approximately equimolar mixture of its two isomers. While the two isomers separated well in the chromatograph column, indicating a difference in their infinite dilution activity coefficients, their values could not be computed since we could not determine which retention time corresponded to which isomer.

Conclusions

A relative measurement technique has been used to determine the infinite dilution activity coefficients and Henry's law coefficients in water of some priority pollutants. This relative gas chromatographic method is not only accurate, but equally important, it is easy to implement and experimentally very quick. The infinite dilution activity coefficient and Henry's law coefficient data reported here can be used directly for estimating environmentally important properties such as solubilities in water, multimedia partitioning, and octanol–water partition coefficients. Such data are also useful for the further development of group contribution and other prediction methods for infinite dilution activity coefficients.

Registry No. (*E*)-ClCH=CHCl, 156-60-5; Cl₂CH₂, 75-09-2; ClCH₂CHClCH₃, 78-87-5; Cl₃CCH₂Cl, 630-20-6; Cl₂CHCHCl₂, 79-34-5; Cl₃CCH₃, 71-55-6; Cl₂CHCH₂Cl, 79-00-5; Cl₂C=CHCl, 79-01-6.

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Sensitized Photolysis of Polychlorobiphenyls in Alkaline 2-Propanol: Dechlorination of Aroclor 1254 in Soil Samples by Solar Radiation[†]

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■ Photodechlorination of Aroclor 1254 (1000 mg/L) in an alkaline 2-propanol solution at $\lambda = 254$ nm proceeded with a high quantum yield ($\Phi = 35.0$) as determined by Cl⁻ release. The Aroclor was completely dechlorinated in 30 min and gave predominantly biphenyl (BP). After 20 h of solar irradiation, only partial dechlorination (25%) was observed, and no BP was formed. In the presence of phenothiazine (PT) sensitizer (5 mM) the Aroclor was completely dechlorinated to BP in 1 h at 350 nm ($\Phi = 2.33$) and in 4 h by exposure to sunlight. Under the same conditions, Aroclor 1254 extracts of contaminated soil (730 mg/L) were dechlorinated in 2 h at 350 nm ($\Phi = 0.28$) and in 20 h on exposure to sunlight. The photoreaction was completely quenched by oxygen and nitrobenzene (0.1 M). Moreover the Aroclor was thermally (ca. 80 °C) dechlorinated to BP using di-*tert*-butyl peroxide. A free-radical chain reaction was suggested in which the aryl radical anion, Ar⁻–Cl, was a key intermediate in the dechlorination process.

Introduction

The unique thermal and chemical stability that makes polychlorobiphenyls (PCBs), e.g., Aroclor 1254, industrially useful has also made them a threat to the environment. They are resistant toward solar photodegradation and microbial biodegradation and therefore tend to persit in-

definitely. A common and deceptive practice to prevent PCBs from reaching our ecosystem is to dispose of them in landfills; however, this has proved to be potentially dangerous and costly. For example, in a recent accident (Saint-Basile-le-Grand, Québec, Canada, on August 23, 1988) 1500 barrels of PCB-laden oil caught fire in a warehouse sending clouds of toxic smoke into the atmosphere, forcing the evacuation of more than 3000 people and costing several millions of dollars to clean up the site and several hectors of surrounding contaminated soil.

Presently, incineration is the most widely used technology for the destruction of PCBs, but incineration often leads to the formation of more toxic oxygenated derivatives (e.g., polychlorinated benzofurans and dioxins) if not carefully controlled. Intensive chemical (*1, 2*), photochemical (*3–5*), and joint physicochemical–microbial dechlorination processes (*6, 7*) have been reported on the dechlorination of PCBs. Solar photodegradation is one of the most natural and most economical degradation routes for environmental pollution. Unfortunately, most PCB congeners do not absorb strongly above 300 nm, and their direct photolysis often proceeds with very low quantum efficiency (*8, 9*). Sensitizers and other additives such as amines (*10, 11*), borohydrides (*12*), alkaline alcohols (*13*), and hydroquinones (*14*) have been used to enhance photodechlorination. One striking example has been reported by Nishiwaki in which photodechlorination of Kanechlor, KC-300, at 298 nm in an alkaline 2-propanol solution proceeds with high quantum yield ($\Phi = 36$) (*13*). One drawback of this reaction is its inability to proceed with the same efficiency at longer wavelengths, particularly if

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using sunlight radiation. However, the process could be modified through photosensitization for use of longer wavelengths and hence for field application.

