

Degradation of Polychlorinated Biphenyls Induced by Ionizing Radiation in Aqueous Micellar Solutions

DANIEL C. SCHMELLING,[†]
 DIANNE L. POSTER,[‡]
 MAHNAZ CHAYCHIAN,[†]
 PEDATSUR NETA,[§]
 JOSEPH SILVERMAN,[†] AND
 MOHAMAD AL-SHEIKHLY*,[†]

*Department of Materials and Nuclear Engineering,
 University of Maryland at College Park, College Park,
 Maryland 20742-2115, Analytical Chemistry Division,
 Chemistry Building, Room B208, National Institute of
 Standards and Technology, Gaithersburg, Maryland 20899,
 and Physical and Chemical Properties Division, Chemistry
 Building, Room A261, National Institute of Standards and
 Technology, Gaithersburg, Maryland 20899*

This investigation examines the γ -radiation-induced degradation of polychlorinated biphenyls (PCBs) in aqueous surfactant solutions. Dichloro-, tetrachloro-, and decachlorobiphenyl congeners were solubilized in water using a commercially available non-ionic surfactant, Triton X-100, and subsequently irradiated by a ^{60}Co γ -source. Rates and extent of dechlorination were determined at different surfactant concentrations, and intermediate species and byproducts were quantified. Pulse radiolysis was used to measure rates of reaction between PCBs and the solvated electron as well as rates of electron scavenging by the surfactant. Experiments were also conducted in organic solvents, and these results have been compared to those observed in the aqueous surfactant solutions. Each PCB congener was fully dechlorinated by ionizing radiation in the micellar systems. Initial chloride yields were directly proportional to the level of chlorination of the PCB congeners. Scavenging of the aqueous electron by the surfactant was significant, and PCB degradation efficiency improved markedly at lower surfactant concentrations. PCB transformation occurred primarily through reductive dechlorination, forming lower chlorinated PCBs and biphenyl. Rates of PCB degradation were substantially higher in aqueous surfactant solutions than in diethyl ether and petroleum ether. This suggests that solubilizing PCBs in water using a surfactant prior to irradiation may provide a considerable improvement in contaminant degradation efficiency in comparison to using an organic solvent or irradiating PCBs directly in oil.

Introduction

Polychlorinated biphenyls (PCBs) are a class of 209 congeners that were widely used in numerous industrial applications. PCBs were produced in the United States from 1929 until 1977 when concern over adverse environmental effects led to a ban on their industrial manufacture under the Toxic Substances Control Act of 1976 (TSCA) (1). During this period world production of PCBs was approximately 1.5 million t with 650 000 t generated in the United States (2). It has been estimated that 20–30% of this amount entered the environment as contamination (3), while in the United States in 1992 approximately 200 000 t of PCBs were still in use as insulating oils in capacitors, transformers, and other electrical equipment (4).

The widespread release of PCBs into the environment presents a serious problem due to their persistence and toxicity. In humans and laboratory animals, PCBs have been shown to elicit an array of toxic responses (5–7) that are compounded by the tendency of PCBs to bioaccumulate (8, 9). Additionally, PCBs exhibit high thermal and chemical stability and do not decompose or biodegrade significantly in natural systems (10). As a consequence of these factors, the United States Environmental Protection Agency (U.S. EPA) has identified remediation of PCB-contaminated soil and sediment as a high priority (11).

The radiation-induced decomposition of PCBs has been investigated in a variety of organic solvents (12–27), including mineral oils (22–25, 27), and in a 2-propanol soil slurry (14). Detailed scavenger studies by Mincher *et al.* (25) and Arbon *et al.* (22) implicated the solvated electron as the major reactive species in the γ -radiation-induced destruction of PCBs in neutral solutions of both 2-propanol (25) and isooctane (22). The reaction efficiency has been observed to vary significantly in different solvents (12, 13, 17, 18, 24), and a chain dechlorination reaction has been reported to occur in alkaline solutions of 2-propanol (13). In addition, the yield for radiation-induced dechlorination of different PCB congeners has, in general, been demonstrated to increase with an increasing degree of chlorine substitution (12, 21), consistent with the corresponding decrease in the energy level of the lowest unoccupied molecular orbital (21).

In the current investigation, we examine the γ -radiation-induced degradation of PCBs in aqueous surfactant solutions. Surfactants have been used in earlier work to extract PCB contaminated oil from soil (28–32), and ionizing radiation may be effective in degrading the extracted PCBs in this matrix. In addition, the free electron yield in nonpolar solvents, such as mineral oil, is usually quite small in comparison to that measured in water (33). Therefore, mixing water with contaminated oil in an emulsion prior to radiolysis has the potential to substantially increase the PCB destruction efficiency by raising the overall yield of solvated electrons.

We have used a commercially available non-ionic surfactant, Triton X-100, to solubilize in water dichloro-, tetrachloro-, and decachlorobiphenyl congeners and subsequently irradiated the solutions using a ^{60}Co γ -source. Rates and extent of dechlorination have been determined at different surfactant concentrations, and intermediate species and byproducts have been quantified. Pulse radiolysis was used to measure rates of reaction between PCBs and the solvated electron in micellar solutions as well as rates of electron scavenging by the surfactant. Experiments were also conducted in organic solvents, and these results have been compared to those observed in the aqueous surfactant solutions. To our knowledge, this is the first presentation of

* To whom correspondence should be sent. Telephone: 301-405-5214; fax: 301-314-9467; e-mail: mohamad@eng.umd.edu.

