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Richard M. Pagni, Major Professor

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THE PHOTOCHEMISTRY OF PCB's

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Theresa Ann Moore

June 1985

ACKNOWLEDGMENTS

In the course of this research, Professor Richard M. Pagni was of great assistance. I am indebted to him for his patience and never-failing guidance. Professor Gary S. Sayler was generous in providing support and the use of laboratory equipment, including HPLC and GC.

I am also grateful to Lan T. Evans for her contribution to this study by performing several experiments utilizing clay. Thanks also to Professor George W. Kabalka for his aid.

ABSTRACT

Polychlorinated biphenyls (PCBs), which were once so widely utilized, have been detected in worldwide environmental samples. Their stability makes them persistent pollutants.

The purpose of this work was to determine the chemical fate of this class of compounds in water, rather than in a cosolvent mixture. The study began simply—observing monochlorinated biphenyls in distilled water under anaerobic conditions. One variable was added at a time in order to understand only its effects instead of trying to unravel the workings of several simultaneously. The reactions were followed under various conditions, alone or in conjunction with others, some of which are as follows: in the absence or presence of oxygen, in distilled water and in lake water, and with or without the addition of clays.

When monochlorinated biphenyls were irradiated in water, phenylphenols were formed in addition to other unidentifiable reaction products. Surprisingly, biphenyl was not a photoproduct. Both meta- and para-phenylphenol were produced photochemically by 4-chlorobiphenyl. The presence of oxygen reduced the reaction rates considerably. Finally, all monochlorinated biphenyls did not react at the same rate.

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CHAPTER I

INTRODUCTION

Manufacture and Use of PCBs

The identification of polychlorinated biphenyls (PCBs) in worldwide environmental samples (e.g., air, water, sediment, wildlife samples, human blood, adipose tissue and breast milk)[1] coupled with toxicity data[2] led to the ban of their production. Yet, since some 750,000 tons have been produced and have either entered the environment, are in landfills or are still in service,[3] it is of great value to know the fate of these compounds. Do they break down in the environment, remain unchanged or possibly convert to even more harmful products?

Commercially produced PCBs, available since 1929, are mixtures of isomers blended to match specification in chlorine content and quality.[3] These PCB mixtures have found widespread applications due to their general stability and inertness, as well as their excellent dielectric properties.[2] The uses include dielectric fluid in capacitors and transformers, industrial fluids in hydraulic systems, gas turbines, and vacuum pumps, fire retardants, heat transfer applications, plasticizers in adhesives, textiles, surface coatings, sealants, printing and copy paper.[2,3]

Chlorinated biphenyls, used alone or in blends with other materials such as trichlorobenzene, met the need for a fire-resistant dielectric fluid with a high resistivity, a high dielectric strength, a

relatively high dielectric constant, and a very low power factor.[4] By replacing hydrocarbon oil with chlorinated biphenyls, it was possible to redesign equipment with a great reduction in size for the same capacity and voltage. At the same time, fire hazards were eliminated.

In paints and varnishes, the hard resinous chlorinated biphenyls were used to impart increased hardness to the films and the softer resins were used to give flexibility. Chlorinated biphenyls were used as lubricants under extreme conditions such as highly oxidizing conditions, high temperatures, extreme pressures or submerged locations.[4]

Fire-retarding paints contained chlorinated biphenyl plus antimony oxide or barium sulfate. Fireproof fiberboard was made by adding emulsified chlorinated biphenyl to the fiber stock.[4]

Chlorinated biphenyls were ingredients in sealing compounds for wood or canvas to give protection against moisture, mildew or attacks of organisms. Carbonless reproducing paper was made by an encapsulation procedure using chlorinated biphenyl as part of the formulation.[4]

Entry of PCBs into the environment has been through the following routes:[3]

1. Completely dispersive losses—all materials used in paints, inks, adhesives, cutting oils, etc., must be assumed to have been lost via widely scattered sources, either directly to the waterways, or indirectly from land disposal.

2. Material used for hydraulic and heat transfer fluids and small capacitors and transformers will have been discharged to the environment as under (1) but from a smaller number of sources.

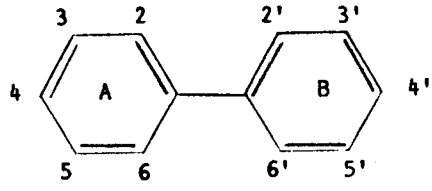
3. Losses from manufacture of PCB and from transformer filling and emptying operations will have entered waterways in the immediate vicinity of these plants, with some being lost to the atmosphere.

Approximately 40-50% of the PCBs produced in the United States was used for capacitors, 15% as transformer oils and 10-15% as heat transfer fluids. Plasticizers accounted for 5% of the use while carbonless copying paper made up 15%. Between 5 and 10% was exported.

4. The bulk of the material used for transformers and capacitors will either still be in service or have been disposed of in large batches, often still in the equipment, on landfill sites.

Of the total cumulative PCB use from domestic sources (Monsanto Chemical was the principal manufacturer under the tradename Aroclor) through 1975, it has been estimated that 38% represents mono-, di-, and trichlorobiphenyl; 23% consists of tetrachlorobiphenyl, while the remaining 39% represents penta- through decachlorobiphenyl.[5]

The biphenyl ring system is numbered as shown:



With ten sites which may contain chlorine, the number of theoretical chlorobiphenyl isomers soars to 209. These may be distributed as shown in Table 1.[2]

In the manufacturing process, the formation of some isomers is unlikely. For example, it is unlikely that one ring would be

Table 1

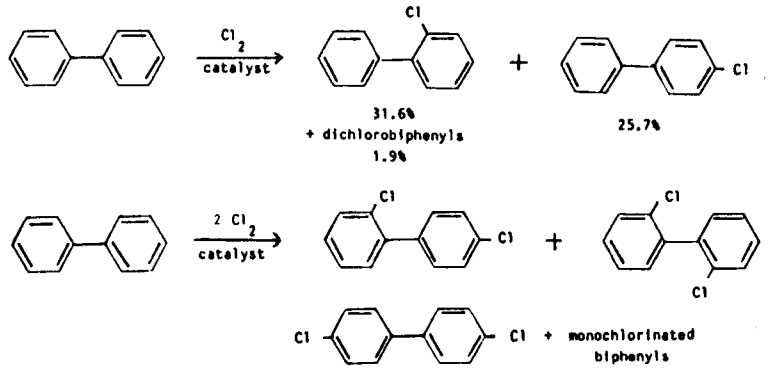
Number of Theoretical Isomers

		Chlorine atoms on Ring A					
		0	1	2	3	4	5
	0	1	3	6	6	3	1
Chlorine	1		6	18	18	9	3
atoms	2			21	36	18	6
on	3				21	18	6
Ring B	4					6	3
	5						1

fully chlorinated while the other possess no chlorine atoms, i.e., 2,3,4,5,6-pentachlorobiphenyl would probably not be formed. One would more readily find a similar number of chlorine atoms on each ring, preferentially in the ortho and para positions.

The most common substitution patterns for chlorobiphenyls are shown in Figure 1.[2]

Polychlorinated biphenyls are produced commercially by the direct anhydrous chlorination of biphenyl, using iron fillings or ferric chloride as a catalyst.[3,4,6,7]



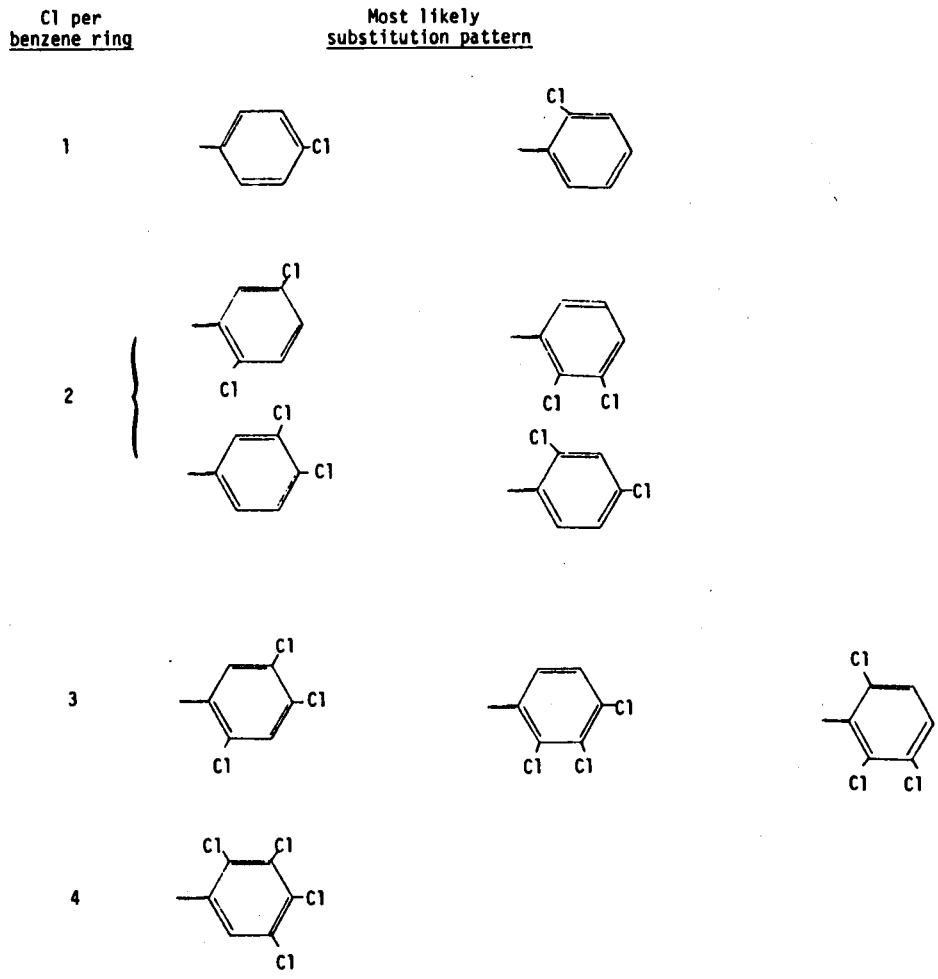


Figure 1. Common Chlorobiphenyl Substitution Patterns.

For industrial purposes, the chlorinators may be cylindrical steel towers, 3 ft. in diameter and 18 ft. high, which are equipped with chlorine distributors at the bottom and with coils for heating and cooling the material undergoing reaction. Pumps provide agitation by circulating the liquid. The lower half of the chlorinators is filled with iron turnings, which have been burned free of oil and moisture. In Germany, the chlorinators are typically agitated 10,000 liter lead-lined

vessels, and ferric chloride is used as a catalyst instead of iron. Fifteen kg. of ferric chloride is used for 6000 kg. of biphenyl. Throughout the chlorination, the temperature is kept well above the melting point of the mixture, and below 150°C, to avoid excessive sublimation and plugging of the line discharging the hydrogen chloride produced by chlorination. Samples are withdrawn for examination from time to time until the desired chlorine content has been reached. The time required for chlorination is 12 to 36 hours, depending upon the chlorine content of the product. Isomers likely to be formed in the manufacturing process are those that have either an equal number of chlorine atoms on both rings or a difference of only one chlorine atom between rings.[5]

Further purification of the crude products is usually necessary to remove the color and traces of hydrogen chloride and ferric chloride.[5] The purification method which is chosen is dependent upon the type of end product. The high melting solid products are distilled in gas-fired retorts at atmospheric pressure. The distillate is flaked on chilled rolls. The liquid and resinous products are distilled at lower temperatures in conventional distillation equipment under reduced pressure. The crude liquid and resinous products are held at an elevated temperature and blown with dry air for several hours, after which a few tenths of 1% of lime or sodium hydroxide is stirred with the material to react with any remaining hydrogen chloride or ferric chloride. This is followed by batch distillation under reduced pressure.

If increased electrical resistance is needed, the material is stirred at an elevated temperature with a few tenths of 1% of well-dried fuller's earth and then filtered.[5]

The stability which was so beneficial in the manufacture of electrically stable and fire-resistant fluids, for example, is the same property which makes PCBs so undesirable in their relationship to the environment. This stability leads to accumulation in fatty tissues, low environmental mobility and resistance to degradation, especially biodegradation.

Degradation Experiments

These compounds are known to accumulate in the environment, particularly in aquatic ecosystems. PCBs' low chemical and metabolic reactivity make them persistent pollutants. They are hydrophobic and so have been observed in lipid phases such as the organic films sometimes found on the surface of natural waters.[8] The aqueous solubility of this class of compounds is said to be a valuable indicator of its environmental fate, such as its tendency to sorb or bioaccumulate.[9] Mackay et al. have compiled aqueous solubility data for PCBs and have developed a method for correlating the isomer solubility from melting point and total surface area data.[9] Their data, shown in Table 2, reiterate the extremely low solubility of these chlorinated biphenyls in water. This has led many researchers to study the photodegration of PCBs in medium other than pure water, such as alcohols or aqueous mixtures.

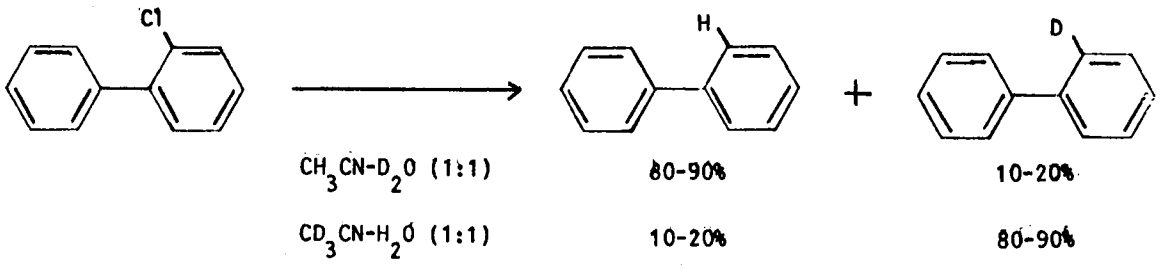
Table 2

Calculated Solubilities for Selected Isomers

Isomer	Calculated Solubility (mg/m^3)
Biphenyl	7455
2 CBP*	5760
3 CBP	6218
4 CBP	1870
22' CBP	1000
244' CBP	266
22' 44' CBP	115
22' 346 CBP	12.9
22' 33' 44' CBP	1.32
22' 33' 44' 55' CBP	0.101
Deca CBP	0.0004

*CBP represents chlorobiphenyl, e.g., 2 CBP represents 2-chlorobiphenyl.

Bunce[10] tested an acetonitrile-water mixture to determine whether or not it would be a good choice of a model for water, but one in which greater solubility could be obtained. It was already known that alcohols such as methanol and ethanol were probably not good models for water because C-H abstraction is greatly preferred over O-H abstraction. In this experiment, Bunce replaced the hydrogens in acetonitrile and then in water with deuteriums. Irradiation of 2-chlorobiphenyl in equimolar mixtures these solvents gave biphenyl and 2-deutero-biphenyl as photoproducts. He was able to show by mass spectrometry that 80 to 90% of the hydrogen abstracted was from acetonitrile. Only 10 to 20% originated from the water.



Bunce was, therefore, able to conclude that acetonitrile is definitely not an inert solvent in the photoreaction. Similar results can be assumed when cosolvents are used from which hydrogens are more easily abstracted than from water.

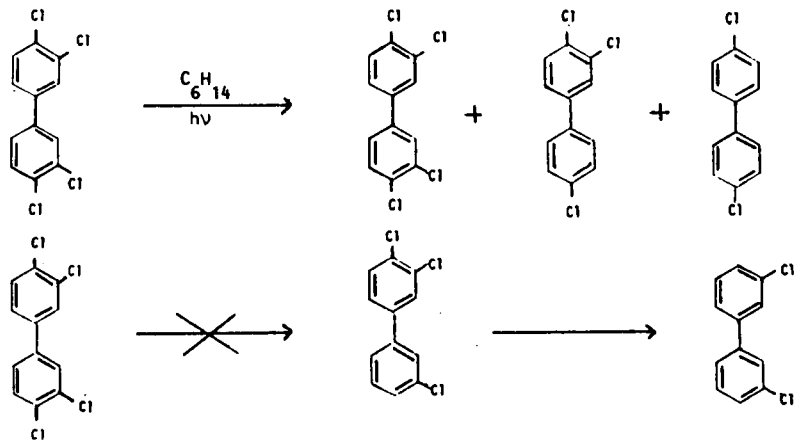
Herring, Hannan and Bills photolyzed a 200 ppm solution of Aroclor 1254 (Monsanto's brand-name for biphenyl chlorinated to 54%) in acetone and diluted 1:100 (2 ppm) with distilled water, hexane and benzene.[11] They found that PCBs degraded fastest in hexane, then water, and slowest in benzene. Over time some peaks increased in size, suggesting that the more highly chlorinated biphenyls were being dechlorinated to form PCBs of lower molecular weight. They also found that not all the PCBs degrade at the same rate. These researchers proposed two possible explanations for the effect of solvent on degradation rate:

1. Solvents which have shorter wavelengths and higher energy radiations are more effective in degradation than those with longer wavelengths and lower energy radiations. Therefore, water, which has a transmission limit of 190 nm, or hexane with a limit of 210 nm

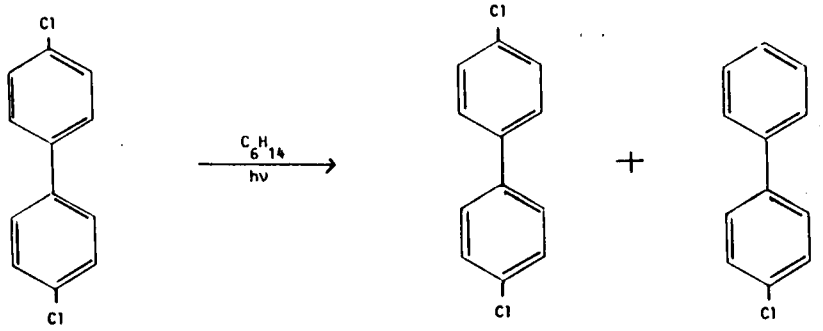
are more efficient solvents in this capacity than benzene with a transmission limit of 280 nm.

2. The solvent may have a participatory role such as hydrogen donation in degradation. Benzene would be expected to be a relatively poor hydrogen donor accounting for its slow rate. Hexane would be expected to be a better hydrogen donor explaining the faster degradation rate in this solvent. The authors reasoned that the faster degradation in hexane as compared to water is due to the relative insolubility of PCBs in water. In addition, the poor hydrogen-donating ability of water should also be considered.

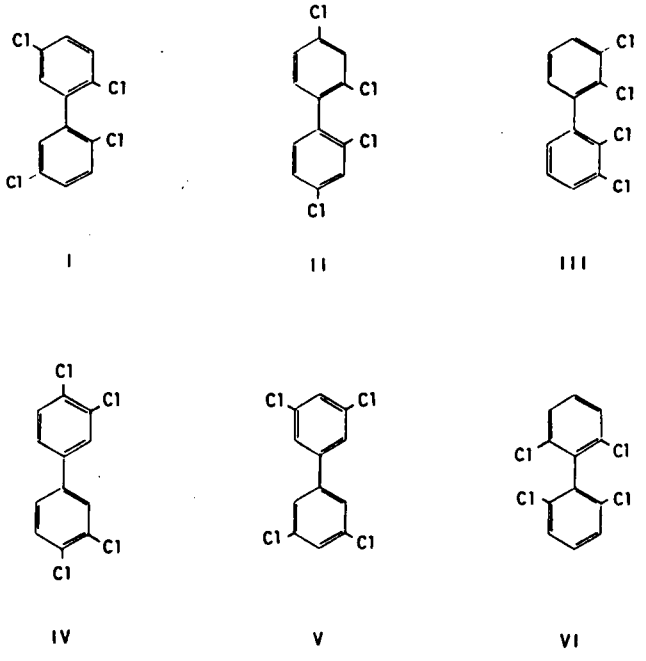
The work of Herring, Hannan and Bills described above indicates a stepwide dechlorination of chlorinated biphenyls. The work of Ruzo, Zabik and Schultz further substantiates this finding.[12] The latter photolyzed 3,,3',4,4'-tetrachlorobiphenyl in n-hexane and obtained the parent compound 3,4,3'4'-tetrachlorobiphenyl, 3,4,4'-trichlorobiphenyl, and 4,4'-dichlorobiphenyl. Since no 3,3'-dichlorobiphenyl was found, they felt that there was no 3,3',4-trichlorobiphenyl included in the trichlorobiphenyl product.



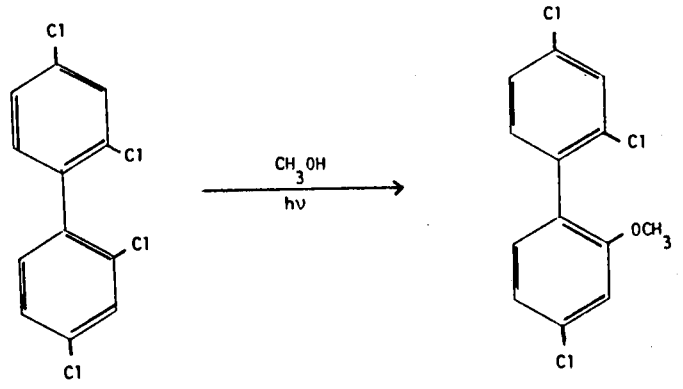
Similarly, when 4,4'-dichlorobiphenyl was photolyzed in n-hexane, the parent compound and 4-chlorobiphenyl were the only products obtained.



In a later study, Ruzo, Zabik and Schultz photolyzed tetrachlorobiphenyls in hexane or methanol.[13] The compounds chosen were 2,2', 5,5' (I) 2,2',4,4' (II), 2,2',3,3' (III), 3,3',4,4' (IV), 3,3',5,5' (V) and 2,2',6,6' tetrachlorobiphenyl (VI).



The primary photoproducts obtained in methanol solutions consisted of dechlorinated PCB; however, methanol substitution products were also observed. They found that methanol substitution took place at the same site from which a chlorine was lost. The methanol substitution product from 2,2',4,4'-tetrachlorobiphenyl photolysis was identified as 2,4,4'-trichloro-2'-methoxybiphenyl. Table 3[13] summarizes the photoproducts in hexane and in methanol.



When tetrachlorobiphenyls containing chlorines in the ortho position were irradiated, products arising from the loss of these chlorines were observed.

Those which contained only meta- and para-chlorines lost the meta-chlorines easier than the para- upon irradiation. The same behavior was observed in formation of the dichlorobiphenyls from the trichlorobiphenyls. Monochlorobiphenyls formed from dichlorobiphenyls were not observed except from compounds I and III. Even for these compounds, the formation accounted for less than 1% yield. The researchers explained the lack of monochlorinated biphenyl products to

Table 3

Photoproducts in Hexane and in Methanol

PCB	Irradiation Time, sec	Solvent	
		Hexane	Methanol
I	167	2,3',5-Trichlorobiphenyl	Trichloromethoxybiphenyl
	128	3,3'-Dichlorobiphenyl	Dichlorodimethoxybiphenyl[a]
		3-Chlorobiphenyl[a]	
II	190	2,4,4'-Trichlorobiphenyl	Trichloromethoxybiphenyl
	148	4,4'-Dichlorobiphenyl	Dichlorodimethoxybiphenyl[a]
		4-Chlorobiphenyl[a]	
III	182	2,3,3'-Trichlorobiphenyl	Trichloromethoxybiphenyl
	129	3,3'-Dichlorobiphenyl	Dichlorodimethoxybiphenyl[a]
IV[b]	192	3,4,4'-Trichlorobiphenyl	Trichloromethoxybiphenyl
	147	4,4'-Dichlorobiphenyl	
V	181	3,3',5-Trichlorobiphenyl[a]	
VI	158	2,2',6-Trichlorobiphenyl	Trichloromethoxybiphenyl[a]
	69	2,2'-Dichlorobiphenyl[a]	

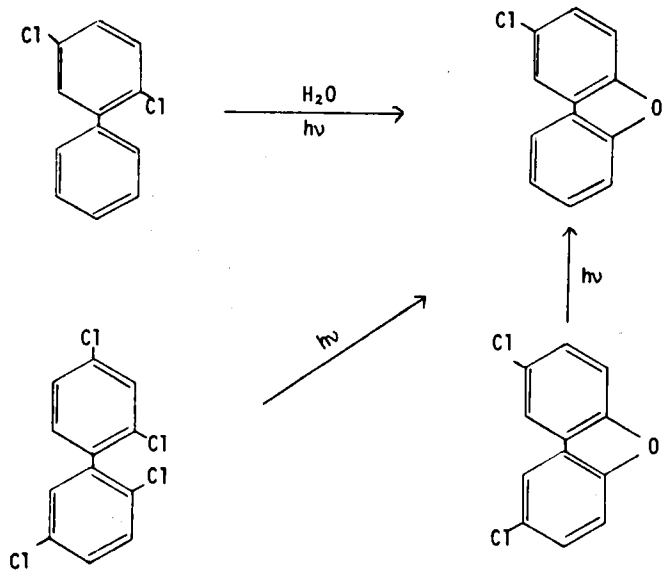
[a]Compound represented less than 1% of total product formation.

[b]3,3',4-Tetrachlorobiphenyl was observed in <2% after 50 hr irradiation.

be the result of insufficient absorption by the dichlorobiphenyls at the wavelengths used (286 nm, max 310 nm) or the result of decreased activity of meta- and para-chlorines relative to those at the ortho position.

When the above-described solutions were degassed prior to irradiation, the reaction rate showed a marked increase. Oxygen is known to act as a triplet quencher by accepting excess electronic energy from excited molecules before any chemical change occurs. An increase in reaction rate was also observed when methanol was used as solvent due to the fact that the increased solvent polarity lowers the energy of π-π^* transitions.

Traces of 2-chlorodibenzofuran were identified as photolysis products of 2,5-dichloro- and 2,2',5,5'-tetrachlorobiphenyl.[14] The irradiation of 2,8-dichlorodibenzofuran also resulted in a trace amount of 2-chlorodibenzofuran.



To determine the multiplicity of photoreactions, Morrison et al.[15] have used xenon which promotes the $S_1 \rightarrow T_1$ conversion. Molecules having a π,π^* S_1 state are particularly susceptible to heavy-atom enhancement, whereas n,π^* S_1 states appear to resist such enhancement.[16] Xenon has been used to determine Φ_{isc} (where Φ_{isc} represents the quantum yield for intersystem crossing) and to probe for the involvement of singlet and/or triplet states in photoproduct formation. The approach is to determine whether xenon quenches or enhances a photoreaction. The less chlorinated PCBs are believed to have relatively small Φ_{isc} and so their efficiency of photodecomposition should be enhanced in the presence of xenon if the triplet is reactive, but reduced if a reactive singlet is involved. PCBs having high Φ_{isc} should not be affected by the presence of xenon.

The results of a xenon assisted reaction for four chlorobiphenyls in isooctane are shown in Table 4.[17]

Table 4

Effect of Xenon on Photodecomposition of PCB

Chlorine Substituents on BP	Fluorescence intensity		Photon flux quanta (s^{-1})	Irradiation times (h)	% decomposed	
	No Xe	Xe			No Xe	Xe
4	28	25	5.0×10^{16}	11	26	37
2,4,6	17	16	1.2×10^{16}	0.167	43	47
2,2',4,4'	15	14	1.2×10^{16}	0.083	25	25
2,2',5,5'	30	29	5.0×10^{16}	0.50	16	18

Heavy atom quenching was first demonstrated using methyl iodide as quencher. Ampoules of PCB in isooctane with and without xenon were irradiated and the measurement of the fluorescence intensity was followed for each. The intersystem crossing yield may be obtained from an analysis of the decrease in fluoresence intensities.

Xenon and methyl iodide were more efficient at quenching the fluoresence of 4-chlorinated analogues. The photodegradation of 4-chlorobiphenyl was enhanced in the presence of xenon which is consistent with a triplet state photoreaction where xenon increases the stock of triplets by its effect on $S_1 \rightarrow T_1$ intersystem crossing. If 4-chlorobiphenyl had reacted from the higher energy singlet, the opposite would have been observed. The efficiencies of reaction of the other compounds studied were almost unaffected by xenon. This is expected when $S_1 \rightarrow T_1$ intersystem crossing is already efficient. Therefore, reaction occurs primarily from the triplet excited state.

Sediments

Suspended solids are present in the aquatic ecosystem of PCBs in various amounts and could have an effect on the rate of photodegradation or even on the mechanism itself. Suspended sediment may reduce the photolysis rate by either shielding the organic from the available light or by quenching the excited states of the organic molecules before they react to form products.[18] It is also possible for suspended particles to enhance the rate of organic photolysis if sediment absorption of light produces excited states or free radicals that can

react with the organic. Therefore, it is possible for organic materials that do not absorb sunlight to be degraded indirectly.

Indirect photolysis has been observed with semiconductors such as TiO_2, which are common constituents of clays, sediments and soils.[19] Oliver, Cosgrove and Carey studied the photodegradation of organics in water.[18] They compared the degradation rate of the compounds in TiO_2 (commonly found in natural sediments and clays in the 5-10% range), in commercially available clays (montmorillonite, kaolinite, bentonite, dolomite and illite), and in samples of suspended sediments collected from rivers flowing into the Great Lakes. All of the above absorbed light strongly in the ultraviolet spectral region. TiO_2 showed a sharp absorption cutoff at about 400 nm. The suspended clay and sediment continued to absorb a significant amount of light in the visible region of the spectrum as seen in Figure 2.[18]

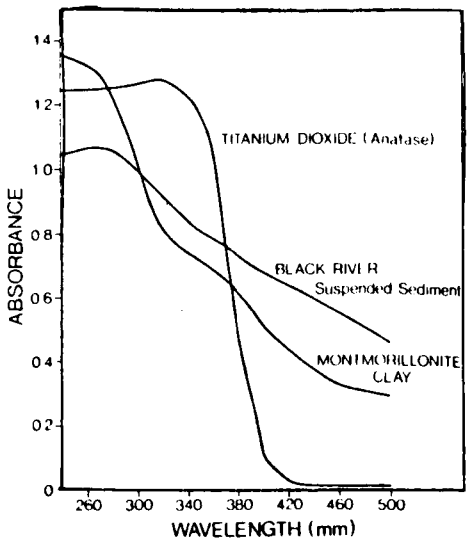


Figure 2. Ultraviolet-Visible Absorption Spectra of TiO_2.

The researchers chose to study p-dichlorobenzene (p-DCB) because it has an absorption maximum of 275 nm and does not absorb significantly at 300 nm, the wavelength of irradiation. When a saturated aqueous solution of p-DCB (47 ppm) was irradiated with 1% TiO_2, it degraded rapidly with a half-life of approximately five minutes. However, when 1% slurries of the clays (montmorillonite, kaolinite, bentonite, illite and dolomite) or the suspended river sediments (from the Ausable, Grand, Black and 40-Mile Rivers) replaced the TiO_2, no decomposition of the p-DCB was observed, even after irradiation of four hours. These researchers concluded that even though ultraviolet irradiation of TiO_2 can result in the photo-decomposition of non-light-absorbing organics in water, naturally occurring suspended sediments and clays do not appear to be capable of undergoing this type of photocalalytic reaction.

Carey, Lawrence and Tosine had previously done work on PCB/ TiO_2 photolysis.[20] Among the compounds they studied were the mono-chlorinated biphenyls. After irradiation on approximately 25 ppb aqueous solutions of 2-, 3-, and 4-chlorobiphenyls, they found no trace of 3- or 4-chlorobiphenyls but the 2-isomer was recovered quantitatively in the solution phase indicating no reaction. Although biphenyl is a primary product from photodechlorination of PCBs in hexane, the researchers detected no biphenyl in the irradiated system. They irradiated the TiO_2 system in the presence of biphenyl for 30 minutes and observed no reaction. These researchers conclude that it

is unlikely that biphenyl is a primary product in the PCB/TiO_2 photolysis.

Dennis[21] reported that PCB concentrations in natural waters rarely exceeded parts per billion. The concentrations in various waterways were as follows: 0.1 μg dm^{-3} for the St. Lawrence River, 0.2-2.9 μg dm^{-3} for the lower Mississippi River, 0.03 μg dm^{-3} for Lakes Erie and Ontario.[22]

Bunce, Kumar, and Brownlee[23] attempted to combine laboratory data for such factors as solar flux, absorbance of water, molar absorptivity of PCBs, and quantum yields of reactions to determine the fate of the PCBs in the waterways. They concluded that at environmental concentrations, such as those given above, a PCB mixture should behave photochemically as the sum of its components. For PCBs in natural waters, of the order of 10 to 100 g km^{-2} yr^{-1} could be decomposed. In shallow waters, such as Lake Erie, on the average of 5% of the lightly chlorinated PCB might lose a chlorine atom per year, but that at least one chlorine should be lost from every highly chlorinated molecule annually. Their predictions are based on experimental data using an acetonitrile-water system, which has already been shown to be a poor representative model for natural water.[10]

CHAPTER II

RESULTS AND DISCUSSION

Monochlorinated Biphenyls

Degradation Experiments

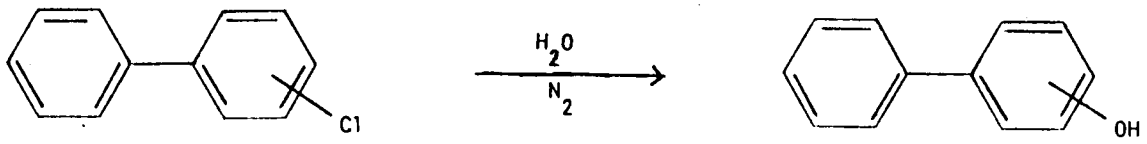
The behavior of PCBs in the aquatic ecosystem is very complex. Many variables come into play for one attempting to understand these reactions. A few of these are the complexity of the reactant, bacterial involvement in degradation, the presence of clays and sediments, the presence of organic matter dissolved in water, and the number of hours of sunlight to which it is exposed. In order to minimize the number of variables simultaneously affecting the reactions thus allowing simpler analysis of data, the project began by studying the photochemistry of a monochlorinated biphenyl in distilled water in the absence of oxygen. After this reaction was understood, one variable was to be added at a time until all were included and a natural environment was simulated in the laboratory.

The question of how monochlorobiphenyls changed over time was to be answered by following the disappearance of reactant and/or the appearance of products through high pressure liquid chromatography (HPLC) data. The identities of the products were to be determined by comparing the HPLC retention times of the photoproducts to those of known compounds.