In this study, results are presented for nonsensitized and phenothiazine- (PT-) sensitized photolysis of commercial Aroclor 1254 by artificial and sunlight irradiation in alkaline 2-propanol and for photolysis of PCBs from a contaminated soil sample taken from a PCB fire site at Saint-Basile-le-Grand Québec, Canada.

Experimental Section

Materials and Reagents. Biphenyl (BP) and 3-chlorobiphenyl (3-ClBP) were from Alfa Products, Danvers, MA. All other polychlorobiphenyl isomers were obtained from Ultra Scientific, Kingstown, RI. Aroclor 1254 was obtained from Chem Service, West Chester, PA. Phenothiazine (PT) was used as received from Aldrich, Milwaukee, WI. All solvents were of pesticide grade and were obtained from Fisher Scientific, Montréal. The soil contaminated with PCB (Aroclor 1254, 730 mg/kg) was obtained from Saint-Basile-le-Grande, Québec, Canada, homogenized, and sieved to less than 500-μm particles before use. Di-*tert*-butyl peroxide (t-BuOOBu-t) was a gift from Witco, Richmond, CA, and *tert*-butyl hypochlorite (t-BuOCl) was synthesized by the method of Mintz and Walling (15). Soil samples contaminated with PCBs were taken from the PCB warehouse fire site at Saint-Basile-le-Grand, Québec, Canada (August 28, 1988). The soil was first cleaned of rough debris and small rocks and then homogenized. A soil sample (5 g) was spiked with 4-bromobiphenyl, as a recovery standard, and PCB was extracted by hexane using a Soxhlet extractor for 12–16 h. The extracts were then cleaned on a silica column, concentrated, and analyzed. GC/ECD and GC/MSD analysis of soil extracts showed that the PCB profile is very similar to that of commercial Arochlor 1254, as shown in Figure 1A. A 1 mg/L standard solution of Aroclor 1254 showed that the PCB content of the soil was 730 mg/kg.