[†] University of Maryland at College Park.

[‡] Analytical Chemistry Division, NIST.

[§] Physical and Chemical Properties Division, NIST.

data on radiation-induced degradation of PCBs in aqueous surfactant solutions. This study investigates the influence of surfactant concentration, solvent type and polarity, dissolved oxygen concentration, and number of chlorine substituents on PCB dechlorination mechanisms and rates.

Radiation Chemistry

In the sample types considered in this study, transformation of PCBs induced by ionizing radiation are expected to occur predominantly through indirect effects. Indirect effects are secondary reactions of a target compound with the primary radicals formed by ionization of the chemical matrix. The initial products formed in a solution upon absorption of ionizing radiation are dependent upon the solvent and solution conditions. For water irradiated by low mean linear energy transfer (LET) radiation, such as ^{60}Co γ -rays and fast electrons, the primary yields in the pH range 3–11 are the following (34):

$$G(e_{\text{aq}}^-) = G(\text{OH}) = G(\text{H}_3\text{O}^+) = 0.28 \mu\text{mol/J}$$

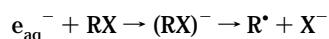
$$G(\text{H}) = 0.062 \mu\text{mol/J}$$

$$G(\text{H}_2) = 0.047 \mu\text{mol/J}$$

$$G(\text{H}_2\text{O}_2) = 0.072 \mu\text{mol/J}$$

Radical yields will be greater in the presence of higher concentrations of electron or hydroxyl radical scavengers (33). Solvated electrons are also formed in organic solvents. However, their yield decreases in nonpolar solvents due to higher rates of recombination with their geminate cations (33).

The hydroxyl radical (OH) is a powerful oxidant that adds to unsaturated bonds at rates near the diffusion-controlled limit and readily abstracts H from C–H bonds. Because of its high reactivity, the hydroxyl radical is not an efficient species in degrading contaminants that are present in relatively low concentrations in matrices with a high background concentration of organics, as is typically the case with PCBs. The OH radical is largely scavenged by the dominant organic material and is unavailable to react with the trace contaminant. In contrast, the solvated electron is a strong reducing agent whose reactivity is dependent upon the availability of a suitable vacant orbital. The reactivity of organic molecules toward the aqueous electron is enhanced by electron-withdrawing substituents, such as chlorine, adjacent to double bonds or attached to aromatic rings (34). Carbon–chlorine bond breakage occurs very rapidly through a dissociative electron capture process:



Because of its high reactivity with aromatic carbon–chlorine bonds, the solvated electron has the potential to be effective in dechlorinating PCBs even when other organic species are present in much higher concentrations.

Experimental Section

Materials. 2,6-Dichlorobiphenyl (PCB 10) (99+%), 2,2',6,6'-tetrachlorobiphenyl (PCB 54) (99+%), and decachlorobiphenyl (PCB 209) (99+%) were purchased from Accustandard (New Haven, CT). PCB congener numbers are listed according to Ballschmiter and Zell (35). Methanol, diethyl ether, sodium carbonate, sodium bicarbonate, and Triton X-100 were purchased from Fisher Chemical. Triton X-100, manufactured by Union Carbide Chemicals and Plastics Co., Inc., is a nonionic surfactant of the type described as ethoxylated alkylphenols; chemical formula: $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{O}-$

$(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ where $n = 9-10$. Petroleum ether was purchased from Burdick and Jackson. All reagents were of the highest grade available and were used without further purification. Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used in all experimental and analytical work (Millipore water purification system). [Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.]

Sample Preparation. Samples consisting of PCBs dissolved in aqueous surfactant solutions were prepared by first dissolving the PCBs in Triton X-100. Dissolution of decachlorobiphenyl was facilitated by stirring and heating ($50-60^\circ\text{C}$). The surfactant/PCB solution was then diluted with water to the desired concentration. Samples of PCBs dissolved in organic solvent solutions were prepared by dissolving the PCB directly into the final solution. All aqueous solutions contained a carbonate buffer ($5 \text{ mmol L}^{-1} \text{NaHCO}_3 + 5 \text{ mmol L}^{-1} \text{Na}_2\text{CO}_3$) that served to hold the pH at 10.3 during irradiation, thereby limiting scavenging of solvated electrons by H_3O^+ .

γ -Irradiation. γ -Irradiation of samples was conducted using the National Institute of Standards and Technology (NIST) (Gaithersburg, MD) Gammacell ^{60}Co radiation source, which had an average dose rate of 3.1 kGy/h during the period when experiments were carried out. Samples were irradiated in 5-mL glass vials, sealed with Teflon-lined caps. The caps were wrapped with paraffin film to further inhibit gas transfer between the sample and the atmosphere during irradiation. Except where noted, all solutions were in equilibrium with the atmosphere prior to irradiation.