In order to photolyze a monochlorinated biphenyl in an aqueous environment rather than in a cosolvent mixture, it was necessary to

get as much starting material into solution as possible. Typically, 4-Cl BP was added to water and stirred magnetically, deoxygenated if desired, and photolyzed. The photoproducts were then analyzed.

When a 2.65×10^{-5} M solution of 3-chlorobiphenyl (3-Cl BP) in distilled water was irradiated under nitrogen for three hours, 3-hydroxybiphenyl (3-OH BP) was the only photoproduct. Unreacted starting material was also observed.



When 3.18×10^{-5} M 2-chlorobiphenyl (2-Cl BP) was irradiated in the same fashion, a 1:1 ratio of 2-hydroxybiphenyl (2-OH BP) and 2-Cl BP was observed. Similar results were obtained from irradiation of 1.29×10^{-4} M 4-chlorobiphenyl (4-Cl BP). Biphenyl (BP) was not observed as a photoproduct of 2-Cl BP, 3-Cl BP, or 4-Cl BP under nitrogen.

Under the HPLC operating conditions, it was not possible to separate isomers with any reliability, e.g., 2-OH BP could not be distinguished from 3-OH BP or from 4-hydroxybiphenyl (4-OH BP); likewise, 2-Cl BP and 3-Cl BP could not be separated from 4-Cl BP. Therefore, it was assumed that 2-OH BP, for example, was formed from irradiation of 2-Cl BP and not one of the other isomers.

By removing aliquots from the reaction vessel periodically, it was possible to obtain a time profile of the photoreactions. A 3.12×10^{-5}

M 2-Cl BP solution was photolyzed during which time measured aliquots were removed every 10 minutes. The results of this and a similar experiment are compiled in Table 5. The retention times of 2.9 minutes, 5.8 minutes and 6.9 minutes correspond to 2-OH BP, BP, and 2-Cl BP, respectively. The increase in the area of 2-OH BP over time is observed alongside the expected decrease in 2-Cl BP area. The presence of BP in the initial aliquot (t = 0) could be the result of a thermal reaction. It is unlikely that BP was an impurity present in the starting material because it was not observed in other reactions. The BP area remained essentially constant but small over the course of the reaction and therefore appears not to be participating in the photoreactions. The observance of a peak with retention time of that corresponding to biphenyl is in contrast to the earlier experiments. The disappearance of 2-Cl BP starting material, as determined by the calculated area, as a function of photolysis time is shown in Figure 3. The reaction is fairly linear for this limited time period.

In the absence of nitrogen, i.e., in the presence of oxygen, a 5.30×10^{-3} M solution of 2-Cl BP was irradiated during which time aliquots were removed at 20-minute intervals. The results are shown in Table 6. The identity of the peaks observed at 7.3 minutes, 8.0 minutes and 9.3 minutes is unknown from comparison of retention times. The retention time of dibenzofuran, a possible product under aerobic conditions, was compared to those of the unknowns. The times did not correspond. The number of products formed in oxygen is greater than that formed in nitrogen. If the area data are considered

Table 5

Time Profile for 2-Cl BP Under Nitrogen

Time hν (min)	Average areas recorded at retention times		
	∿2.9 min[a]	∿5.8 min[b]	∿6.9 min[c]
0	–	9,916	145,895
10	37,512	8,330	127,845
20	62,358	9,811	121,747
40	5,191	3,500	109,500
60	12,951	7,335	94,005
80	30,581	8,289	84,772
100	48,639	8,431	60,054
120	51,366	11,988	39,959

[a]Corresponds to the retention time of 2-OH BP.

[b]Corresponds to the retention time of BP.

[c]Corresponds to the retention time of 2-Cl BP.

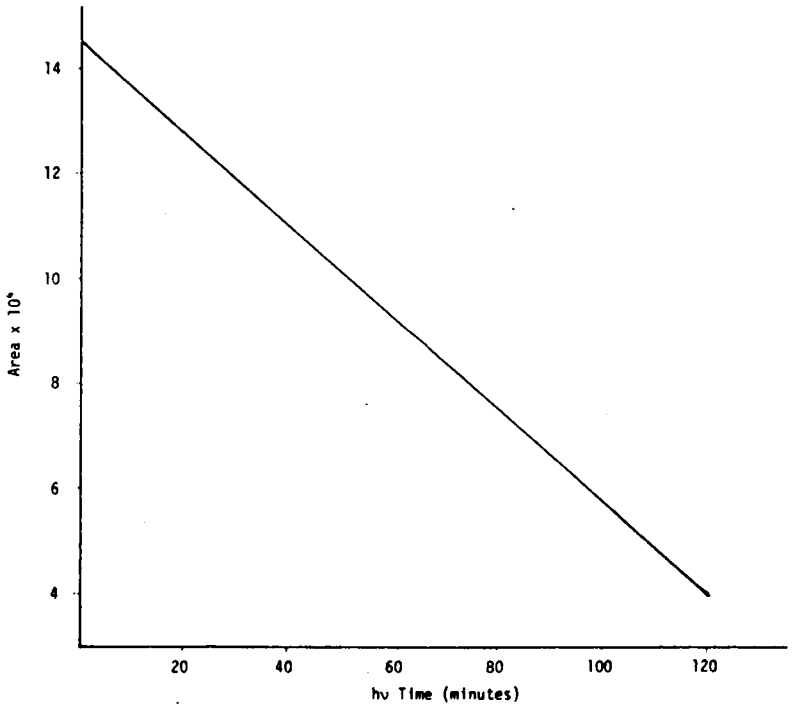


Figure 3. Disappearance of 2-Cl BP Under Nitrogen.

Table 6

Time Profile for 2-Cl BP Under Oxygen

Time hυ (min)	Areas recorded at retention times					
	∿2.9 min[a]	∿5.8 min[b]	∿6.9 min[c]	∿7.3 min[d]	∿8.0 min[d]	∿9.3 min[d]
0	–	–	84,847	–	–	–
20	–	21,145	70,247	35,363	57,539	43,573
40	–	16,542	90,222	81,006	68,953	144,640
60	–	7,316	64,102	–*	121,470	152,750
80	–	9,699	38,932	1,947	18,818	39,762
100	25,552	7,658	47,372	–	84,757	103,340
120	–*	3,608	32,524	–	4,764	35,034
140	16,735	3,480	22,999	–	22,780	38,731
160	11,680	4,833	24,072	–	20,920	44,282
180	–	4,390	28,222	–	33,057	27,059

*Numerical data was not obtainable in these cases, although peaks were visible on the graph.

[a]Corresponds to retention time of 2-OH BP.

[b]Corresponds to retention time of BP.

[c]Corresponds to retention time of 2-Cl BP.

[d]Peak identity unknown from retention times.

for general trends and not for precise figures, it is seen that the concentration of 2-Cl BP decreases over this time period. BP seems to be produced quickly but its concentration, too, dwindles over time indicating that it may play a part in secondary reactions possibly in the formation of the other products. The data indicates that 2-OH BP is not formed until quite late in the reaction. The same trends were noted when the experiment was repeated.

The disappearance of 2-Cl BP as a function of time is plotted in Figure 4. As in Figure 3, linearity is observed within the constraints of experimental error. The slopes of Figures 3 and 4 are not the same. In Figure 3, 877.55 units area are lost per minute while in Figure 4, 350.00 units area are lost per minute. The reaction of 2-Cl BP in distilled water in an oxygen environment is about 2.5 times slower than that in a nitrogen environment.

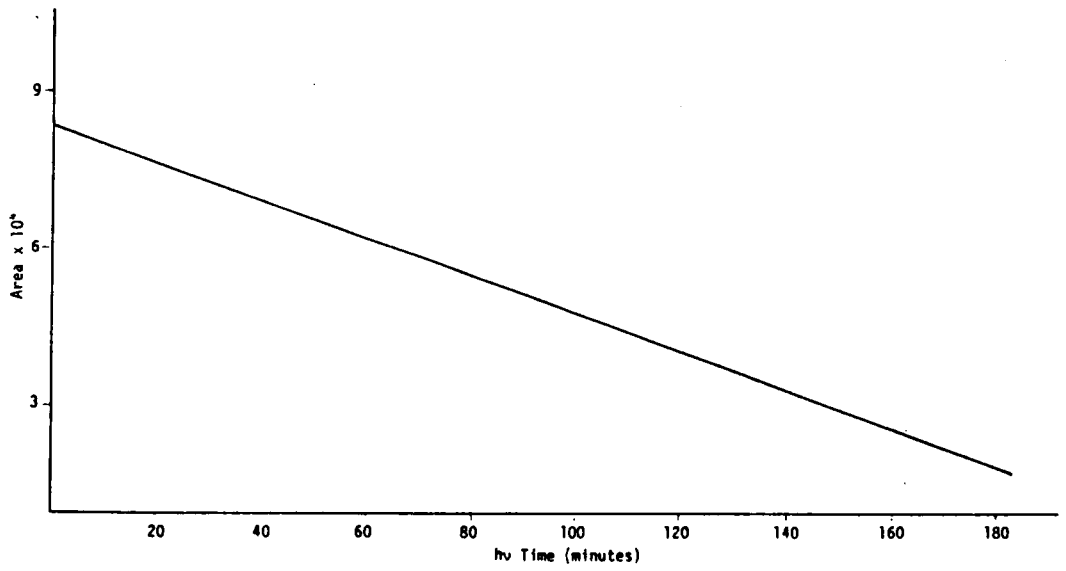


Figure 4. Disappearance of 2-Cl BP Under Oxygen.

In order to calculate concentration from area units, a standard concentration curve was prepared for 2-Cl BP. Standard concentration solutions of 2-Cl BP were made and analyzed. The results are shown in Table 7.

Table 7

Average Areas for Standardized 2-Cl BP Solutions

Concentration $\frac{\text{mg 2-Cl BP}}{\ell\ CH_3OH}$	Average area
23.0	2,933,000
11.5	1,596,800
5.8	728,170
2.9	402,700
1.4	236,550
0.0	–

These values are plotted in Figure 5. The result is linear with a calculated slope of 1.277×10^5 units area/mgl^{-1}.

By combining the slopes of Figures 3 and 5, it was found that per liter of distilled water under nitrogen an average of 6.87×10^{-3} mg of 2-Cl BP reacted each minute. In the same way, per liter of distilled water under oxygen, an average of 2.74×10^{-3} mg of 2-Cl BP reacted each minute, at least for the time period studied. The decomposition of 2-Cl BP proceeded approximately 2.5 times faster under nitrogen than under oxygen.

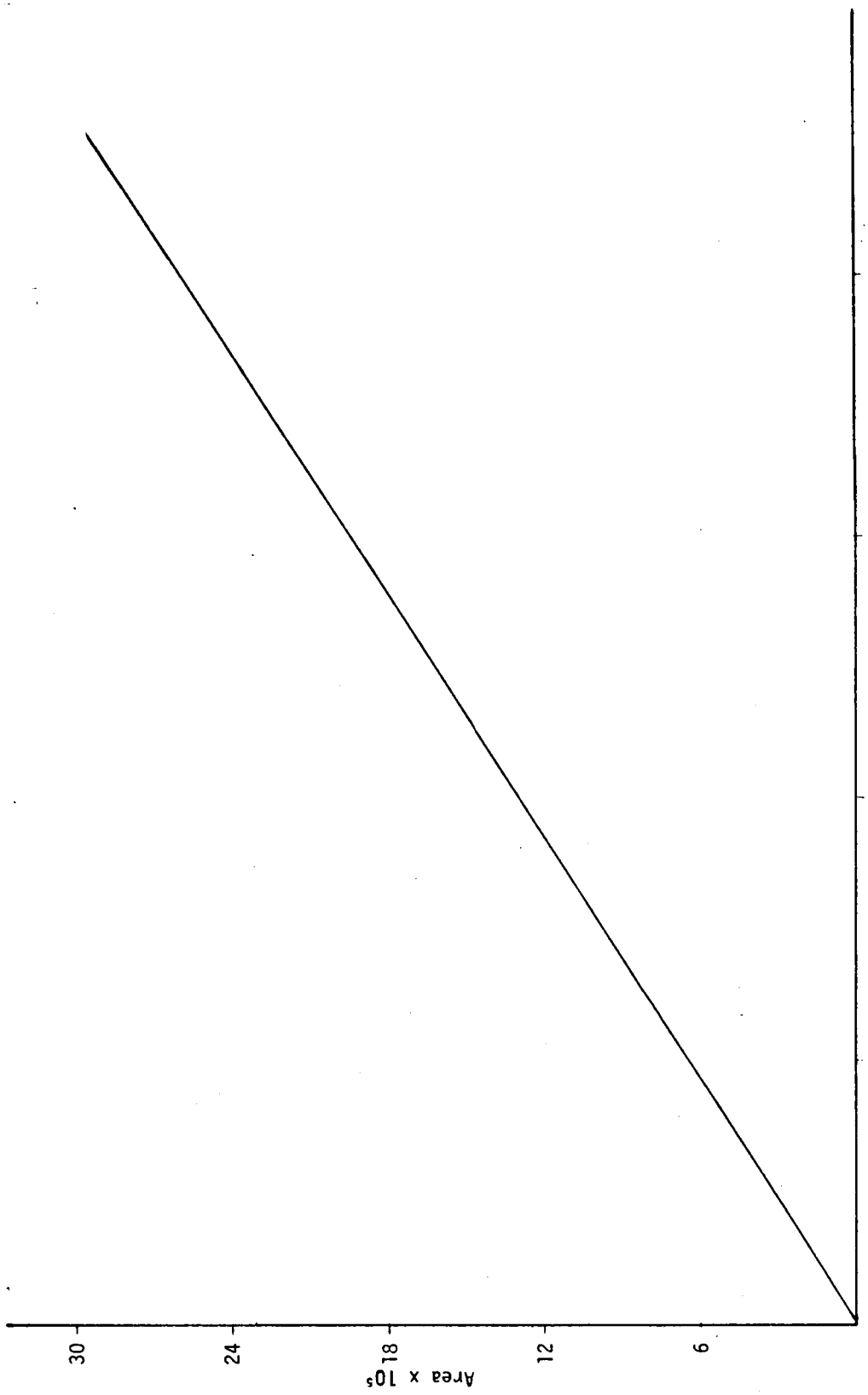
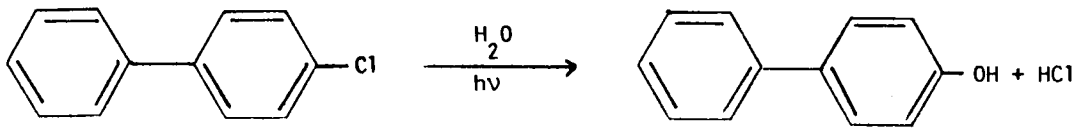


Figure 5. Average Areas vs. Standardized 2-Cl BP Concentrations.

pH Studies

Another method of studying these reactions as a function of time is through pH measurements. pH was chosen as the observed parameter because of the ease of duplicating natural buffer systems in the laboratory and the mobility afforded by the testing equipment in future field studies.

During the course of the photoreaction in water, HCl is produced along with the formation of phenylphenols. The increasing concentration of HCl, as observed by declining pH measurements, signals the parallel increase in concentration of phenylphenol and conversely the decrease in concentration of the chlorinated starting material.



The aqueous solution to be irradiated was circulated continuously between two chambers one of which was exposed to the lamp and the other of which contained the combination electrode and was not exposed to the light. The liquid circulated by means of a magnetic stirring bar. This apparatus design was necessary because if the electrode were positioned so that it was directly exposed to the lamp, erroneous readings resulted. These readings were not associated with a temperature change in the solution.

By monitoring pH change, it was possible to follow the photoreaction of 4-Cl BP in distilled water under nitrogen as a function of

time. Four reactions were performed under these conditions, labelled Reaction A, B, C, and D, and four reactions, labelled Reaction E, F, G, and H, were performed in the same manner with one exception—the solutions were not deoxygenated. The data and plots of pH as a function of time for these reactions are seen in Appendix A.

Figure 6 shows typical pH changes over time for a reaction in nitrogen, Reaction D, and for one in air, Reaction H. The final pH change for both reactions is the same, however, the reaction pathways are quite different. The oxygen or air pathway was much slower at the onset than the nitrogen reaction. This is consistent with the findings that for the decomposition of 2-Cl BP, which was followed for a shorter time period, the oxygen reaction proceeded much slower than the nitrogen. The presence of oxygen seems to act as a reaction quencher at least at the beginning of the reaction.

Similar reactions, in which the photoreaction of 4-Cl BP was monitored by following pH, were performed in lake water. Three reactions were run in lake water under nitrogen and were labelled Reaction I, J, and K. The data and time plots for these reactions are shown in Appendix A. To compare reactions of 4-Cl BP under nitrogen in lake water to those in distilled water, pH changes as a function of time were plotted in Figure 7.

Figure 7 shows that the presence of lake water slows down the ΔpH over time. The lake water in Reaction J appears to be buffered in comparison to the distilled water in Reaction B. This buffering phenomenon is most likely due to the presence of carbonates in the lake water, which are absent from the distilled water.

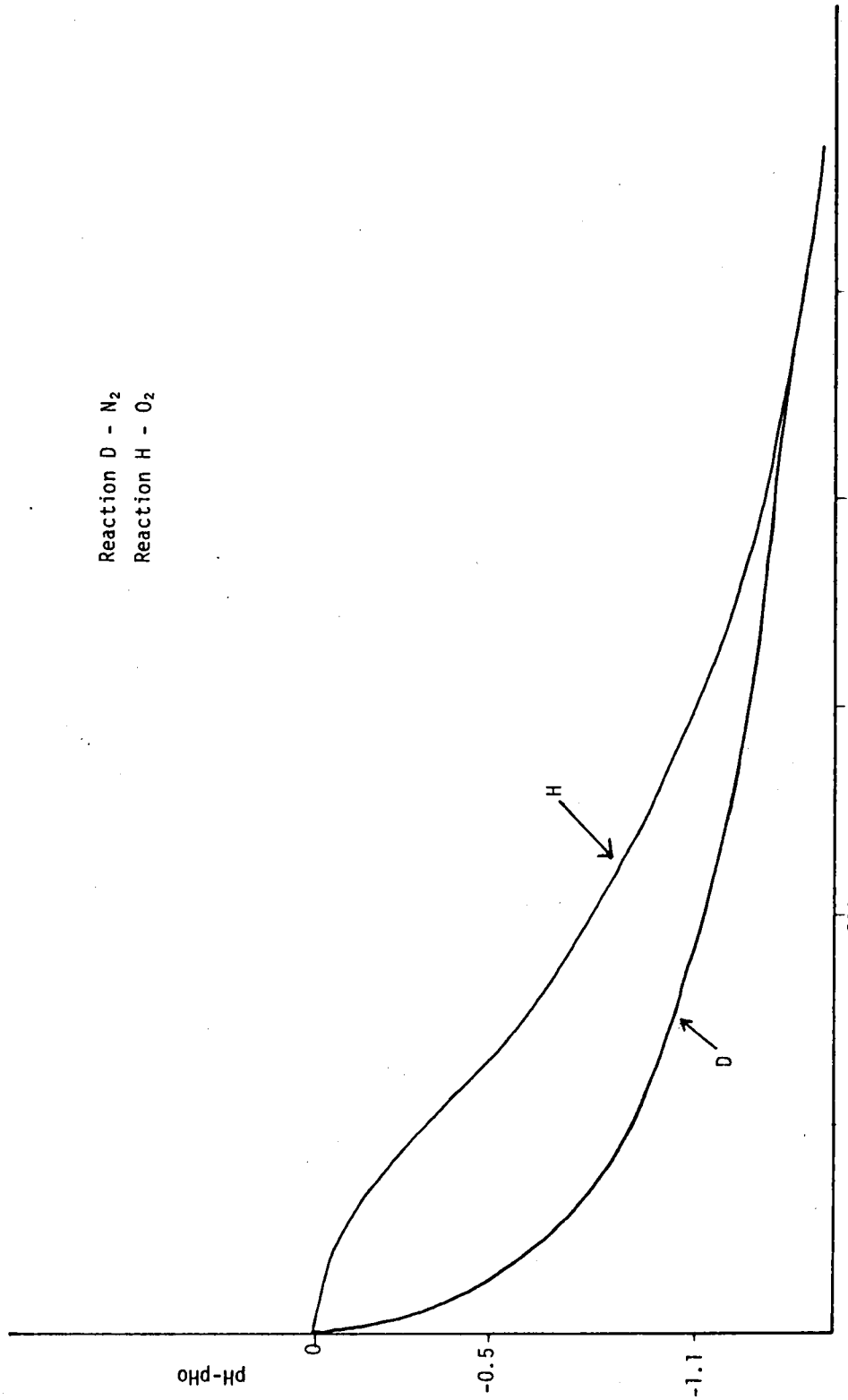


Figure 6. Reactions of 4-Cl BP in Distilled Water—Comparison of N_2 to O_2.

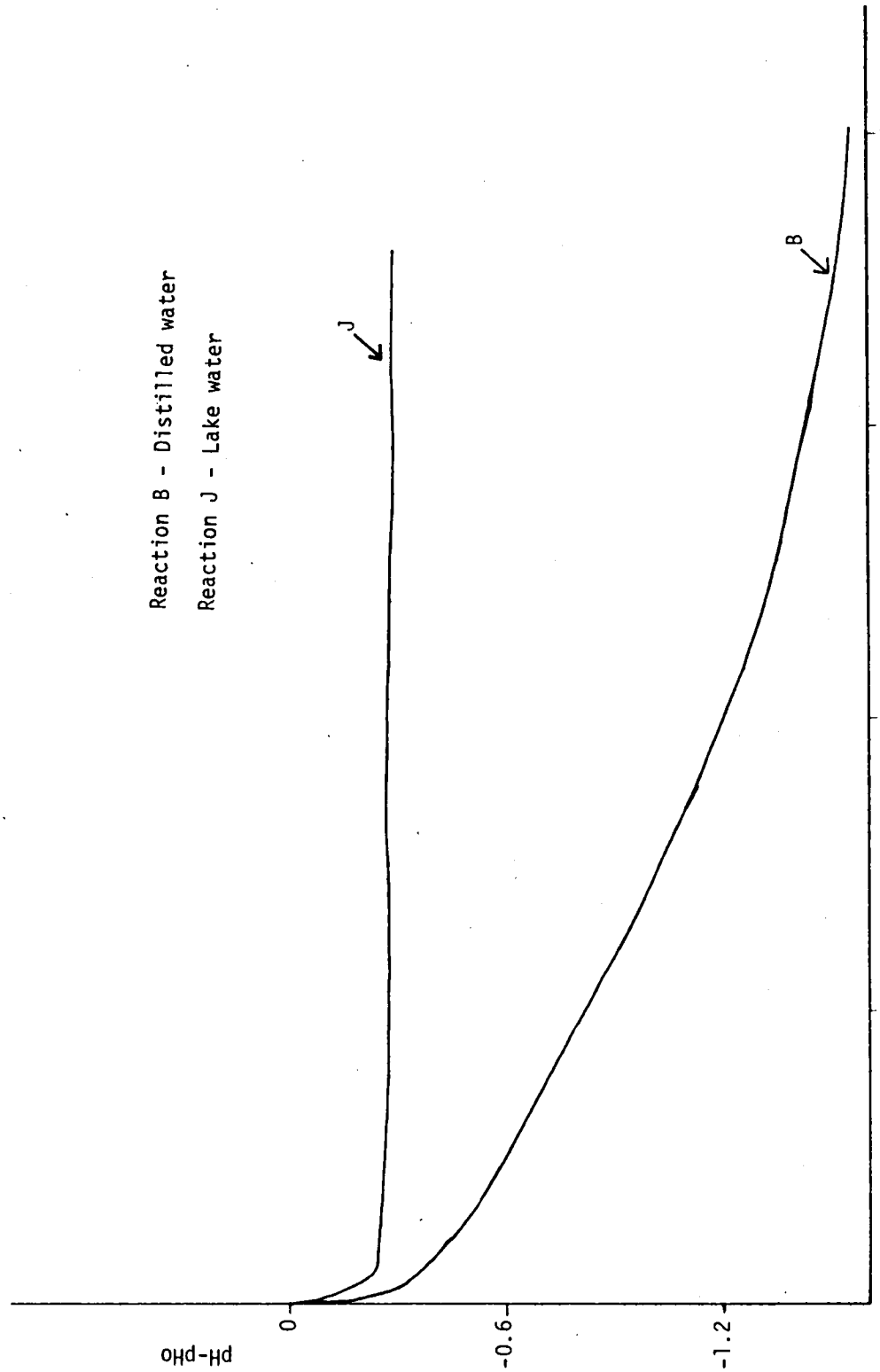


Figure 7. Reactions of 4-Cl BP under N_2—Comparison of Distilled to Lake Water.

Two reactions of 4-Cl BP in lake water in the presence of oxygen were monitored by pH. The data and plots as a function of time for these reactions, labelled reaction L, and M, are found in Appendix A (Tables A-12 and A-13, Figures A-12 and A-13). In Figure 8, ΔpH for the degradation of 4-Cl BP in lake water under nitrogen is plotted against the reaction under oxygen. Again, as seen with analogous reactions in distilled water, it is observed that oxygen slows down the reaction relative to nitrogen.

A comparison of photolysis of 4-Cl BP under oxygen in distilled water to that in lake water is depicted in Figure 9. The pH changes are relatively small over time for the distilled water but almost none at all for the lake water. Again the lake water appears to be acting as a buffer.

In an effort to understand the kinetics of these photoreactions and therefore the order of the reactions, the data were manipulated and plotted in the zero order rate equation for reactions A and C (see Appendix A, Figures A-14 and A-15)

$$kt = [H^+] - [H^+]_o$$

where: k = the rate constant,

t = the reaction time,

$[H^+]$ = the concentration of hydrogen ions at time t, and

$[H^+]_o$ = the concentration of hydrogen ions at the onset of the reaction when $t = 0$.

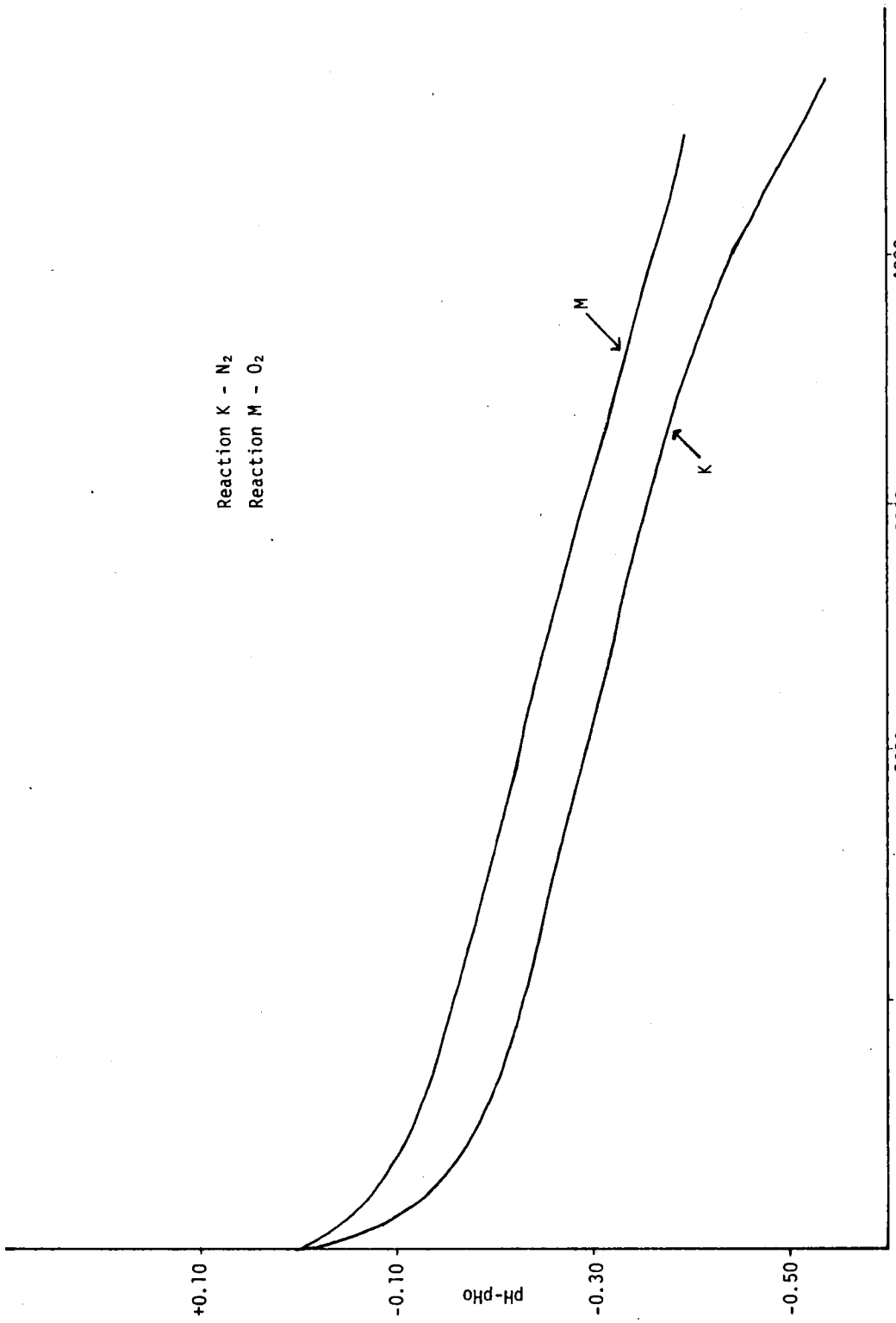


Figure 8. Reactions of 4-Cl BP in Lake Water—Comparison of N_2 to O_2.

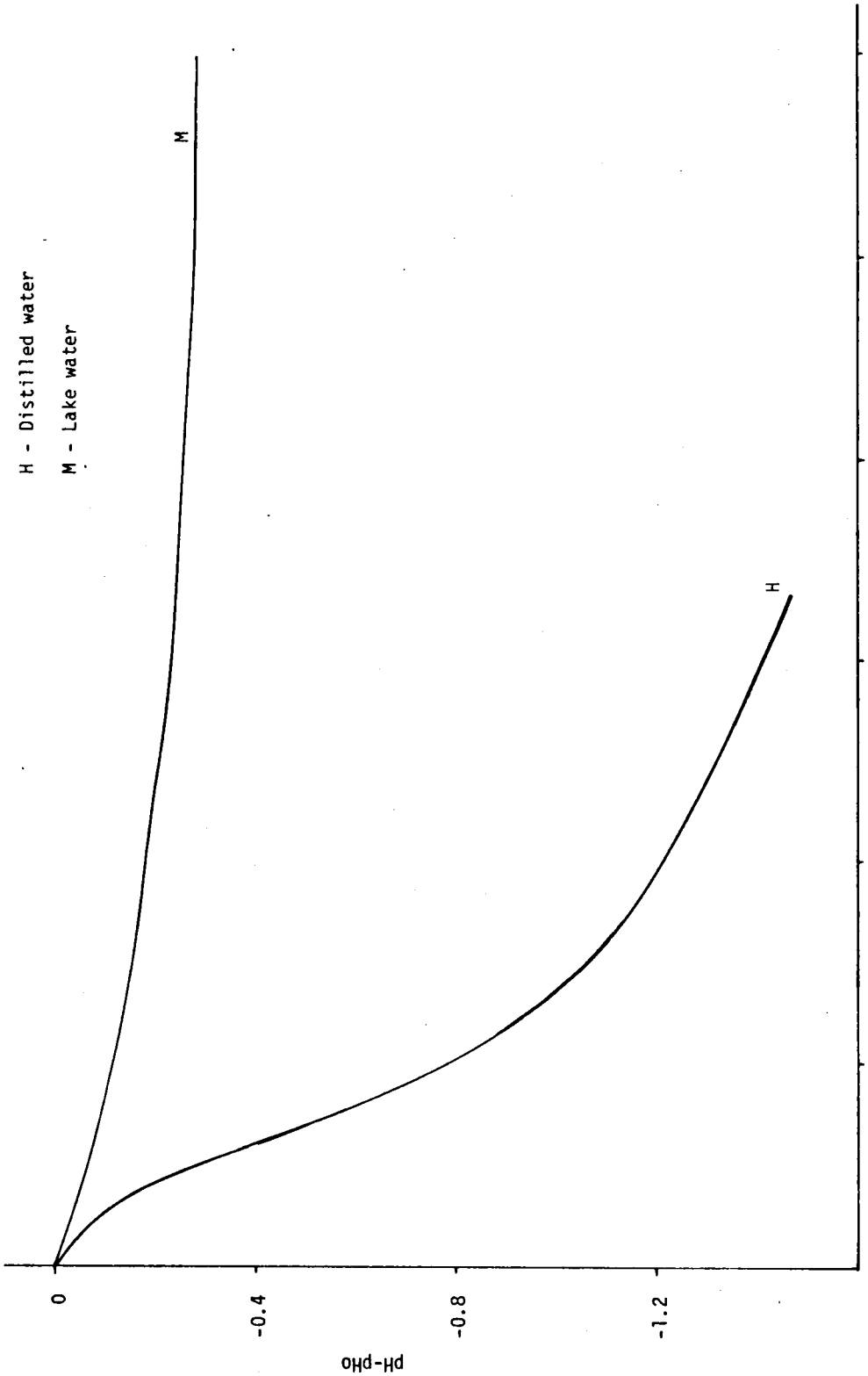


Figure 9. Reactions of 4-Cl BP Under O_2—Comparison of Distilled to Lake Water.

Data from reaction C was also plotted in the first order rate equation

$$kt = \ln \frac{[H^+]_o}{[H^+]}$$

and in the second order rate equation

$$kt = \frac{[H^+]_o - [H^+]}{[H^+]_o ([H^+])} .$$

See Appendix A (Figures A-16 and A-17) for plots. The desired linear plot was not obtained from the zero order, first order or second order rate equations. The reactions may have a fractional order of reaction or involve simultaneous or consecutive reactions in which the order of reaction is difficult to determine.

Scintillation Counting Technique

Because of the extremely low solubilities of PCBs in water, very low concentrations were involved in these experiments, making analysis by HPLC often difficult yielding inconclusive results. Therefore, it was felt that by using C-14 labelled PCBs instead of nonlabelled material, scintillation counting could be coupled with HPLC, adding accuracy and sensitivity to the experimental technique. The HPLC eluent was collected at 1-minute intervals and analyzed by liquid scintillation.

4-Cl BP was photolyzed under nitrogen and aliquots were removed at 18 hours, 87 hours, 90 hours and at the end of 150 hours. Results of averaged data appear in Table 8.

