1254

Hexane solutions of the Aroclor 1254 mixture were separated under the various chromatographic conditions listed below. Each set of conditions will be referred to later by the number associated with each column used.

Gas Chromatographic Conditions

A.)	Instrument:	F and M Model 810
	Type Detector:	Tritium EC
	Column:	1. 122 cm by 4 mm I. D. glass column packed with 2% SE-30 and 2% QF-1 on 70/80 mesh Anakrom ABS
	Operating Conditions:	Injector Temp. - 205°C Detector Temp. - 205°C Column Temp. - 180°C Carrier Gas - 5% Methane, 95% Argon Flow Rate - 60 ml/min.
B.)	Instrument:	Varian Aerograph Model 90P3
	Type Detector:	Micro thermistor (thermal conductivity)
	Column:	2. 6 ft. by 1/4 in. O. D. aluminum column packed with 2% SE-30 and 2% QF-1 on 70/80 mesh Anakrom ABS
	Operating Conditions:	Injector Temp. - 200°C Detector Temp. - 200°C Column Temp. - 180°C Collector Temp. - 240°C Carrier Gas - Helium Flow Rate - 25 ml/min. Filament current - 30 μa
C.)	Instrument:	Varian Aerograph Series 1200
	Type Detector:	Flame Ionization

	Column:	3. 6 ft. by 1/8 in. O. D. Stainless Steel column packed with 5% Dexsil 300 GS (Analabs, Inc.) on 60/80 mesh Chromosorb G
	Operating Conditions:	Injector Temp. - 250°C Detector Temp. - 310°C Column Temp. - 220°C Carrier Gas - nitrogen Flow Rate - 15 ml/min.
D.)	Instrument:	Varian Aerograph Series 1200
	Type Detector:	Flame Ionization
	Column:	4. 300 ft. by .02 in. I. D. capillary column coated with 'Q' Purified Apiezon L (Perkin Elmer)
	Operating Conditions:	Injector Temp. - 250°C Detector Temp. - 310°C Column Temp. - 220°C Carrier Gas - nitrogen Flow Rate - 10 ml/min.

The components eluting from column 2 were individually trapped in 7 cm lengths of Teflon tubing cooled by dry ice. They were then dissolved in hexane, diluted to a suitable concentration, and injected separately on each of the other three columns.

Combined Gas-Liquid Chromatography-Mass Spectrometry (GLC-MS)

Mass spectra were obtained by injecting 16 μg of Aroclor 1254 in 1 μl of hexane into the F and M Model 810 gas chromatograph.

The solvent peak was vented to the atmosphere using the Carle valve, the valve was closed and the column eluate introduced to the mass spectrometer via the molecular separator. A mass spectra was recorded when the 20 eV source showed a positive response. The compounds eluting from both column 2 and column 3 were analyzed. The chromatographic conditions for each column were the same as those listed in the previous section except helium was used as carrier gas. The mass spectrometer conditions are listed below.

MS Conditions

Filament Current:	20 eV source 40 μA 70 eV source 20 μA
Electron Voltage:	20 eV and 70 eV
Accelerating Voltage:	3000 V
Analyzer Pressure:	1.5×10^{-6} Torr for Column 2 7×10^{-7} Torr for Column 3
Multiplier Voltage:	1.60 KV
Scanning Speed:	5.0 seconds from m/e 25 to m/e 250

Preliminary Irradiation Study

A solution of 205 ppm Aroclor 1254 in acetone was used to make 2.05 ppm solutions in distilled water, hexane, and benzene.

Three ml portions of each 2 ppm solution were placed in quartz cuvettes fitted with Teflon caps and irradiated for periods of 5, 15, 30 and 45 minutes. The hexane and benzene samples were concentrated to one ml using a Büchi Rotavapor evaporator. The water samples were extracted with two ten ml portions of hexane. The extracts were dried with anhydrous sodium sulfate and then concentrated to one ml. All the samples were analyzed by GLC using the conditions listed in set A in the previous section.

Trapping and Irradiation Procedure

For more complete explanation of the trapping and irradiation procedures used in this work the reader is directed to the reports of Kaufman (1971) and Kaufman et al. (1972). Their procedures as developed for certain chlorinated insecticides were suitable for application to PCBs without modification.

Briefly, the GLC effluent is split by means of a specially constructed Teflon stream-splitter, half being directed to the detector, half to the atmosphere. A seven cm length of Teflon tubing is placed at the end of the atmospheric leg of the splitter and the sample is condensed on the walls of the tubing, using dry ice to cool the trap. The Teflon tubing is then removed, crimped on one end and placed in a spring-loaded paper clip. Fifty µl of hexane is added to dissolve

the sample, being careful to wash down the inside walls of the tubing, and the open end is crimped and placed in a second clip. The sealed tube is then placed in a special irradiation chamber equipped with a light-tight sliding shutter and positioned 14 cm directly in front of the uv lamp. The shutter is closed and the lamp allowed to warm-up for four minutes. Then the shutter is opened and the sample irradiated the desired length of time. The entire contents of the tube is then reinjected into the gas chromatograph with the atmospheric leg of the splitter closed so the entire sample goes to the detector.