Pulse Radiolysis. Pulse radiolysis experiments were performed using the NIST Febetron pulse radiolysis apparatus. Rate constants for reactions of solutes with the aqueous electron were determined by monitoring the decrease in absorbance of the electrons at 700 nm. Measurements of rates of reaction of the aqueous electron with PCBs in Triton X-100 micelles were made at PCB concentrations of 0.1 mmol L^{-1} , 0.05 mmol L^{-1} , and a blank in solutions containing 34 mmol L^{-1} Triton X-100 plus $5 \text{ mmol L}^{-1} \text{Na}_2\text{CO}_3$ and $5 \text{ mmol L}^{-1} \text{NaHCO}_3$. Rates of reaction of the aqueous electron with Triton X-100 micelles were measured at Triton concentrations of 34 mmol L^{-1} , 17 mmol L^{-1} , and a blank in aqueous solutions containing $5 \text{ mmol L}^{-1} \text{Na}_2\text{CO}_3$ and $5 \text{ mmol L}^{-1} \text{NaHCO}_3$. Dilution of the Triton solution from 34 to 17 mmol L^{-1} was performed by addition of an aqueous solution containing the carbonate buffer and 2% methanol (volume fraction). The methanol was used to maintain a relatively constant concentration of organic carbon in the solution. The bimolecular rate constants were calculated by a linear least squares curve fit through pseudo-first-order rate constants. All samples analyzed using pulse radiolysis were sparged with argon for 30 min to remove molecular oxygen prior to irradiation. UV-vis absorption analysis indicated that the composition of samples was not altered by sparging.

Sample Analysis. The concentration of chloride in aqueous surfactant solutions was measured using a Dionex DX-500 ion chromatograph (ED40 electrochemical detector, GP40 gradient pump, $25 \mu\text{L}$ injection loop) with a Dionex AS11 column (4 mm) and NaOH eluant (gradient method: increase from 0.2 to 15 mmol L^{-1} NaOH over 15 min). Five point calibration curves were generated for each analysis, and duplicate analyses were performed on each sample.

Concentrations of PCB congeners were determined by capillary gas chromatography (GC), electron capture detection (ECD), and mass spectrometry (MS) using a Hewlett

Packard 5890 Series II GC and a 6890 GC, respectively. The mass spectrometer was a Hewlett Packard 5970 with electron ionization. Both GCs were equipped with 60 m of 5% phenyl-methylpolysiloxane capillary columns (0.25 mm i.d., 0.25 μ m film thickness). Aqueous surfactant solutions were prepared for GC analyses by liquid-liquid partitioning into hexane, followed by concentration to <0.5 mL under nitrogen. Solvent-free Na_2SO_4 was used to break up the slight emulsion formed during liquid-liquid partitioning. Concentrated nonpolar samples were processed through silica solid-phase extraction cartridges (SPEs) to remove traces of water/surfactant that may have been soluble in hexane. SPEs were rinsed once with the mobile phase (10 mL of 2% methylene chloride:hexane) prior to sample processing, and two 10 mL aliquots were used to elute each sample. Collected eluants were reduced to 0.5 mL under nitrogen, transferred to amber vials, sealed with Teflon caps, and stored at -20°C in the dark until quantification by GC. Perdeuterated 4,4'-DDT was added to each solution prior to liquid-liquid partitioning for use as an internal standard. In addition, calibration standards were processed alongside the samples to generate response factors for each of the three PCB congeners studied in this work (PCBs 10, 54, and 209) relative to the internal standard. Identification of PCBs formed as byproducts was made using mass spectra data that allowed determination of the number but not the position of chlorine substituents. Reported concentrations of these assume a constant response factor relative to the internal standard.

The ability of the liquid-liquid partitioning procedure to isolate the desired hydrophobic compounds was evaluated by determining recoveries of analytes present in unirradiated aqueous surfactant PCB solutions. Specifically, four samples of aqueous surfactant solutions of PCB 54 and two samples of aqueous surfactant solutions of 11 other PCB congeners were processed using the method described above, and concentrations of the individual compounds were determined using GC/ECD. The average recovery of the 12 PCB congeners was 95–100%, indicating that the liquid-liquid partitioning and SPE cleanup procedures described above were efficient at isolating PCB congeners from aqueous surfactant solutions.

Results and Discussion

γ -Irradiation of PCBs in Micellar Solutions. The formation of chloride during γ -irradiation of aqueous surfactant solutions of three PCB congeners, 2,6-dichloro- (PCB 10), 2,2',6,6'-tetrachloro- (PCB 54), and decachlorobiphenyl (PCB 209) is displayed in Figure 1. These three PCB congeners were chosen for study because their chlorination levels span a wide range of values. The solutions were buffered and contained 2% Triton X-100 by volume, a nonionic surfactant. The initial concentration of PCB in each experiment was 100 $\mu\text{mol L}^{-1}$. For each congener, essentially all of the initial organic chlorine was converted to chloride. Thus, 0.2 mmol L^{-1} chloride was generated from 0.1 mmol L^{-1} dichlorobiphenyl; 0.1 mmol L^{-1} tetrachlorobiphenyl produced 0.4 mmol L^{-1} chloride; and 1 mmol L^{-1} chloride was released from 0.1 mmol L^{-1} decachlorobiphenyl. These results demonstrate that PCBs can be fully dechlorinated by γ -radiation in aqueous micellar systems.