Table 8

Average CPM for Periodic Aliquots Under Nitrogen

HPLC Retention Time (min)	18 hours hυ CPM	87 hours hυ CPM	90 hours hυ CPM	150 hours hυ CPM
1	187	71	2,115	205
2	15,470	168,908	2,700	7,017
3	13,437	50,591	17,969	1,847
4	3,751	11,432	5,854	997
5	901	2,537	964	729
6	510	5,019	1,053	1,039
7	362	4,675	2,664	389
8	285	2,466	793	236
9	263	1,536	1,076	211
10	249	760	970	176
11	718	548	688	158
12	460	489	525	150
13	315	358	451	226
14	205	198	518	309
15	287	361	504	135
16	281	787	466	157
17	202	319	2,893	186
18	158	237	648	146
19	1,059	295	428	153
20	83,965	203	620	146
21	68,379	163	398	12,063
22	23,673	220	335	17,980
23	11,066	14,449	290	2,078
24	4,956	49,035	327	1,491
25	982	10,107	187	1,260
26	772	5,170	291	1,197
27	856	3,814	3,334	511
28	383	2,852	13,191	243
29	271	2,008	19,207	367
30	231	1,253	23,972	552

When HPLC retention times are plotted against counts per minute (CPM), the result is a graph which gives a picture similar to what would be obtained from a plot of absorbance vs. retention time. The 18-hour data are shown in Figure 10. While the vast majority of the 4-Cl BP had not reacted, a small amount of 4-OH BP was formed. At 87 hours, Figure 11, more of the starting material had reacted which is seen in the growth in size of the 4-OH BP peak. A peak around 16 minutes, which is approximately the retention time of BP, begins to be visible. The 90 hour graph, Figure 12, reveals larger peaks at approximately the same retention times as 4-OH BP and BP. At the end of 150 hours, Figure 13, a large portion of the starting material had still not reacted and the peak near BP had disappeared while the 4-OH BP peak was somewhat reduced in size. A peak appears to be forming at the tail end of the 4-CL BP peak but it is unclear whether this is actually another peak or whether it is the unresolved 4-Cl BP peak.

Four photolysis of the same kind were run for 96 hours. The data from these experiments performed under nitrogen were averaged and are compiled in Appendix B, Table B-1, and plotted in Figure 14. After 96 hours, no 4-Cl BP starting material is present. The peak at approximately 9 minutes corresponds to the retention time of 4-OH BP. The identity of the peak at 15 minutes is unknown. Its retention time does not match that of BP. This is consistent with the findings shown in Figure 12 at close to the same time.

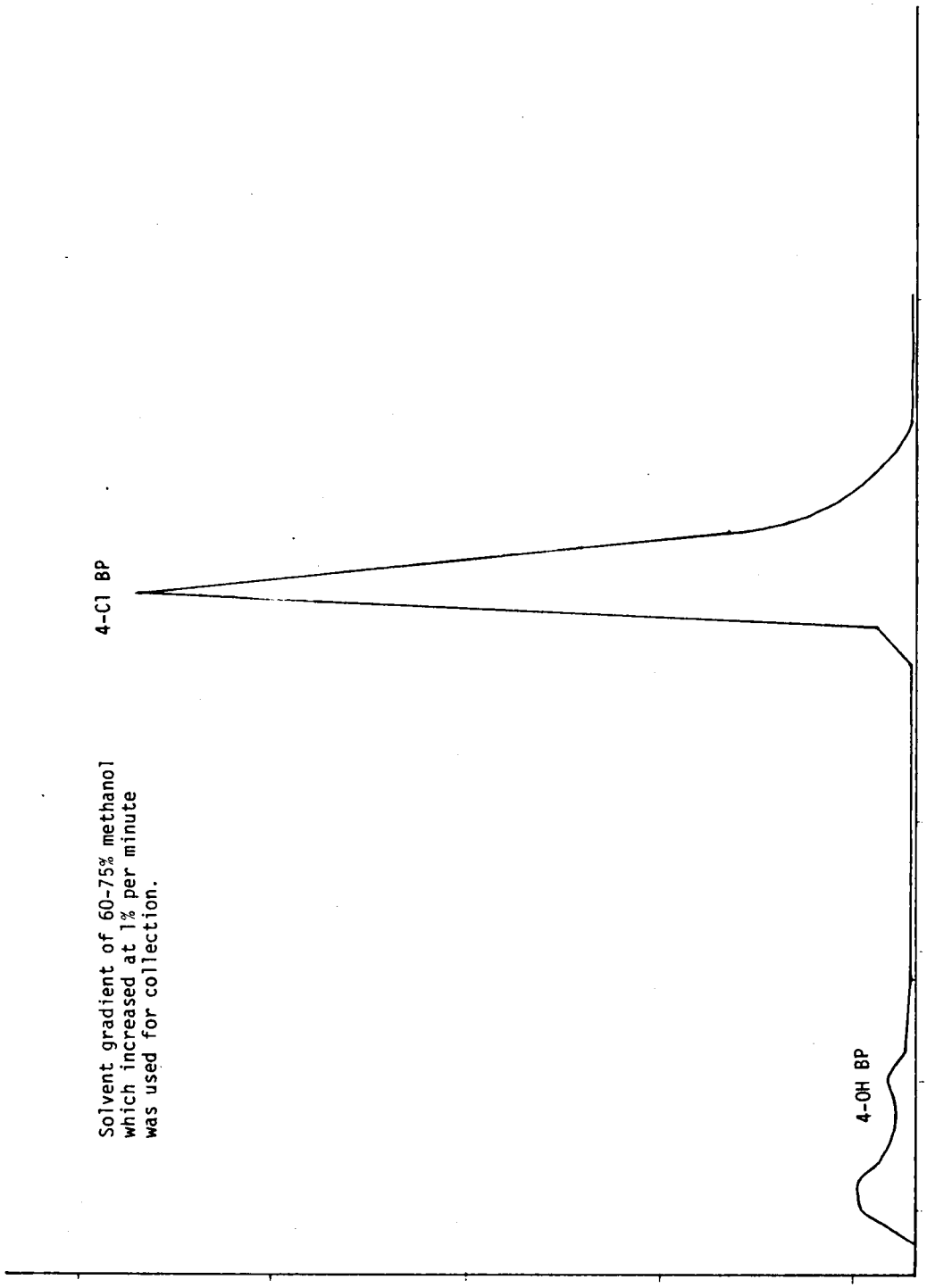


Figure 10. 18 Hours of 4-Cl BP Under N_2.

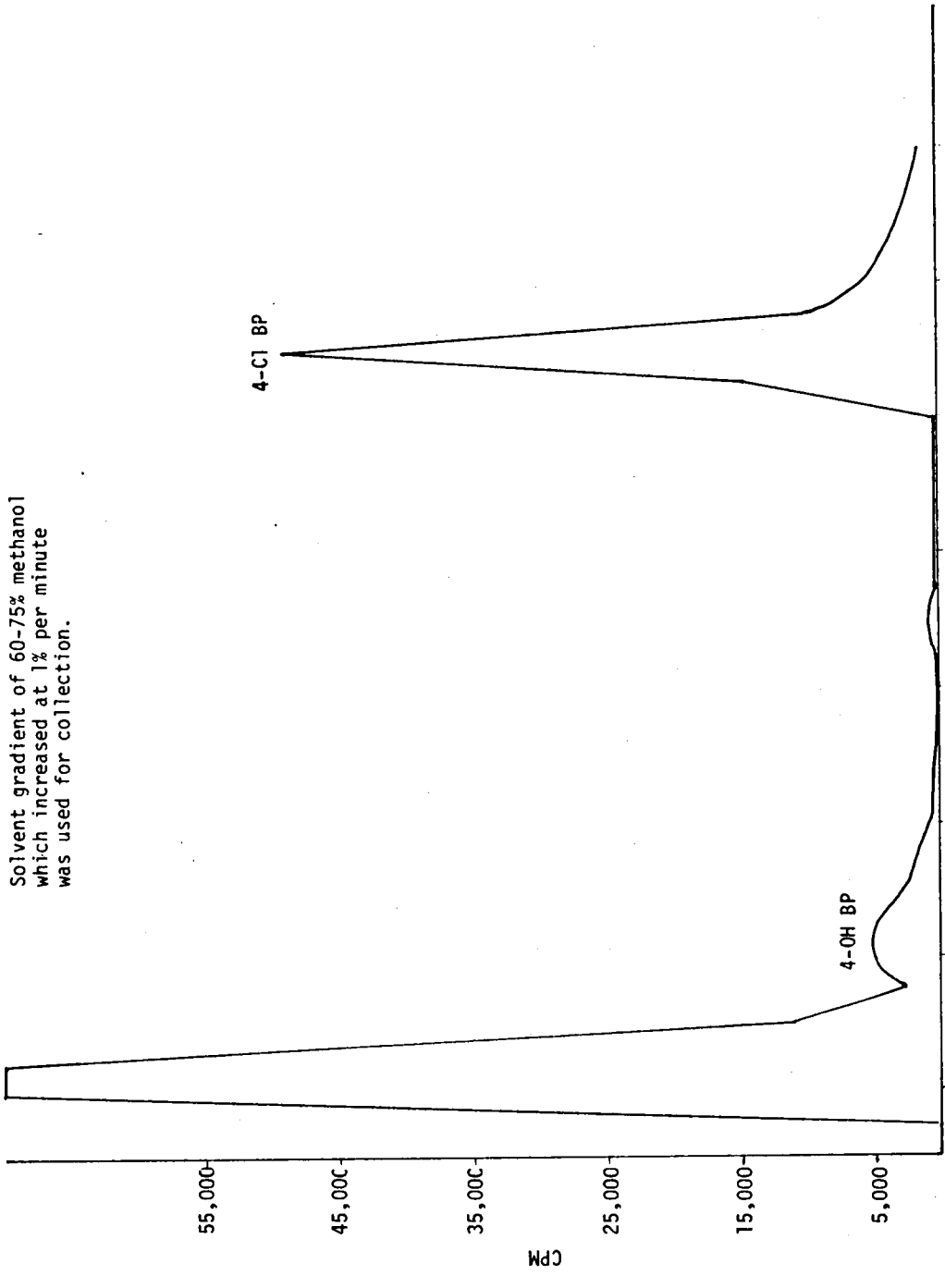


Figure 11. 87 Hours of 4-Cl BP Under N_2.

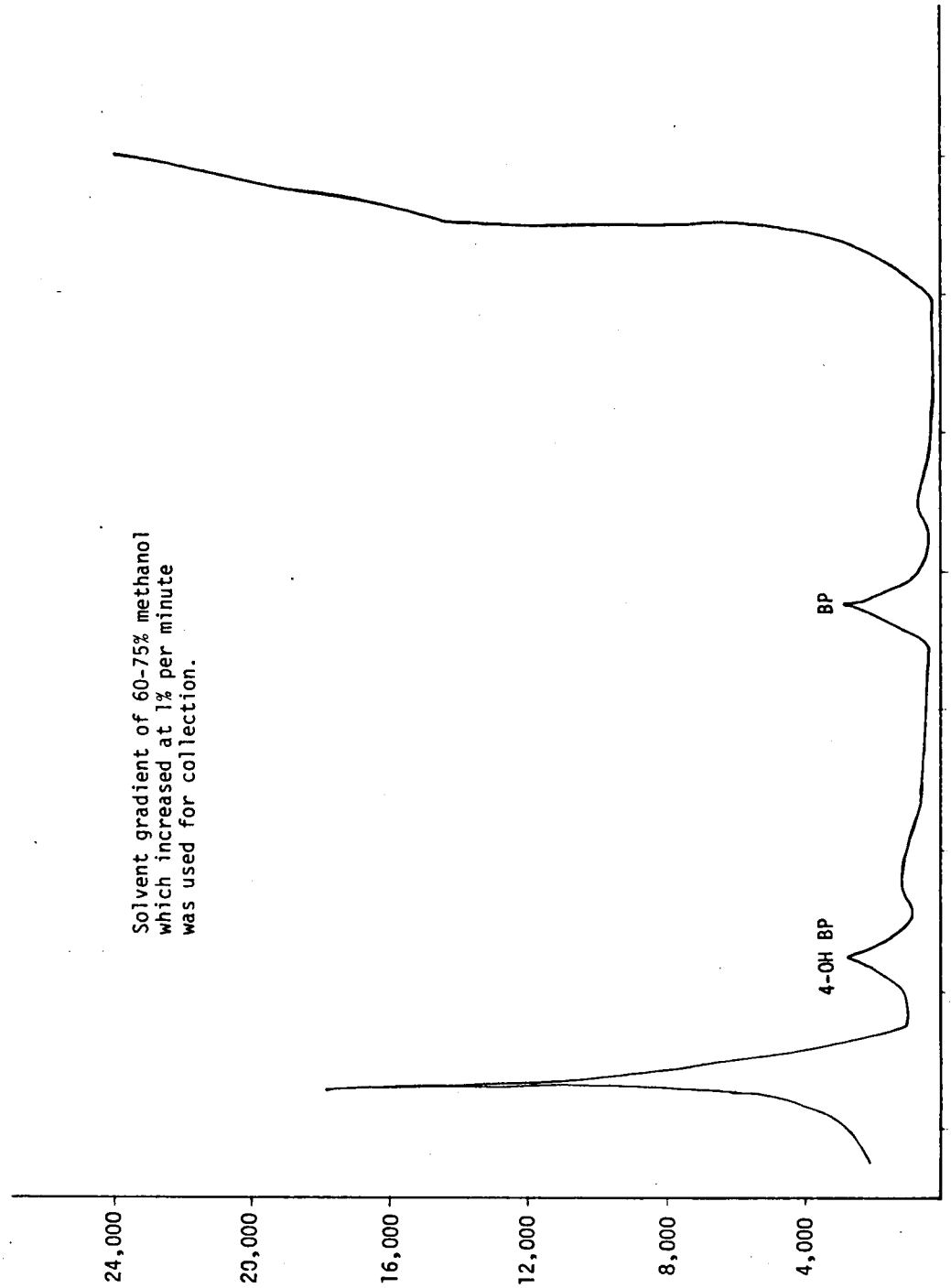


Figure 12. 90 Hours of 4-Cl BP Under N_2.

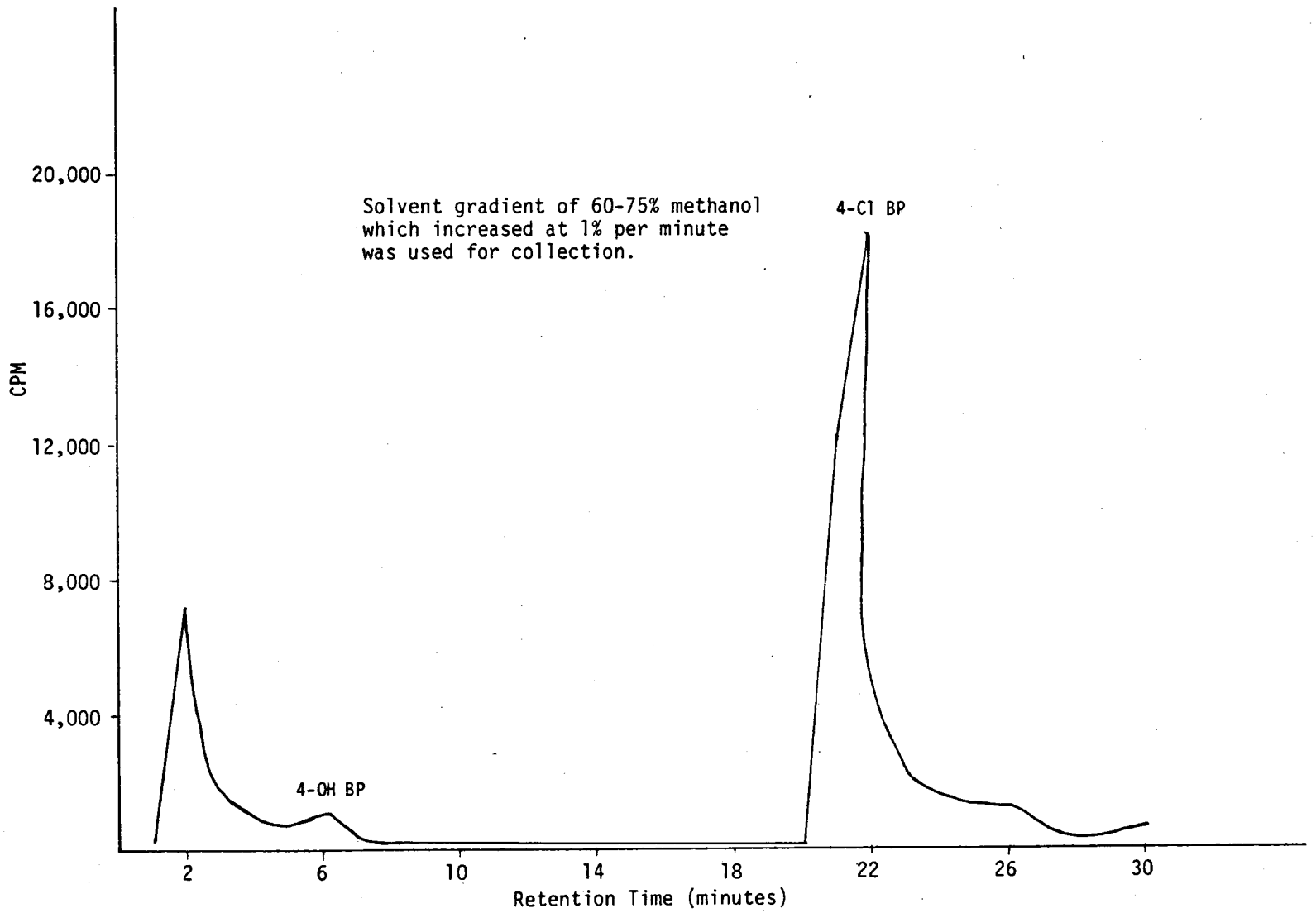


Figure 13. 150 Hours of 4-Cl BP Under N_2.

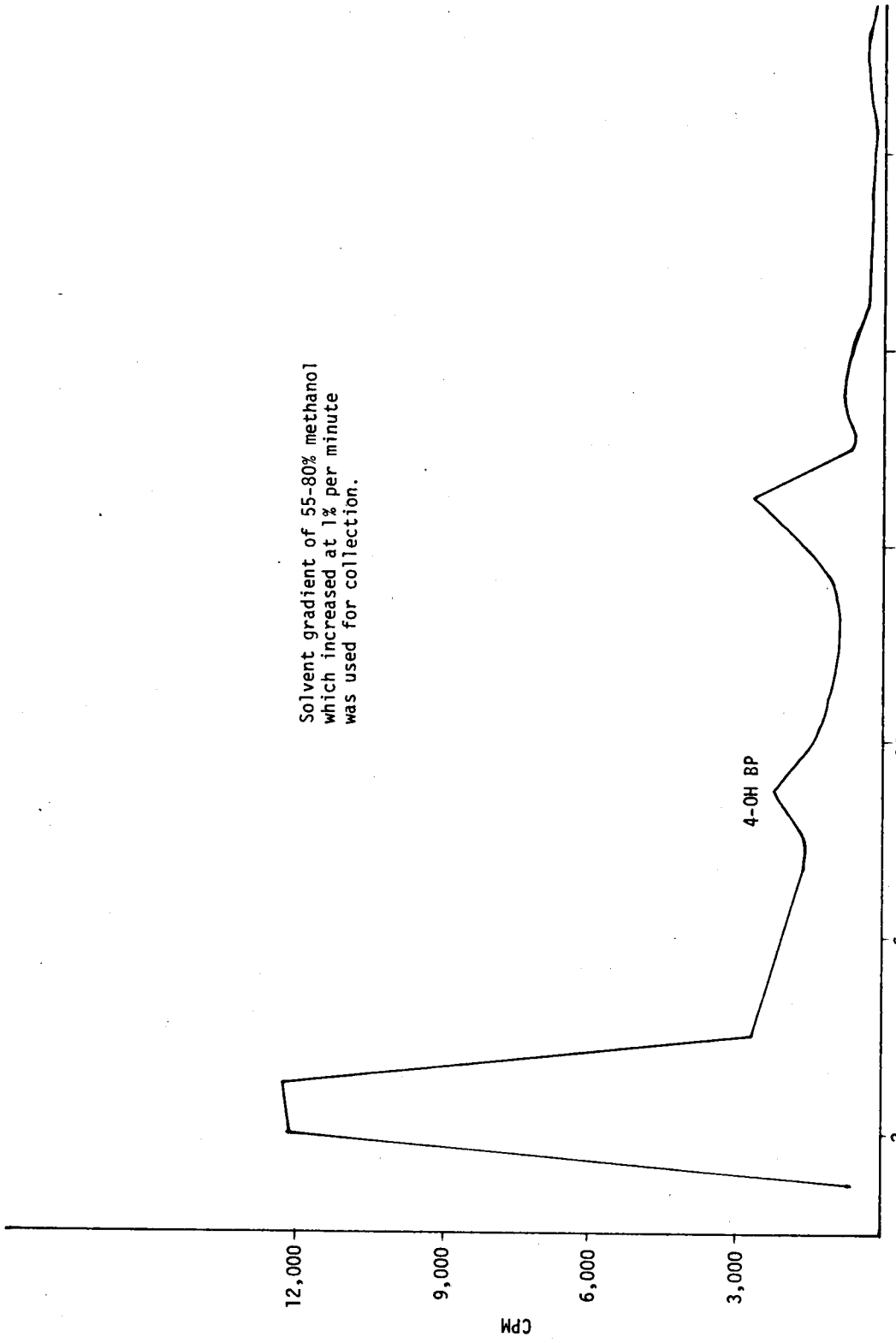


Figure 14. Reaction of 4-Cl BP Under N_2.

Irradiating 4-Cl BP under nitrogen yielded only 4-OH BP. No other photoproducts were detected.

$$\text{4-Cl BP} \xrightarrow[h\nu]{H_2O/N_2} \text{4-OH BP}$$

The photolysis of 4-Cl BP was repeated in the presence of oxygen. Aliquots were removed and analyzed at 40 hours, 80 hours and at the end of 100 hours. Average number of counts for those times are summarized in Table 9.

When 4-Cl BP was photolyzed in the presence of oxygen, many more products were formed. At 40 hours, Figure 15, peaks at retention times of 21 minutes, 15 minutes and at 7 minutes correspond to 4-Cl BP, BP, and 4-OH BP, respectively. The identity of the others is unknown. At 80 hours, Figure 16, most of the parent peak has disappeared. At the same time the concentration of 4-OH BP and BP has increased. The peak at 12 minutes in Figure 14 has disappeared completely while the others have increased. At the end of 100 hours, Figure 17, the most prominent peak corresponds to the retention time of BP. There is no parent peak visible. The majority of those unknown products have also been reduced in size. What is most outstanding about these studies in oxygen is the presence of a large number of products and the large amount of product whose retention time closely approximates that of BP.

Four experiments were also performed in which 4-Cl BP was photolyzed in distilled water under oxygen for 96 hours. The average data for these four runs, shown in Appendix B, Table B-2, are

Table 9

CPM for Aliquots Taken from Photolysis of 4-Cl BP Under Oxygen

HPLC Retention Time (min)	40 hours hυ CPM	80 hours hυ CPM	100 hours hυ CPM
1	75	570	66
2	2,617	655	132
3	1,078	436	947
4	468	281	292
5	766	447	1,659
6	1,742	756	149
7	1,298	952	1,094
8	2,692	1,201	978
9	680	600	132
10	403	289	115
11	340	251	112
12	4,545	181	786
13	242	155	122
14	211	155	127
15	1,214	150	658
16	175	1,715	4,508
17	133	290	149
18	306	96	281
19	154	2,205	173
20	154	102	178
21	1,575	314	177
22	282	220	226
23	1,978	283	203
24	96	101	222
25	111	76	204
26	103	77	173
27	102	2,105	149
28	1,172	167	1,285
29	94	1,215	142
30	79	84	531

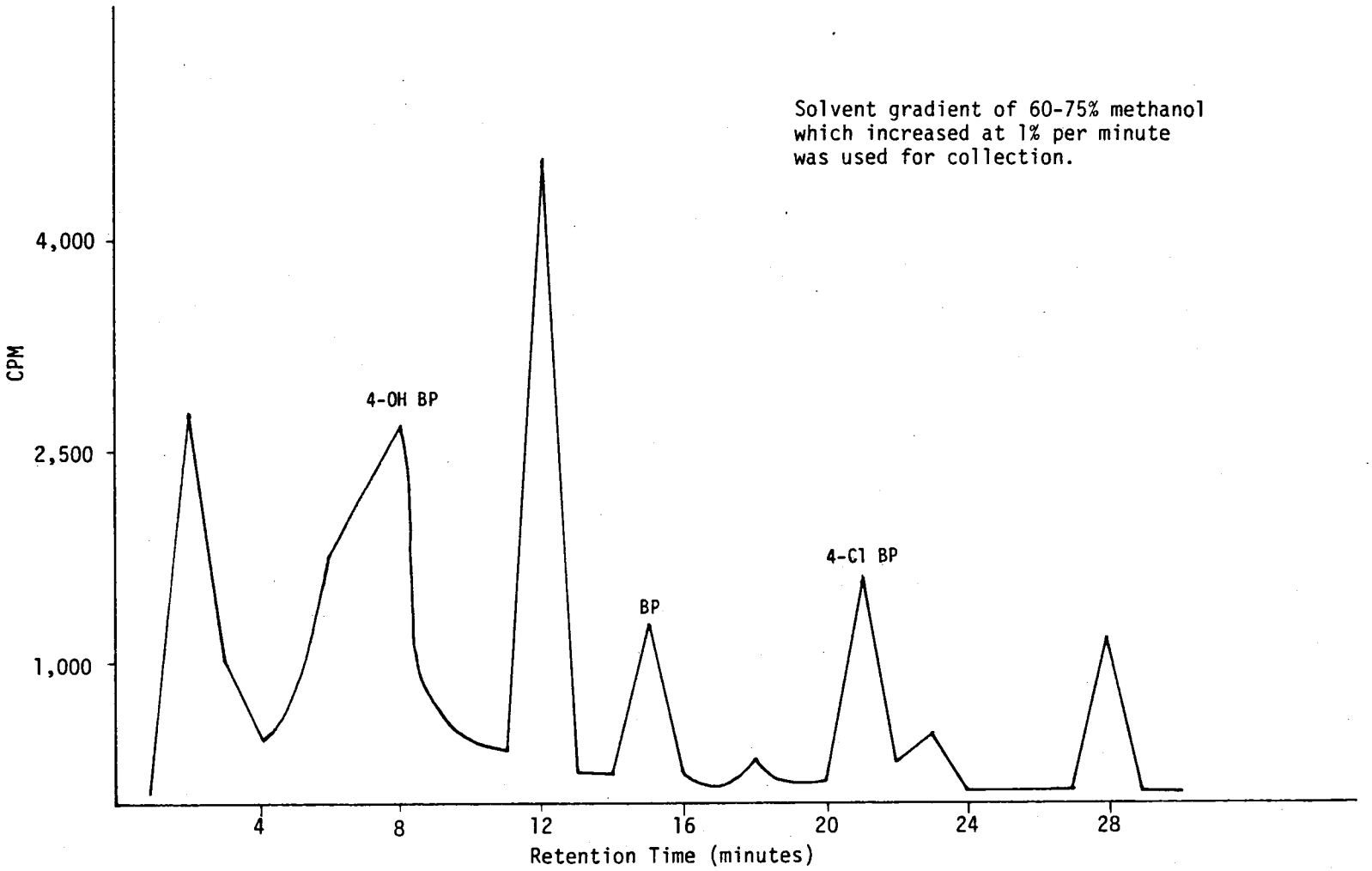


Figure 15. 40 Hours of 4-Cl BP Under O_2.

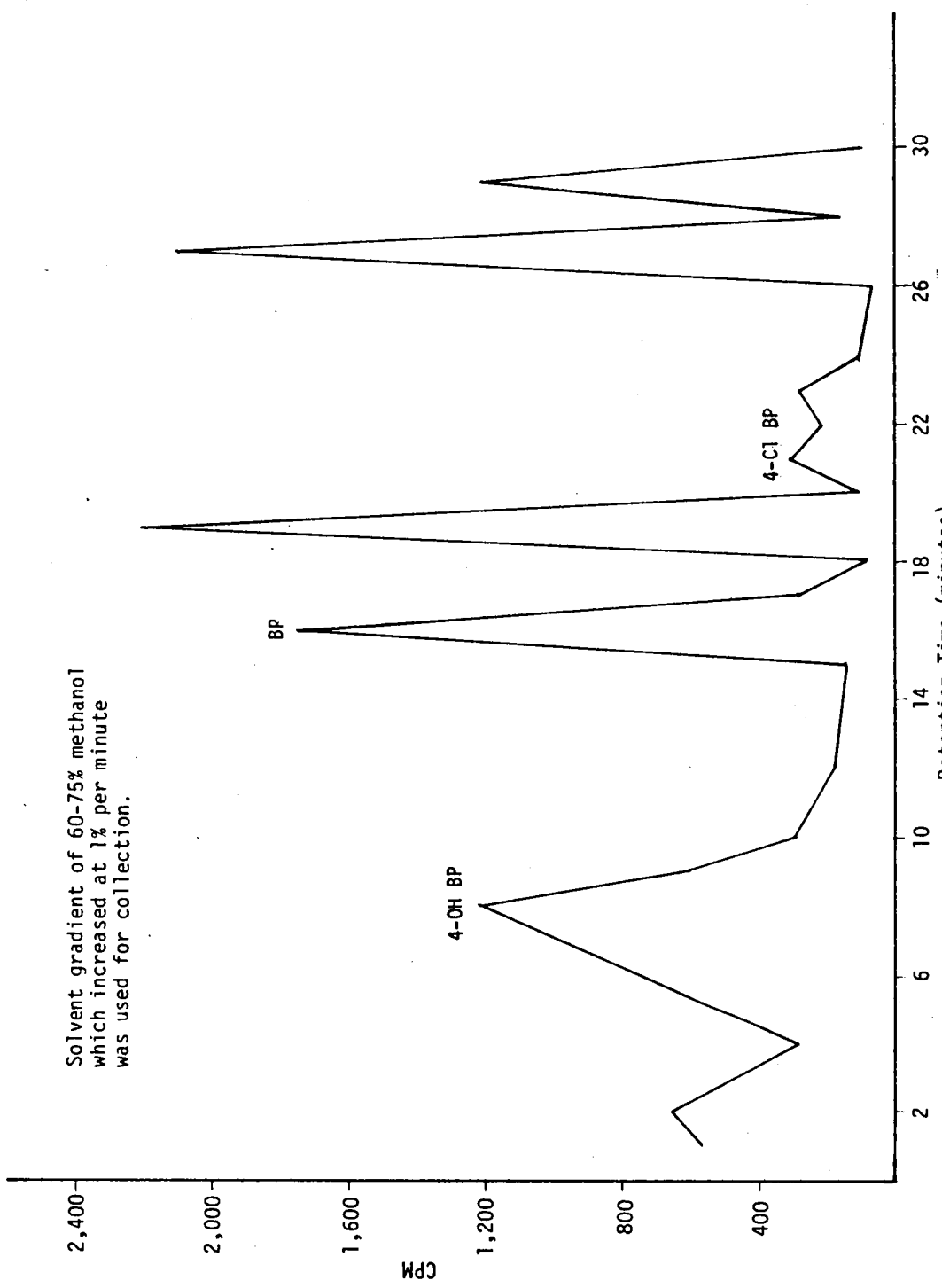


Figure 16. 80 Hours of 4-Cl BP Under O_2.

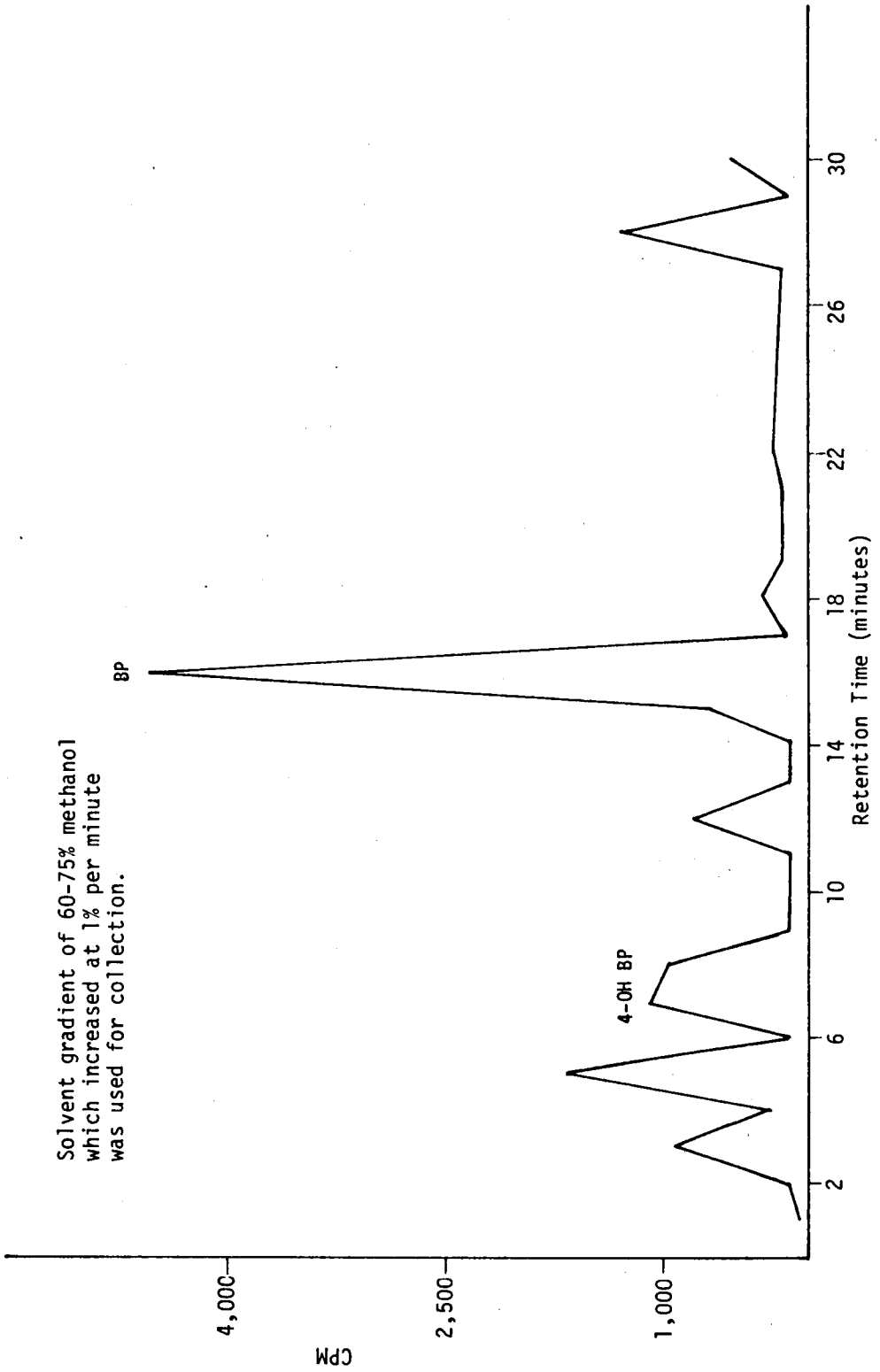


Figure 17. 100 Hours of 4-Cl BP Under O_2.

graphed in Figure 18. Surprisingly, the 4-Cl BP had reacted very little, if at all. There was nothing other than it and the solvent peak observed.