Column 1 was used for trapping and irradiation of the PCB components. The optimum irradiation time for the components was determined by injecting 88.6 ng Aroclor 1254 in 10 µl hexane, trapping each component and irradiating it for various lengths of time as described above. The irradiation time chosen was the minimal time that yielded approximately equal areas for the largest degradation peak and for the parent peak.

Trapping Efficiency

The ratio of sample going to the detector and that going to the atmosphere was determined by measuring the gas velocity in both legs. The trapping efficiency was then determined by trapping each peak, closing the atmospheric leg of the splitter, and reinjecting

the sample, using the same attenuation setting for both injections. The efficiency was determined by the following equation:

$$\text{Percent trapping efficiency} = \frac{\text{Flow rate in detector leg}}{\text{Flow rate in atmospheric leg}} \times \frac{\text{Area of Peak on Second Injection}}{\text{Area of Peak on First Injection}} \times 100$$

Analysis in Presence of Pesticides

Solutions of the individual PCB components separated on column 2 were made by injecting 1.2 mg Aroclor 1254, trapping each peak in a 7 cm length of Teflon tubing cooled by dry ice, and dissolving them in 100 ml hexane. Approximately equal amounts of PCB and the interfering pesticide with the same GLC retention time were then determined by GLC peak area and combined in a Teflon trap. This mixture was irradiated and analyzed as described previously. The organochlorine insecticides used in this study were aldrin, dieldrin, p,p'-DDE, and p,p'-DDT. The optimum irradiation time for these PCB-pesticide mixtures was selected to yield the clearest pattern for demonstrating the simultaneous occurrence of the two.

Analysis of Samples

The samples were extracted by petroleum ether-acetonitrile partitioning (Pesticide Analytical Manual, 1968). The extracted

samples were further purified by placing them on an 11.5 cm x 2.2 cm Florisil column and eluting them with 250 ml petroleum ether. Selected peaks from the resulting chromatograms were then trapped and irradiated by the procedure described previously. The two samples used in this work were herring oil and salmon oil.

RESULTS AND DISCUSSION

Gas Chromatographic Separations

Figures 8 and 9 represent typical chromatograms obtained using columns 1 through 3 and 4, respectively. Columns 1 and 2 were very similar and gave similar patterns. On column 1 the Aroclor 1254 mixture was separated into 13 major peaks. Using column 2, only the first ten major peaks could be readily distinguished. The most striking difference between the two patterns is the differences in the relative peak areas. It can be seen that with the electron capture detector, the tendency is for much greater response with longer retention time. This would be expected since the degree of chlorination also increases with increasing retention time. The disadvantage of the microthermistor detector was that it was less sensitive than the EC detector by a factor of about 10^5. For this reason the microthermistor detector is useful only for preparative separations of large amounts of material, i.e., one to ten mg.

Column 3, coated with Dexsil 300 GS, and used in conjunction with flame ionization detection gave an improved separation over columns 1 and 2, however, the sensitivity was still poorer than with EC detection. The Aroclor 1254 mixture yielded 35 distinguishable