Soil Extraction for Photolysis. The contaminated soil (5 g) was spiked with 4-bromobiphenyl as a recovery standard and mixed with 10 mL of alkaline 2-propanol solution (NaOH, 0.5% w/v). The resulting slurry was shaken (200 rpm) for 30 min (New Brunswick G-24 shaker) at room temperature, then centrifuged, and filtered, and the filtrate was spiked with 1,2,3-trichlorobenzene as an internal standard. Subsequent analysis of the filtrate showed that close to 75% of the PCBs was extracted from the soil. Successive extractions of the soil with fresh alkaline alcohol solutions (5 × 10 mL) increased the efficiency of extraction to ca. 98%. By increasing the temperature to 60 °C, only one extraction was necessary to remove 95–99% of the PCBs from the soil. Traces of PCBs that remained adsorbed onto the soil particles were extracted by hexane using Soxhlet extraction for several hours. The extraction process was also attempted by means of continuously flowing 2-propanol through the soil sample. Gravimetric flow of the alkaline 2-propanol solution (40 mL, 1 mL/min) through a column bed (i.d. 2 cm) of the contaminated soil (5 g) removed 95% of PCBs. For photolysis purposes, the final concentration of NaOH in the soil extracts was adjusted to 0.1 M. The UV spectrum of the soil extract showed a strong absorption (OD >2) at 300 nm with a continuum tailing to 450 nm (OD 0.1). This was attributed to various humic substances (HS), such as fulvic acids (FA) and humic acids (HA), that were coextracted with the Aroclor. HS are known to be rich in chromophores and tend to absorb strongly above 300 nm (16). To minimize their presence during photolysis, the soil was first prewashed with 0.1 N NaOH, and then
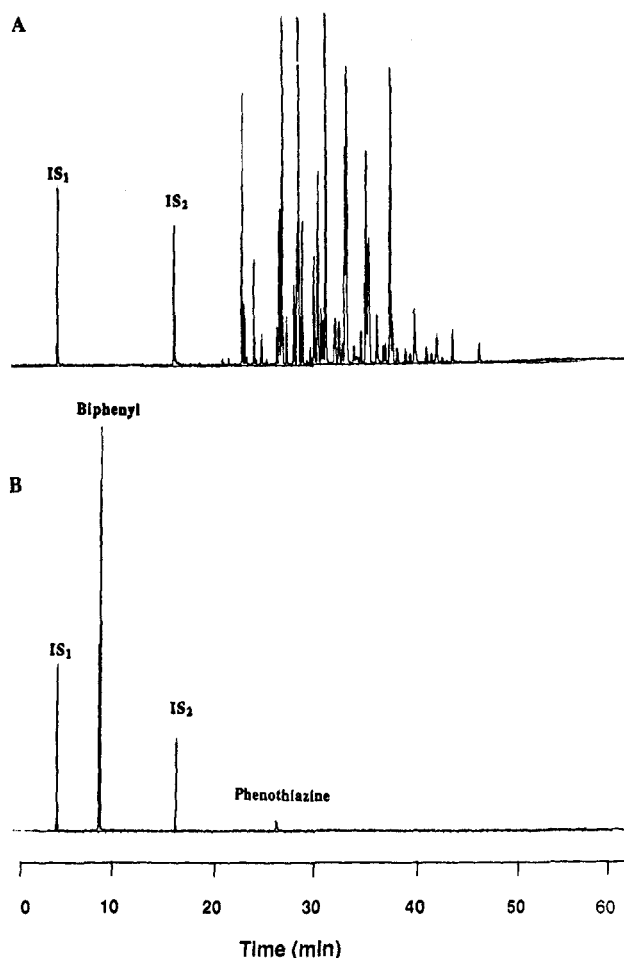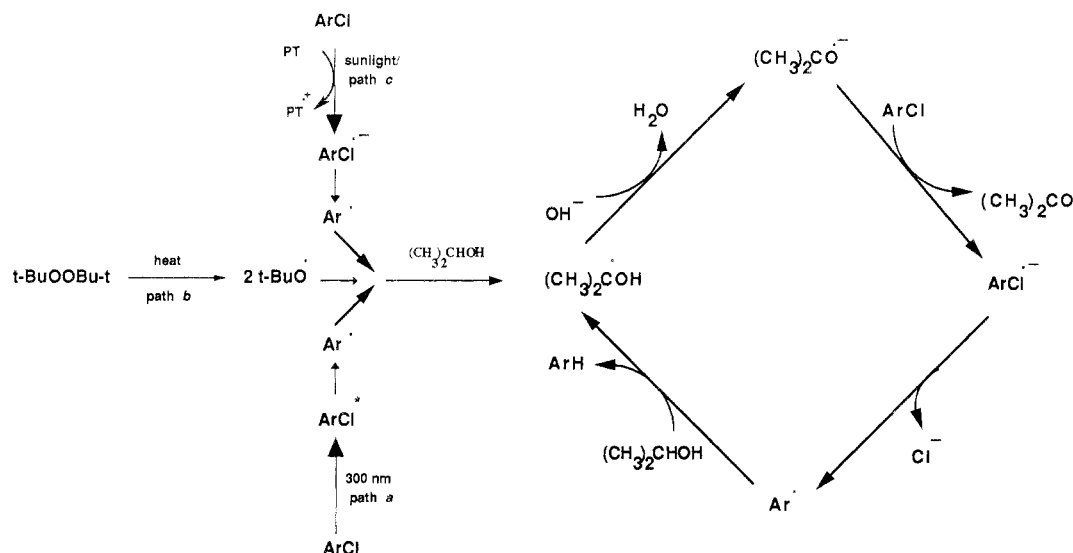

Figure 1. Total ion chromatogram of Aroclor 1254 (1000 mg/L) (A) before photolysis and (B) after 20-min photolysis at 350 nm in NaOH (0.1 M)/2-propanol solution. IS$_1$ = 1,2,3-Cl$_3$Bz and IS$_2$ = 4-BrBP as internal standards.

PCB was extracted with neutral rather than alkaline 2-propanol. UV spectra of the soil extracts after the base wash (OD$_{300nm}$ 0.7) showed that the use of neutral rather than alkaline 2-propanol reduced extracted HA and FA by a factor of 3.

Irradiation Experiments. Solar radiation or a Rayonet photoreactor RPR-100 fitted with a merry-go-round apparatus (Southern New England Co., Hamden, CT) equipped with 16 254- or 350-nm lamps were used as light sources. Sample tubes were made of either quartz for photolysis at 254 nm or pyrex for photolysis at 350 nm. Each tube was charged with 10 mL of the NaOH (0.1 M) 2-propanol solution of either commercial Aroclor 1254 or PCB-contaminated soil extract. The sensitizer PT (5 mM) was added as indicated to samples. Control experiments were carried out in tubes filled with the above solutions and kept in the dark covered with aluminum foil. The solutions were degassed before photolysis by either 3–5 freeze-pump–thaw cycles or bubbling with oxygen-free N$_2$. In some experiments photolysis was carried out in the presence of nitrobenzene (0.1 M) or oxygen. The temperature of the reactor was maintained at 40–42 °C by maintaining a stream of air current through the apparatus during irradiation. Sunlight irradiation experiments were conducted during the months of August and September in sealed pyrex or borosilicate tubes placed on special racks facing the sun horizontally. For quantum yield (Φ) measurements, PCB samples (prepared and sealed as described above) were photolyzed in a Rayonet photoreactor fitted with a merry-go-round apparatus to a maximum of 20%