When 4-Cl BP was irradiated under oxygen instead of under nitrogen, many more photoproducts were observed. 4-OH BP and BP were identified as two of these products.

$$\text{4-Cl BP} \xrightarrow[h\nu]{H_2O/O_2} \text{4-OHBP + BP + other products}$$

Two experiments in which labeled 4-Cl BP was photolyzed in lake water under nitrogen for 96 hours were performed. An initial aliquot was removed, analyzed and showed only the starting material. The results of the 96-hour experiments, shown in Appendix B, Table B-3, are graphed in Figure 19. The 4-Cl BP had reacted and three photoproducts were formed, one of which was identified as 4-OH BP. The identity of the other products is not known. This is quite similar to what was observed for distilled water under nitrogen (Figure 14).

The results of photolyzing 4-Cl BP in lake water under oxygen for 96 hours are graphed in Figure 20. Results are compiled in Appendix B, Table B-4. Some unreacted starting material is still present. Also identifiable by retention times are 4-OH BP and BP. Two other peaks, one at approximately 13 minutes and the other at 16 minutes, are visible, but neither of their identities is known.

In lake water as opposed to distilled water, irradiating 4-Cl BP under nitrogen yielded other photoproducts in addition to 4-OH BP. BP was not identified among the other products.

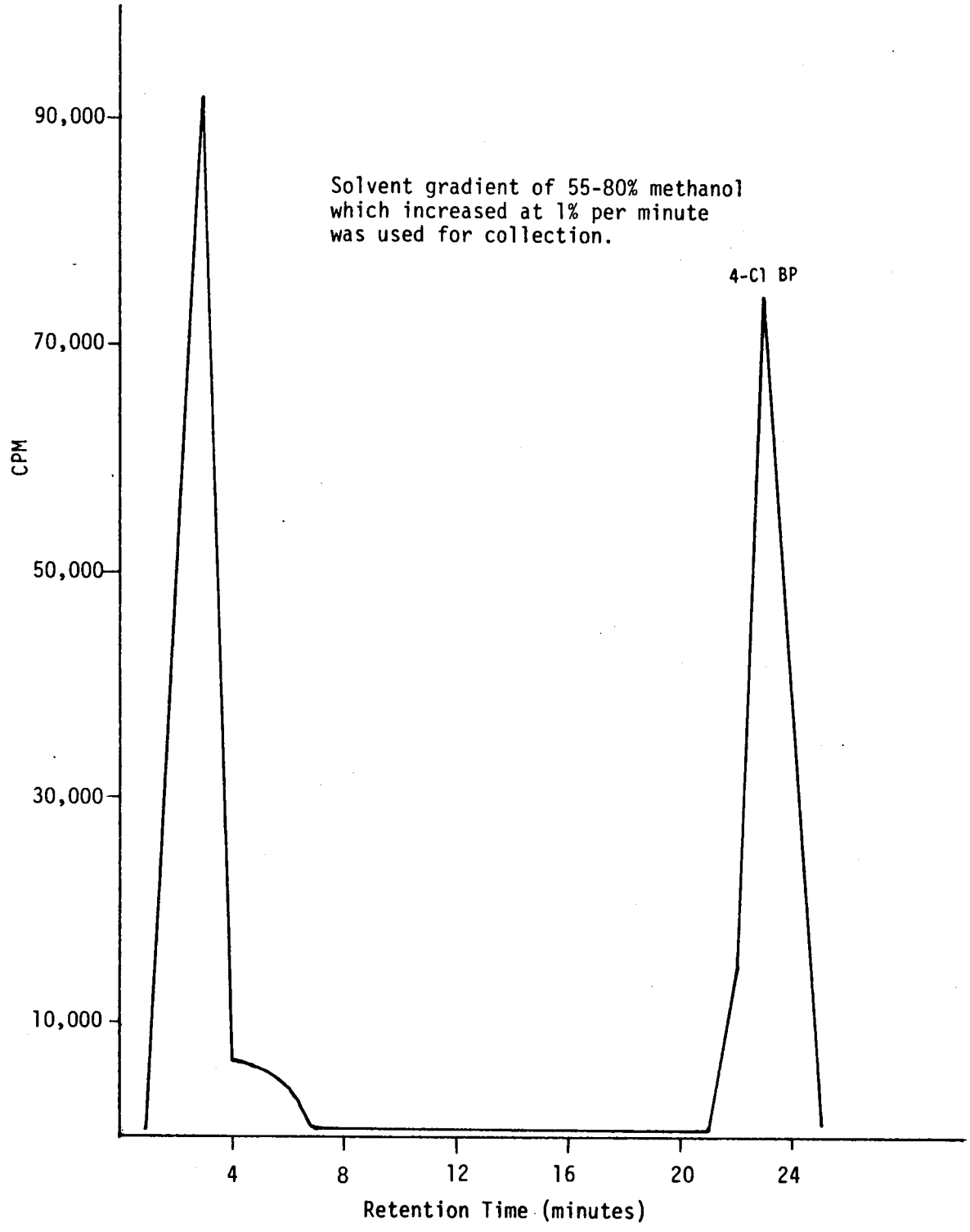


Figure 18. Reaction of 4-Cl BP Under O_2.

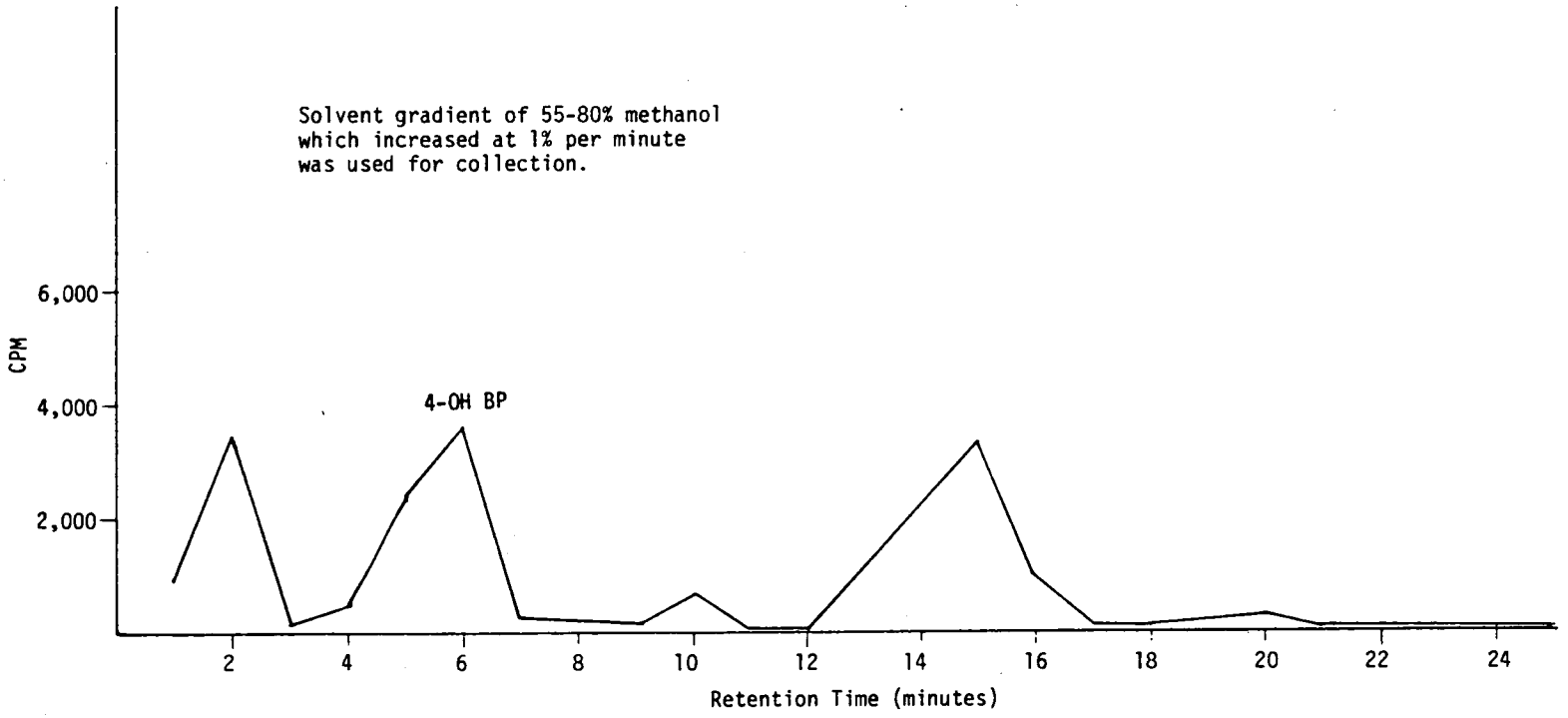


Figure 19. Reaction of 4-Cl BP in Lake Water Under N_2.

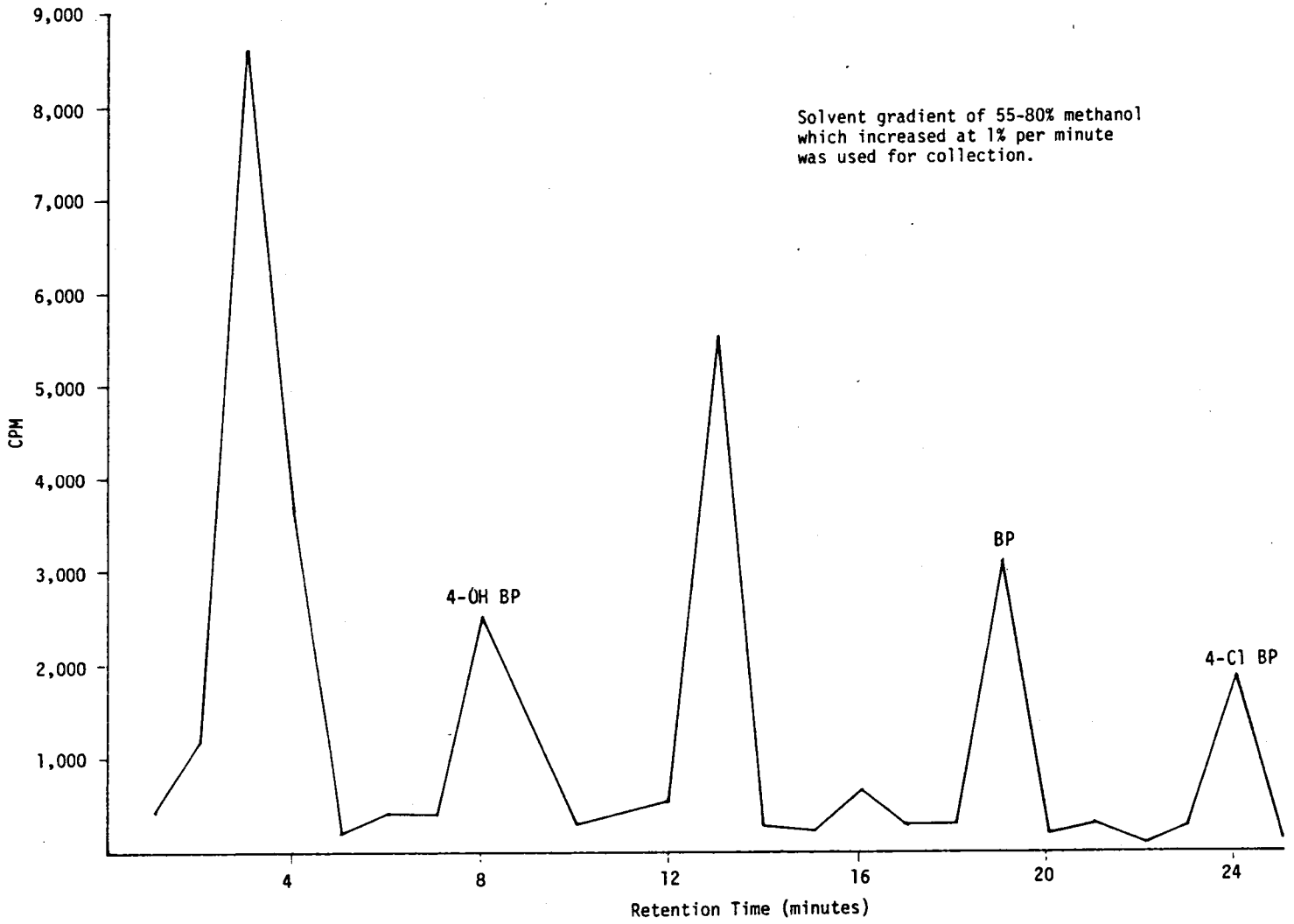


Figure 20. Reaction of 4-Cl BP in Lake Water Under O_2.

$$\text{4-Cl BP} \xrightarrow[h\nu]{\text{Lake Water}/N_2} \text{4-OH BP + other products}$$

However, under oxygen, reactions of 4-Cl BP in both distilled and lake water produced BP and 4-OH BP in addition to other unidentifiable products.

$$\text{4-Cl BP} \xrightarrow[h\nu]{H_2O/O_2} \text{4-OH BP + BP + other products}$$

Clays

Since suspended sediments and clays are present in the aquatic ecosystem, a clay, kaolin, was chosen for several experiments. The purpose in its introduction was to observe whether or not the 4-Cl BP adhered to or interacted with this material, and if so, in what ways. Inferences could then be made as to how clays effect the photodegradation of PCBs in the environment.

Clay, by definition,[24] is a dispersive system of mineral fragments of hydrated aluminum silicate of which particles smaller than 2 microns predominate. The term "clay" refers to a physical condition and not a definite chemical composition. Because hydrogen ions are preferentially absorbed by clay particles, most natural clays contain hydrogen, in part at least, as their exchangeable cation.[25] Consequently, when such clays are suspended in water, dissociation occurs and the hydrogen ion concentration in the suspension is increased.

If an acid is added to the water the content of free hydrogen ions is increased in proportion to the amount of acid added and to the degree to which it is dissociated. The pH value of most clay

suspensions lies between 4.2 and 7.0 indicating that they behave as weak acids.

Many clays owe their acidity to associated organic matter in addition to the exchangeable hydrogen ions which they have absorbed. Humic and other soil acids[25] are frequently associated with clays as protective colloids and these, even in small amounts, may produce marked acidity in clay suspensions. This acidity will have an effect on the way clays interact with the compounds, such as PCBs, with which they come into contact.

Kaolin may be defined as a clay derived by decomposition or weathering of an aluminous mineral such as feldspar or mica.[24] Its most important commercial source is the Cornwall district of England. However, moderately large deposits are located in California, Delaware, Georgia, Idaho, North Carolina and Vermont.

Kaolin is a group of at least four minerals: kaolinite, nacrite, dickite and anauxite.[26] These minerals have the general formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The Al:Si ratio may vary from 2:1 to 3:1 but the major characteristics, as indicated by x-ray diffraction patterns, remain the same.

The kaolin group is based on layers of single sheets of silicon-oxygen linkages bound through common anions to aluminum atoms arranged as in a gibbsite sheet and surrounded by six anions of oxygen and hydroxyl units. This arrangement, shown in Figure 21,[27] is a crystal structure wherein the gibbsite sheet is condensed with one silica sheet forming a stable nonexpanding type crystal lattice.

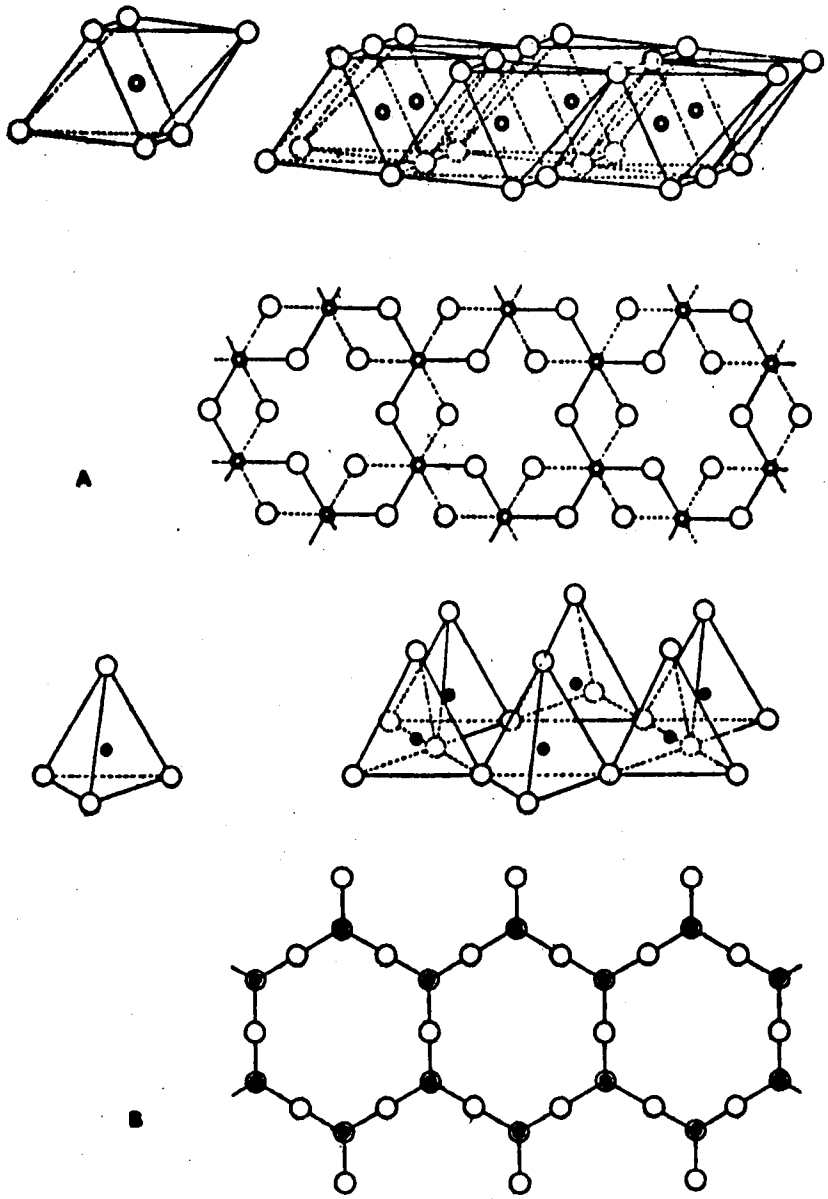


Figure 21. The Structure of a Kaolin Layer. The gibbsite unit (A) showing an octahedral $AL(OH)_6$ unit and the planar construction from side and top elevations; the silica plane (B) showing a tetrahedral unit and the planar construction from side and top projections.

Dickite, nacrite and kaolinite are chemically identical but differ in the manner of stacking of the sheets.[26] Water is not absorbed between the sheets of these minerals since there is relatively strong hydrogen bonding between two adjacent sheets. Clays composed of the nonexpanding lattice structures are said to possess moderate surface activity and generally form relatively freer flowing systems in water.

Commercial kaolins contain between 80-90% of clay mineral kaolinite contaminated mainly with quartz and fine-grained mica or hydrous micas but seldom with appreciable proportions of felspar[28].

Following the standard irradiation procedure for 4-Cl BP, to which kaolin was added and separating the clay portion from the aqueous portion prior to extraction, yielded data which are tabulated for the aqueous layer in Appendix C, Table C-1, and for the clay layer in Appendix C, Table C-2.

By plotting time vs. counts per minute it is possible to obtain a graph similar to one which would have been produced by plotting of absorbance vs. retention time. This type graph for the aqueous layer, Figure 22, shows the main photoproduct to be 4-OH BP in addition to unreacted starting material. This analysis was made by comparison of retention times to those of known compounds. The clay extract, Figure 23, revealed neither 4-OH BP nor 4-Cl BP. Three photoproducts were observed but not identified as the retention times did not correspond to those of known compounds including BP or dibenzofuran.

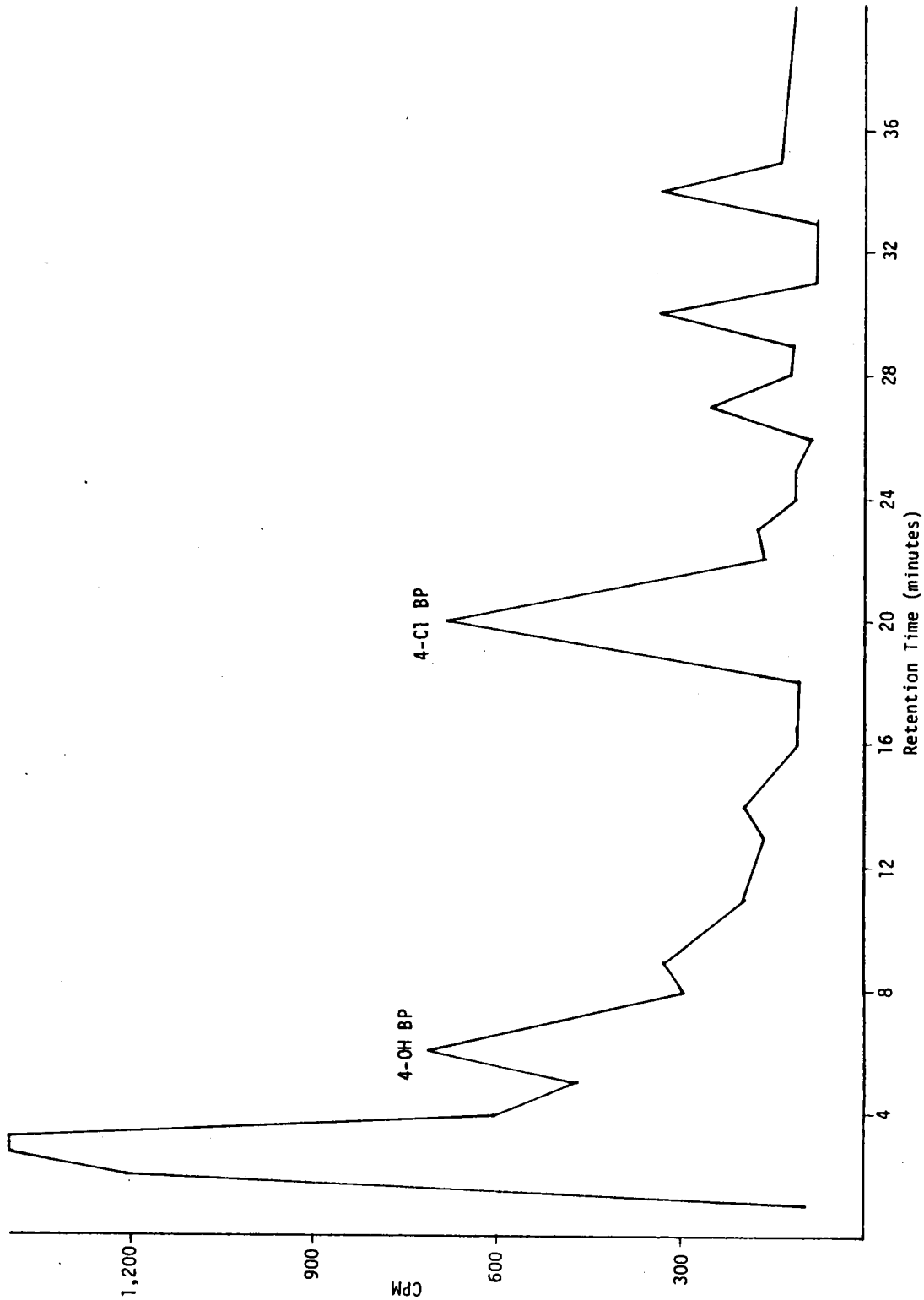


Figure 22. Aqueous Layer from Irradiation of 4-Cl BP.

An experiment was performed in which labeled 4-Cl BP was introduced into a tube containing clay and distilled water. It was shaken and allowed to remain in the dark for 21.75 hours. This was the control tube. A tube prepared in an identical fashion was photolyzed for 21.75 hours after deoxygenating with nitrogen. The results of scintillation counting are shown below in Appendix C, Tables C-3 through C-6.

A plot of time vs. counts for the experimental aqueous layer compared to that for the control aqueous layer is shown in Figure 24. The control aqueous layer showed essentially no photoproducts including the starting material implying no reaction occurred in the absence of light. The experimental aqueous layer, which had been exposed to light for 21.75 hours, revealed the presence of two photoproducts in addition to the solvent peak. The retention times of these products are dissimilar to those of known quantities of 4-OH BP, BP or 4-Cl BP, and their identities unknown.

A similar plot comparing the results of the clay extracts of the experimental tube to those of the control tube is shown in Figure 25. The clay extract from the control reveals the presence of four products, one of which is identifiable by retention time data and found to be a small quantity of 4-OH BP. The clay extract of the experimental tube also shows the presence of four products. A small amount of unreacted starting material can be seen. The retention times of two of the other products correspond to those of 4-OH BP and BP. The identity of the third product, also observed in the control flask, is not available from retention time data.

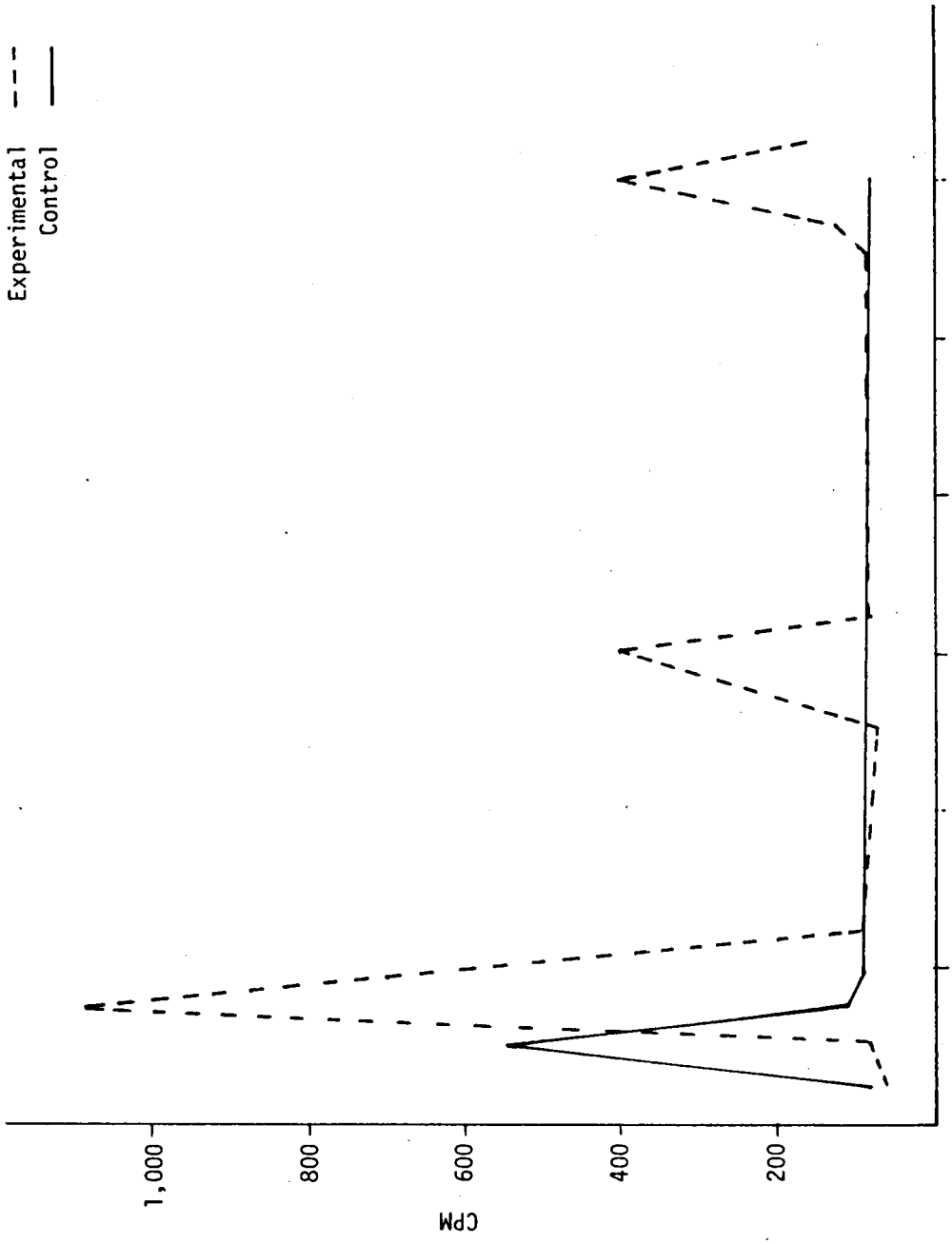


Figure 24. Experimental vs. Control Aqueous Layer for Irradiation of 4-Cl BP.

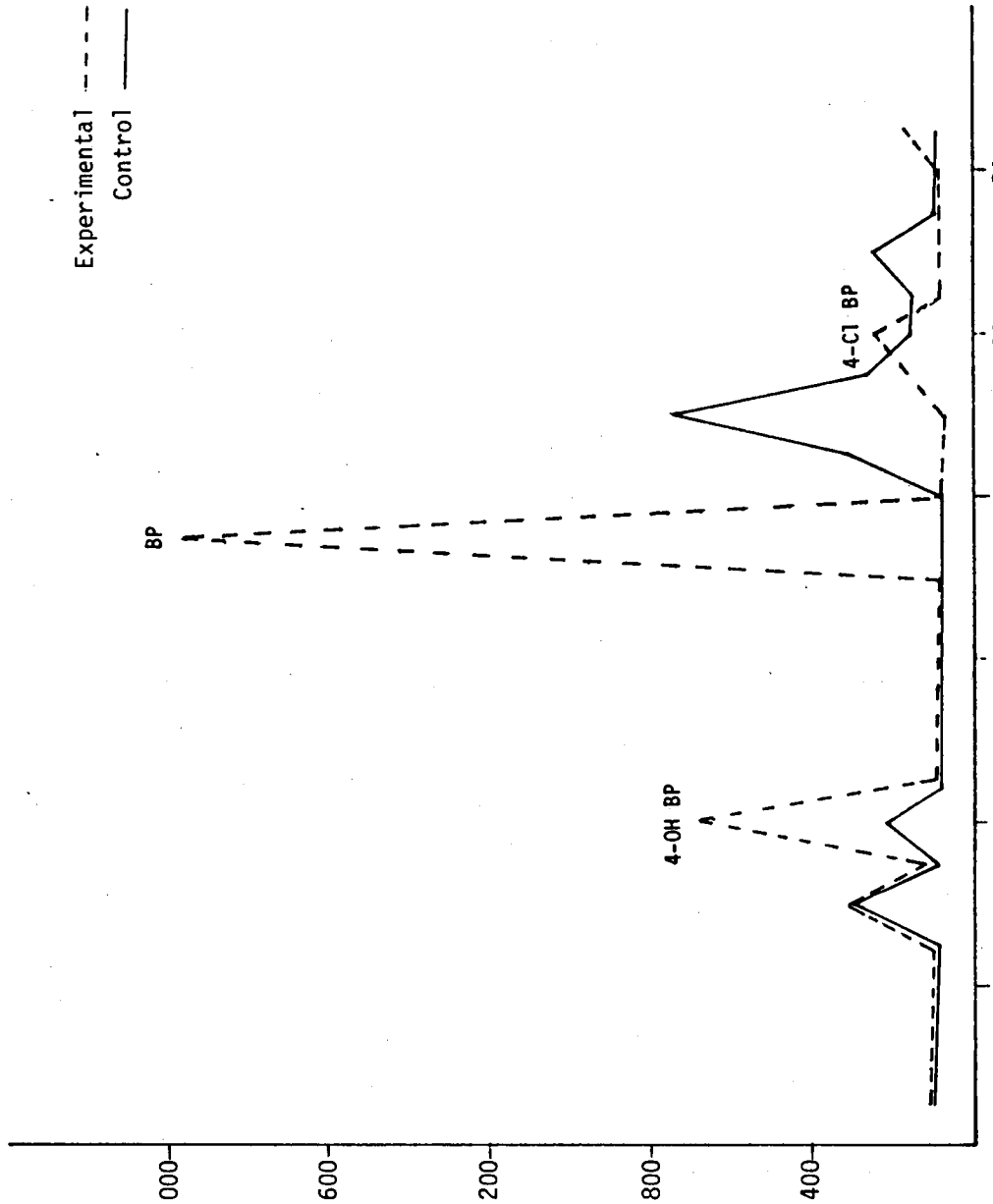


Figure 25. Experimental vs. Control Clay Extract for Irradiation of 4-Cl BP.

Figure 26 compares the clay extract and aqueous extract from the experimental tube, which was photolyzed under nitrogen. The aqueous layer contains only two products in addition to the solvent peak which elutes first. Product identity could not be determined in this case as the retention times of known compounds do not match experimental times.

The clay layer, in contrast, shows three clearly defined peaks which have been identified in the same manner as 4-OH BP, BP, and a small amount of unreacted 4-Cl BP starting material. The products of the clay are clearly quite different from those of the aqueous layer. This is possibly due to the fact that although it is possible to deoxygenate the aqueous layer before photolysis, it is not possible to deoxygenate the clay in the same fashion. Two different photolysis atmospheres lead to different photoproducts.

The labeled 4-Cl BP was irradiated with clay in distilled water under oxygen for 43.15 hours. Results are compiled in Appendix C (Tables C-7 and C-8).