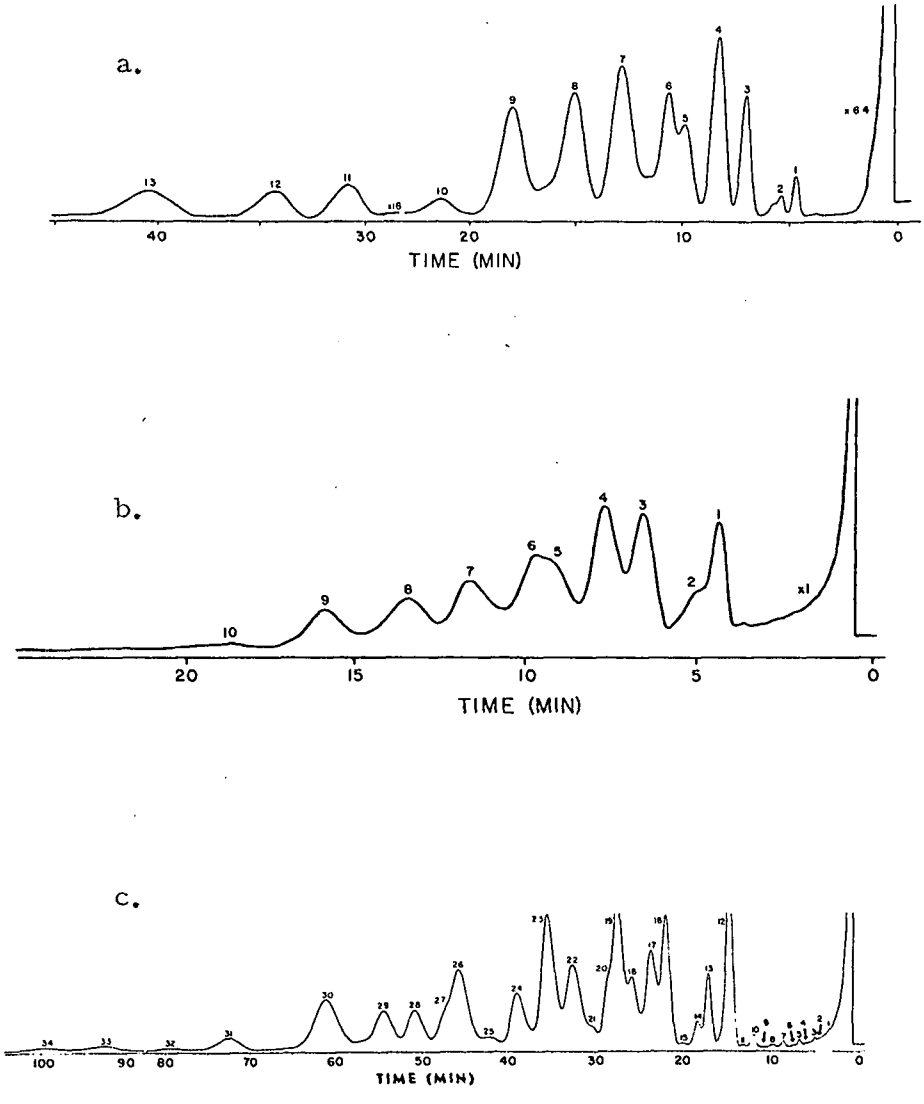


Figure 8. Chromatograms of Aroclor 1254 separated on a.) column 1, b.) column 2, and c.) column 3. See text for column descriptions and instrumental conditions.