Scheme I. Reductive Dechlorination Cycle of Aroclor 1254 in Alkaline 2-Propanol[a]

ArCl

PT sunlight/ path c

PT

ArCl·⁻

Ar·

t-BuOOBu-t —heat→ path b 2 t-BuO· —(CH₃)₂CHOH→ (CH₃)₂C·OH

Ar·

ArCl*

300 nm path a

ArCl

(CH₃)₂CO·⁻

H₂O   ArCl

OH⁻   (CH₃)₂CO

(CH₃)₂C·OH   ArCl·⁻

ArH

(CH₃)₂CHOH   Cl⁻

Ar·

[a] The cycle was initiated by (a) direct photolysis at 350 nm, (b) thermolysis in the presence of t-BuOOBu-t at 80 °C, and (c) sunlight irradiation in the presence of PT.

conversion. Light intensities I_{254} = 3.5 × 10⁻⁶ einstein mL⁻¹ s⁻¹ (RPR 254-nm lamp tubes emitting ca. 99% of their energy at 253.7 nm) and I_{350} = 3.0 10⁻⁶ einstein mL⁻¹ s⁻¹ (RPR 350-nm lamp tubes emitting >90% of their energy at 350 nm) were measured using ferrioxalate actinometry (17). UV spectra were measured using a Beckman DU-7 spectrometer, and the Beer–Lambert law was used to compensate for the light that was not absorbed in the photolysis cell. The concentration of Cl⁻ was used to calculate Φ for Aroclor disappearance and the formation of BP to calculate Φ for the photolysis of 3-ClBP.
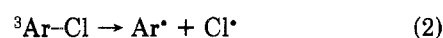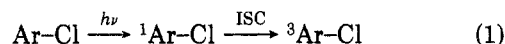
Product Analysis. A sample aliquot (100 μL) was withdrawn from the photolyzed mixture and then diluted with water, and the pH was adjusted to 5–6 by treatment with nitric acid (0.1 M). The acidified samples were spiked with 4-bromobiphenyl as the recovery standard and extracted with hexane (2 × 2 mL). 1,2,3-Trichlorobenzene was added to the hexane extracts as an internal standard for GC quantitation. Products were analyzed by GC on a Perkin-Elmer Sigma 2000 capillary gas chromatograph equipped with an electron capture detector, a 30 m × 0.25 mm DB-5 capillary column (J&W Scientific Inc), a Perkin-Elmer LC1-100 integrator, and a Perkin-Elmer AS-2000B autosampler (1 μL, splitless) injection. Argon/methane (5%) was used as the makeup gas and helium as the carrier gas. In cases where high resolution was required to separate various PCB products, a Hewlett-Packard 50 m × 0.2 mm Ultra-1 capillary column was employed. Photoproducts were identified by GC/MS (Hewlett-Packard 5970 MSD connected to a HP 5890 GC) and by comparison with reference compounds. The aqueous layer which remained after the hexane extraction of the above photolyzed mixture was analyzed for chloride ions with an SP 8100 HPLC with a 25 × 0.46 cm PRP-X 100 Hamilton column and a Waters 431 conductivity detector. Methanol (10%) in a buffer solution (pH 8.5) of p-hydroxybenzoic acid/NaOH was used as mobile phase. Analytical-grade sodium chloride was used as the standard.
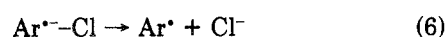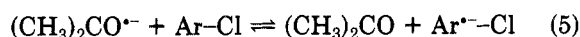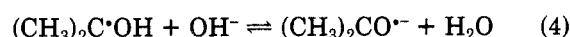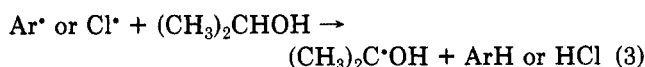
Results and Discussion

Nonsensitized Photolysis of Chlorobiphenyls. Photolysis of Aroclor 1254 (1000 mg/L) in an NaOH (0.1 M)/2-propanol solution at 254 nm was found to proceed with an apparent high dechlorination quantum yield (Φ

= 35) (Table I) similar to that which has been observed in the photodechlorination of Kanechlor, KC-300, (Φ = 36) at 298 nm (13). Bunnet and co-workers (18) reported earlier that aromatic halides are photodehalogenated in the presence of ionic metal alkoxides through a radical-chain reaction. We found that the reaction could be thermally initiated using peroxides (described later) and that photolysis was strongly quenched by either oxygen or nitrobenzene (0.1 M).