The product formation and distribution is somewhat different in the nitrogen and oxygen environments. A comparison of the clay extract to the aqueous extract in an oxygen environment is shown in Figure 27. Seven products are observable from the aqueous layer, but the identity of only three can be ascertained from retention time data. These are 4-OH BP, BP and 4-Cl BP, and the unreacted starting material. Five products are observed from the clay extract, two of which are identified as 4-OH BP and BP. No unreacted starting

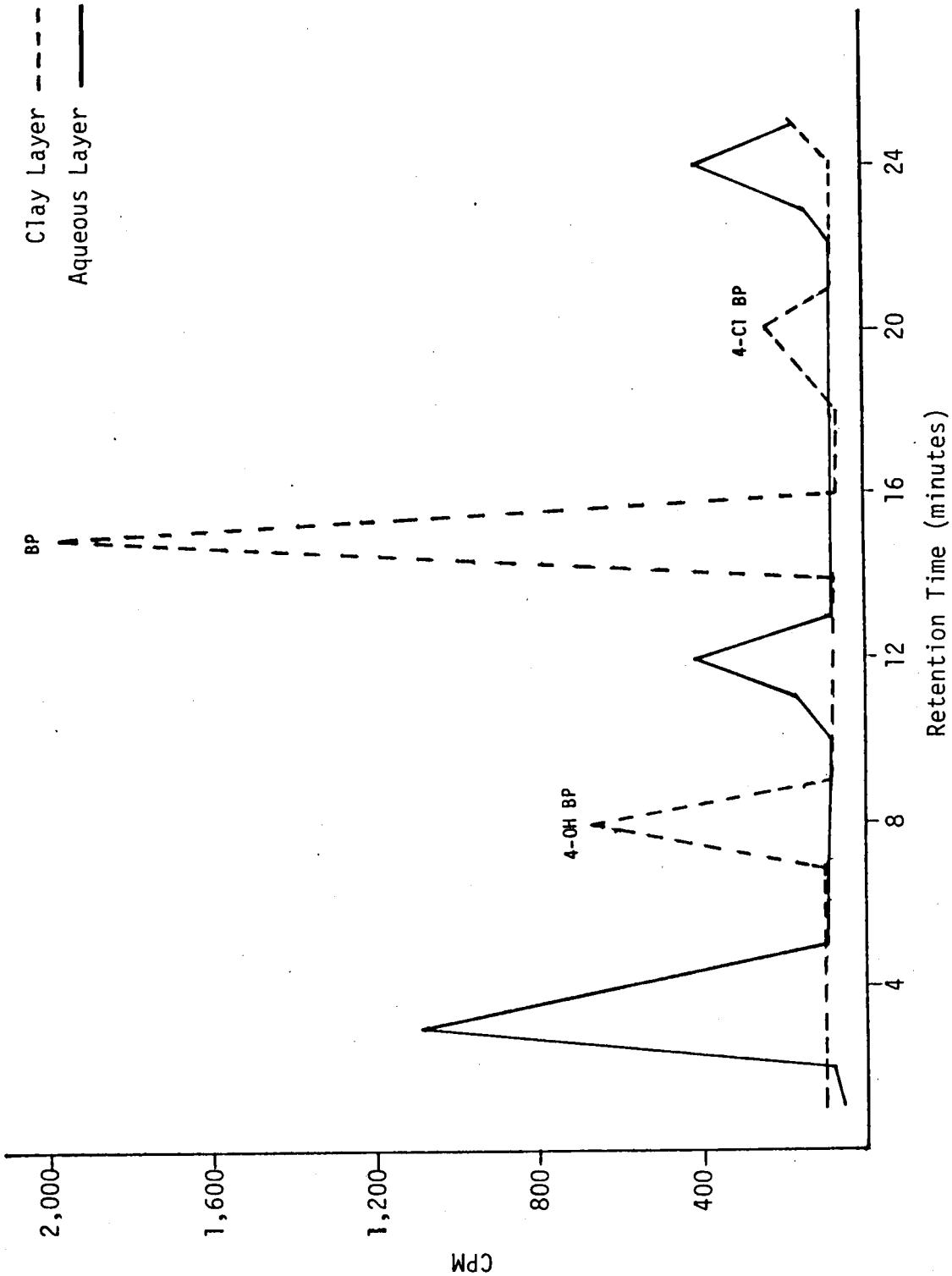


Figure 26. Aqueous vs. Clay in N_2 for Irradiation of 4-Cl BP.

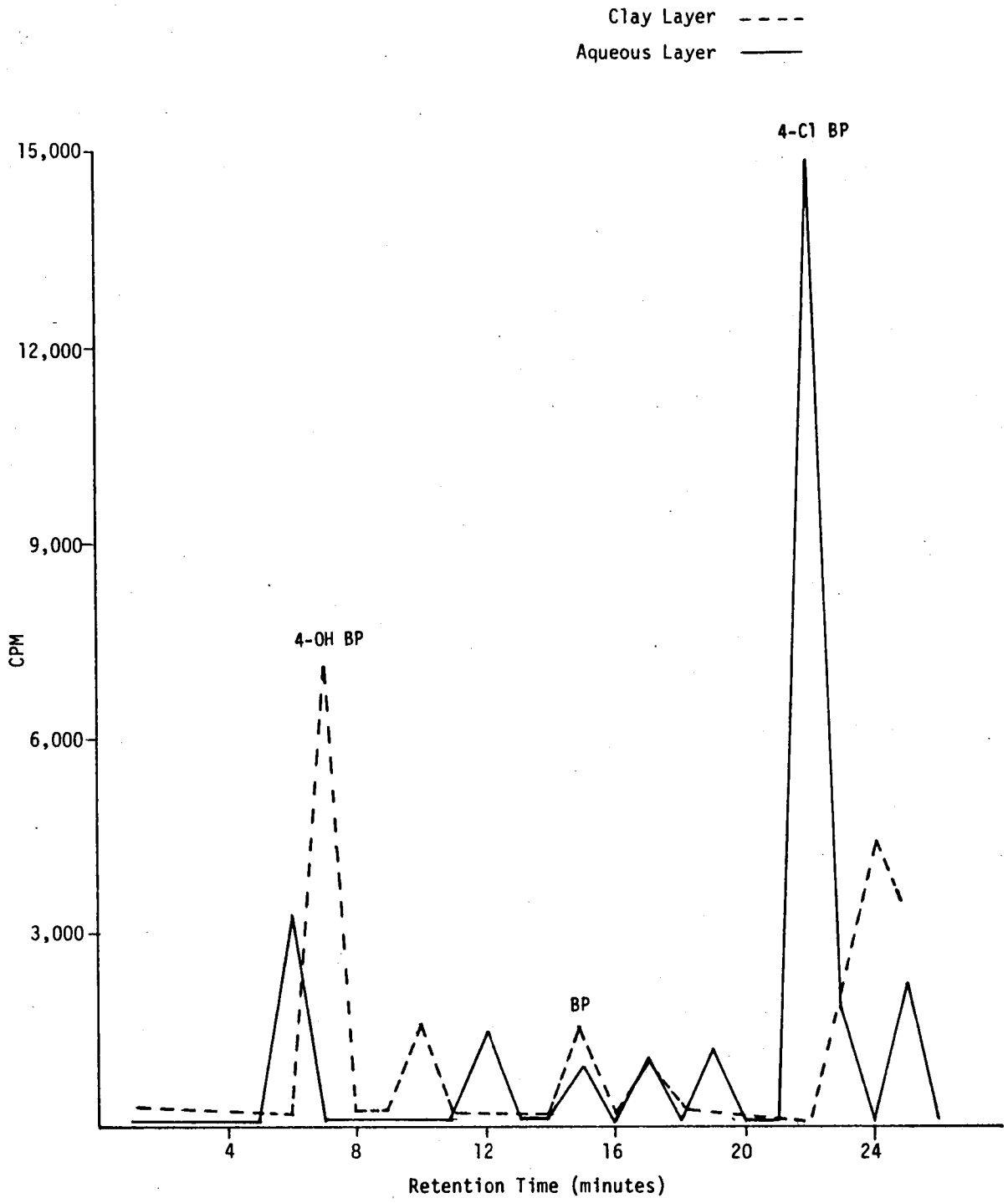


Figure 27. Aqueous vs. Clay in O_2 for Irradiation of 4-Cl BP.

material was observed. The unidentified product peaks may correspond to secondary products.

How are the products formed in the aqueous layer in the absence of oxygen, i.e., in the presence of nitrogen, different from those formed in the presence of oxygen? The products' identities and distributions are quite dissimilar in the two media as seen in Figure 28. Only qualitative data may be derived from this graph. No quantitative comparison can be made because of differing experimental conditions, e.g., amount of starting material and reaction time. This comparison is still useful, however, for noting what products are formed in each environment.

There were two peaks in addition to the solvent peak which were observed for the aqueous layer photolyzed in nitrogen. Neither of these could be identified. The aqueous layer photolyzed in oxygen yielded multiple products—a finding consistent with previous observations made in the presence of oxygen. The majority of starting material was still unreacted and had a retention time of approximately 22 minutes. Of the products which were formed, the one which had a retention time of about 12 minutes matched one at the same time in the nitrogen environment. Two of the other peaks were identified as 4-OH BP and BP. The identity of the remainder is unknown.

Finally, a comparison of the clay extract in nitrogen to that in oxygen is shown in Figure 29. The clay is not truly in a nitrogen environment as previously mentioned. Observations similar to those

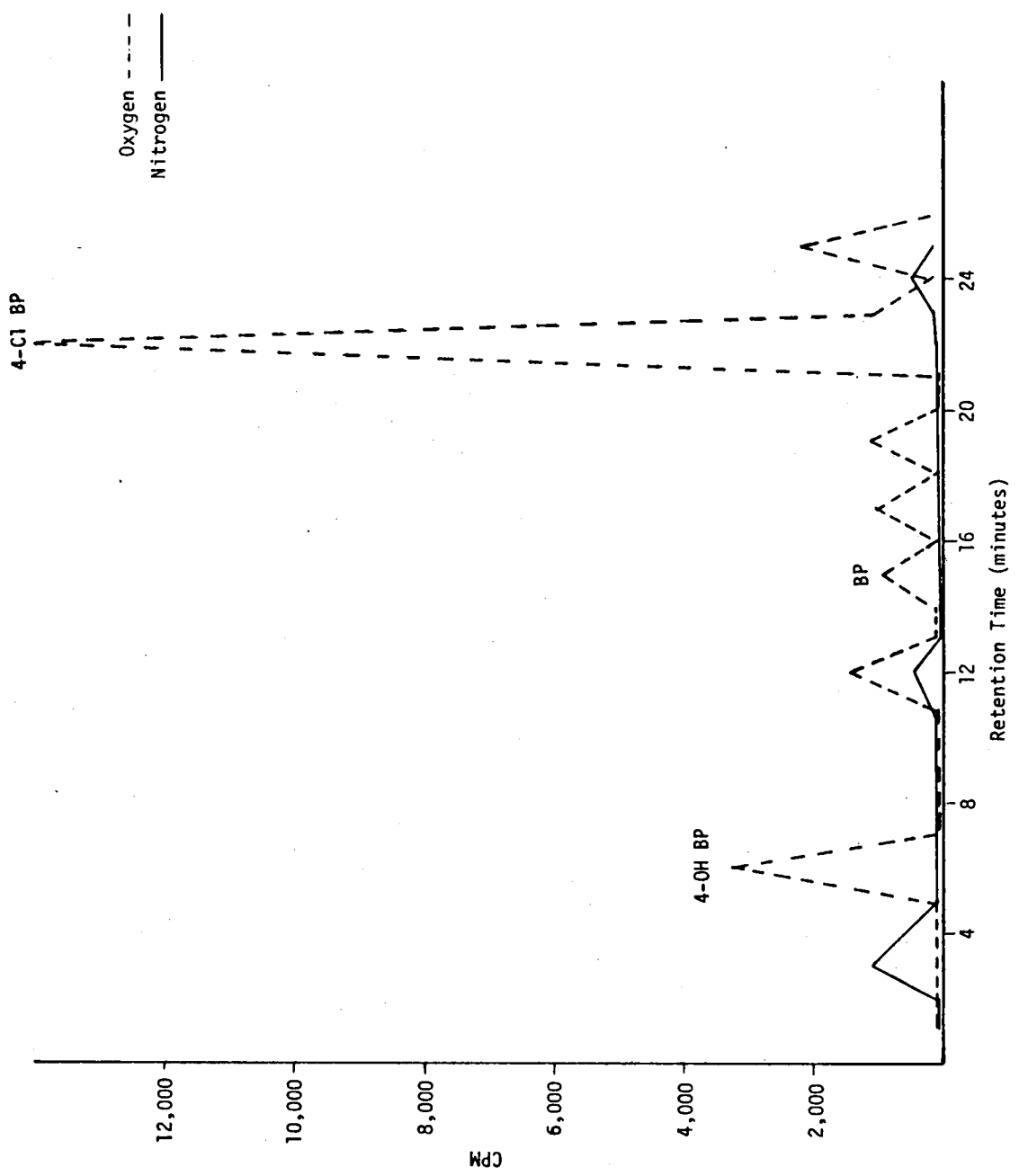


Figure 28. O_2 vs. N_2 in Aqueous Layer for Irradiation of 4-Cl BP.

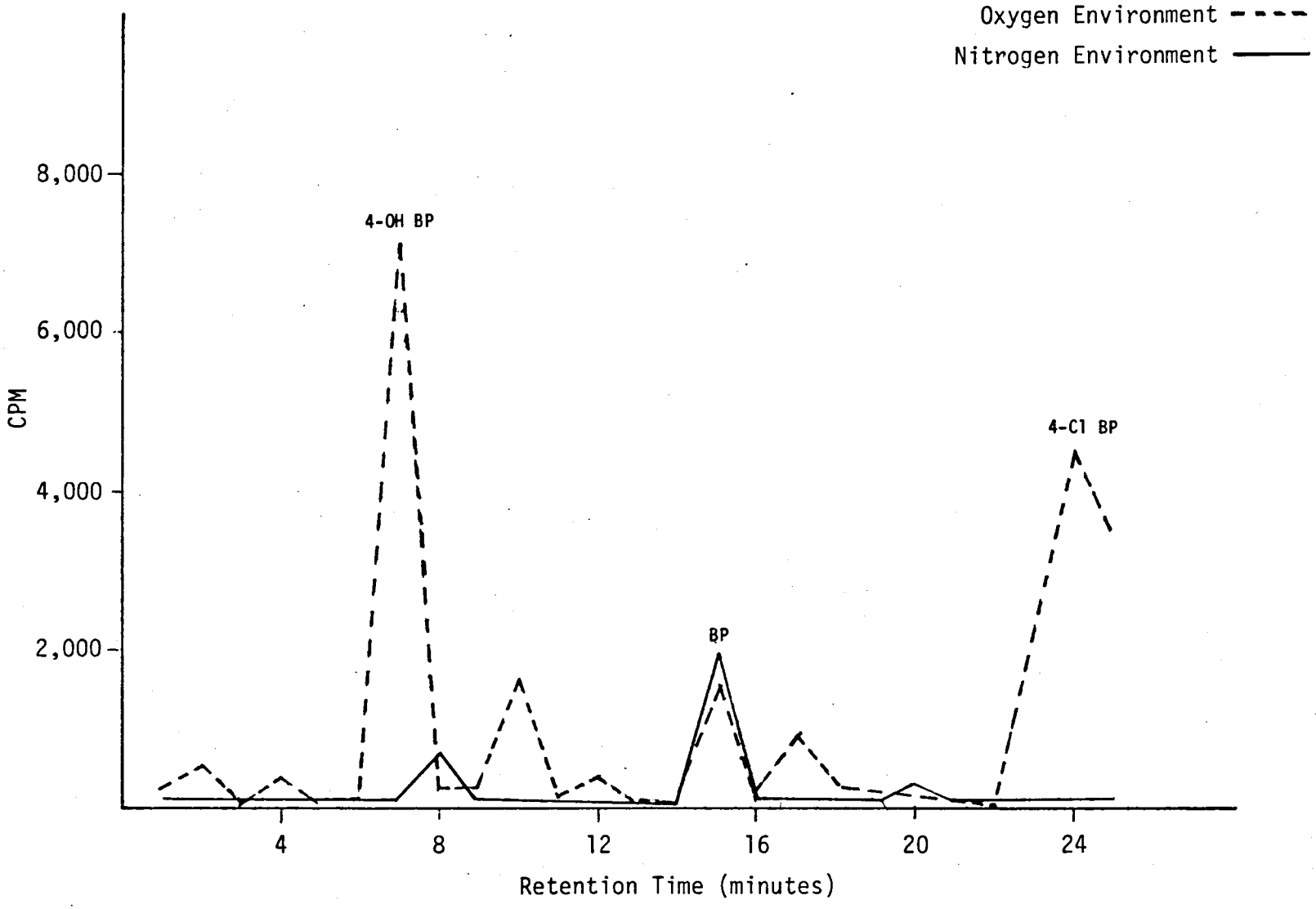


Figure 29. O_2 vs. N_2 in Clay Extract for Irradiation of 4-Cl BP.

made for the aqueous medium are applicable in this medium as well. The number of products formed under oxygen is greater than the number formed under nitrogen. It is again noted that unreacted starting material is present with the oxygen but absent with the nitrogen environment. The triplet O_2 could be quenching either or both singlet and triplet states[29] so that a much slower reaction rate is observed in its presence. It is presumed, however, that the complexity of photoproducts in oxygen is greater.

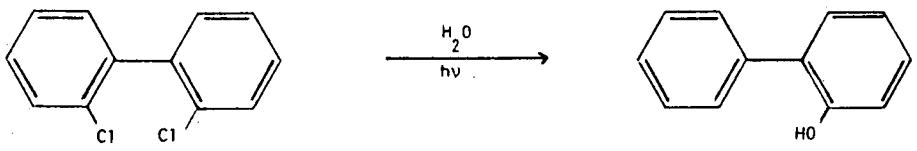
In Figure 27 for the irradiation under oxygen, both the clay and aqueous extracts exhibited a peak with retention time close to that of biphenyl. To determine whether or not this peak was truly biphenyl, an isotopic dilution experiment was performed using a portion of the aqueous extract as the source of radioactivity. At this time carbon-14 labelled 4-Cl BP was irradiated under the specified conditions. During analysis of the products of the aqueous extract with HPLC, the labelled eluent was collected. This was added to pure unlabelled BP and the combination was recrystallized to constant melting point and activity. Scintillation counting of this revealed no more counts than were normally in the background, leading to the conclusion that the peak whose retention time was close to BP was not actually BP, although its true identity is unknown. If BP were a photoproduct, its presence would have been indicated by the radioactivity level. This isotopic dilution technique is so sensitive that even a few parts per billion can be detected.

Dichlorobiphenyl

2,2' Dichlorobiphenyl

A 9.88×10^{-6} M solution of 2,2'-dichlorobiphenyl in distilled water was prepared. It was divided into two photolyzing tubes, into one of which nitrogen was introduced and the other was allowed to remain in the oxygen environment. Both were photolyzed for three hours.

The solution which had remained in oxygen yielded two photolysis products. The retention time of the major one corresponds to 2-OH BP, or a phenylphenol isomer. The identity of the other, which is very small in comparison, is unknown. Its retention time does not match that of biphenyl, dibenzofuran or 2,2'-dihydroxybiphenyl.



The solution half which had been deoxygenated yielded two photoproducts in addition to a small amount of starting material. The vast majority of product could be identified as a phenylphenol. The second product which had the same retention time as the one described for the oxygen environment and was likewise not identifiable.

pH studies were performed on 2, 2'-dichlorobiphenyl under nitrogen in distilled water and in lake water, labelled reactions N and O, respectively. The results are compiled in Appendix D (Tables D-1 and D-2). Figure 30 depicts a plot of ΔpH vs. time for these reactions.

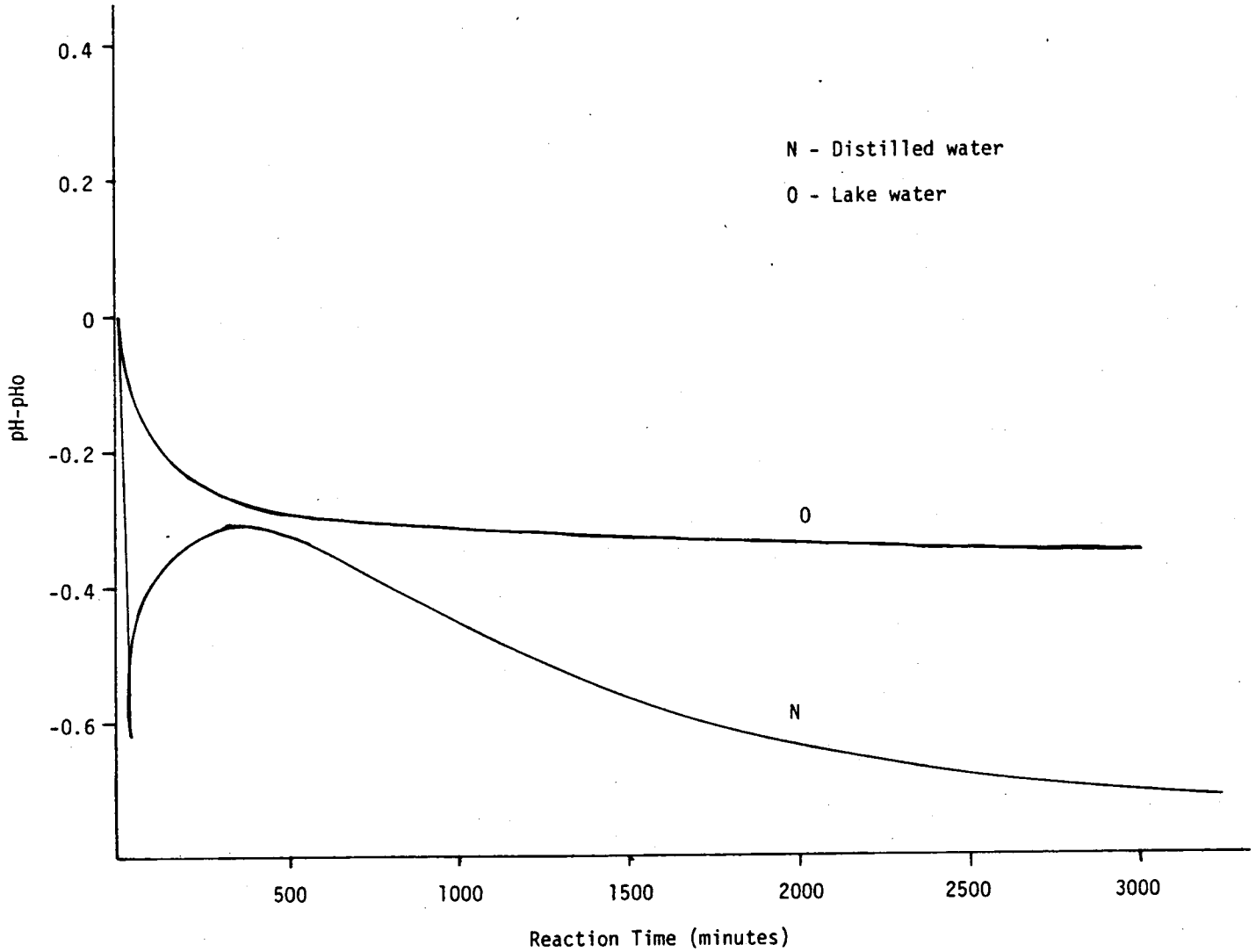


Figure 30. Photolysis of 2,2'-dichlorobiphenyl Under N_2.

Observed here, as with 4-Cl BP photodegradation, was the slower reaction signaled by little change in pH in the lake water medium.

From observing pH changes, it was noted that the behavior of 2,2'-dichlorobiphenyl is more complex than 4-Cl BP indicating that reversible and/or competing reactions may be taking place. It is known that ortho-substituted BPs react very rapidly in order to relieve unfavorable steric strain, which would be even more unfavorable with two ortho-substituents.[30]

2,2',4,4'-Tetrachlorobiphenyl

A 8.49×10^{-7} M solution of 2,2',4,4'-tetrachlorobiphenyl in distilled water was prepared. It was photolyzed under nitrogen for a total of 95.3 hours during which time aliquots were removed for analysis at 22.3 hours and at 52.8 hours. The results are shown in Table 10.

While the identity of the photoproducts of tetrachlorobiphenyl is not certain, it is clear that there are very many in number. It is reasoned from this experiment that the photoproducts of more highly chlorinated biphenyls, such as the once commonly used Aroclor 1254, would be a very complex mixture which would be quite difficult to separate and identify.

Summary and Conclusions

It has been shown that the presence of oxygen in the reaction medium retards the photoreaction. Several explanations are possible:

Table 10

Time Profile for Tetrachlorobiphenyl[a,b]

22.3 hours		52.8 hours		95.3 hours	
Retention time (min)	Area	Retention time (min)	Area	Retention time (min)	Area
5.13	13,110	3.76*	174,414	3.71*	432,280
7.08	42,146	9.48	8,456	4.09	17,526
9.12	13,112	9.70	7,846	10.20	10,772
10.14	18,690	13.54*	4,654	13.79*	15,108
11.12	21,229	15.47	32,496	19.49	3,793
12.09	22,719	16.15*	74,536	20.60	9,775
13.16	27,184	22.47	62,770	21.13	7,117
14.11	52,265	22.55	66,220		
15.14	11,961				
16.35*	14,070				
17.15	47,695				
18.65	244,310				
19.78	15,400				
20.30	10,988				

[a]Photolyzed in distilled water under nitrogen.

[b]HPLC solvent ratio of 70% methanol:30% water was used.

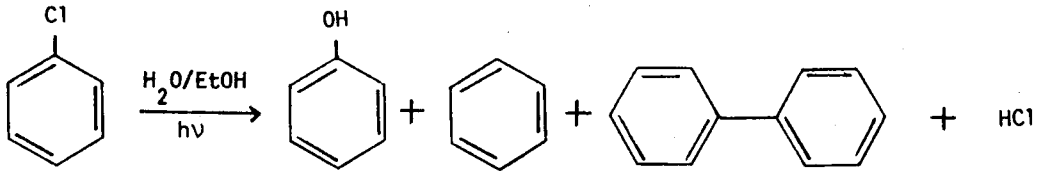
*For this solvent ratio, the retention times of standard solutions are as follows:

4-Cl BP	3.73	BP	13.58
4-OH BP	17.96	tetrachlorobiphenyl	16.27

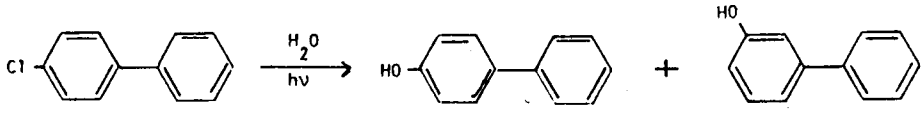
(1) oxygen acts as a quencher so that a much slower reaction rate is observed, (2) it affects the rate of intersystem crossing (ISC), or (3) competing reactions are involved which inhibit the production of phenylphenols and HCl.

Simply to assume a compound's identity by favorably comparing its retention time to the retention time of known compounds has proven unwise. This proved to be true in this study. At one point it was assumed that the photoreaction products of 4-Cl BP in water under aerobic conditions were BP and 4-OH BP in addition to unreacted starting material. In an effort to be certain of the identities of these compounds, further testing was done.

Was the compound assumed to be BP actually BP? An isotopic dilution experiment, similar to that described on p. 67, using the photoproducts from labelled 4-Cl BP proved that BP was not formed from irradiation of 4-Cl BP in H_2 under O_2. The products of a similar photoreaction were similarly analyzed with HPLC and the eluent collected for the time which corresponded to the retention time of the peak in question. The solvent was removed and analysis was done using mass spectrometry. The actual identity was not determined; however, by comparison of the mass spectrum to those of BP and p-quaterphenyl, those possibilities were ruled out. Quaterphenyl was considered as the possible identity because in analogous work[31] a small amount of BP was formed from irradiation of chlorobenzene. The other photoproducts of chlorobenzene were HCl, phenol and benzene. This, like other studies in which dechlorination is predominant, was performed in a cosolvent mixture rather than in an aqueous medium.



In an isotopic dilution experiment similar to that previously described, it was shown that irradiation of 4-Cl BP yielded not only 4-OH BP but also 3-OH BP in approximately equal amounts. The presence of both isomers was confirmed by making chloroacetate derivatives[33] from the phenylphenols which could be separated by gas chromatography (GC). The separation and the presence of both isomers is shown in Figure 31.



By irradiating standard aqueous solutions of 4-OH BP and 3-OH BP independently and making chloroacetate derivatives of the photoproducts, it was determined that neither isomer interconverted. Therefore the explanation that 4-OH BP, formed from irradiation of 4-Cl BP, converts to 3-OH BP is not a valid one. Likewise, 4-Cl BP does not form 3-Cl BP nor does the meta isomer convert to the para.

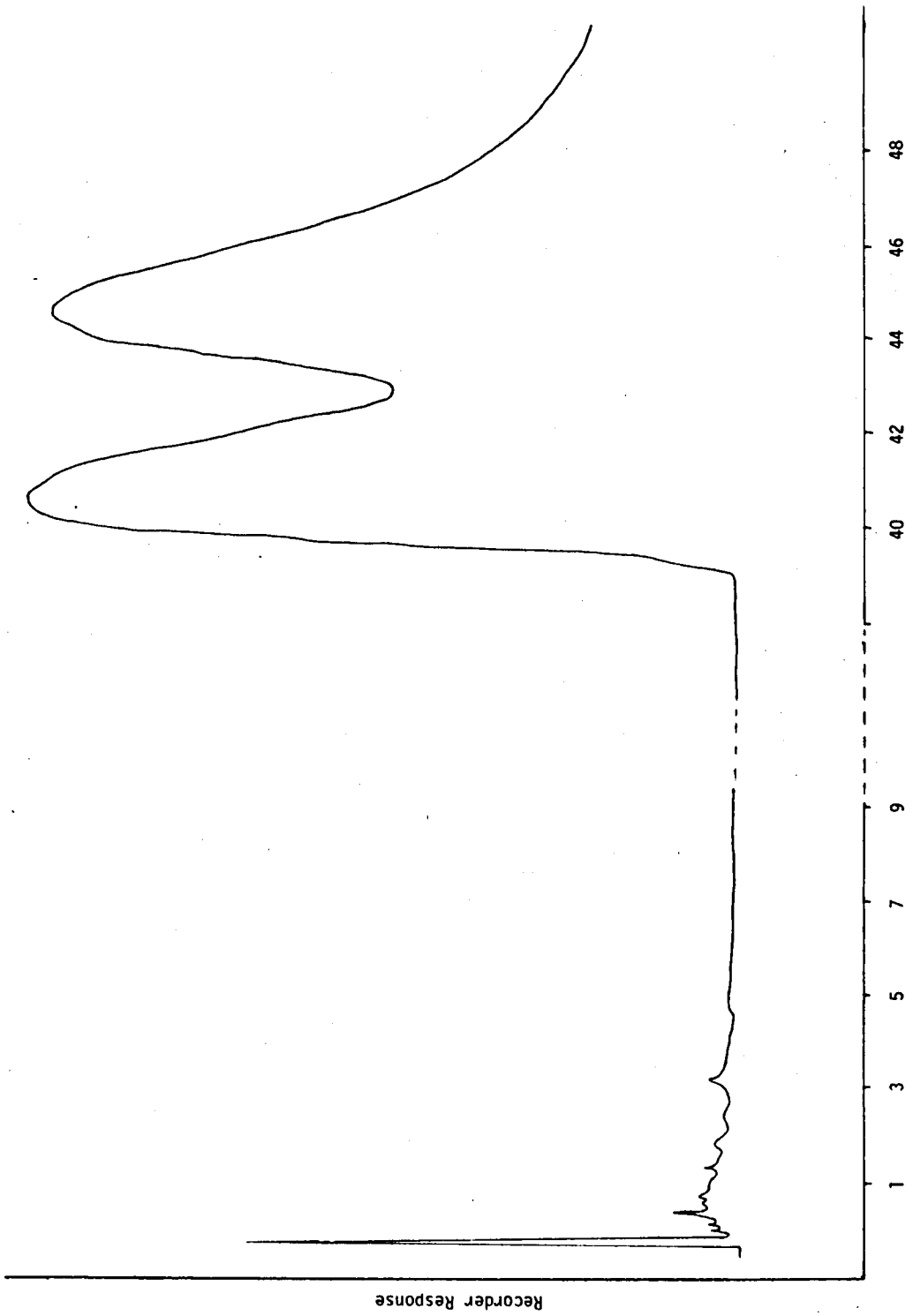
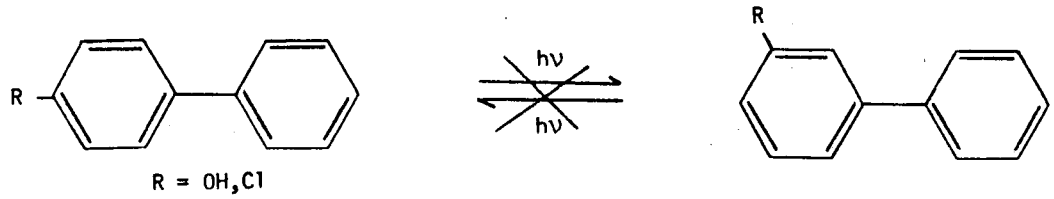


Figure 31. Separation of Phenylphenols.



The rates of photodegradation of monochlorinated biphenyls were found to be in the following order: 2-Cl BP > 3-Cl BP > 4-Cl BP. The same degradation rate order was observed by Kong and Sayler[34] with biological degradation as opposed to photochemical degradation. Using ^{14}C-labeled chlorobiphenyl, total mineralization (defined as CO_2 production from the chlorobiphenyl ring) was observed for 4-Cl BP but not for 2-Cl BP. They found that natural mixed microbial populations degrade monohalogenated biphenyls through halogenated benzoate intermediates.

The total degradation of 4-Cl BP was accomplished by the combined effort of two bacterial strains under laboratory conditions.[34] One strain converts 4-Cl BP to 4-chlorobenzoate and the second utilizes 4-chlorobenzoate. Natural selection, under the PCB-contaminated situation, may have effected the coexistence of these two sets of degradation genes within an aquatic ecosystem.

Reichardt[35] found that the comparative rates of biodegradation in seawater were in the order BP > 2-Cl BP > 4-Cl BP > 3-Cl BP. There the turnover time of monochlorinated biphenyls in an Alaskan estuary was estimated to be on the order of one year at a concentration of

0.1 μg/l or less, but with longer turnover times at higher concentrations. No significant buildup of partially degraded products was observed.