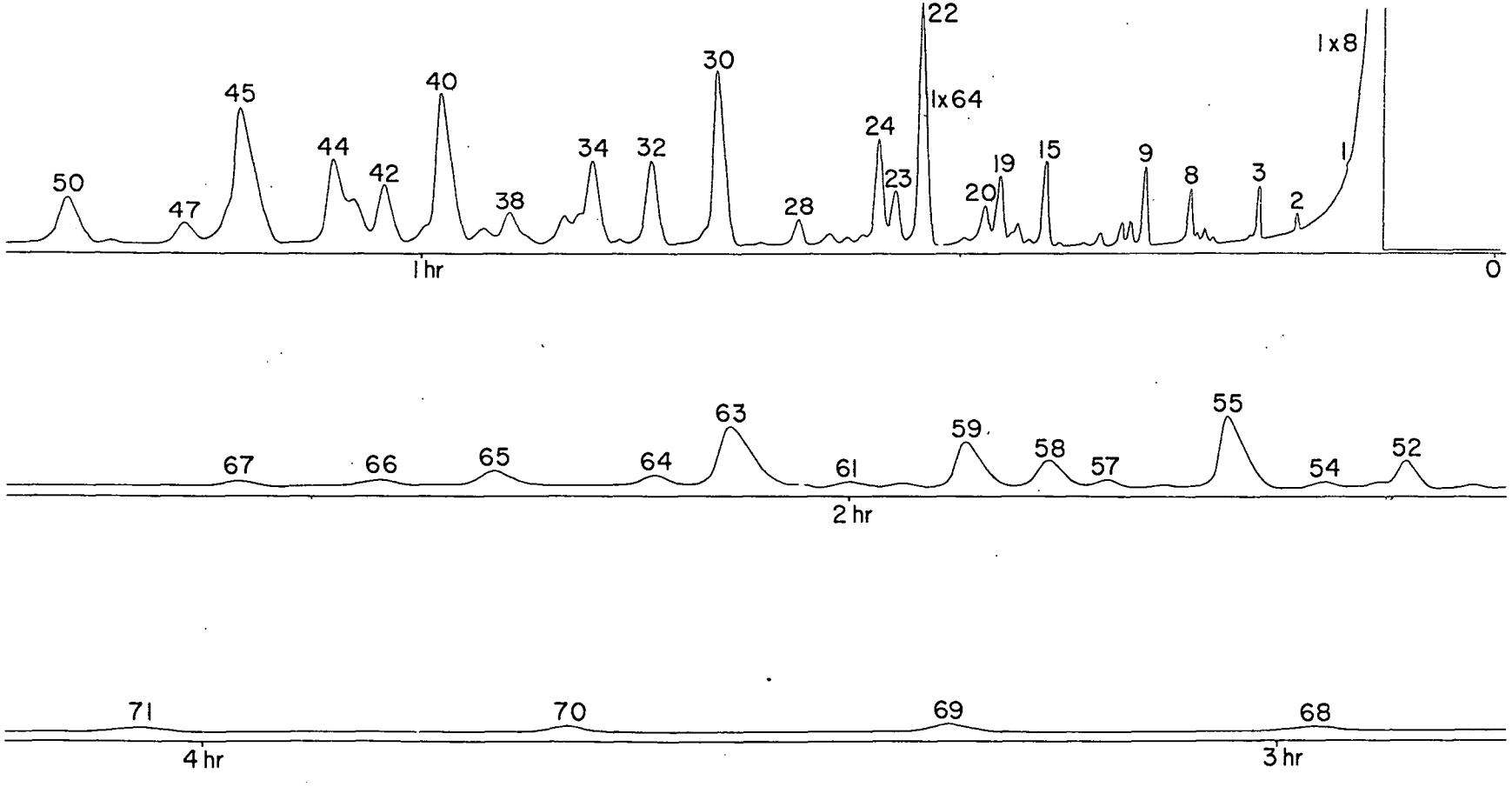


Figure 9. Chromatogram of Aroclor 1254 separated on column 4. See text for description of column and conditions.

components using this column, the last of which is not shown in Figure 8c. It was possible to distinguish several minor components prior to the major peaks which could not be seen on the first two columns. Several of the major peaks on columns 1 and 2 were also partially resolved into more than one component on this column. The analysis time was increased, however, by a factor of 2.5 over column 1 and five over column 2.

The capillary column, number 4, gave the best separation of all, however, the analysis time was also the longest, over four hours. The Aroclor 1254 mixture was separated into 71 distinguishable peaks. Again, as with column 3, there were a number of minor components prior to the major peaks and the major peaks were resolved even further. Based on this resolution, which was by no means complete, it seems evident that a great number of the possible PCB isomers are present in the mixture, though many are present only in small quantities.

By trapping the peaks separated on column 2 and injecting them on column 1, it was found that the peaks on these two columns coincided. By injecting these peaks on columns 3 and 4, it was found that each peak on columns 1 and 2 may be composed of as many as 11 components. Table 3 shows the peaks which correspond to one another on the four columns.

Column 1 was chosen for use in further qualitative analysis based on sensitivity and analysis time. A third consideration was that these column conditions are similar to those reported by other investigators. It was hoped that any new identification technique developed would be as compatible as possible with existing analytical methods.

It is important to keep in mind, however, that the individual peaks separated on column 1 are not single compounds but combinations of many different PCB isomers.

Mass Spectral Results

The results of the mass spectral analysis of Aroclor 1254 as separated on columns 2 and 3 are given in Table 4. The structure and number of chlorines per molecule were confirmed by the mass of the molecular ion. The results for column 2 agree with those reported by Biros, Walker and Medbery (1970). Using column 3, it was possible to identify mono-, di-, and tri-chlorinated PCBs in addition to the molecules containing 4, 5 and 6 chlorines/molecule. Sissons and Welti (1971) also reported the lesser chlorinated biphenyls as well as molecules containing seven chlorines per molecule. In this work, the minor components of long retention time could not be analyzed due to an increasing resistance to cross the molecular separator as the retention time increased. For this reason, no hepta-

Table 3. Peaks eluting from columns 2, 3 and 4 which correspond to the peaks eluting from column 1.

Peak # [(a)]	Column 2	Column 3	Column 4
		1-11	1-21
1	1	12	22, 23
2	2	11-15	24-29
3	3	16, 17	30, 32, 34-36
4	4	18-21	31-33, 38, 40-42
5	5	21, 22	39-44
6	6	23, 24	44-46
7	7	24-26	45-55
8	8	27-29	51, 54, 56-58
9	9	30	59-63
10	10	31, 32	64-66
11	11	33	67
12	12	34	68, 69
13	13	35	70

(a) Column 1

Table 4. Mass Spectra Results for Column 2 and Column 3.

# Chlorines/ molecule	m/e molecular ion	Peak Numbers	
		Column 2	Column 3
1	188		1
2	222		3, 4, 5
3	256		6, 7, 8
4	290	1, 2	10-14
5	324	3, 4, 5	16-19, 21, 22
6	358	6, 7, 8, 9	23, 24, 26, 28, 30
7	392		

chloro molecules were observed.

Irradiation of Aroclor 1254

The results of irradiating the entire PCB mixture in hexane, benzene and water are shown in Tables 5 through 7. The percentages listed in each case represent the portion of the original peak area remaining after the indicated length of exposure. As indicated the PCBs were degraded in all three solvents. The fastest degradation occurred in hexane with all the peaks dissappearing after 30 minutes. In water there were still peaks present after 45 minutes, and in benzene roughly 50% of the PCBs remained after 45 minutes.

The fact that some peaks increased in size suggests that the more highly chlorinated PCBs were being dechlorinated to form PCBs with lower molecular weights and shorter retention times. In view of the results of Hutzinger, Safe and Zitko (1972), one would expect dechlorination to take place in the organic solvents. It was also concluded from the variability in the percentages remaining for different peaks of the same sample that the PCBs do not all degrade at the same rate.