The initial yields of chloride were 0.0045, 0.0092, and 0.0023 $\mu\text{mol J}^{-1}$ for dichloro-, tetrachloro-, and decachlorobiphenyl, respectively. These chloride yields are low relative to the yields of primary radicals formed by ionization of water, and they reflect the scavenging of reactive radicals by the surfactant, Triton X-100. It is also interesting to note that the initial chloride yields were directly proportional to the level of chlorination of the PCB congeners. Hence, the initial yield for chloride formation in the solution containing decachlorobiphenyl was approximately 2.5 times higher than

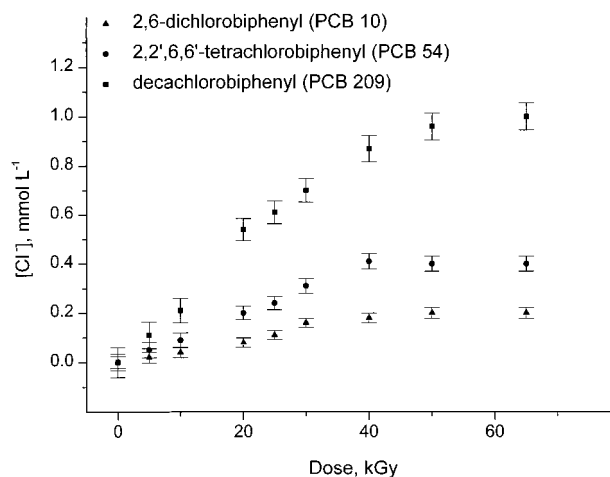


FIGURE 1. Formation of chloride during γ -irradiation of 0.1 mmol L^{-1} 2,6-dichloro (PCB 10), 2,2',6,6'-tetrachloro (PCB 54), and decachlorobiphenyl (PCB 209) in aqueous solutions of 2% (v/v) Triton X-100.

that observed for an equal concentration of tetrachlorobiphenyl and 5 times higher than the yield measured for dichlorobiphenyl.

The Triton X-100 was used at a 2% concentration (34 mmol L^{-1}) because this was found to be the lowest level that could solubilize 0.1 mmol L^{-1} decachlorobiphenyl in a stable solution. A 2% surfactant concentration is also typical of what has been used in washing PCB-contaminated oil from soil (29–32). The critical micellar concentration for Triton X-100 is approximately 0.3 mmol L^{-1} (36), which is well below the concentration used in these experiments. Considering this as well as the very low solubility of PCBs in water, it is assumed that essentially all of the PCBs were contained within micelles.

On the basis of previous work, the aqueous electron, e_{aq}^- , is well established as the radical primarily responsible for PCB dechlorination in these systems (22, 25, 34). In general, rates of reaction between e_{aq}^- and solutes contained within nonionic micelles are reduced in comparison to homogeneous aqueous-phase reactions (37, 38). This is due to lower rates of diffusion and to the higher chemical potential of an electron in the lipoidic interior of the micelle (39). In this research, the rate constant for the reaction between e_{aq}^- and Triton X-100 was determined by pulse radiolysis to be $1.2 \times 10^7 \text{ mol L}^{-1} \text{ s}^{-1}$, a value slightly lower than that reported in earlier work (38). For the reaction between decachlorobiphenyl and e_{aq}^- in the 2% Triton solution, the rate constant was measured as $2.6 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$. Rates of reaction with e_{aq}^- could not be quantified for either tetrachlorobiphenyl or dichlorobiphenyl because they were not sufficiently higher than the background scavenging of electrons by the surfactant. When it is considered that the initial concentration of the surfactant was approximately 340 times greater than the PCBs, these rate data demonstrate that a greater fraction of the solvated electrons in the micellar solutions reacted directly with the surfactant rather than with the PCBs.

The effect of the surfactant in suppressing PCB dechlorination rates is further illustrated in Figure 2, which shows the release of chloride during γ -irradiation of aqueous solutions of 2,2',6,6'-tetrachlorobiphenyl, solubilized using Triton X-100 at concentrations of 0.5%, 1.0%, and 2.0% (volume fraction). The efficiency of PCB dechlorination increased significantly as the surfactant concentration decreased. This was due to lower rates of reaction between the surfactant and the primary radicals generated radiolytically. Initial chloride yields were 0.0031, 0.0020, and 0.0092 $\mu\text{mol J}^{-1}$ for surfactant concentrations of 0.5%, 1.0%, and 2.0%, respectively.

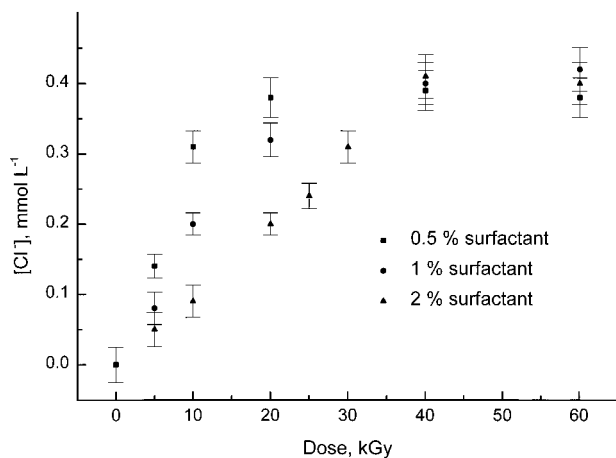


FIGURE 2. Formation of chloride during γ -irradiation of 0.1 mmol L^{-1} 2,2',6,6'-tetrachlorobiphenyl (PCB 54) in aqueous solutions of Triton X-100 at various concentrations.