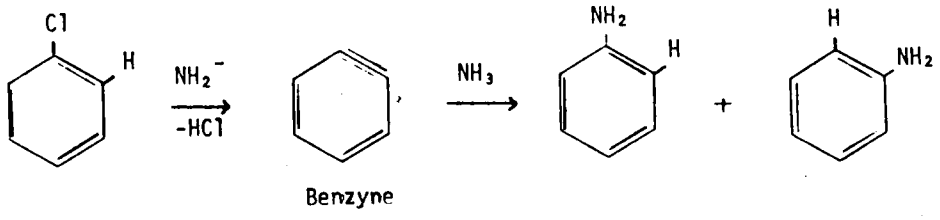
The order of degradation of monochlorobiphenyls can be explained by relief of steric strain. An ortho-chlorine substituent will, due to its size, increase the activation energy for the biphenyl system to achieve planarity.[30] Its expulsion will lead to far greater relief of strain than if the chlorine had been at the 3- or 4- position, and therefore 2-chloro-substituents are lost more easily.

What is the mechanism by which the meta- and para-phenylphenols are formed from 4-Cl BP? One possibility is that the aryl halide reacts via an S_N1 mechanism, that is, dissociation to an aryl cation ($C_6H_5^+$) followed by nucleophilic attack.[36] The $C_6H_5^+$ cation is an extremely high energy species.

$$C_6H_5Cl \longrightarrow C_6H_5^+ + Cl^- \xrightarrow{Nu^-} C_6H_5Nu$$

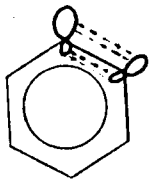
The positive charge originates from a vacant orbital in the plane of the ring, orthogonal to the π system and not stabilized by delocalization other than a little hyperconjugation with the ortho C-H bonds.

An elimination-addition mechanism was proposed by Roberts[37] to explain cine-substitution, where the incoming nucleophile may attack the position ortho to the vacated by the leaving group.



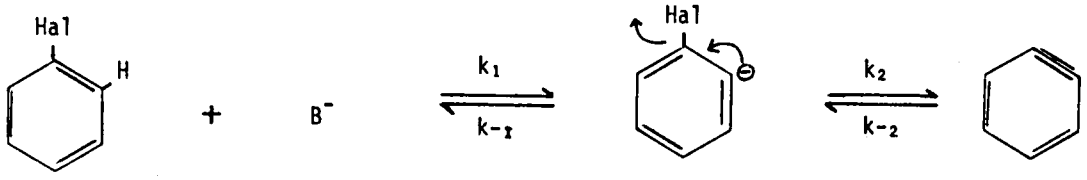
Benzyne

The intermediate benzyne (dehydrobenzene) has a weak extra bond formed by diagonal interaction of the sp^2 orbital. The overlap is about half that of an ordinary benzene π bond.



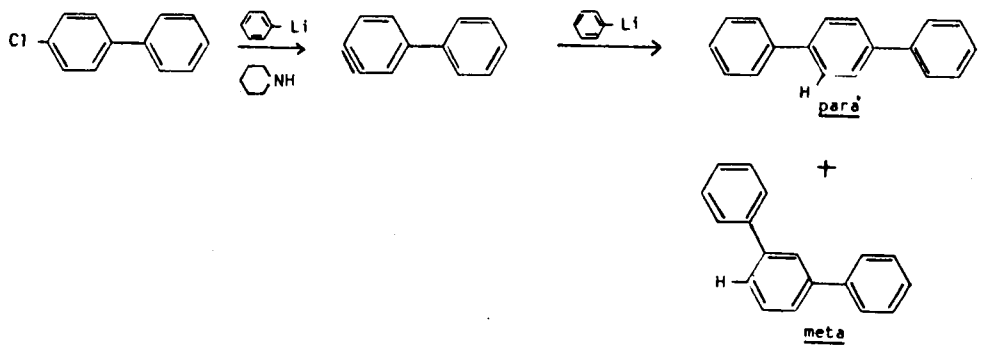
Benzene

The behavior of this elimination-addition mechanism is understood in terms of a two-step formation of the aryne:[7]



Chloride, although somewhat more reactive than fluoride, still leaves slowly and step 2 is rate-determining.

In the piperdine-catalyzed reaction of p-chlorobiphenyl with phenyllithium, which Huisgen, Sauer and Hauser studied, both the para- and meta-isomers were formed.[38]



The results of their work are shown in Table 11. These demonstrate that, although a small percentage more meta-isomer was formed than para-, the product distribution is close to equal when no piperdine was present. The amount of meta-isomer formed increased as greater amounts of piperdine were added.

Table 11

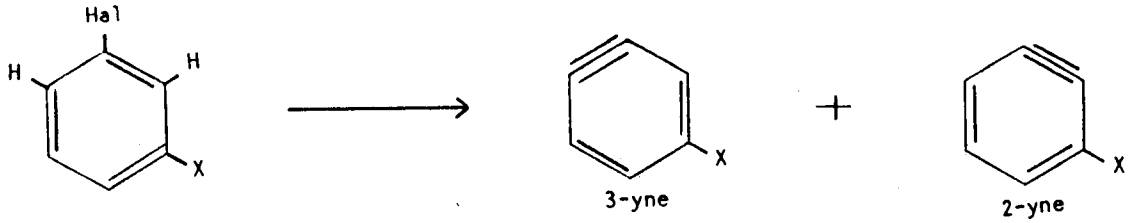
Piperdien-Catalyzed Reaction of P-Chlorobiphenyl with Phenyllithium[a]

mmol Piperdine and time of addition	rxn time (hrs)	Product distribution[b] %para:%meta
0	6	48:52
3 mmol added after 0, 1 and 2 hrs	6	45:55
5 mmol added after 0, 2.5 and 5 hrs	9	44:56

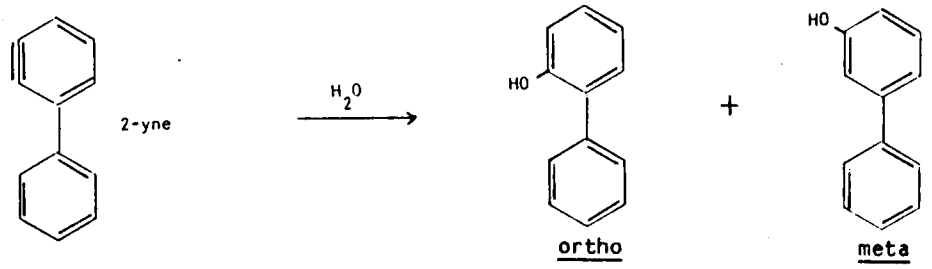
[a] 25 mmol para-chlorobiphenyl was mixed with 58 mmol C_6H_5Li in 110 ml ether and heated under reflux.

[b] Analyzed by IR with a calculated error of ±1.5%.

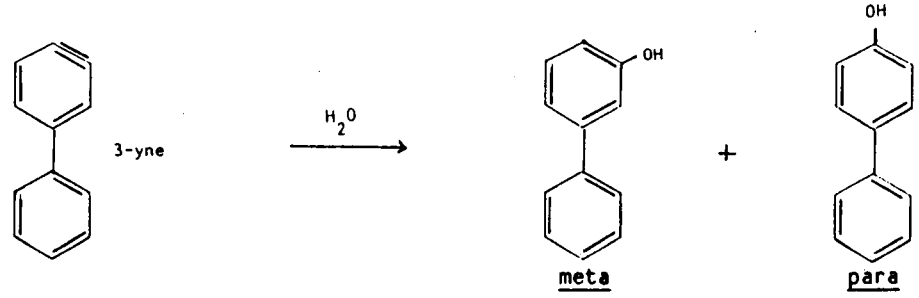
Irradiation of 4-Cl BP yields both meta- and para-phenylphenol. It is not known whether or not the 3-chlorobiphenyl and the 2-chlorobiphenyl likewise yield a mixture of isomers. Meta-substituted halogenobenzenes can generate two different arynes.[7]



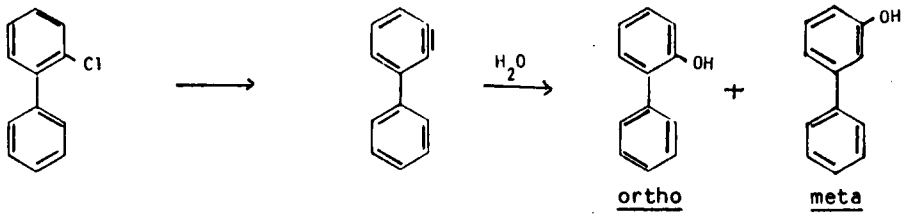
Which aryne predominates depends upon the substituent X and on which step in the dehydrohalogenation is rate-determining. With meta-chlorobiphenyl, the formation of the 2-yne, below, would give ortho- and meta-phenylphenol.



The dominance of the 3-yne, shown below, would yield the meta- and para-phenylphenolds, identical to what was observed from 4-Cl BP in the previous experiments.



Ortho-chlorobiphenyl would yield the ortho- and meta-phenylphenolds if the same mechanism controls the hydroxy addition in this case.



Which phenylphenol isomers are formed could be readily determined by performing isotopic dilution experiments on the photoproducts of labelled 2-Cl BP and 3-Cl BP.

In conclusion, while future studies can resolve the question of which mechanisms control the photoreactions and provide more specific data about the fate of higher chlorinated species, this study yielded much information about monochlorinated biphenyls. One can now begin to imagine their fate in the environment.

In terms of the chlorinated biphenyls already present in the aqueous ecosystem, it has been shown that the presence of oxygen inhibits their breakdown. The photoproducts formed in the presence of clay, which is also present naturally, are the same as those produced in the presence of oxygen and their formation is also relatively slow. Other researchers[34] have shown that bacterial greakdown of chlorinated biphenyls occurs in the laboratory, and presumably in the environment.

Of the monochlorinated biphenyls, the ortho-substituted isomer breaks down faster than the meta-, which in turn, reacts more readily than the para-isomer. While it was already known from Bunce's work[10] that the products formed in cosolvent mixtures were not

necessarily the same as those formed in water, this study corroborated that finding. Different photoproducts were observed here, namely the absence of BP from irradiation of 4-Cl BP, than were reported for photoreactions performed in cosolvent solutions.[2] Therefore the photoproducts formed as a result of irradiating PCBs in cosolvents cannot be assumed to be the same as those formed in water in the environment. Further studies must be performed in the laboratory in water to postulate as to what happens in the environment in water.

CHAPTER III

EXPERIMENTAL SECTION

Sample Preparation

At the beginning of this project, aqueous solutions of 4-chlorobiphenyl (99% purity from Ultra Scientific) were prepared by adding a known amount of 4-Cl BP to water and stirring magnetically for about two days. The mixture was then filtered through sintered glass before its introduction into the photolysis tube. This method later proved to be unsatisfactory and so the weighed sample was introduced directly to the photolysis tube equipped with a magnetic stirrer.

In preparing solutions of C-14 labelled 4-Cl BP, the compound itself was dissolved in a small amount of acetone. The desired amount was measured by syringe into the photolysis flask. Ring-uniformly labelled ^{14}C-4-chlorobiphenyl was obtained from Pathfinder Laboratories. It was greater than 98% pure and had a specific activity of 9.86 mCi/mmol. Typically, a concentration of approximately 1.25×10^{-3} mg/l or 5.65×10^{4} CPM per ml was prepared.

While doubly distilled water was used for some experiments, lake water was used for others. Lake water was collected from Center Hill Reservoir, Tennessee, and filtered through a micropore filter prior to use. A UV-visible spectrum showed no absorbance in the 200-600 nm range.

Sample irradiation was accomplished by exposure to a 450-watt water-cooled medium pressure Hanovia mercury lamp for a set time

between 3 and 100 hours. A pyrex sleeve, which cuts off transmission below 275 nm, was positioned around the lamp and both were fitted into a quartz well for cooling.

After photolysis, the photoproducts were removed from the aqueous layer by extracting with four portions of ethyl acetate equal in volume to the aqueous layer. These were dried over magnesium sulfate, filtered and the solvent removed via rotary evaporation. An appropriate amount between 1-3 ml of methanol or ethyl acetate was reintroduced to the photoproducts in preparation for analysis.

The kaolin used in these experiments, which were performed by L. T. Evans, was acid-washed American standard obtained from Fisher Scientific. Typically, 750 µl of labelled 4-Cl BP in acetone was added to 150 mg of kaolin clay and 50 ml of water. The mixture was stirred magnetically, under nitrogen if desired, for about 30 minutes. The nitrogen stream was removed and the flask sealed. The flask was then irradiated for a predetermined time period.

After irradiation, the flask was centrifuged to separate the aqueous layer from the solid. The liquid was decanted from the solid and the photoproducts extracted. The material adhering to the clay was removed by adding ethyl acetate and shaking vigorously for several minutes on a mechanical shaker. This extract was labelled as the clay layer extract while the other was the aqueous layer extract. These extracts were analyzed with HPLC and liquid scintillation.

Analytical Techniques

The samples were analyzed on a Perkin-Elmer Series 2 liquid chromatograph using a C 18/10 0.46 x 25 CMLC column and Perkin-Elmer LC-75 Spectrophotometric detector. The following conditions were set as standards, unless specified otherwise in the text:

solvent ratio	75% methanol-25% water
flow rate	2 ml/min
detector wavelength	247 nm

In addition, a Hewlett-Packard model 3390A integrator-recorder was used.

For some experiments, fractions were collected using a solvent gradient of 60-75% methanol which increased at a rate of 1% per minute. Fractions were collected at 1-minute intervals by positioning a scintillation vial beneath the HPLC output. At the end of 1 minute, another vial was put into the same position for the same time period. At the end of the run, 15 ml of scintillation cocktail (to each 1 l of dioxane was added 8 g. of omnifluor which is a mixture of 98% 2.5-diphenyl-oxazole plus 2% bis-MSB) was pipetted into each vial containing the collected 2 ml. These vials were allowed to equilibrate overnight prior to counting.

These radiolabelled fractions were analyzed using a Tracor Analytic Model 6892 liquid scintillation system which was programmed to count each vial for two minutes. The level of channel A was set to 90-620 while that for channel B was 350-620. Channel A levels were considered for data analysis. Reliable data is considered to be

approximately four times background or about 300 counts per minute (CPM).

In order to separate the meta- and para-phenylphenols for analysis by gas chromatography (GC), chloroacetate derivatives were prepared using the procedure of R. J. Argauer.[33] Following this procedure, 10 µl of the phenylphenol in benzene (approximate concentrations of 1 µg/µl) was introduced into a flask to which was added 15 ml of 0.25 N NaOH and 10 ml reagent (1 g of chloroacetic anhydride per 200 ml benzene). The flask was shaken for exactly 2 minutes on a mechanical shaker. The benzene and water layers readily separated and so 5-µl aliquots were removed directly from the benzene layer for injection into the gas chromatograph.

A Perkin-Elmer Model 3920 Gas Chromatograph was equipped with a capillary column containing dimethyl silicone polymer maintained at 140°C. The injection heater was at 220°C while the interface was at 180°C. Nitrogen carrier gas was used. The electron capture detector was heated to 350°C. Under these conditions retention time had to be sacrificed for better separation; therefore, the 3-OH BP derivative had an approximate retention time of 40.7 minutes while that of the 4-OH BP derivative was 44.5 minutes.

pH Measurements

Reactions in which pH was studied as a function of time were performed in a circulating photolysis apparatus, Figure 32. This apparatus, made from the suggestions of G. H. Weeks, allowed the pH

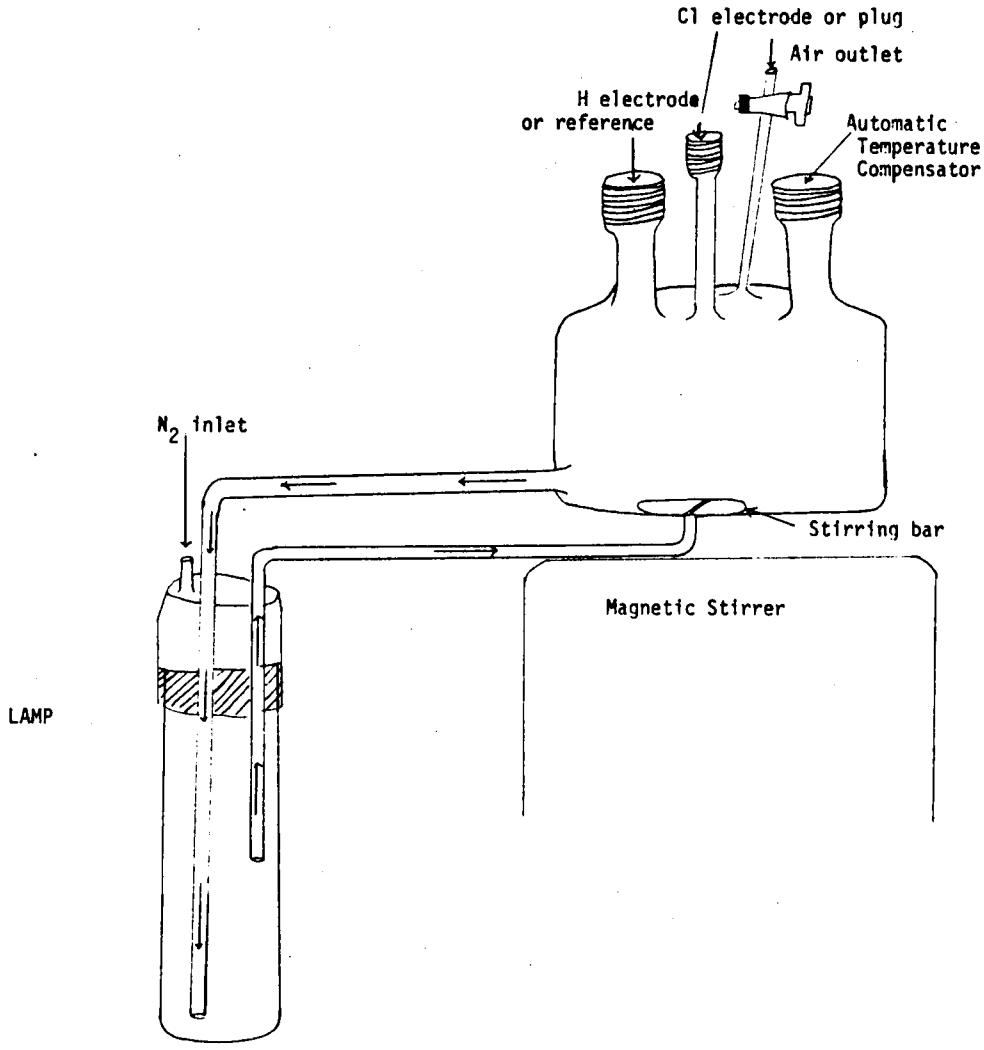


Figure 32. Circulating Photolysis Apparatus.

to be measured with no interruption of the light. The combination electrode, Ross model 81-02, and automatic temperature compensator, Fisher model 13-636-17, were fitted into the upper right portion and did not come into contact with the lamp. The lower left side was clamped next to the lamp and both were covered with aluminum foil during the irradiation.

If it was desired, nitrogen is introduced as indicated. The magnetic stirrer kept the solution constantly circulating.

A Fisher Accumet Model 810 pH meter was used for measurement.

pCl Measurements

It was thought that by using a chloride ion specific electrode and following the pCl instead of pH of the degradation experiments, the buffering effect of the carbonates in lake water could be eliminated, giving a more accurate representation of the reactions. A Lazer Research Laboratories Model IS-146 chloride specific electrode was used in the apparatus depicted in Figure 32 along with a Lazer Model DPH-1 double junction reference electrode.

At the onset of the reaction, an initial millivolt datum was recorded, but after this time erroneous results were observed. The millivolt values jumped erratically as if the electrodes were not actually in the solution. Since the electrodes maintained good contact with the solution at all times and these same results were obtained in several attempts, it was postulated that the 4-Cl BP compound present in the solution actually coated the electrode. This resulted in the electrode

being in direct contact only with the chloride coating but not with the aqueous solution. A solution to this problem was never found, so the use of the chloride sensitive electrode was abandoned.

Deoxygenation

The nitrogen gas used to deoxygenate the solutions was prepurified from MG Scientific. Prior to its entry into the sample, it flowed through a deoxygenating line which consisted of four bubblers. The procedure of L. Meites and T. Meites[39] was slightly modified. The first two bottles contained 0.1 M vanadyl sulfate over amalgamated zinc.[40] Concentrated sulfuric acid was added dropwise to each of these solutions until the characteristic blue color returned and stabilized. The third bottle contained water and the fourth drierite crystals.

Occasionally, the solution in the first two bottles turned brown. At this time they could be revitalized simply by adding H_2SO_4 until the blue color was once again stable.

Isotopic Dilution Experiments

Biphenyl

A sample of ^{14}C-labelled 4-Cl BP (with specific activity of 9.86 mCi/mmol) was shown to have 5.50×10^4 CPM/μl in acetone.

Biphenyl was recrystallized in a 3:1 ratio of carbon tetrachloride: toluene a total of three times for a constant melting point of 70.0°C, 7.50 mg of this was dissolved in 1 ml of acetone and 1 ml of water in a

vial to which dioxane scintillation cocktail was added. The average counts obtained were 168 CPM, well within the background range, therefore this BP had no inherent radioactivity.

To 57.0 mg of BP was added a portion of an aqueous layer extract, obtained from irradiation of 4-Cl BP under oxygen in distilled water to which clay was added. This combination was recrystallized three times to constant melting point. Finally, 7.65 mg of this solid was dissolved in 1 ml acetone and 1 ml water in a scintillation vial to which was added the cocktail. The average number of counts (250.9 CPM) was well within the background range. This experiment showed that BP was not formed under the experimental conditions described above.

Analogously, a sample of eluent, which was obtained from the irradiation of 4-Cl BP in distilled water under oxygen but without clay, was treated as described for the clay reaction above. The final counting in this case yielded an average of 268.0 CPM. If BP had been formed, it would have been detected by this technique which is so sensitive that as little as 5.33×10^{-9} grams can be detected reliably.

Phenylphenols

A sample of 4-Cl BP (^{14}C ring labelled) was irradiated and during HPLC analysis, the eluent for the retention time of phenylphenols was collected. Meanwhile, 3-OH BP and 4-OH BP were recrystallized in methanol. The procedure outlined for BP was followed in this case. After several recrystallizations of 3-OH BP plus radioactive

eluent and likewise 4-OH BP plus eluent, the final counting yielded an average of 44,676 CPM for 3-OH BP and an average of 46,858 CPM for 4-OH BP. This leads to the conclusion that both isomers are produced from irradiation of 4-Cl BP. Approximately 49% 3-OH BP and 51% 4-OH BP are being formed.

Extraction Efficiency

In order to determine whether or not the extraction method which was chosen to remove the photolysis products from the water was adequate for this application, the following experiment was performed to determine the efficiency extraction. Labelled 4-chlorobiphenyl dissolved in 0.5 ml ethyl acetate was added to 25 ml of distilled water. Two 5 ml samples were pipetted into scintillation vials labelled 0 to which was added 10 ml of the dioxane scintillation cocktail.

Of the remaining 15 ml, 5 ml were removed by pipette to a separatory funnel to which was added an equal amount of ethyl acetate. The funnel was shaken and the layers separated. The ethyl acetate layer which now should contain the radiolabelled compound was put into a scintillation vial labelled 1 to which the same cocktail was added. The water layer was returned to the separatory funnel and the procedure repeated with another 5 ml of ethyl acetate. The organic layer was labelled 2. The procedure outlined above was repeated until five organic layers from five extractions were produced. Appropriate amounts of scintillation cocktail were added to each vial. The vials were allowed to equilibrate overnight. These vials were then

put into the scintillation counter for analysis. The results of two repetitions were averaged in Table 12.

Table 12

Extraction Efficiency

Vial #	CPM	% of total collected
0	2,653,324	–
1	2,412,228	90.91
2	117,848	95.35
3	29,558	96.46
4	17,623	97.12
5	7,876	97.42

By numerically averaging the data, it was shown that 90.91% of the total sample is collected in the first extraction. The next extraction yields 4.44% of the total and the third, fourth and fifth produce 1.11%, 0.66%, and 0.30% respectively. After five extractions, 97.42% of the total sample is collected from the aqueous layer. Further extractions would increase the percentage of the total sample but with only marginal utility. This technique was proven to be sufficiently sensitive for the bulk of the experiments to be performed.

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APPENDIXES

APPENDIX A

pH STUDIES OF 4-CHLOROBIPHENYL

Table A-1

pH Values for Reaction A[a]

Reaction time (min)	pH	pH-pHo*
15	6.66	0
35	6.41	-0.25
75	6.11	-0.55
1,425	5.21	-1.45
2,150	5.11	-1.55
2,860	5.07	-1.59
3,540	5.07	-1.59
4,185	5.07	-1.59
4,320	4.87	-1.79
4,500	4.85	-1.81
5,625	4.78	-1.88
5,700	4.78	-1.88

[a] 4.72×10^{-6} M 4-Cl BP in distilled water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 6.66.

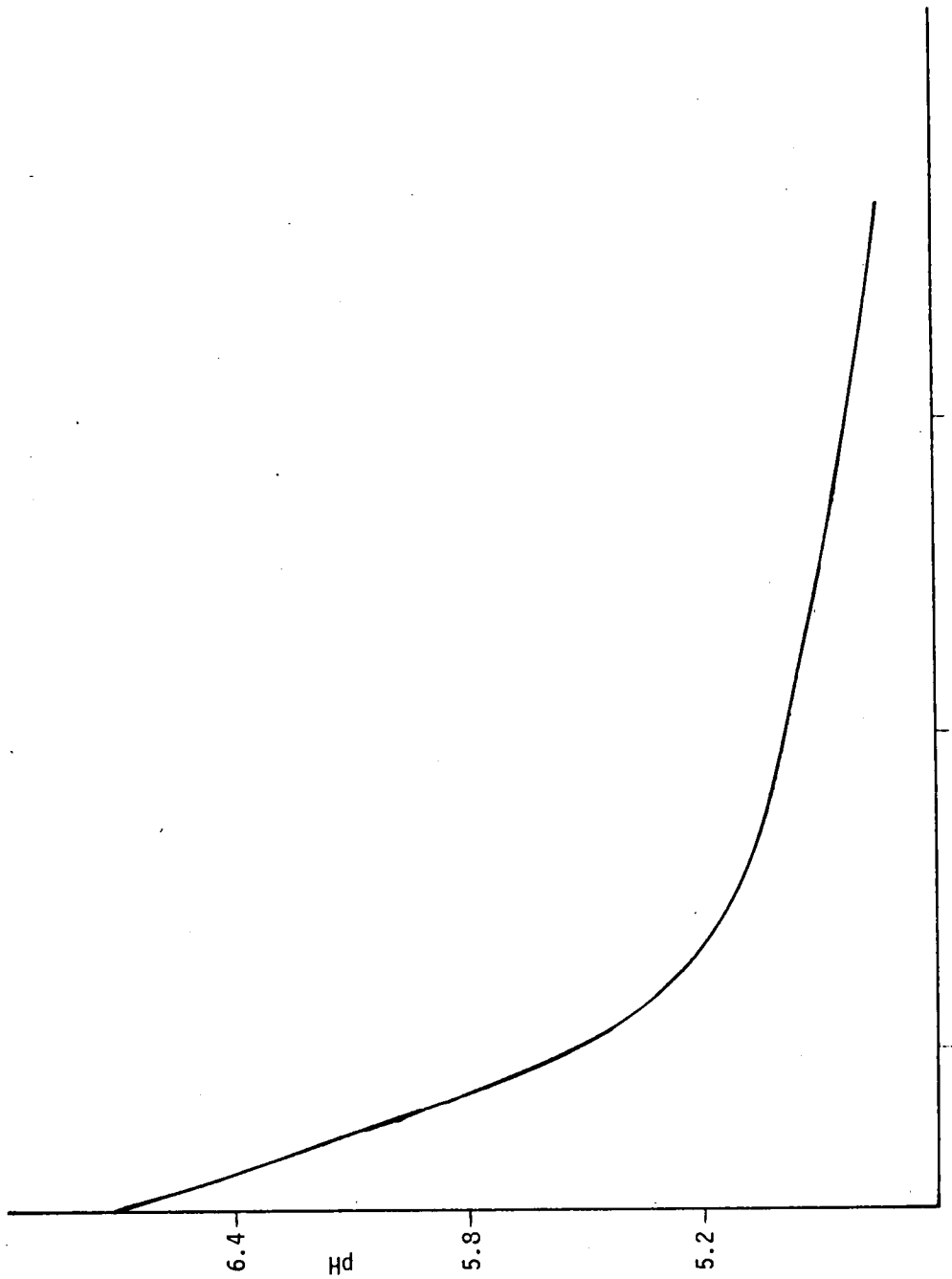


Figure A-1. Reaction A.

Table A-2

pH Values for Reaction B[a]

Reaction time (min)	pH	pH-pHo*
0	7.12	0
10	7.04	-0.08
20	6.97	-0.15
30	6.90	-0.22
40	6.86	-0.26
50	6.83	-0.29
60	6.78	-0.34
320	6.73	-0.39
1,160	6.31	-0.81
1,210	6.28	-0.84
1,435	6.14	-0.98
2,630	5.77	-1.35
4,075	5.61	-1.51
4,195	5.59	-1.53
4,255	5.59	-1.53
5,490	5.53	-1.59
5,740	5.51	-1.61

[a] 1.42×10^{-5} M 4-Cl BP in distilled water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 7.12.

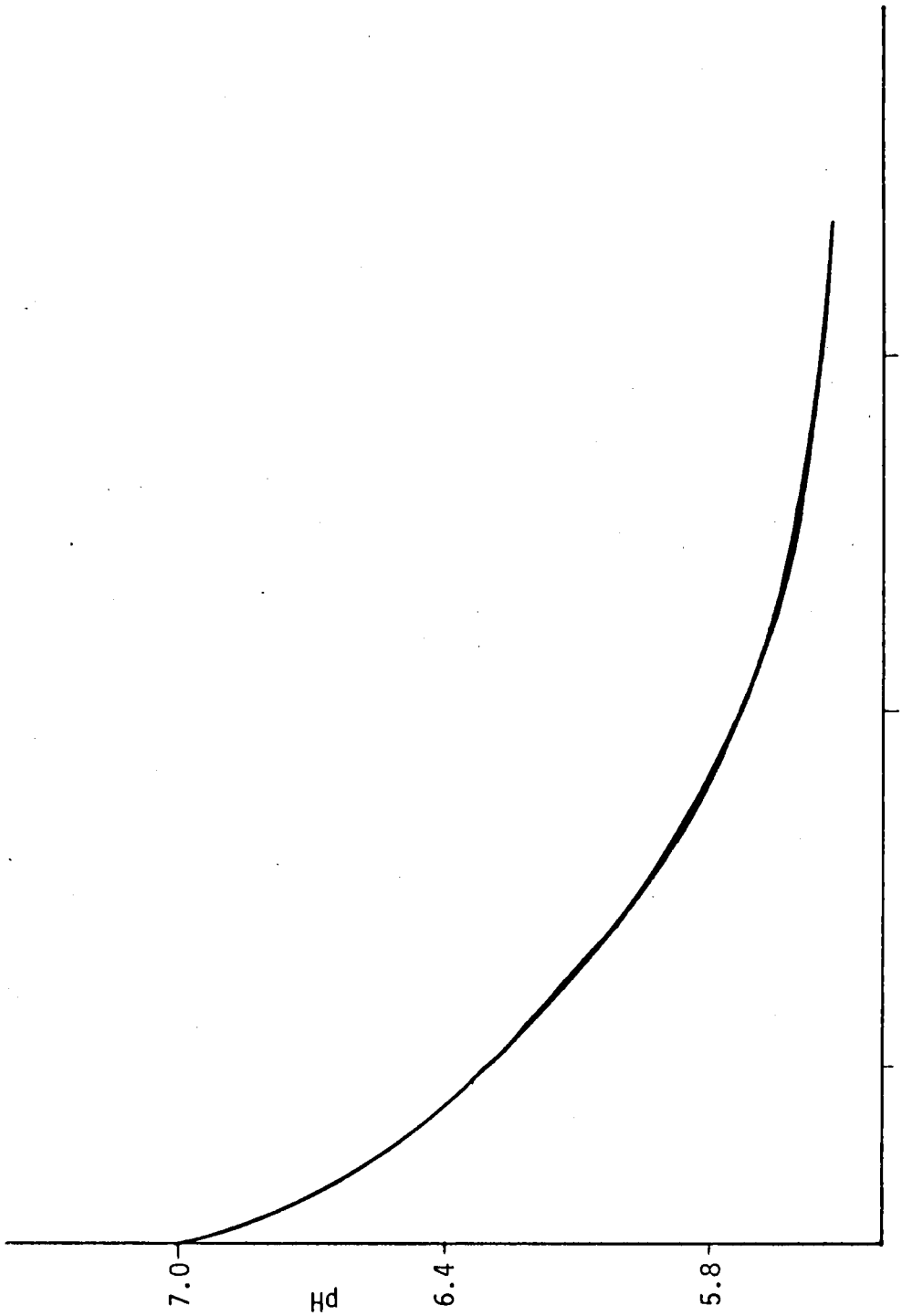


Figure A-2. Reaction B.

Table A-3

pH Values for Reaction C[a]

Reaction time (min)	pH	pH-pHo*
0	7.50	0
30	7.14	-0.36
60	6.89	-0.61
210	6.66	-0.84
1,290	6.73	-0.77
1,700	6.64	-0.86
2,070	6.62	-0.88
2,820	6.57	-0.93
4,200	6.47	-1.03

[a] 9.44×10^{-6} M 4-Cl BP in distilled water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 7.50.