These observations support the presence of a free-radical chain reaction. We assume that upon absorption of light the Aroclor ArCl produces a singlet excited state, ¹ArCl, which through intersystem crossing (IST) gives a triplet, ³ArCl, which upon dissociation produces the chlorine atom, Cl· and the aryl radical, Ar·, reactions 1 and 2. We have no data to support the claim that under these conditions PCBs react through a triplet; however, it has been reported that the efficiency of $S_1 \rightarrow T_1$ intersystem crossing of PCBs is near unity at room temperature (8).

$$\text{Ar-Cl} \xrightarrow{h\nu} {}^1\text{Ar-Cl} \xrightarrow{\text{ISC}} {}^3\text{Ar-Cl} \qquad (1)$$

$$^3\text{Ar-Cl} \rightarrow \text{Ar}^\bullet + \text{Cl}^\bullet \qquad (2)$$

Subsequent hydrogen abstraction from 2-propanol by either Cl· or Ar· gave the ketyl radical $(CH_3)_2C^\bullet OH$ (reaction 3), which after the loss of a proton to the alkaline medium produced the ketyl radical anion $(CH_3)_2CO^{\bullet -}$ (reaction 4). The reaction of $(CH_3)_2CO^{\bullet -}$ with the Aroclor singlet ground state through an electron-transfer process gave the unstable aryl radical anion Ar·⁻–Cl, which on cleavage provided the chloride anion Cl⁻ and Ar·, reactions 5 and 6, respectively. The generated Ar· would in turn start the reductive chain cycle as depicted in Scheme I, path a.

$$\text{Ar}^\bullet \text{ or } \text{Cl}^\bullet + (CH_3)_2CHOH \rightarrow$$
$$(CH_3)_2C^\bullet OH + \text{ArH or HCl} \qquad (3)$$

$$(CH_3)_2C^\bullet OH + OH^- \rightleftharpoons (CH_3)_2CO^{\bullet -} + H_2O \qquad (4)$$

$$(CH_3)_2CO^{\bullet -} + \text{Ar-Cl} \rightleftharpoons (CH_3)_2CO + \text{Ar}^{\bullet -}\text{-Cl} \qquad (5)$$

$$\text{Ar}^{\bullet -}\text{-Cl} \rightarrow \text{Ar}^\bullet + \text{Cl}^- \qquad (6)$$

The concentration of 2-propoxide anion, $(CH_3)_2CHO^-$, in alkaline 2-propanol is very low, pK_a = 20.6, and its

Table I. Photolysis of Polychlorobiphenyls in Alkaline (NaOH, 0.1 M)/2-Propanol Solution

substrate[a,b]	λ, nm	time, h (dechlorination %)	quantum yield,[c] Φ
Aroclor 1254	sun	20 (25)	
Aroclor 1254[d]	sun	4 (100)	
Aroclor 1254	254	0.5 (100)	35.0
Aroclor 1254[d]	350	1 (100)	2.33
soil	350		0.02
soil[d]	350	2	0.28
soil	254	55	0.67
soil	sun	20 (30)	
soil[d]	sun	20 (100)	

[a] Aroclor 1254 was a commercial sample (1000 mg/L). [b] The soil was contaminated with 730 mg/L Aroclor 1254. [c] Calculated at 20% conversion and based on the Cl⁻ release. [d] In the presence of phenothiazine (5 mM).

contribution to the overall kinetics of the chain reaction is insignificant (19). In contrast to Nishiwaki (13), we thus believe that the ketyl radical, $(CH_3)_2C^\bullet OH$, reacts with the hydroxyl anion, OH^-, rather than with the 2-propoxide anion, $(CH_3)_2CHO^-$, to give $(CH_3)_2CO^{\bullet -}$. Furthermore, both reactions 4 and 5 are reversible, for example, the equilibrium constant for reaction 4 is $K = 93$ (20) whereas the reduction potentials (E_0) of $(CH_3)_2CO^{\bullet -}/(CH_3)_2CO$ (20) and chlorobiphenyls, $PCB^{\bullet -}/PCB$, (21) (reaction 5) are very similar, i.e., -2.1 V and -2.1 to -2.3 V, respectively. The chain reaction can be terminated if intermediates such as $(CH_3)_2C^\bullet OH$ and $(CH_3)_2CO^{\bullet -}$ are removed from the reaction by either reacting with each other or with other quenchers such as oxygen and nitrobenzene. The suggested mechanism is in line with a universal mechanism proposed by Bunnet and co-workers for the photoreduction of aromatic halides by alkoxide ions (18), which predates the proposal of Nishiwaki (13) and Bunce (22).