Triton X-100 was chosen for this initial work because it solubilizes hydrophobic organic compounds well, and a previous study demonstrated alkylphenol ethoxylates, like Triton X-100, to be highly effective in washing transformer oil from contaminated soil (30). However, its pejorative influence on the overall radiolytic dechlorination rate of PCBs makes it a poor choice for use in this process application. We are currently testing different surfactants. These results, therefore, illustrate the importance of surfactant type and concentration when utilizing ionizing radiation to degrade contaminants within micellar systems.

The decay of the parent compound and the formation of lower chlorinated biphenyls during γ -irradiation of decachlorobiphenyl in the Triton X-100 micellar solution are shown in Figure 3. The solution conditions were the same as those described for Figure 1. Each data point in Figure 3 is equal to the molar sum of all measured PCBs whose number of chlorine substituents corresponds to the prefix shown in the legend. Initially decachlorobiphenyl degraded predominantly through reductive dechlorination, forming less chlorinated PCBs as a result. The conversion of the biphenyl radicals, formed through reactions of solvated electrons with PCBs, into biphenyl products suggests that these radicals, like other aryl radicals (40, 41), are good H-abstractors and react rapidly with Triton X-100. After a radiation dose of 5 kGy, approximately $70 \mu\text{mol L}^{-1}$ decachlorobiphenyl had degraded and $64 \mu\text{mol L}^{-1}$ lower chlorinated PCBs, primarily nonachloro- and octachloro-, had been produced. These PCB concentrations were also consistent with measurements of chloride (Figure 1). A mass balance on chlorine indicates that at a dose of 5 kGy, 30% of the initial organic chlorine was still present in decachlorobiphenyl, 54% in lower chlorinated PCBs, and 11% had formed chloride. However, as the average number of chlorine substituents on the PCBs decreased at higher radiation doses, mechanisms other than reductive dechlorination became increasingly important in PCB transformation. For example, essentially no decachlorobiphenyl remained after a radiation dose of 20 kGy. At this point approximately half of the initial organic chlorine had been released as chloride, but measured PCB concentrations could account for only 14% of the remaining chlorine; the remainder was in the form of unidentified organic chlorides. Cleavage of the aromatic rings, hydrogenation, and reactions with the surfactant are likely to have contributed to this behavior. Similar observations have been made by other researchers (18, 42).

Comparison of Micellar and Organic Solvent Systems. Results from the γ -radiation-induced degradation of 2,2',6,6'-tetrachlorobiphenyl in a 2% Triton X-100 surfactant solution

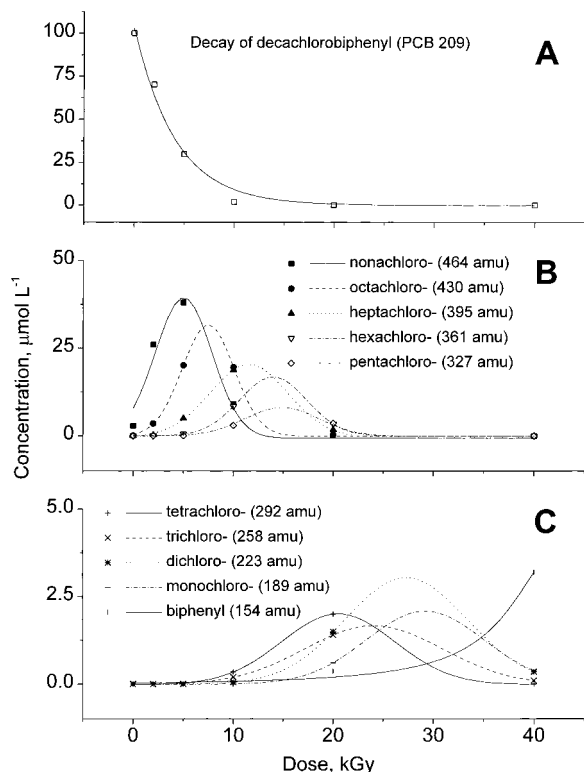


FIGURE 3. γ -Radiation-induced decay of 0.1 mmol L^{-1} decachlorobiphenyl (PCB 209) in aqueous solution of 2% (v/v) Triton X-100 (A) and formation of lower chlorinated biphenyls (B and C). Fitted first-order exponential decay gives the following equation: $y = 103e^{-(x)/4.1}$. Gaussian curves are fitted to the formation data to demonstrate doses of radiation that likely produced the peak amounts of the lower chlorinated biphenyl congeners. Biphenyl production was not detected until the highest dose (40 kGy).