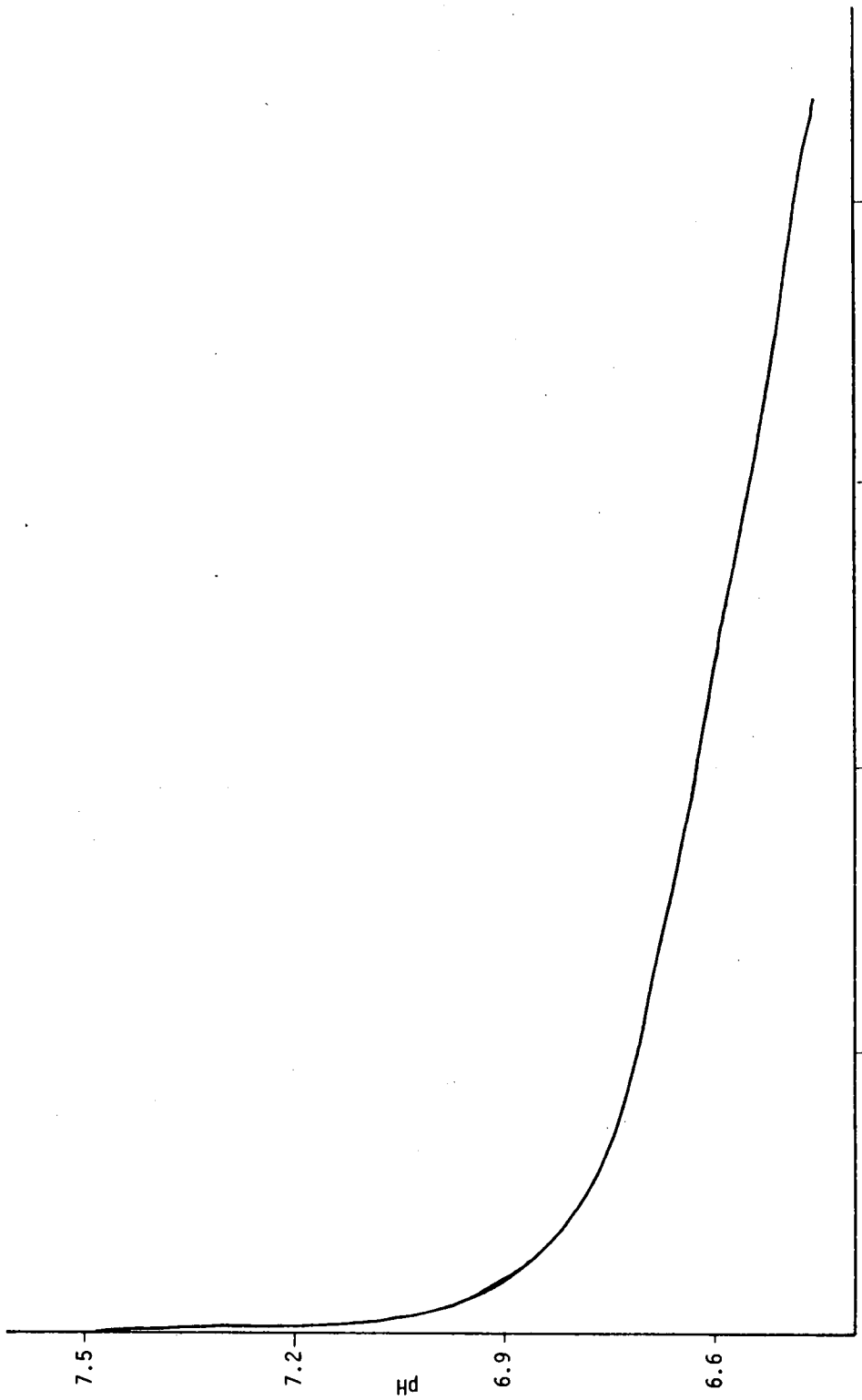


Figure A-3. Reaction C.

Table A-4

pH Values for Reaction D[a]

Reaction time (min)	pH	pH-pHo*
0	7.73	0
20	7.36	-0.37
35	7.28	-0.45
45	7.25	-0.48
60	7.23	-0.50
125	7.21	-0.52
375	6.98	-0.93
1,130	6.41	-1.32
1,190	6.39	-1.34
1,220	6.35	-1.38
1,250	6.34	-1.39
1,300	6.33	-1.40
1,395	6.32	-1.41
1,440	6.33	-1.40
1,585	6.28	-1.45
1,680	6.25	-1.48
2,665	6.10	-1.63
2,725	6.10	-1.63
2,925	6.10	-1.63
4,035	6.07	-1.66
4,775	6.03	-1.70
5,625	5.97	-1.76
5,685	5.97	-1.76
5,725	5.96	-1.77
5,910	5.95	-1.78
6,960	5.89	-1.84

[a] 4.72×10^{-6} M 4-Cl BP in distilled water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 7.73.

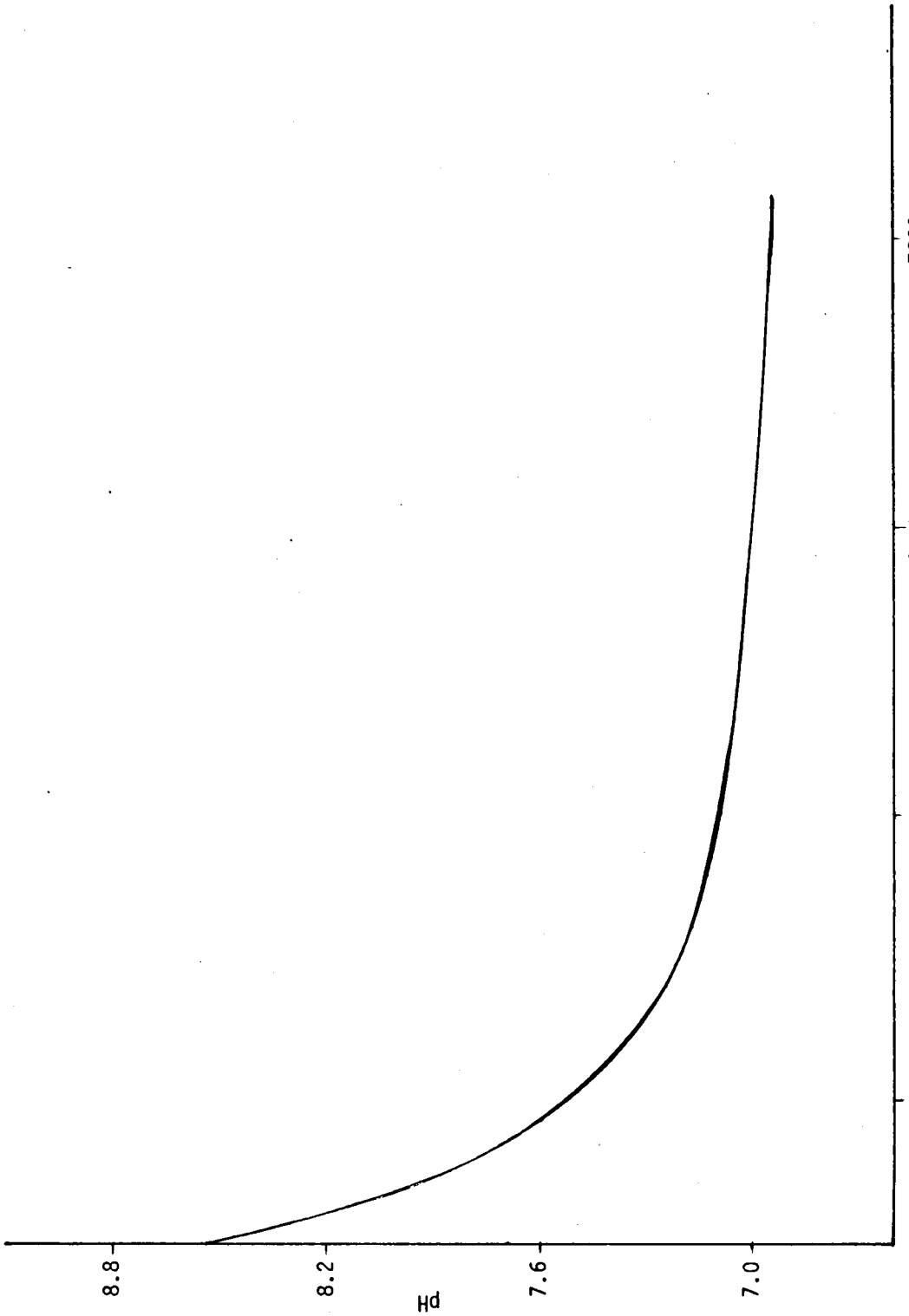


Figure A-4. Reaction D.

Table A-5

pH Values for Reaction E[a]

Reaction time (min)	pH	pH-pHo*
0	7.00	0
15	6.27	-0.73
30	5.98	-1.02
45	5.88	-1.12
55	5.81	-1.19
75	5.71	-1.29
90	5.65	-1.35
105	5.61	-1.39
120	5.57	-1.43
135	5.53	-1.47
150	5.51	-1.49
165	5.49	-1.51
180	5.47	-1.53
195	5.44	-1.56
210	5.42	-1.58
225	5.40	-1.60
240	5.38	-1.62

[a] 1.24×10^{-5} M 4-Cl BP in distilled water under oxygen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 7.00.

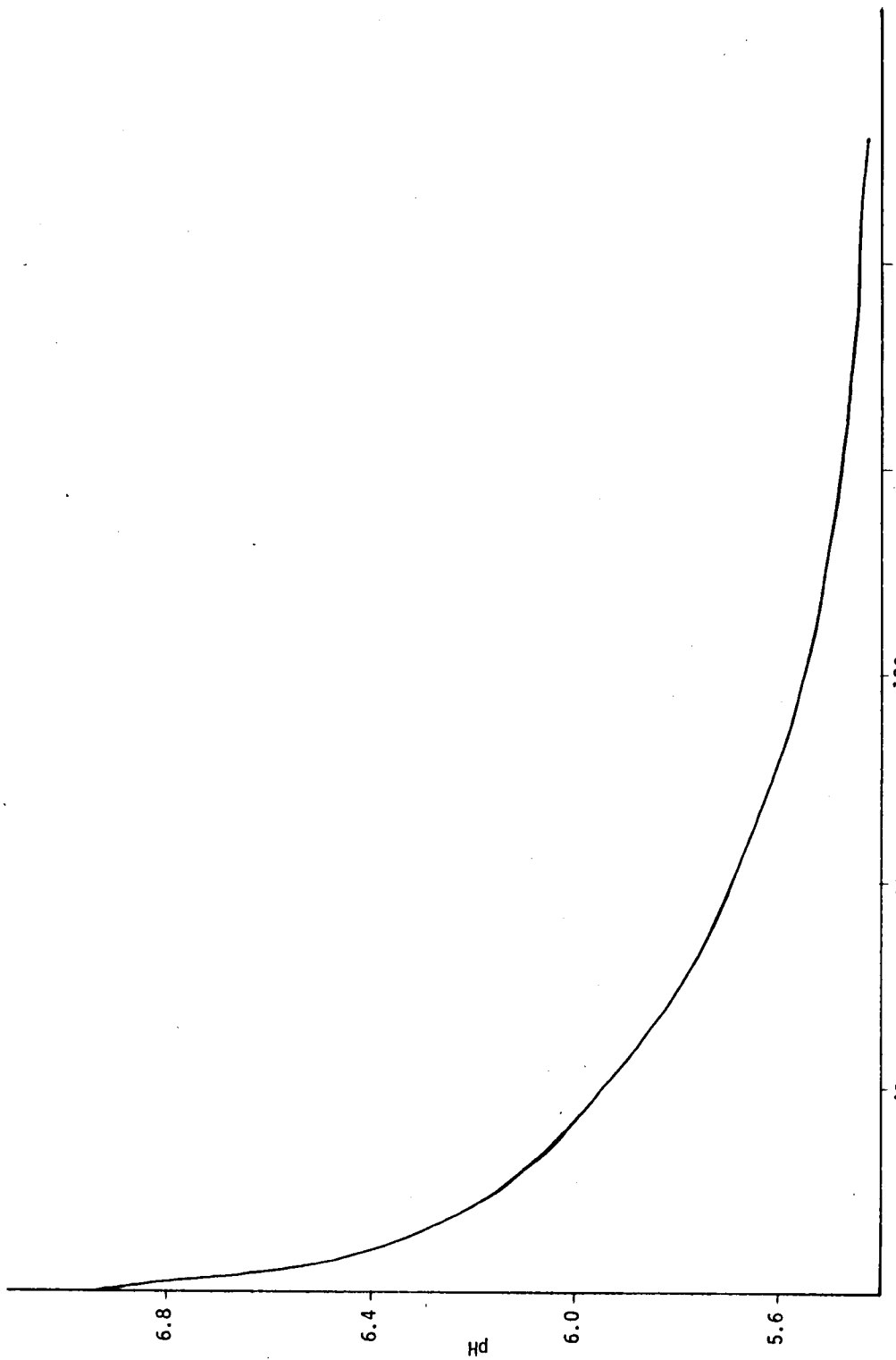


Figure A-5. Reaction E.

Table A-6

pH Values for Reaction F[a]

Reaction time (min)	pH	pH-pHo*
0	7.54	0
20	7.10	-0.44
50	6.74	-0.80
70	6.62	-0.92
90	6.60	-0.94
110	6.58	-0.96
130	6.58	-0.96
160	6.59	-0.95
190	6.60	-0.94
195	6.48	-1.06
215	6.48	-1.06
250	6.51	-1.03
325	6.58	-0.96

[a] 8.48×10^{-6} M 4-Cl BP in distilled water under oxygen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 7.54.

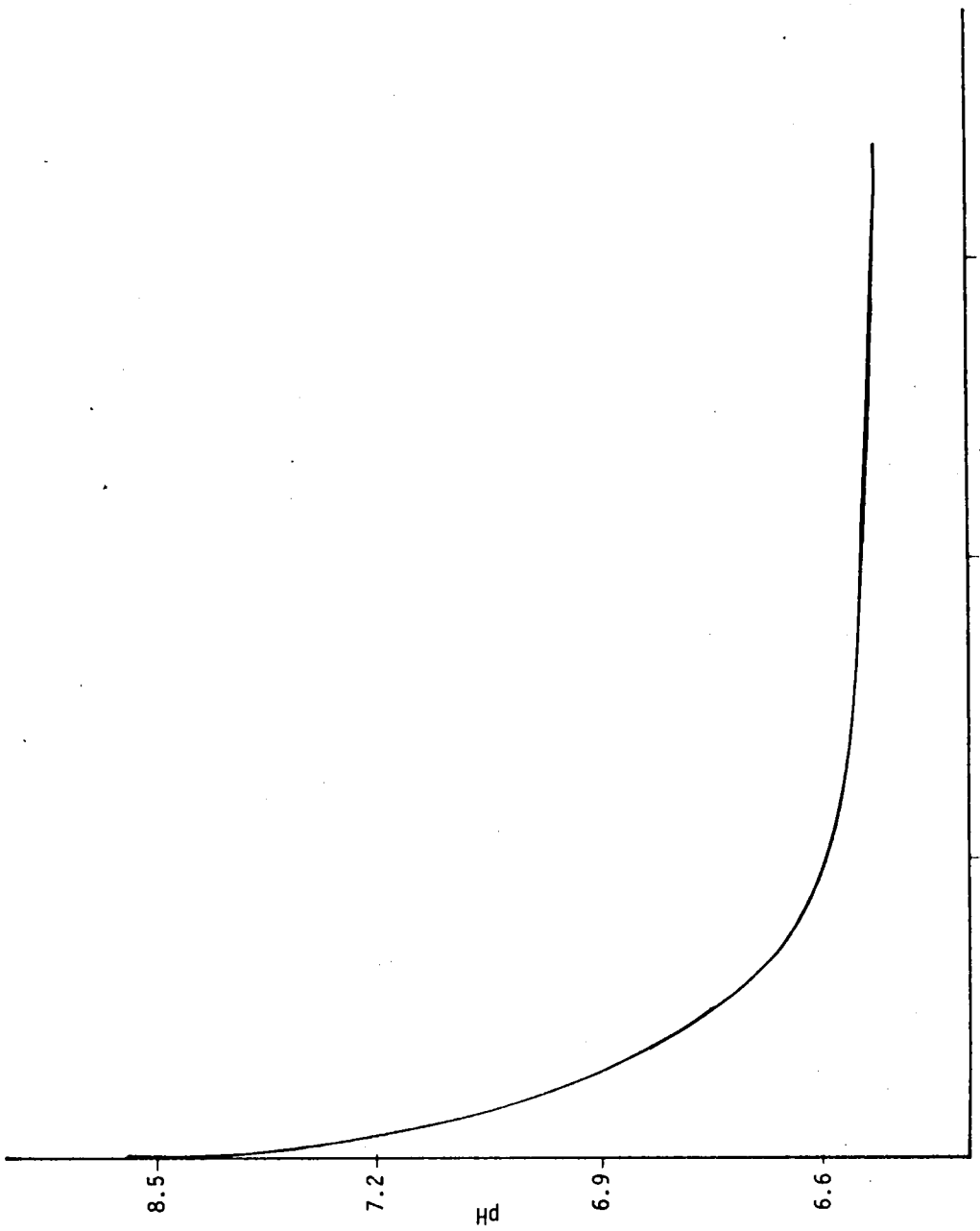


Figure A-6. Reaction F.

Table A-7

pH Values for Reaction G[a]

Reaction time (min)	pH	pH-pHo*
0	6.64	0
15	6.75	+0.11
30	6.66	+0.02
50	6.58	-0.06
60	6.55	-0.09
72	6.53	-0.11
85	6.51	-0.13
110	6.49	-0.15
120	6.48	-0.16
135	6.48	-0.16
150	6.47	-0.17
210	6.46	-0.18
240	6.44	-0.20
270	6.44	-0.22
330	6.32	-0.32
535	5.86	-0.78

[a] 1.24×10^{-5} M 4-Cl BP in distilled water under oxygen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 6.64.

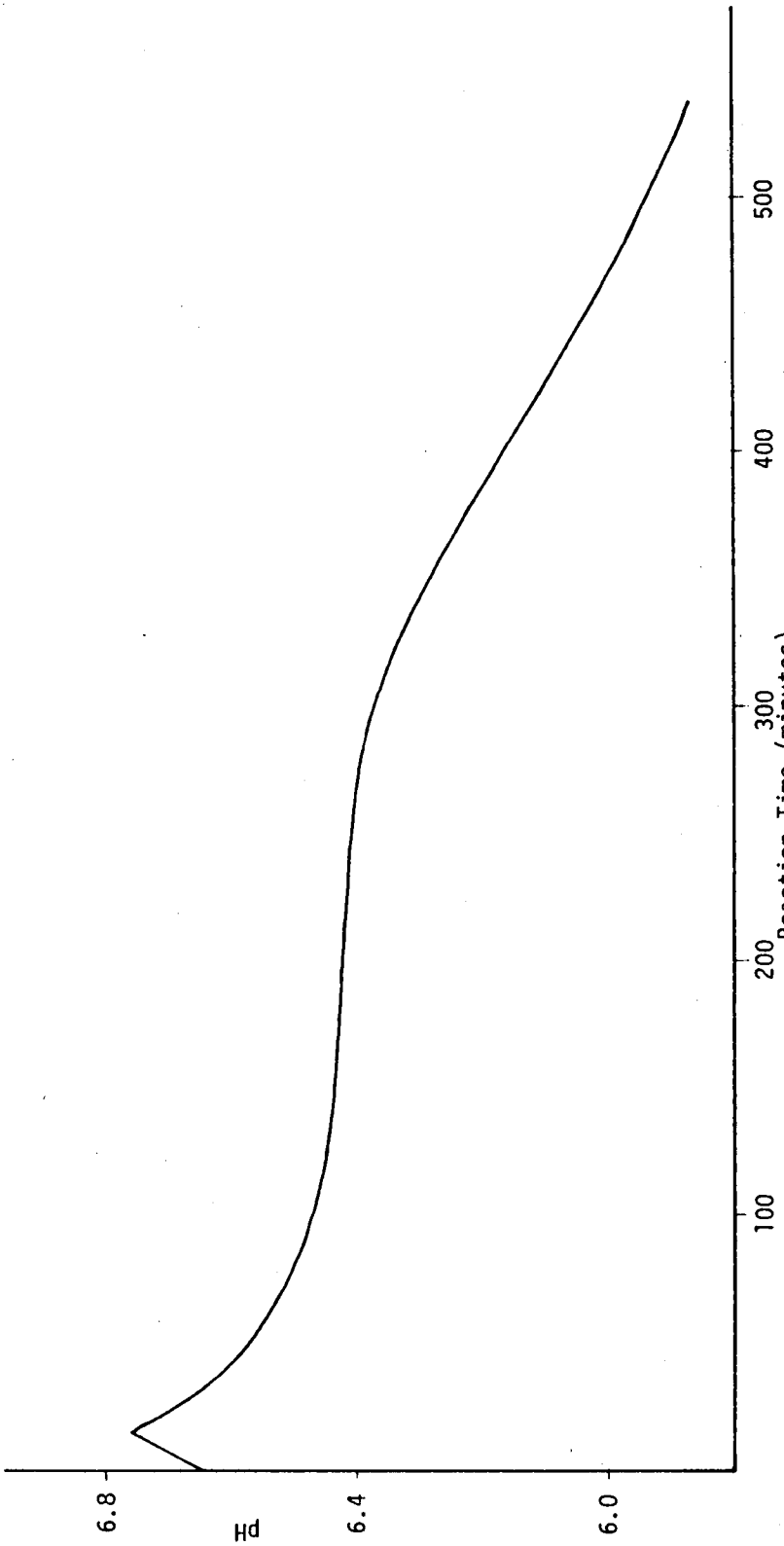


Figure A-7. Reaction G.

Table A-8

pH Values for Reaction H[a]

Reaction time (min)	pH	pH-pHo*
0	5.78	0
20	5.74	-0.04
50	5.78	0
80	5.78	0
110	5.74	-0.04
150	5.69	-0.09
185	5.62	-0.16
215	5.55	-0.23
252	5.48	-0.30
277	5.43	-0.35
340	5.37	-0.41
363	5.31	-0.47
410	5.18	-0.60
1,190	4.49	-1.29
1,242	4.47	-1.31
1,268	4.46	-1.32
1,305	4.44	-1.34
1,410	4.40	-1.38
1,450	4.38	-1.40
1,640	4.32	-1.46

[a] 5.30×10^{-6} M 4-Cl BP in distilled water under oxygen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 5.78.

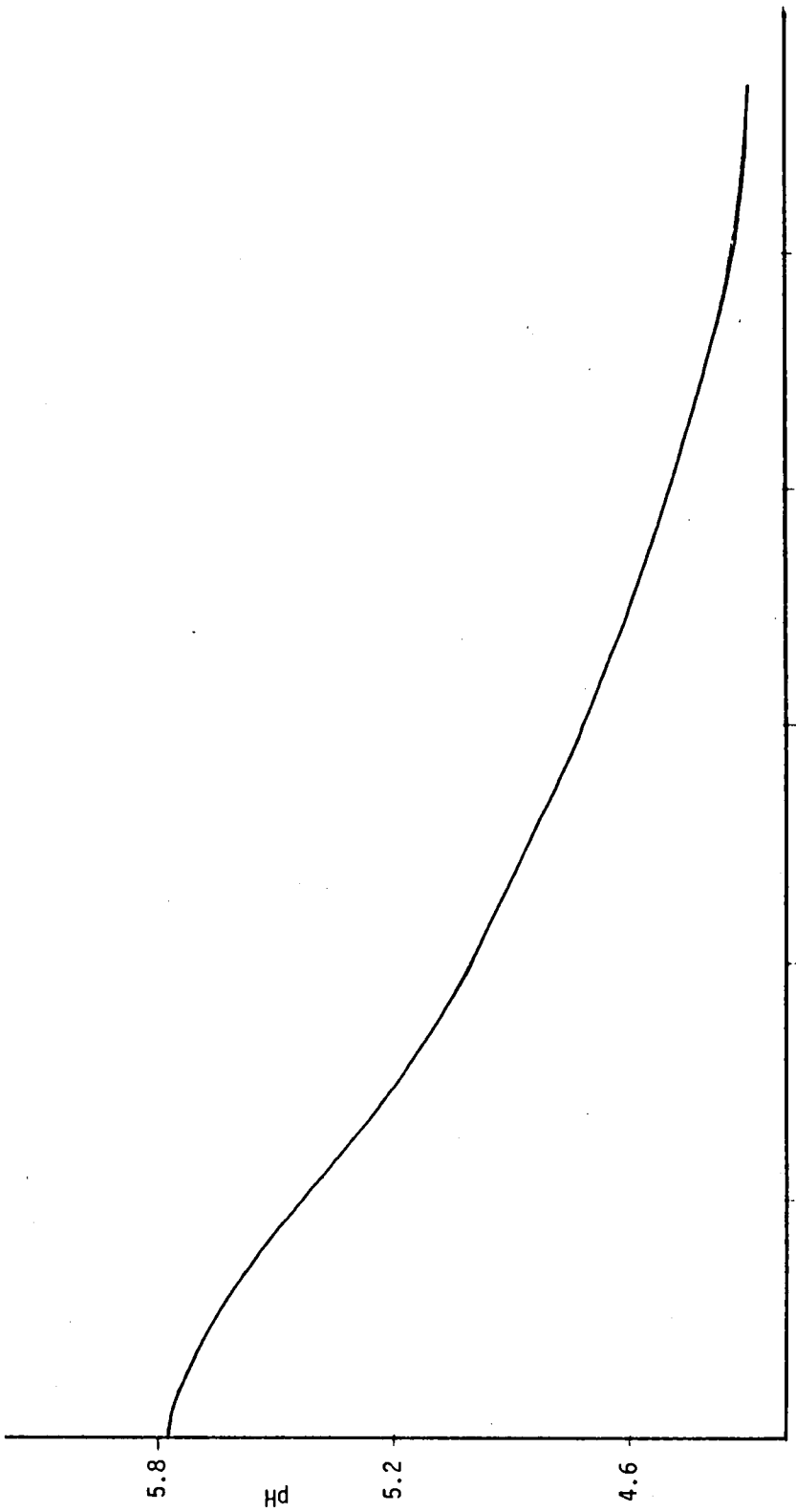


Figure A-8. Reaction H.

Table A-9

pH Values for Reaction I[a]

Reaction time (min)	pH	pH-pHo*
0	8.96	0
10	8.94	-0.02
20	8.87	-0.09
35	8.81	-0.15
40	8.80	-0.16
60	8.76	-0.20
95	8.72	-0.24
110	8.72	-0.24
140	8.71	-0.25
320	8.73	-0.23
1,200	8.71	-0.25
1,265	8.71	-0.25
1,315	8.69	-0.27
1,395	8.68	-0.28
1,440	8.68	-0.28
1,530	8.67	-0.29
2,630	8.62	-0.34
2,720	8.61	-0.35
2,765	8.61	-0.35
2,810	8.61	-0.35
2,885	8.60	-0.36
2,940	8.60	-0.36
3,030	8.60	-0.36
4,115	8.55	-0.41
4,255	8.54	-0.42
4,310	8.54	-0.42

[a] 9.44×10^{-6} M 4-Cl BP in lake water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 8.96.

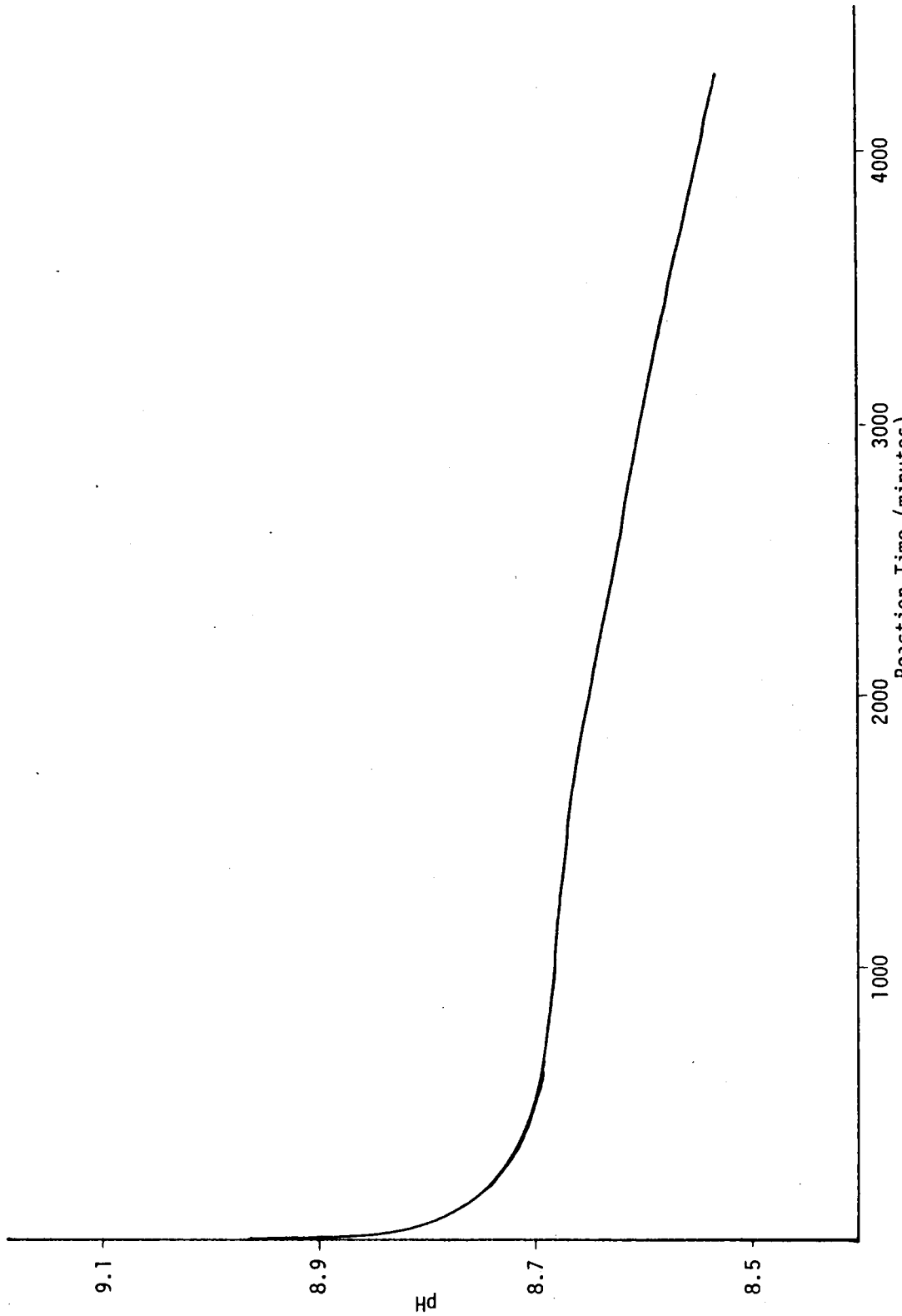


Figure A-9. Reaction 1.

Table A-10

pH Values for Reaction J[a]

Reaction time (min)	pH	pH-pHo*
0	9.00	0
15	8.96	-0.04
30	8.88	-0.12
45	8.83	-0.17
75	8.80	-0.20
120	8.77	-0.23
1,310	8.77	-0.23
1,385	8.77	-0.23
1,455	8.76	-0.24
1,670	8.74	-0.26
2,800	8.71	-0.29
2,905	8.70	-0.30
3,170	8.68	-0.32
3,510	8.72	-0.28

[a] 1.42×10^{-5} M 4-Cl BP in lake water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pH = 9.00.

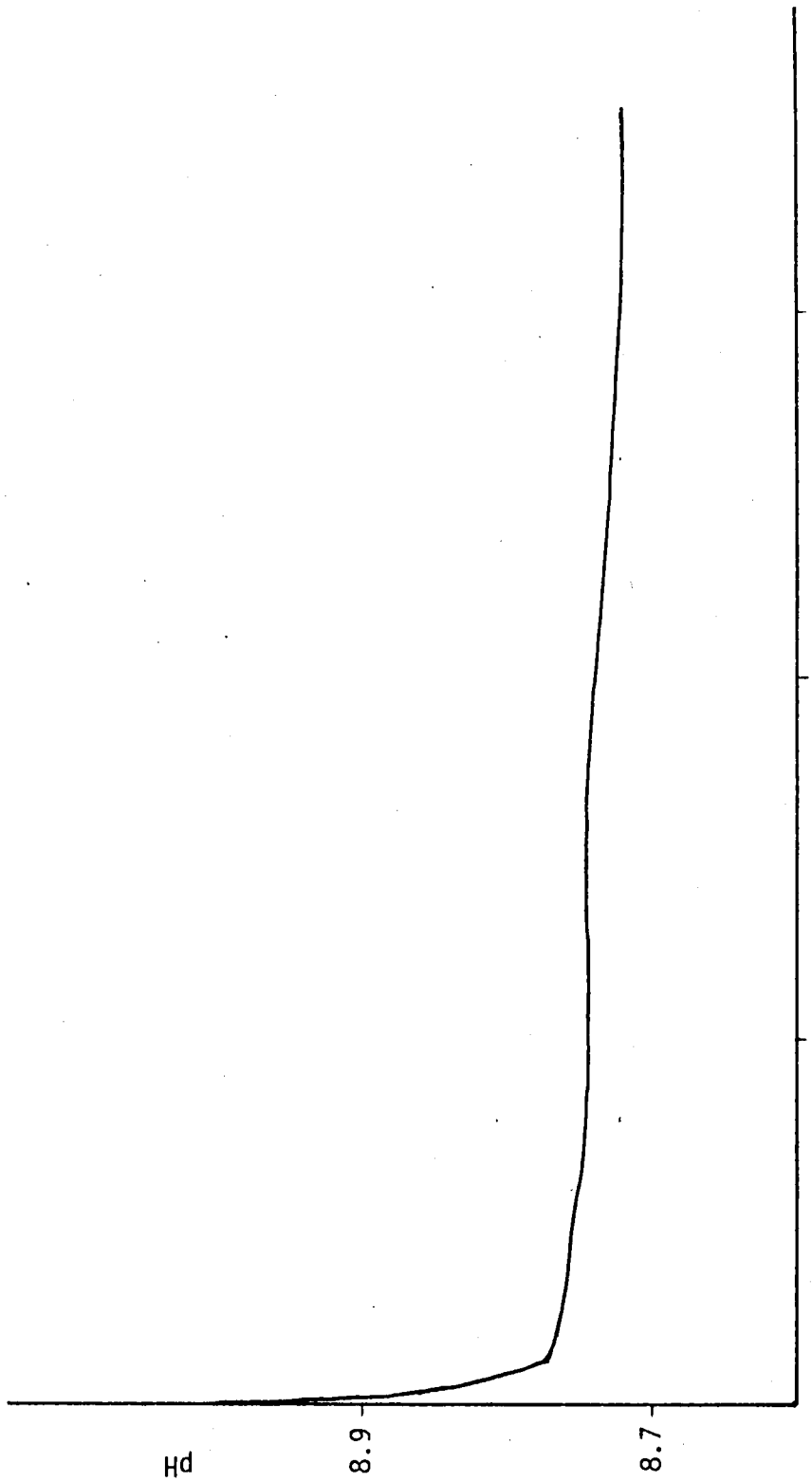


Figure A-10. Reaction J.