In line with the above mechanism, the reductive dechlorination cycle summarized in reactions 3–6 was reproduced thermally using di-tert-butyl peroxide as a free-radical initiator. When an alkaline (NaOH, 0.1 M) 2-propanol solution of Aroclor 1254 (1326 mg/L) was heated at 80 °C in the presence of t-BuO-OBu-t (0.1 M) under nitrogen for 3 h, the Aroclor was dechlorinated to BP. Di-tert-butyl peroxide is thermally unstable, and at 80 °C it decomposes to give the tert-butoxyl radical, t-BuO•, which after H abstraction from 2-propanol gives the ketyl radical $(CH_3)_2C^\bullet OH$. Subsequent reaction of $(CH_3)_2C^\bullet OH$ with the hydroxyl anion would give $(CH_3)_2CO^{\bullet -}$ and regenerate the reductive dechlorination cycle as shown in Scheme I, path b. The α-H abstraction from 2-propanol by t-BuO• is thermodynamically and kinetically feasible. For example, the α-C–H bond energy ($D_{CH} =$ ca. 376 kJ/mol) in 2-propanol is weaker than that of the OH bond in t-BuOH ($D_{OH} =$ ca. 418 kJ/mol) (23). Furthermore, the t-BuO• radical is reported to react with 2-propanol with a relatively high rate constant, $k = 1.8 \cdot 10$ $M^{-1} s^{-1}$ (24). Other radical initiators such as tert-butyl hypochlorite were found to be unsuitable to initiate the reaction due to a severe reaction involving the hypochlorite and the alkaline medium.

Interestingly, the aryl radical anion intermediate, $Ar^{\bullet -}-Cl$, is also implicated as a key intermediate in the electrochemical dechlorination of polychloroaromatics (25). In contrast, direct photolysis of PCBs in nonpolar solvents,

e.g., hexane, is found to be inefficient and at best gives partially dechlorinated photostable congeners (22). It thus seems that dechlorinatioin mechanisms involving the formation of aryl radical anion intermediates are relatively fast and efficient and may serve as a basis for a PCB destruction technology. However, the above photolysis is still restricted by the light wavelength (λ < 300 nm) and by the presence of air.

Phenothiazine-Sensitized Photodechlorination of Chlorobiphenyls. Photolysis of Aroclor 1254 (1000 mg/L) in an alkaline 2-propanol solution by solar radiation alone for 20 h gave less than 25% dechlorination. No biphenyl or monochlorobiphenyls were detected. Instead products such as 3,3′-dichlorobiphenyl, 2,3′,5-trichlorobiphenyl, and PCB congeners with average chlorine content of 3–4 Cl atoms/PCB molecule were detected. When the above photolysis was repeated in the presence of PT sensitizer (5 mM), photodechlorination was completed after 4-h exposure to sunlight and in about 1 h by irradiation at 350 nm. A relatively high dechlorination quantum yield was obtained (Φ = 2.33) although it was lower than the values obtained for the 254-nm nonsensitized photolysis of Aroclor 1254 (Φ = 35.0) (Table I). On the basis of the initial concentration of Aroclor 1254 and taking into account that 54% (w/w) of commercial Aroclor 1254 is chlorine, the chloride ion recovery was quantitative (100%). As Figure 1 shows, biphenyl was formed as a final organic product. For example, when the photolyzed solution was acidified (pH 1–2) and extracted by ethyl acetate, no hydroxybiphenyls or any products derived from an aryl radical attack on 2-propanol were observed. In a few cases, traces (<1%) of tetraphenyl, Ar_2 ($m/z = 306$), were formed apparently by a dimerization reaction involving biphenyl radicals, $2Ar^\bullet$.

Light absorption by PCBs above 300 nm is very weak ($\epsilon_{320} = 15$ L³ mol⁻¹ cm⁻¹). Relatively, phenothiazine absorbs strongly (ϵ_{320} 4800 L³ mol⁻¹ cm⁻¹) with a spectral cutoff reaching 450 nm. This implies that dechlorination of PCBs by direct photolysis (reactions 1 and 2) is negligible and that most dechlorination results from photosensitization by PT.

Light absorption by PT in alcoholic solvents has been reported to produce a triplet with relatively long lifetime ($t_{1/2} = 3.5 \mu s$) and high quantum yield (Φ = 0.96) (26). Furthermore, the triplet state of phenithiazine ³PT is known to be an efficient electron donor (27). It is thus believed that upon the absorption of light, PT is excited to triplet phenothiazine ³PT, which in the presence of ArCl is oxidized through an electron-transfer process giving the phenothiazine radical cation $PT^{\bullet +}$ and the aryl radical anion $Ar^{\bullet -}-Cl$. The dechlorination of the aryl radical anion would produce once again the aryl radical $Ar^\bullet$, thus regenerating the reduction cycle as shown in Scheme I, path c.