are compared with those observed in two organic solvents, petroleum ether and diethyl ether, in Figure 4. The petroleum ether was composed of low molecular weight alkanes, primarily C5 and C6 (99.9%). γ -Irradiation of petroleum ether yields hydrogen and hydrocarbons with a range of molecular weights (33). This behavior is similar to what would be observed in the irradiation of paraffinic-base mineral insulating oils, which are found in PCB-contaminated transformers (43). The yield of solvated electrons in diethyl ether is greater than that measured for the paraffins found in petroleum ether (44), and it solubilizes PCBs well. As shown by Figure 4, PCB degradation in all three solvents occurred predominantly through reductive dechlorination, leading to formation of lower chlorinated PCBs and biphenyl. However, PCB degradation took place with a significantly higher yield in the surfactant solution than in either the petroleum ether or diethyl ether. A reduction of 90% in the initial tetrachlorobiphenyl concentration occurred at a dose of 8.3 kGy in the surfactant solution while doses of 18 and 26 kGy were required to achieve this level of degradation in the diethyl ether and petroleum ether solutions, respectively. At a dose of 20 kGy, the total PCB concentration in the surfactant solution was reduced from an initial concentration of $100 \mu\text{mol L}^{-1}$ to less than $0.2 \mu\text{mol L}^{-1}$. The total PCB concentration was only reduced to $50 \mu\text{mol L}^{-1}$ in the diethyl ether solution and to $59 \mu\text{mol L}^{-1}$ in the petroleum ether solution after a 20 kGy radiation dose.

Previous work has noted rates of radiation-induced PCB dechlorination to increase in more polar solvents (12, 17, 18, 24), as a result of higher yields and longer lifetimes of solvated electrons (18). However, significant deviations from this trend have been reported. Arbon *et al.* (22) observed

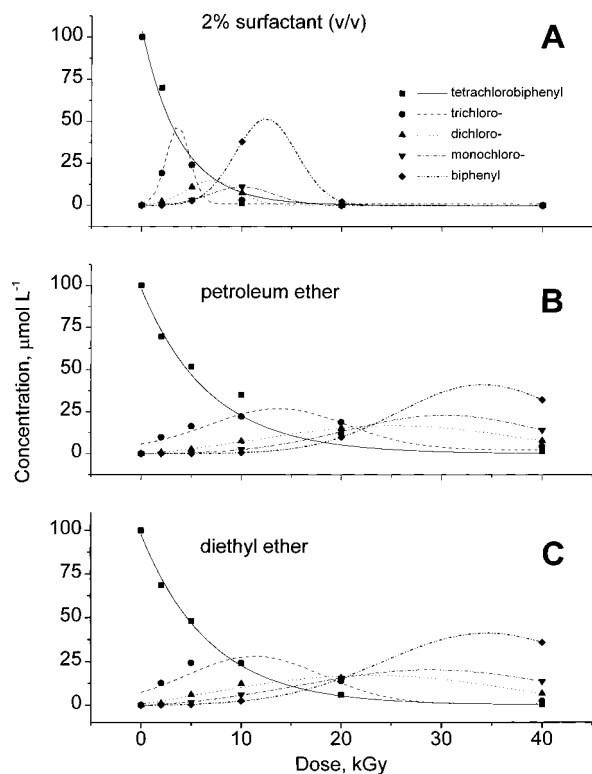


FIGURE 4. γ -Radiation-induced decay of 0.1 mmol L^{-1} 2,2',6,6'-tetrachlorobiphenyl (PCB 54) in various solutions and the formation of lower chlorinated biphenyls. (A) 2% (v/v) Triton X-100; $y = 103e^{-(x)/3.8}$. (B) Petroleum ether; $y = 95e^{-(x)/9.0}$. (C) Diethyl ether; $y = e^{-(x)/6.8}$. Gaussian curves are fitted to the formation data to demonstrate doses of radiation that likely produced the peak amounts of the lower chlorinated biphenyl congeners.

radiation-induced PCB degradation to be more efficient in isooctane than 2-propanol even though 2-propanol has a solvated electron yield more than an order of magnitude greater than isooctane. Moreover, in a comparison by Lepine and Massé (18) of the γ -irradiation of 2,2',6,6'-tetrachlorobiphenyl in solutions of petroleum ether and methanol:water (80:20), a substantially higher degradation rate occurred in the petroleum ether, which is far more hydrophobic than methanol. This behavior was attributed to the *ortho* position of the chlorine substituents in the PCB inhibiting reaction with $\cdot\text{CH}_2\text{OH}$ radicals generated in the methanol solution. Hence, our observation of a higher PCB degradation rate in the 2% Triton X-100 solution relative to those measured in petroleum ether and diethyl ether suggests that solubilizing PCBs in water using a surfactant prior to irradiation may provide a considerable improvement in contaminant degradation efficiency in comparison to using an organic solvent or irradiating PCBs directly in oil.

Influence of Oxygen. Molecular oxygen reacts rapidly with many nucleophilic radicals (33). Consequently, the presence of dissolved oxygen might be expected to reduce radiation-induced PCB degradation efficiency through scavenging reactive species, such as solvated electrons. Arbon *et al.* (22) reported an increase in the destruction rate of PCBs in isooctane when the solution was sparged with nitrogen prior to irradiation. However, both Sawai and Shinozaki (12) and Mincher *et al.* (25) observed that molecular oxygen did not affect the γ -radiation-induced dechlorination of PCBs in methanol and 2-propanol.