It was felt that there are two possible explanations for the effect of solvent on degradation rate. The first is the uv transmission limit of the solvent. This limit is approximately 190 nm, 210 nm and

Table 5. Percent of each peak[(a)] remaining after irradiation of Aroclor 1254 in hexane.

Peak #	Time of Exposure (minutes) 5	15	30
1	104	29	0
2	275	83	0
3	99	0	0
4	62	0	0
5	0	0	0
6	140	75	0
7	9	0	0
8	28	0	0
9	7	0	0
10	0	0	0

(a) Column 1

Table 6. Percent of each peak[(a)] remaining after irradiation of Aroclor 1254 in water.

Peak #	Time of Exposure (minutes) 5	15	30	45
1	97	20	0	0
2	30	0	0	0
3	121	43	21	10
4	96	45	23	10
5	66	14	0	0
6	80	38	26	15
7	110	78	55	32
8	79	54	35	20
9	75	35	27	10
10	0	0	0	0

(a) Column 1

Table 7. Percent of each peak[(a)] remaining after irradiation of Aroclor 1254 in benzene.

Peak #	Time of Exposure (minutes)			
	5	15	30	45
1	104	72	31	55
2	116	48	30	43
3	94	73	57	60
4	96	77	31	55
5	106	61	26	44
6	99	67	43	47
7	75	47	22	15
8	90	68	46	40
9	90	64	45	44
10	106	71	67	63

(a) Column 1

280 nm for water, hexane and benzene, respectively. Comparing the rates in hexane and water to that in benzene, it appears that the shorter wavelength, higher energy radiation is more effective.

The second possible explanation is that the solvent participates in the reaction, possibly as a hydrogen donor. In this case, both the reactivity and the polarity of the solvent would be important. One would expect benzene to be a relatively poor hydrogen donor compared to either hexane or water, thus explaining the slower rate in benzene. The fact that the rate was slower in water than in hexane

may be due to the relative insolubility of PCBs in water. The hexane molecules could be much more closely associated with the PCB molecules due to their low polarities.

From these findings, hexane was chosen to be used as the solvent for the irradiation of the individual components trapped from the PCB mixture. The decision was based on its low uv transmission limit, its good solubility properties, and the apparent high degradation rate of PCBs in it.

Irradiation of Individual Components from Aroclor 1254

Table 8 shows the optimum irradiation times for the nine major peaks of Aroclor 1254, as separated on column 1. There is a general tendency for shorter irradiation time as the retention time increases. This agrees with the findings of Hutzinger et al. (1972).

The irradiation times using the 0.053 inch diameter Teflon tubes for trapping and irradiating were considerably shorter than those noted by Hutzinger et al. (1972), Kharasch et al. (1966) and in the previous section of this paper. With the Teflon tubing, all of the PCB molecules in the solution are within a maximum distance of 1.4 mm of the incident photons compared to the maximum distance of 10 mm in the quartz cuvettes used previously. This shorter distance would facilitate exposure of all the pesticide molecules to photon interaction in a much shorter time.

Table 8. Retention times and optimum irradiation times for Aroclor 1254 components.

Peak #	Retention Time (min.)[a]	Optimum Irradiation Time (sec.)
1	4.9	120
2	5.6	90
3	7.4	120
4	8.8	180
5	10.6	30
6	11.2	45
7	13.7	45
8	16.1	90
9	19.0	30

(a) As separated on Column 1

The results of the irradiation of the individual Aroclor 1254 components are given in Table 9 and Figure 10. The degradation patterns in Figure 10 are represented as bar charts with the height of the bar being relative to the degradation peak area/parent peak area (DPA/PPA) ratio.

In all cases the degradation patterns consisted of a number of peaks with shorter retention times than the parent peak. In many cases the retention times of the degradation peaks corresponded closely to the retention times of peaks in the original mixture. This supports the suggestion that dechlorination was occurring. It is clear that isomerization or rearrangement was also taking place.

Table 9. Irradiation results at optimum irradiation times for individual components of Aroclor 1254.

Peak # [a]	Retention time (min) [a]	Relative retention time [b]	Peak area (mm^2)	DPA/PPA [c]
1	3.7	.76	33	.45
	4.9	1.00	73	---
2	3.8	.67	37	.47
	5.6	1.00	78	---
3	3.7	.50	31	.27
	4.9	.66	65	.57
	5.7	.77	80	.70
	7.4	1.00	114	---
4	4.9	.56	52	.31
	6.0	.68	115	.68
	7.4	.84	63	.37
	8.8	1.00	169	---
5	5.8	.55	41	.23
	7.7	.73	129	.74
	9.2	.87	27	.15
	10.6	1.00	175	---
6	5.7	.51	98	.29
	7.4	.66	325	.97
	8.5	.76	72	.21
	11.2	1.00	336	---

Table 9. Continued.