We do not have enough experimental details to outline a conclusive mechanism; however, our observation tends to support our argument. For example, ³PT, $E = 255$ kJ/mol (27), is known to undergo a reversible energy transfer with other molecules such as naphthalene to create other triplets. However, this is not the case with PCBs whose triplet energies are much higher, i.e., $E = 300$ kJ/mol for PCBs without ortho Cl and 275 kJ/mol for PCBs with ortho Cl (22). It thus appears that the electron-transfer process which involves both ³PT and the Aroclor singlet ground state is dominant over the energy-transfer process.
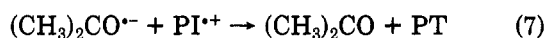
As we discussed earlier, the apparent quantum yield of the sensitized photodechlorination of Aroclor 1254 (350

Table II. Effect of Water and Methanol on Photodechlorination of Aroclor 1254 (1326 mg/L) and 3-Chlorobiphenyl (5.38 mM) in NaOH (0.1 M)/2-Propanol Solution at 350 nm in Presence of Phenothiazine (5 mM)

substrate	additive (20% v/v)	quantum yield,[a] Φ
3-chlorobiphenyl	MeOH	0.56[b]
3-chlorobiphenyl	H$_2$O	0.50[b]
3-chlorobiphenyl	N/A[d]	0.67[b]
Aroclor 1254	MeOH	1.30[c]
Aroclor 1254	H$_2$O	1.00[c]
Aroclor 1254	N/A[d]	1.57[c]

[a] Quantum yields were calculated at 5% conversion. [b] Based on biphenyl production. [c] Based on the Cl⁻ ion release. [d] N/A means none added.

nm) is much lower than that of the nonsensitized one (λ = 254 nm), Φ = 2.33 and 35, respectively (Table I). The apparent difference in Φ should not be solely attributed to a difference in the wavelength of photolysis, it is probably due to some other side physical and chemical processes undertaken by PT which are not completely understood. Presumably, PT and its radical cation PT$^{\bullet+}$ may react with the radical anions Ar$^{\bullet-}$–Cl and $(CH_3)_2CO^{\bullet-}$ by a back-electron-transfer process as shown in reactions 7 and 8, thus reducing their counts in the chain reaction and consequently decreasing its chain length. In fact an increase in the concentration of PT from 5 to 25 mM lowered the apparent Φ from 2.33 to 1.57.

$$(CH_3)_2CO^{\bullet-} + PI^{\bullet+} \rightarrow (CH_3)_2CO + PT \qquad (7)$$

$$Ar^{\bullet-}–Cl + PT^{\bullet+} \rightarrow ArCl + PT \qquad (8)$$

When the sensitized photolysis of Aroclor 1254 (1000 mg/L) was carried out in the presence of pure oxygen (sample tubes were saturated with pure oxygen and then sealed) or nitrobenzene (0.1 M), no photodechlorination was observed after 4 h of photolysis. Interestingly, air (sample tubes were exposed to the atmosphere during photolysis) had little effect on the reaction. For example, parallel photolysis of degassed and undegassed alkaline 2-propanol solutions of Aroclor 1254 (1000 mg/L) in the presence of PT at 350 nm for 10 min gave the following amounts of chloride ions: 140 and 138 mg/L, respectively. Continued photolysis for 1 h led to quantitative chloride recoveries and to the formation of BP with no sign of oxygen-derived products.

The severe quenching effects of pure O$_2$ on the reaction supports the free-radical nature of the reaction. However, the small retarding effect observed when the photolyzed mixtures are exposed only to the atmosphere may be due to the presence of insufficient O$_2$ concentrations. Interestingly, Epling has recently reported that oxygen has a slight effect on the sensitized photolysis of aromatic halide in the presence of amines (11). Furthermore, PT has been reported (27) to undergo photooxidation with O$_2$ to give the superoxide anion O$_2^{\bullet-}$ which has been recently used to mineralize PCBs in DMF (28).

We have also studied the effect of water and methanol on the above reaction and found that both did not quench the reaction when their respective concentrations were <5% (v/v). When either concentration was increased to 20% (v/v), the apparent Φ for the reaction dropped from 2.67 to 1.00 and 1.30, respectively (Table II). The above slight quenching effects of MeOH and H$_2$O on the reaction may seem to contradict the previously suggested chain reaction. We have, therefore, photolyzed 3-ClBP (5.38 mM), under similar conditions and observed slight variations in Φ, i.e., 0.67, 0.50, and 0.56, respectively (Table II).