A comparison of the chloride released during γ -irradiation of aerated and nitrogen sparged solutions of 1.0 mmol L^{-1} 2,2',6,6'-tetrachlorobiphenyl in 77% methanol:23% water is presented in Figure 5. Solutions were sparged prior to

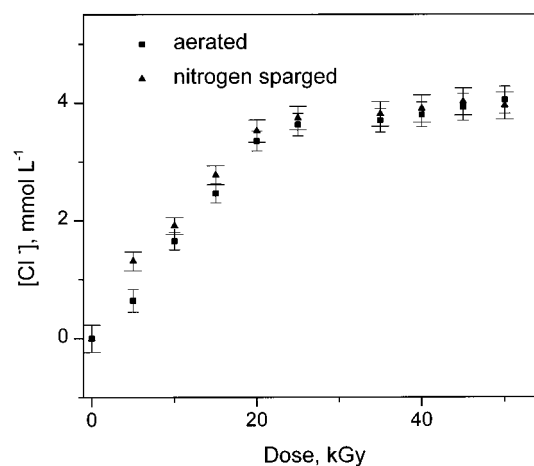


FIGURE 5. Comparison of chloride formation during γ -irradiation of aerated and nitrogen sparged solutions of 1.0 mmol L^{-1} 2,2',6,6'-tetrachlorobiphenyl (PCB 54) in 77% methanol:23% water (v/v). Solutions were sparged prior to irradiation and were contained in sealed gas-tight vials during the experiment.

irradiation and were contained in sealed gas-tight vials during the irradiation. Irradiated samples were first analyzed after a dose of 5 kGy. At this point, approximately twice as much chloride had formed in the deaerated sample as in the sample that was initially aerated, such that the initial chloride yields were 0.26 and $0.13 \mu\text{mol J}^{-1}$, respectively. The significantly lower chloride yield observed in the aerated solution suggests that the radicals responsible for PCB dechlorination in this system were effectively scavenged by molecular oxygen. After a dose of 5 kGy, the aerated solution displayed essentially the same relative chloride yield per dose as the deaerated solution, indicating that most of the initial molecular oxygen had been reduced and was no longer acting as a radical scavenger.

When aqueous solutions of methanol containing dissolved oxygen are irradiated, O_2 reacts with methanol radicals ($\cdot\text{CH}_2\text{OH}$), eventually producing formaldehyde and formic acid, and scavenges solvated electrons and hydrogen atoms to form a superoxide anion (O_2^-), and the perhydroxyl radical (HO_2) (33, 45, 46). The combined yield of H , e_{solv}^- and $\cdot\text{CH}_2\text{OH}$, in these solutions is estimated as $0.54 \mu\text{mol J}^{-1}$ based on proportionately averaging the yields of these species in pure solutions of water and methanol (33). The initial concentration of dissolved oxygen in the aerated solution was 1.7 mmol L^{-1} . Accordingly, a radiation dose between 3 and 6 kGy should have generated enough radicals to fully eliminate the dissolved oxygen initially present in the aerated solution. These data indicate that this was the case. Thus, while molecular oxygen had an inhibitory effect on PCB dechlorination in these systems, the radiation dose required to reduce the dissolved oxygen initially present in an aerated sample was relatively small in comparison to the dose required to fully dechlorinate the PCBs.

Comparison of the initial chloride yield for 2,2',6,6'-tetrachlorobiphenyl in the aerated 77% methanol solution to those measured in the aerated Triton X-100 solutions shown in Figure 2 shows that the yield in the alcohol solution was substantially higher. However, the starting PCB concentration in the methanol solution was 10 times higher than in the surfactant solutions, and the data in Figure 1 indicate that the initial chloride yields in this concentration range are proportional to the concentration of organic chlorine. If the yields in the two solutions are normalized by their initial PCB concentrations, then the specific chloride yield per dose in the alcohol solution is greater than that observed in the solution with 2% surfactant and less than that in the 1% surfactant solution.

Acknowledgments

We thank Robert Huie of the Physical and Chemical Properties Division of NIST for helpful suggestions throughout this study. This project was supported in part by the National Science Foundation through Grant BES-9320339.