Peak #[a]	Retention time (min)[a]	Relative retention time[b]	Peak area (mm^2)	DPA/PPA[c]
7	6.2	.45	57	.13
	7.7	.56	73	.16
	9.2	.67	159	.36
	12.2	.89	451	1.01
	13.7	1.00	446	---
8	6.1	.38	74	.31
	7.6	.47	72	.30
	9.0	.56	128	.54
	11.9	.74	253	1.06
	16.1	1.00	238	---
9	5.9	.31	48	.11
	7.4	.39	44	.10
	8.9	.47	98	.22
	11.6	.61	329	.75
	13.5	.71	363	.83
	19.0	1.00	463	---

(a) As separated on Column 1

(b) Relative to Parent Peak

(c) Degradation Peak Area/ Parent Peak Area

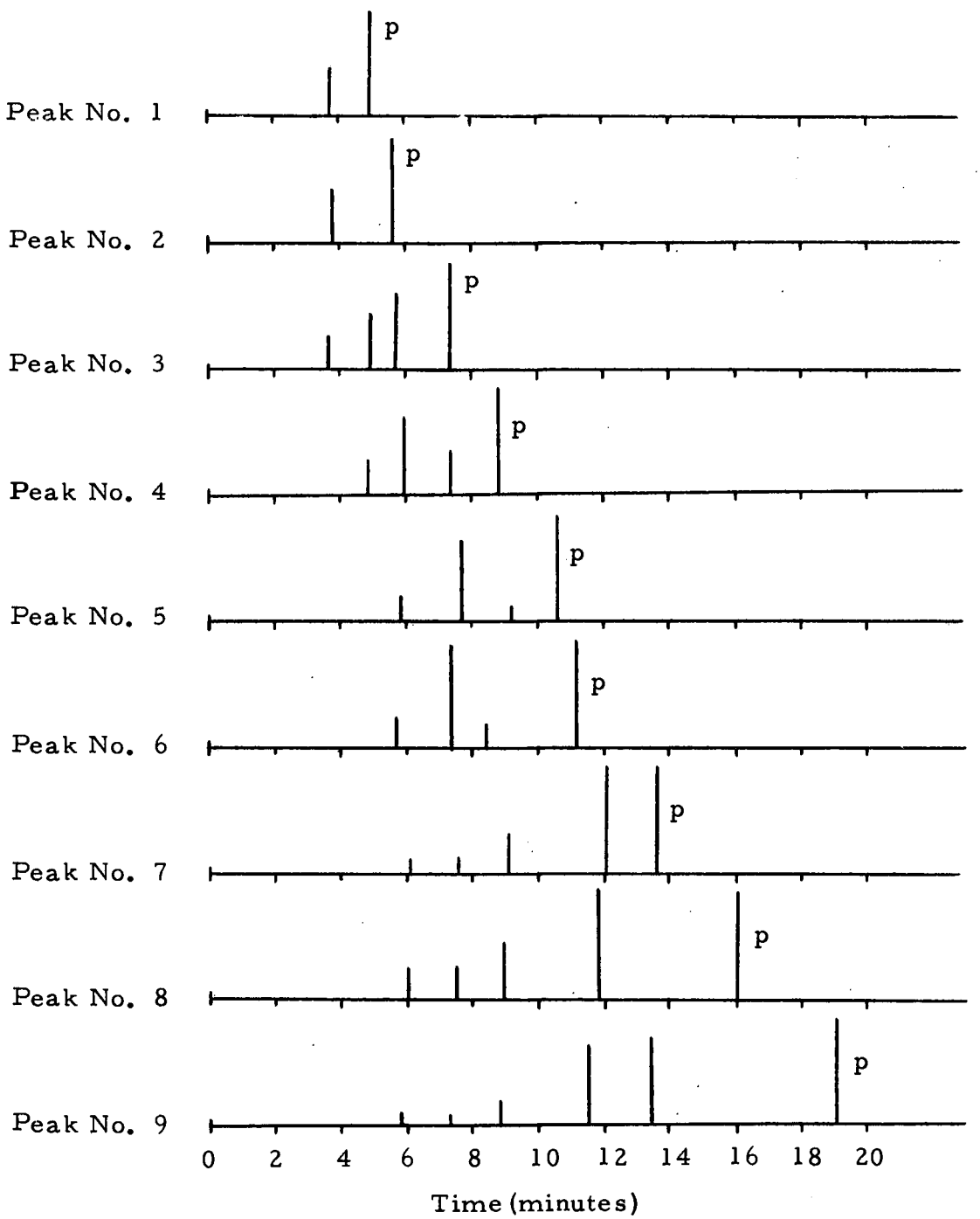


Figure 10. Degradation patterns of peaks 1-9 of Aroclor 1254, as separated on column 1, and irradiated at optimum irradiation times. Presented as Degradation Peak Area/Parent Peak Area ratio vs. retention time. p = parent peak.