Table A-11

pH Values for Reaction K[a]

Reaction time (min)	pH	pH-pHo*
0	8.97	0
5	8.98	+0.01
10	8.97	0
20	8.94	-0.03
30	8.90	-0.07
45	8.87	-0.70
60	8.90	-0.07
90	8.84	-0.13
1,195	8.91	-0.06
1,245	8.69	-0.28
3,175	8.61	-0.36
4,075	8.53	-0.44
4,215	8.52	-0.45
4,370	8.50	-0.47
4,610	8.41	-0.56

[a] 1.65×10^{-5} M 4-Cl BP in lake water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 8.97.

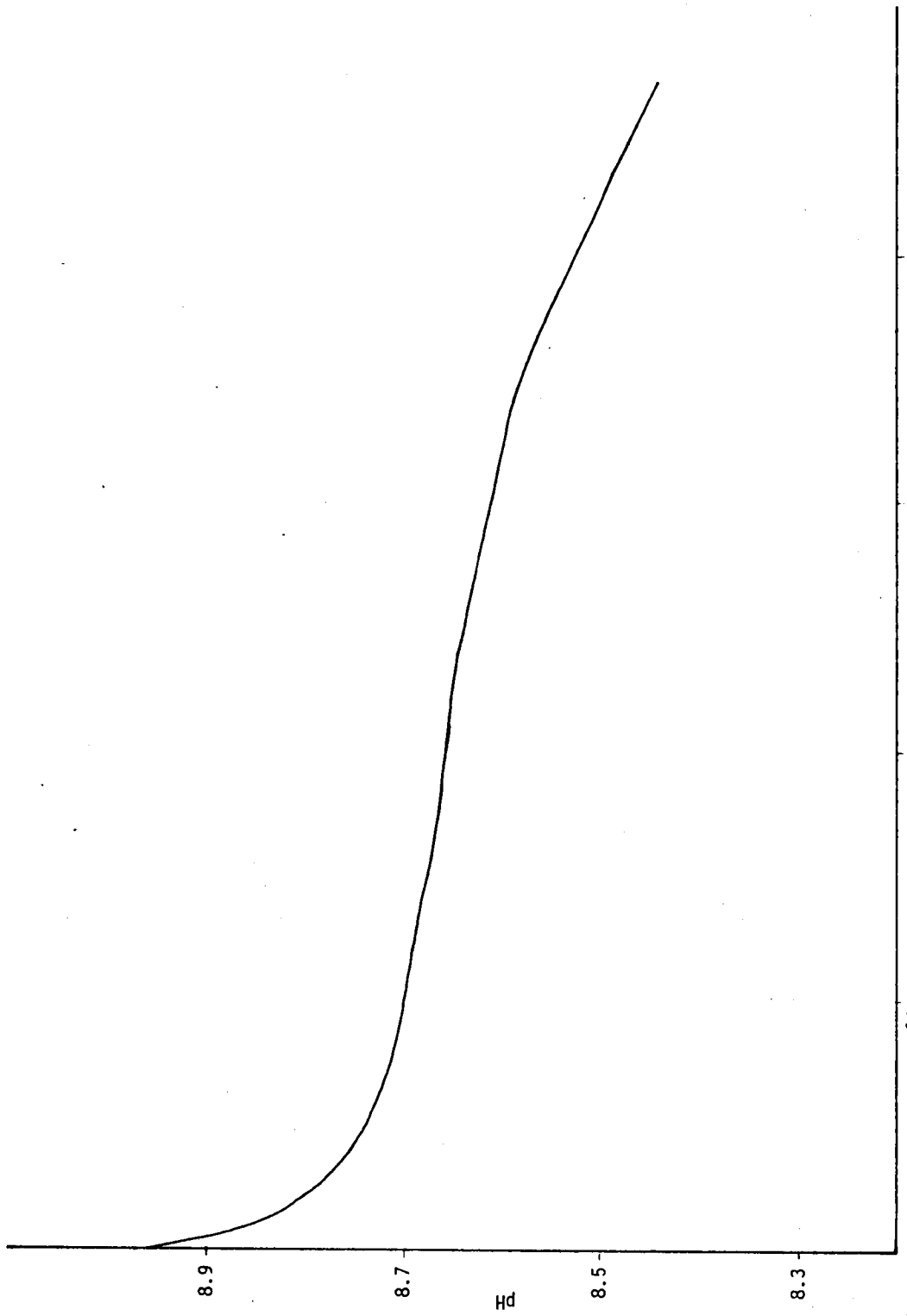


Figure A-11. Reaction K.

Table A-12

pH Values for Reaction L[a]

Reaction time (min)	pH	pH-pHo*
0	8.18	0
10	8.15	-0.03
465	8.11	-0.07
500	8.11	-0.07
1,155	8.09	-0.09
1,185	8.09	-0.09
1,250	8.10	-0.08
1,440	8.08	-0.10
1,470	8.08	-0.10
1,530	8.08	-0.10
2,600	8.12	-0.06
2,625	8.12	-0.06

[a] 1.33×10^{-5} M 4-Cl BP in lake water under oxygen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 8.18.

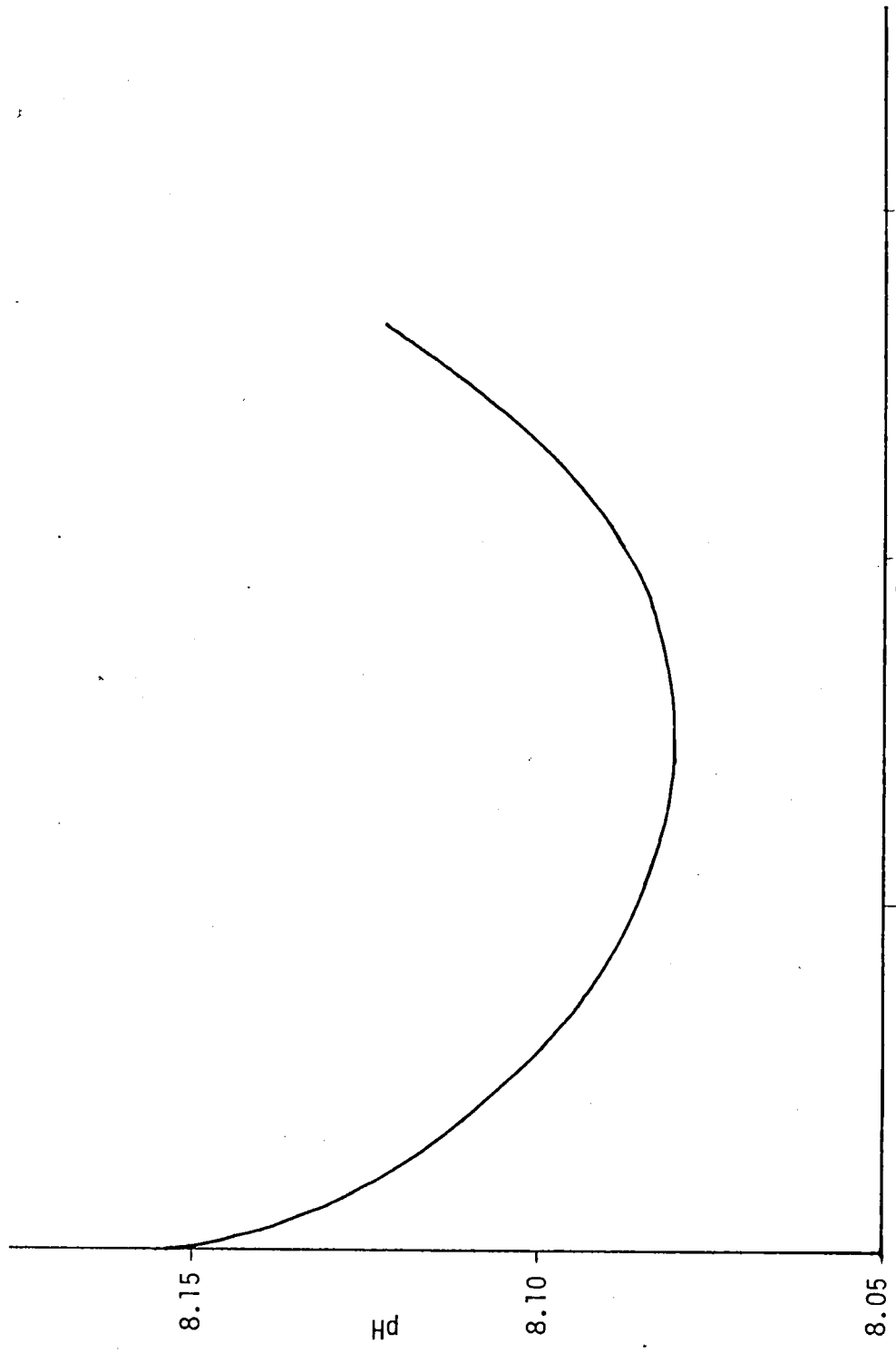


Figure A-12. Reaction L.

Table A-13

pH Values for Reaction M[a]

Reaction time (min)	pH	pH-pHo*
0	8.17	0
50	8.10	-0.07
110	8.08	-0.09
140	8.08	-0.09
295	8.10	-0.07
420	8.09	-0.08
468	8.03	-0.14
558	8.02	-0.15
678	8.01	-0.16
868	8.00	-0.17
2,860	7.88	-0.29
2,985	7.87	-0.30
3,210	7.85	-0.32
3,305	7.85	-0.32
4,295	7.78	-0.39

[a] 1.77×10^{-5} M 4-Cl BP in lake water under oxygen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 8.17.

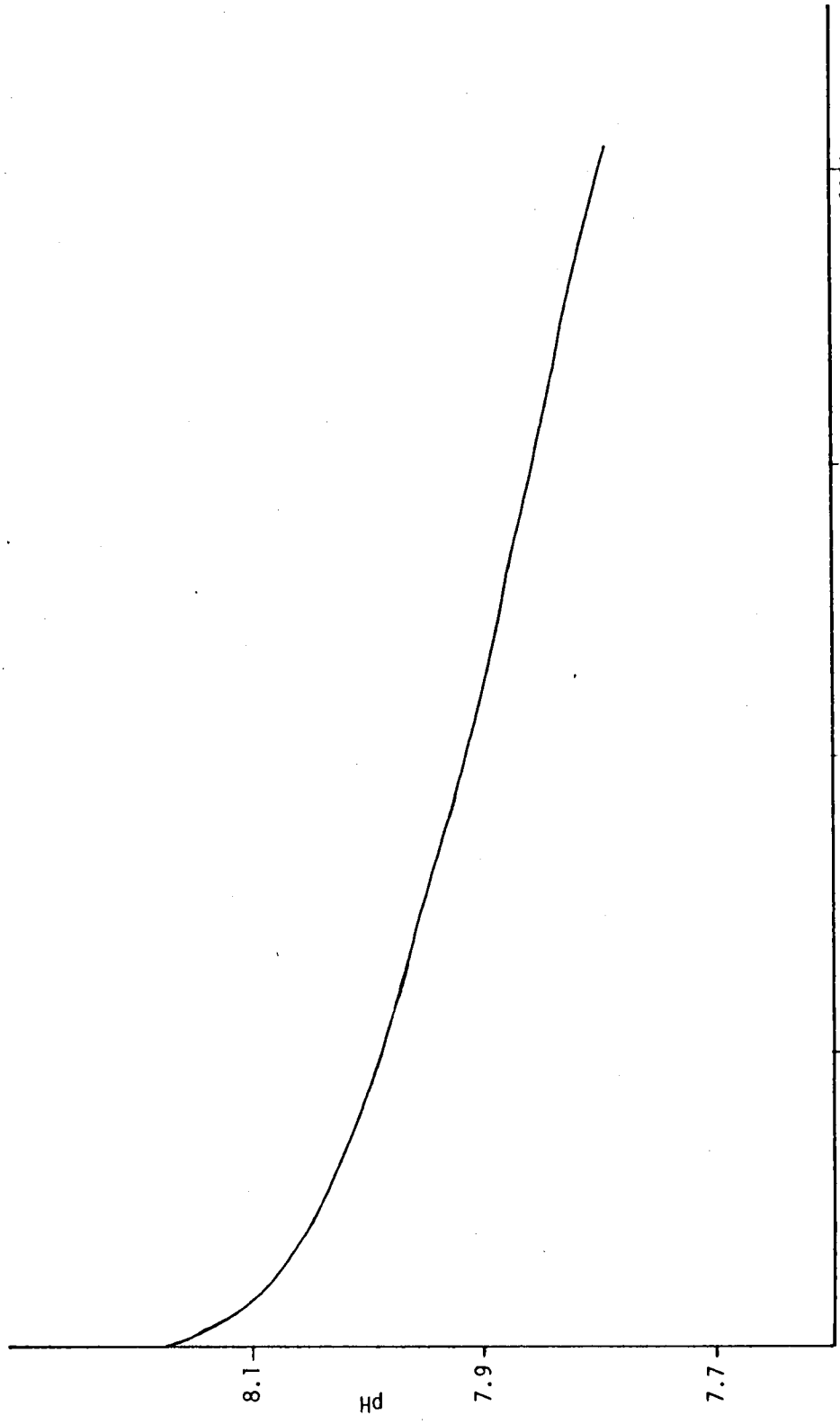


Figure A-13. Reaction M.

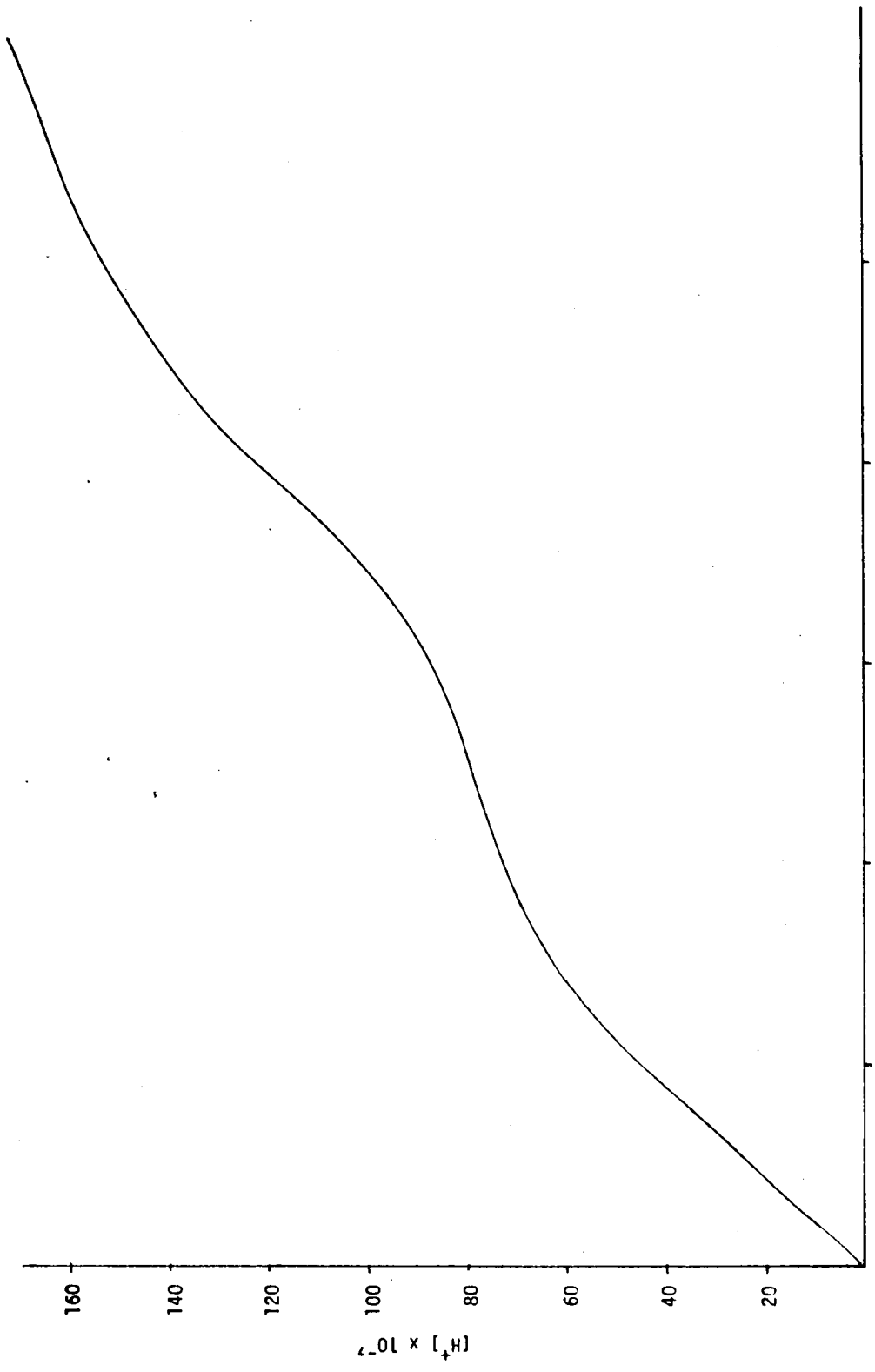


Figure A-14. Reaction A Fitted to Zero-Order Rate Equation.

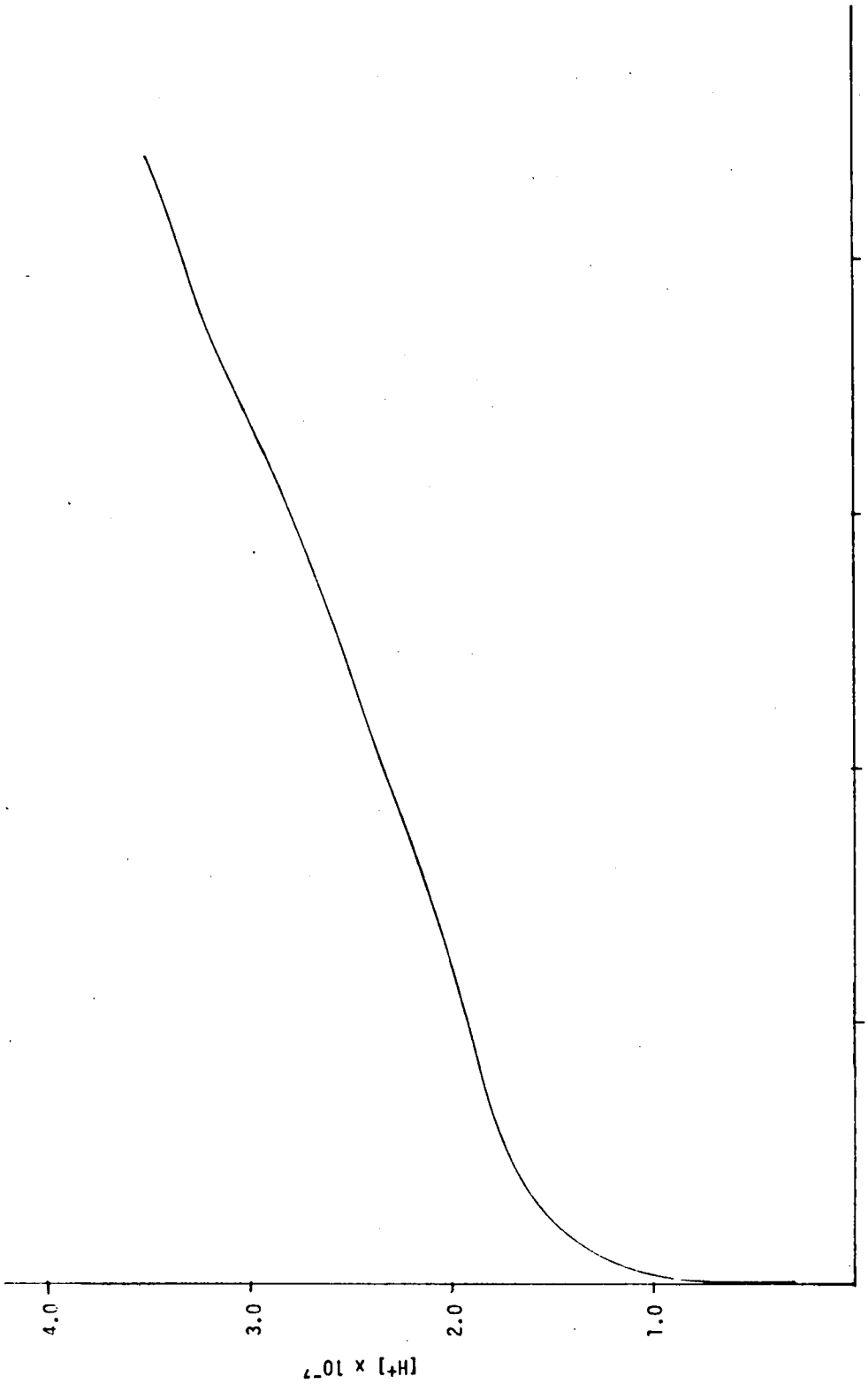


Figure A-15. Reaction C Fitted to Zero-Order Rate Equation.

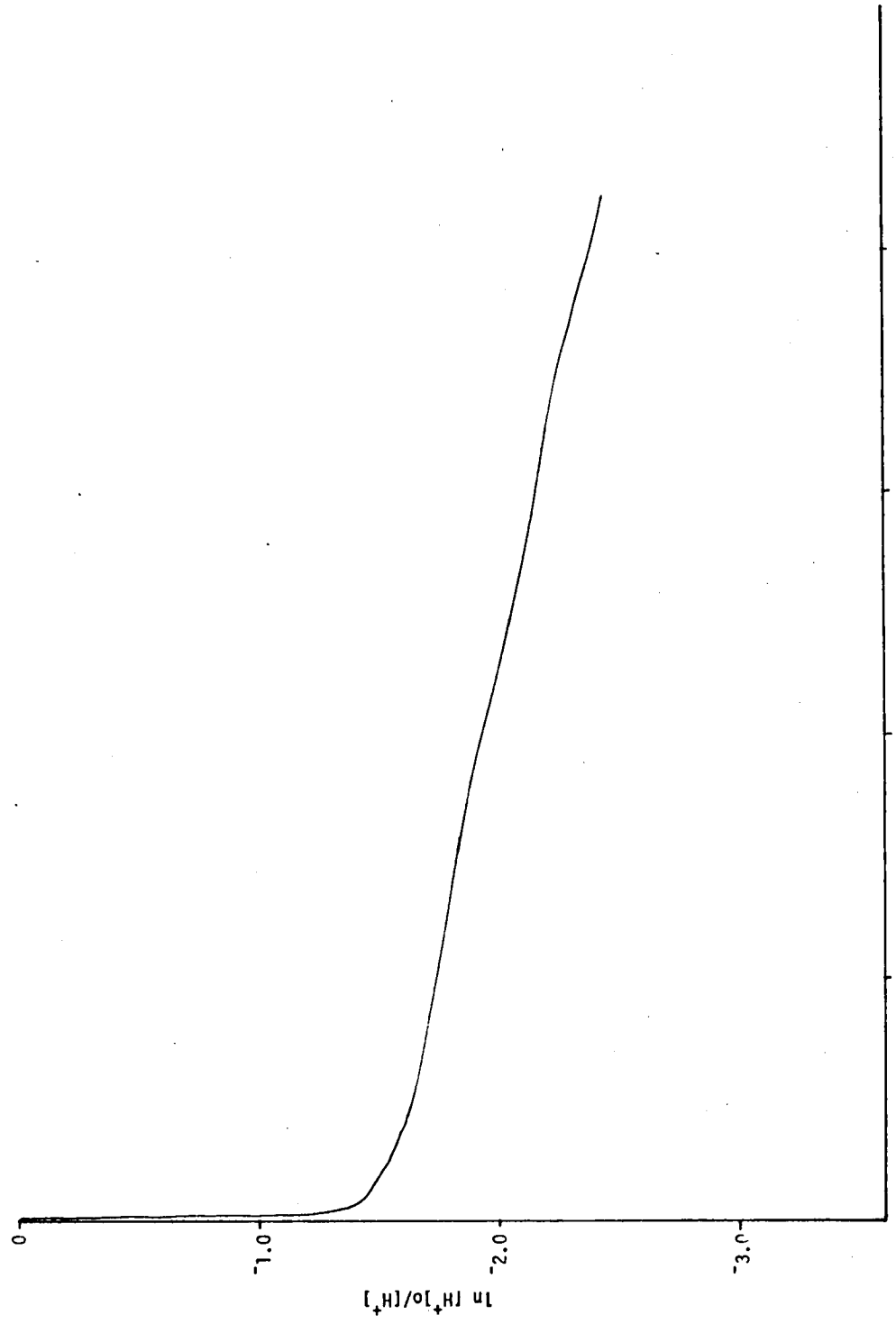


Figure A-16. Reaction C Fitted to First-Order Rate Equation.

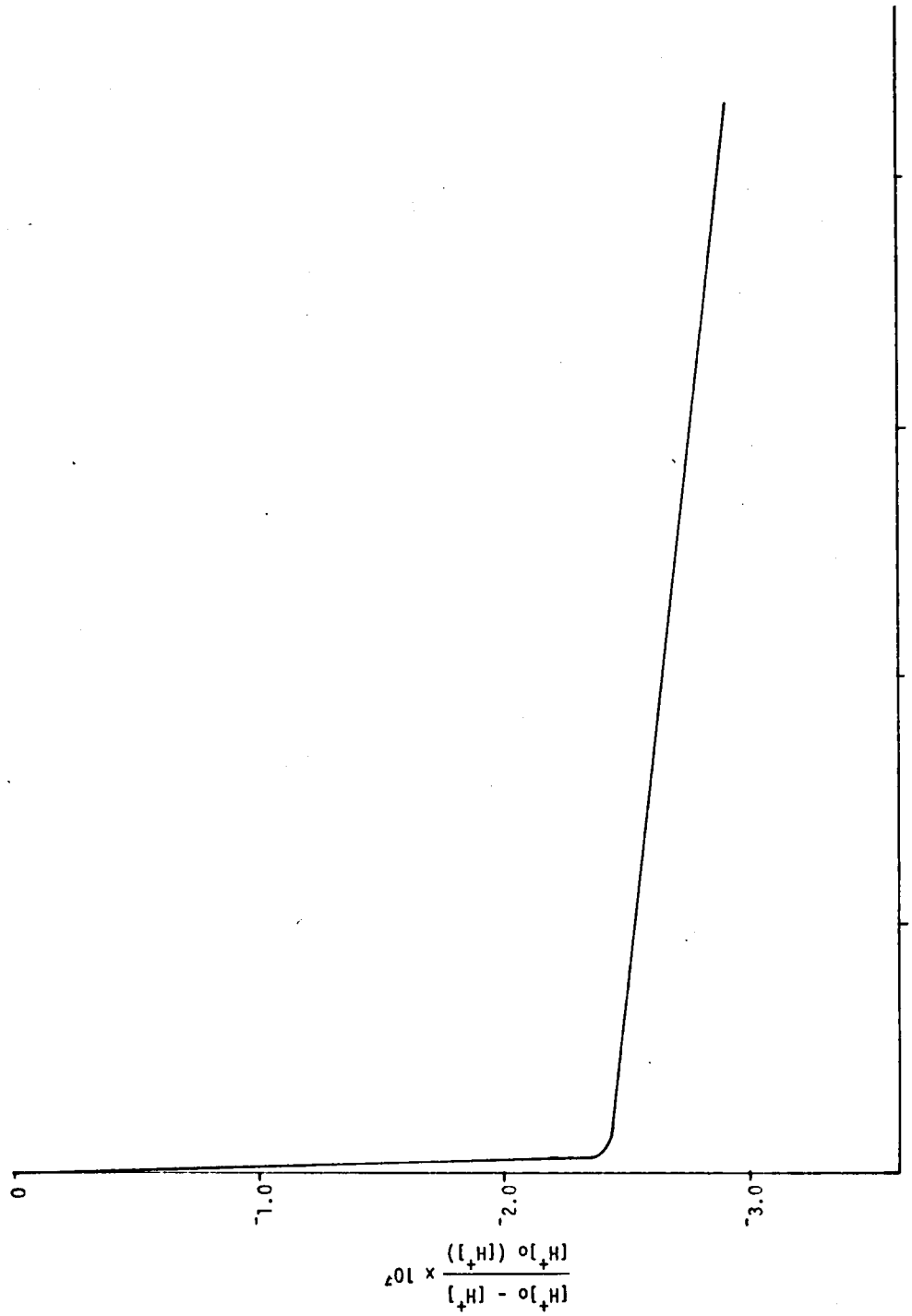


Figure A-17. Reaction C Fitted to Second-Order Rate Equation.

APPENDIX B

SCINTILLATION TECHNIQUE

Table B-1

Average CPM for Photolyses Under Nitrogen (96 Hours)

Retention time (min)	Average CPM
1	590
2	12,167
3	12,265
4	2,680
5	2,333
6	2,039
7	1,706
8	1,660
9	2,170
10	1,301
11	1,296
12	883
13	874
14	1,888
15	2,636
16	611
17	799
18	560
19	327
20	258
21	283
22	224
23	285
24	373
25	172

Table B-2

Average CPM for Photolysis Under Oxygen (96 hours)

Retention time (min)	Average CPM
1	901
2	42,382
3	91,828
4	6,687
5	6,036
6	4,518
7	849
8	501
9	378
10	267
11	345
12	345
13	397
14	402
15	187
16	153
17	233
18	328
19	228
20	135
21	858
22	14,587
23	74,319
24	59,418
25	1,186

Table B-3

Average CPM for Photolysis in Lake Water Under Nitrogen
(96 hours)

Retention time (min)	Average CPM
1	906
2	3,476
3	163
4	441
5	2,392
6	3,558
7	224
8	72
9	147
10	655
11	63
12	67
13	1,108
14	10,714
15	3,033
16	933
17	116
18	173
19	285
20	285
21	60
22	79
23	87
24	87
25	74

Table B-4

Average CPM for Photolysis in Lake Water Under Oxygen
(96 hours)

Retention time (min)	Average CPM
1	422
2	1,617
3	8,590
4	3,584
5	215
6	409
7	368
8	2,519
9	1,120
10	285
11	407
12	561
13	5,510
14	227
15	191
16	660
17	266
18	261
19	3,119
20	151
21	282
22	88
23	276
24	1,850
25	172

APPENDIX C

CLAYS

Table C-1

Aqueous Layer

Retention time (min)	Average CPM
1	87
2	1,203
3	1,473
4	604
5	469
6	716
7	508
8	296
9	327
10	259
11	199
12	181
13	165
14	197
15	169
16	111
17	112
18	101
19	374
20	689
21	388
22	164
23	173
24	112
25	115
26	87
27	254
28	123
29	118
30	341
31	79
32	75
33	78
34	339
35	135
36	93
37	133
38	103
39	173
40	93

Table C-2

Clay Extract

Retention time (min)	Average CPM
1	95
2	210
3	161
4	109
5	97
6	95
7	124
8	127
9	117
10	89
11	94
12	2,821
13	112
14	158
15	115
16	99
17	110
18	106
19	103
20	118
21	441
22	1,685
23	7,583
24	219
25	221
26	203
27	213
28	115
29	3,671
30	511
31	136

Table C-3

Control—Aqueous Layer

Retention time (min)	Average CPM
1	79
2	548
3	112
4	92
5	80
6	91
7	91
8	73
9	71
10	83
11	74
12	76
13	75
14	70
15	83
16	90
17	77
18	82
19	91
20	97
21	97
22	95
23	85
24	89

Table C-4

Control—Clay Extract

Retention time (min)	Average CPM
1	106
2	96
3	88
4	71
5	81
6	148
7	77
8	121
9	66
10	61
11	82
12	91
13	83
14	78
15	75
16	77
17	149
18	746
19	263
20	163
21	146
22	250
23	86
24	85
25	86

Table C-5

Experimental—Aqueous Layer

Retention time (min)	Average CPM
1	60
2	76
3	1,087
4	696
5	93
6	107
7	85
8	85
9	68
10	71
11	160
12	420
13	79
14	70
15	73
16	75
17	71
18	98
19	84
20	78
21	85
22	69
23	144
24	412
25	156

Table C-6

Experimental—Clay Extract

Retention time (min)	Average CPM
1	97
2	122
3	104
4	78
5	81
6	199
7	114
8	683
9	96
10	73
11	86
12	74
13	64
14	78
15	1,963
16	68
17	66
18	72
19	161
20	238
21	82
22	90
23	69
24	82
25	167

Table C-7

Aqueous Layer in Oxygen

Retention time (min)	Average CPM
1	73
2	138
3	90
4	83
5	59
6	3,287
7	104
8	126
9	75
10	213
11	70
12	1,462
13	102
14	107
15	903
16	79
17	1,041
18	79
19	1,186
20	101
21	83
22	14,874
23	1,073
24	78
25	2,231
26	80

Table C-8

Clay Extract in Oxygen

Retention time (min)	Average CPM
1	222
2	550
3	90
4	363
5	78
6	72
7	7,119
8	235
9	250
10	1,657
11	122
12	344
13	74
14	83
15	1,515
16	122
17	915
18	279
19	85
20	84
21	78
22	93
23	1,881
24	4,531
25	3,407

APPENDIX D

pH STUDIES OF 2,2'-DICHLOROBIPHENYL

Table D-1

pH Values for Reaction N[a]

Reaction time (min)	pH	pH-pHo*
0	6.79	0
40	6.17	-0.62
75	6.39	-0.40
315	6.49	-0.30
1,350	6.24	-0.55
1,370	6.23	-0.56
1,470	6.21	-0.58
1,560	6.20	-0.59
2,790	6.11	-0.68
2,920	6.09	-0.70
3,620	6.07	-0.72
4,250	6.07	-0.72
5,710	6.06	-0.73

[a] 9.88×10^{-7} M 2,2'-dichlorobiphenyl in distilled water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 6.79.

Table D-2

pH Values for Reaction O[a]

Reaction time (min)	pH	pH-pHo*
0	9.08	0
20	8.96	-0.12
90	8.93	-0.15
110	8.89	-0.19
135	8.85	-0.23
165	8.83	-0.25
195	8.82	-0.26
355	8.81	-0.27
1,375	8.78	-0.30
1,450	8.77	-0.31
1,830	8.75	-0.33
2,860	8.72	-0.36
4,390	8.65	-0.43

[a] 9.97×10^{-6} M 2,2'-dichlorobiphenyl in lake water under nitrogen.

*pHo refers to the pH at the onset of the reaction (t = 0). In this case, pHo = 9.08.

VITA

Theresa Ann Moore was born in Detroit, Michigan on October 23, 1957. She attended elementary schools in Livonia, Michigan, but was graduated from Putnam County High School in Cookeville, Tennessee in June 1975. The following September, she entered The University of Tennessee, Knoxville, and received a Bachelor of Arts degree in June 1980.

The author accepted a research assistantship at The University of Tennessee in the fall of 1981 and began study towards a Master's degree. This degree was awarded in June 1985 with a major in organic chemistry.