Bunnet (18) has previously reported that photodehalogenation of aryl halides in alkaline methanol proceeds in a chain reaction via the formaldehyde radical anion HCHO$^{\bullet-}$. The slight quenching effects from MeOH are presumably due to the replacement of $(CH_3)_2CO^{\bullet-}$ (E_0 = -2.1 V) by the less efficient radical-chain carrier HCHO$^{\bullet-}$ (E_0 = -1.81 V) (20), possibly through hydrogen atom abstraction from MeO⁻ (18), $(pK_a)_{MeOH}$ = 16.7 compared to $(pK_a)_{2-PrOH}$ = 20.6 (19).

The observed tolerance from water on the dechlorination process, which contrasts with the suggestion of Bunce (22), is of practical significance if photodechlorination of PCBs in soil samples is desired. Additionally, the use of methanol or aqueous methanol to extract PCB from the soil would be more cost effective.

Photodechlorination of PCBs from Contaminated Soil.

Sunlight irradiation of neutral propanol extracts of the PCB-contaminated soil (final PCB concentration in the extract was 350 mg/L) did not produce any photodechlorination for more than 20 h. In the presence of NaOH (0.1 M), under otherwise identical conditions, only 30% dechlorination was achieved with the formation of only partially dechlorinated products, whose average chlorine content ranged from 3 to 4 Cl/PCB congener. However, in the presence of phenothiazine sensitizer (5 mM), the soil extracts were completely dechlorinated to biphenyl in about 20 h by solar irradiation and in 2 h by photolysis at 350 nm using a Rayonet photoreactor (Table I). Interestingly, the Φ in the present case was lower than that obtained from the photolysis of commercial Aroclor 1254, i.e., 0.67 and 2.33, respectively (Table I).

The above observed differences in Φ may indicate that despite the fact that 350-nm artificial light is more intense than sunlight irradiation, other chemical compositions in the soil such as FA and HA retard rather than enhance photodechlorination. For example, it has been reported that HS has a significant free-radical content (10^{17} spin/g) and therefore may act as spin traps (sink) for the free-radical initiators generated in reactions 1 and 2 or other chain carriers necessary to the above photolysis (29). Reactions 1 and 2 and Scheme I clearly show the essential role of free-radical intermediates in the photodechlorination process. Quenching any of these intermediates will lead to a reduction in the photoreaction chain length and in the quantum yield.

Washing the soil with NaOH (0.1 M) followed by extraction with neutral rather than alkaline propanol reduced the amount of extracted humic acids in the final photolyzed mixtures by a factor of 3. Subsequent solar photolysis of these extracts (final PCB concentration 125 mg/L) under alkaline conditions (NaOH, 0.1 M), in the presence and absence of the sensitizer (PT), gave quantitative dechlorination in 4 and 12 h, respectively. Interestingly, we found that the photolyzed PCB extracts stayed clear and transparent to light throughout photolysis, making the use of this solvent system practical for soil photodecontamination.

To examine the possibility of directly decontaminating the soil, we suspended the soil in 2-propanol (20 g/100 mL) in pyrex containers sealed with Teflon-coated serum caps to prevent solvent evaporation. The suspensions were then photolyzed either at 350 nm in a Rayonet photoreactor or by exposure to sunlight with occasional agitation. An average of 70–80% dechlorination could be achieved in 2 days of photolysis at 350 nm or in 1 week of sunlight irradiation with the formation of biphenyl as end product. Further sunlight irradiation for another week did not lead to extra dechlorination unless a more vigorous and con-

tinuous agitation mechanism such as sonication was employed to help desorb PCBs from the soil particles.

In general, photodecontamination on soil is much slower than in solution because the pollutant is shielded from light by the soil and furthermore is photochemically quenched by other chemicals in the soil (*30*).

Environmental Significance

The present work clearly demonstrates that solar radiation is effectively used to dechlorinate PCBs to biphenyl in 2-propanol in the presence of a trace amount of phenothiazine. The sensitized photolysis can tolerate significant concentrations of water, methanol, and above all air (not pure oxygen), thus making the above photolysis attractive for field application. Additionally, 2-propanol is widely used for domestic purposes and is biodegradable, and its use as an additive in the above photolysis is relatively safe.

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Registry No. O_2, 7782-44-7; $PhNO_2$, 98-95-3; Aroclor 1254, 11097-69-1; phenothiazine, 92-84-2; 3-chlorobiphenyl, 2051-61-8.

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