For instance, peak 9 breaks down into five peaks which are very similar in retention time to peaks 7, 6, 4, 3, and 2. From the mass spectral results it was shown that peaks 6, 7, and 9 all contained six chlorines/molecule. Dechlorination alone could not account for this transformation. It may be that dechlorination, recombination reactions occur resulting in a shift of the chlorine positions.

As stated above, the degradation peaks do not correspond exactly to the retention times of peaks in the original mixture. This might be expected since on column 1 the peaks have been shown to be combinations of molecules and not single compounds. Variations in the composition of the components of each peak may cause slight shifts in the retention time.

It was found that the actual peak areas of the degradation patterns were quite variable. This was probably due to the fact that it is difficult to trap the same amount and portion of each peak from one run to another. The ratio of the degradation peak area to the parent peak area was much more precise, being independent of the initial concentration. For this reason the DPA/PPA ratio is a much more useful parameter for comparing results from one day to another than peak area.

The same relationship was found to be true for retention time. While the absolute retention time would vary from one run to

another, the relative retention time of the degradation peaks (relative to the parent peak) was constant. The relative retention time is felt to be a much better means of expressing the degradation pattern than absolute retention time.

Trapping Efficiency

The trapping efficiencies determined for the nine major peaks of the Aroclor 1254 mixture are shown in Table 10. The values ranged from 61% to 78%. While these values are somewhat lower than those obtained for certain pesticides (Kaufman, 1971) they are certainly good enough to allow qualitative analysis. In a situation where not enough sample could be trapped at one time, multiple trappings could be made.

Table 10. Trapping Efficiency.

Peak # [a]	Trapping Efficiency
1	67
2	64
3	68
4	76
5	78
6	77
7	64
8	75
9	61

(a) Column 1

Analysis in the Presence of Interfering Insecticides

The results of irradiating the individual PCB peaks plus the interfering insecticides are shown in Figure 11. In each bar chart the parent peak is labeled with a P, the PCB degradation peaks with an (a) and the insecticide degradation peaks with a (b). The DPA/PPA ratio is for the individual PCB component or pesticide before they were mixed. It was demonstrated that the patterns were unaffected when the substances were irradiated together.

The optimum irradiation times and degradation patterns for the pesticides used were reported by Kaufman (1971). In most cases the optimum irradiation times differ for the PCB components and the insecticides so an intermediate time was picked to show the presence of both substances in a mixture.

As can be seen in Figure 13, there was good separation of the degradation peaks for all four pesticides and PCBs studied. This technique, then, is a useful method for identifying PCBs in the presence of these four insecticides. If the degradation peaks did happen to overlap, it would still be possible to demonstrate the presence of an interfering compound by comparing the DPA/PPA ratio to those of PCB standards. This approach, however, would not be as unambiguous as when there are clearly separated degradation peaks.

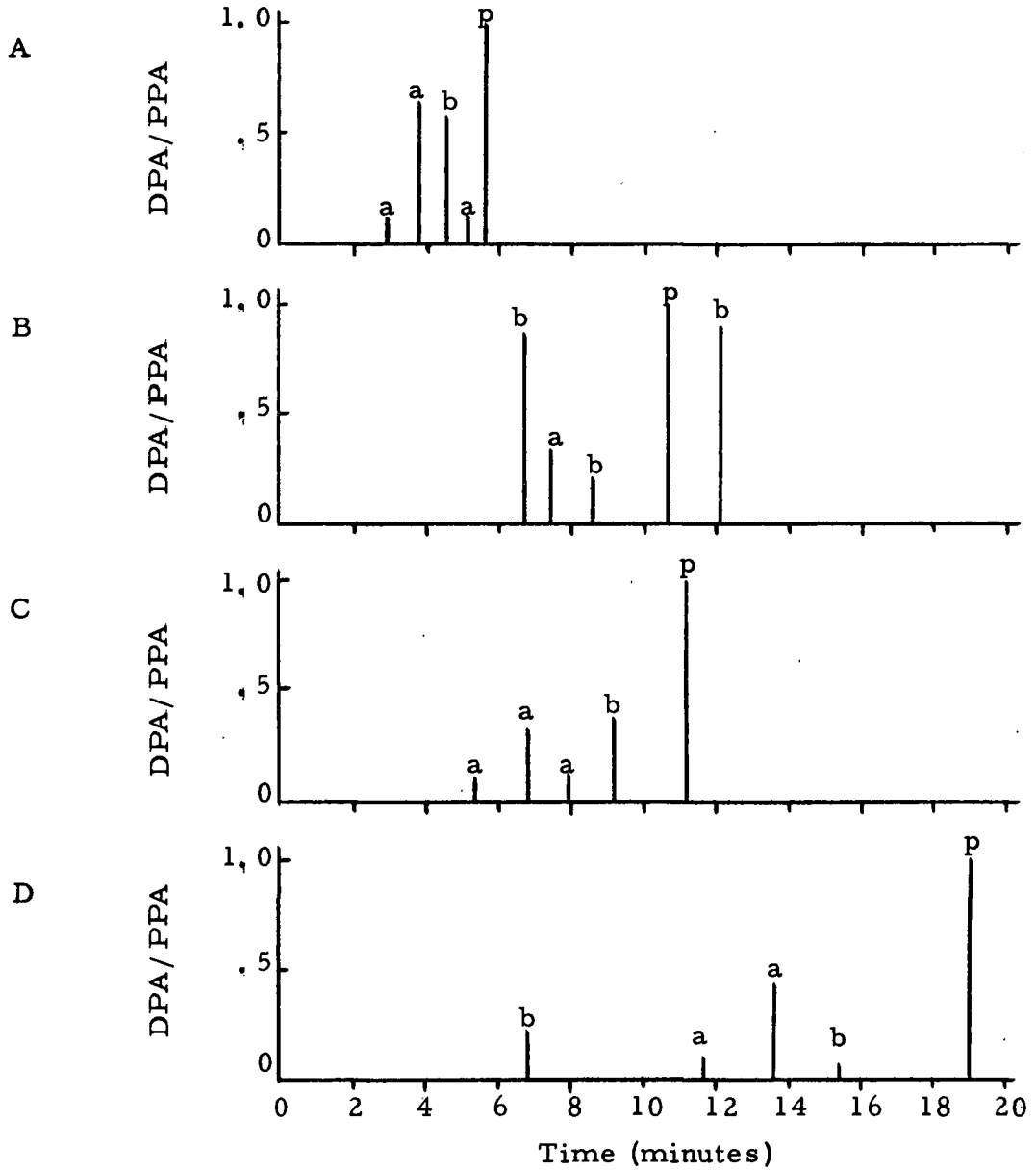


Figure 11. Degradation patterns for individual Aroclor 1254 peaks plus insecticides. A, peak 2 plus aldrin, irradiated 75 seconds; B, peak 5 plus p, p'-DDE, irradiated 25 seconds; C, peak 6 plus dieldrin, irradiated 50 seconds; D, peak 9 plus p, p'-DDT, irradiated 30 seconds. p= parent peak, a= PCB degradation peak, b= insecticide degradation peak.

Analysis of Herring and Salmon Oils

Both the herring oil and salmon oil samples gave chromatograms containing peaks which corresponded in retention times to peaks in the Aroclor 1254 standard. The ratio of the peak areas was not the same as the standard, however. When these compounds were trapped and irradiated, they gave degradation patterns similar to those of the standard. In some cases the DPA/PPA ratios were not the same as the standard, but this might be expected if preferential metabolism or degradation of the PCBs had occurred in the biological samples.

The presence of p, p'-DDE in both samples was also demonstrated by its degradation pattern. The DDE was combined with two PCB peaks under one peak on the sample chromatograms, but by trapping both halves of the peak separately the presence of both PCBs as well as the pesticide was shown.

The use of a pre-fractionation procedure such as chromatography on Florisil as employed in this study is beneficial in that it simplifies the original chromatogram. However, it has been shown that it is not necessary to remove interfering pesticides in order to get confirmation of the presence of PCBs. The analysis of these two samples demonstrates the utility of this technique for the qualitative analysis of PCBs.

SUMMARY AND CONCLUSIONS

A commercial mixture of polychlorinated biphenyls, Aroclor 1254, was separated into 13 components using GLC-EC and a packed column similar to those reported by most workers. The same mixture, however, was separated into 71 components using GLC-FID and a .02 inch by 300 foot capillary column. Combined GLC-MS was used to confirm the presence of mono- through hexachlorobiphenyls. When the mixture was exposed to laboratory uv light, it was found that the GLC-EC peaks disappeared with time.

The compounds represented by single gas chromatographic peaks obtained using the 2% SE-30 and 2% QF-1 packed column were trapped in Teflon tubes, irradiated with the laboratory uv light, and reinjected into the gas chromatograph. The resulting gas chromatograms showed decreases in the original peak area along with the appearance of peaks with shorter retention times than the parent peak. These "fingerprint" degradation patterns were specific and reproducible for each component of the original mixture. The degradation patterns were unaffected by the presence of certain organochlorine insecticides.

Compounds isolated from herring and salmon oil samples were identified as PCBs by this method. The presence of p, p'-DDE was also observed.

As a result of this study the following conclusions were reached.

1. Gas chromatographic peaks of Aroclor 1254 separated on the packed columns reported by most workers do not represent single compounds but may be composed of as many as 11 compounds.

2. PCBs are degraded by uv light, and the solvent has a major effect on the rate of decomposition.

3. The individual gas chromatographic components yield unique and reproducible uv degradation patterns.

4. Dechlorination and rearrangement reactions appear to be responsible for the appearance of the degradation compounds.

5. The use of gas-liquid chromatography and uv degradation is a practical technique for the identification of PCBs in organochlorine residue extracts.

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