Literature Cited

- (1) Woodyard, J. P.; King, J. J. *PCB Management Handbook*, 2nd ed.; Executive Enterprises Publications Co., Inc.: New York, 1992; pp 3–12.
- (2) De Voogt, P.; Brinkman, U. In *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*; Kimbrough, R. D., Jensen, A. A., Eds.; Elsevier: Amsterdam, 1989.
- (3) Webster, T.; Commoner, B. In *Overview of the Dioxin Debate*; Schechter, A., Ed.; Plenum: New York, 1994; pp 1–50.
- (4) Amend, L. J.; Lederman, P. B. *Environ. Progr.* **1992**, *11*, 173–177.
- (5) Mousa, M. A.; Quensen, J. F., III; Chou, K.; Boyd, S. A. *Environ. Sci. Technol.* **1996**, *30*, 2087–2092.
- (6) Safe, S. H. *Crit. Rev. Toxicol.* **1994**, *24*, 87–149.
- (7) Sittig, M. In *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 3rd Ed.; Noyes Publications: New York, 1991.
- (8) Gobas, F. A.; Z'Graggen, M. N.; Zhang, X. *Environ. Sci. Technol.* **1995**, *29*, 2038–2046.
- (9) Strachan, W. M. J. *Polychlorinated Biphenyls (PCBs)—Fate and Effects in the Canadian Environment*; report prepared for Toxic Chemicals Steering Committee, Canadian Council of the Resource and Environment Ministers; Report EPS 4/HA/2; 1988.
- (10) McDonald, C. J.; Tourangeau, R. E. *PCBs: Question and Answer Guide Concerning Polychlorinated Biphenyls*, Commercial Chemicals Branch, Environmental Protection Service, Environment Canada, Catalog No. EN40-335/1986E, 1986.
- (11) Davila, B.; Whitford, K. W.; Saylor, E. S. *EPA Engineering Issue: Technology Alternatives for the Remediation of PCB-Contaminated Soil and Sediment*; EPA/540/S-93/506; U.S. EPA: Washington, DC, 1993.
- (12) Sawai, T.; Shinozaki, Y. *Chem. Lett.* **1972**, 865–868.
- (13) Sawai, T.; Shimokawa, T.; Shinozaki, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1889–1893.
- (14) Singh, A.; Kremers, W.; Smalley, P.; Bennett, G. S. *Radiat. Phys. Chem.* **1985**, *25*, 11–19.
- (15) Monig, J.; Asmus, K.-D.; Robertson, L. W.; Oesch, F. *J. Chem. Soc. Perkin Trans. 2* **1986**, 891–896.
- (16) Anklam, E.; Asmus, K.-D.; Robertson, L. W. *J. Chem. Soc. Perkin Trans. 2* **1989**, 1573–1576.
- (17) Lepine, F.; Massé, R. *Bull. Environ. Contam. Toxicol.* **1990**, *44*, 549–554.
- (18) Lepine, F.; Massé, R. *Environ. Health Perspect.* **1990**, *89*, 183–187.
- (19) Lepine, F.; Milot, S.; Gagne, N. *J. Agric. Food Chem.* **1990**, *38*, 1873–1876.
- (20) Arbon, R. E.; Mincher, B. J.; Meikrantz, D. H. *Gamma radiolysis of chlorinated hydrocarbons*; Report prepared for U.S. Department of Energy, Office of Technical Development; EGG-M92301, DE92 018028, NTIS CONF-920851-59.
- (21) Arbon, R. E.; Mincher, B. J.; Knighton, W. B. *Environ. Sci. Technol.* **1994**, *28*, 2191–2196.
- (22) Arbon, R. E.; Mincher, B. J.; Knighton, W. B. *Environ. Sci. Technol.* **1996**, *30*, 1866–1871.
- (23) Mincher, B. J.; Meikrantz, D. H.; Arbon, R. E.; Murphy, R. J. *High energy decomposition of halogenated hydrocarbons, FY91 final report*; prepared for U.S. Department of Energy, Office of Technical Development; EGG-WTD-9935; 1991.
- (24) Mincher, B. J.; Arbon, R. E.; Meikrantz, D. H. *High energy decomposition of halogenated hydrocarbons, FY92 final report*; Prepared for U.S. Department of Energy, Office of Technical Development; EGG-PHY-10446, DE93 005268; 1992.
- (25) Mincher, B. J.; Arbon, R. E.; Meikrantz, D. H. *High energy decomposition of halogenated hydrocarbons, FY93 final report*; Prepared for U.S. Department of Energy, Office of Technical Development; EGG-NRP-10991; 1993.
- (26) Al-Sheikhly, M.; Silverman, J.; Neta, P.; Karam, L. *Environ. Sci. Technol.* **1997**, *31*, 2473–2477.
- (27) Matthews, S. M.; Boegel, A. J.; Caulfield, R. A.; Jovanovich, M. C.; Loftis, J. A. *Radiolytic decomposition of environmental contaminants using an electron accelerator*; Paper prepared for submittal to the Waste Minimization/Pollution Prevention Conference San Francisco, CA, April 13–15, 1993.
- (28) Scholz, R.; Milanowski, J. *J. Hazard. Mater.* **1984**, *91*, 241–252.
- (29) Nash, J.; Traver, R. P. *Field evaluation of in situ washing of contaminated soils with water/surfactants*; Proceedings of the 12th annual research symposium; EPA/600/9-86/022; U.S. EPA: Washington, DC, 1986.
- (30) Abdul, A. S.; Gibson, T. L.; Rai, D. N. *Ground Water* **1990**, *28*, 920–926.
- (31) Abdul, A. S.; Gibson, T. L. *Environ. Sci. Technol.* **1991**, *25*, 665–671.
- (32) Abdul, A. S.; Gibson, T. L.; Ang, C. C.; Smith, J. C.; Sobczynski, R. E. *Ground Water* **1992**, *30*, 219–231.
- (33) Spinks, J. W.; Woods, R. J. In *An Introduction to Radiation Chemistry*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1990.
- (34) Buxton, G. V. In *Radiation chemistry of the liquid state: (1) Water and homogeneous aqueous solutions, Radiation Chemistry, Principles and Applications*; Farhatziz, Rodgers, M. A., Eds.; VCH Publishers Inc.: New York, 1987; pp 321–376.
- (35) Ballschmiter, K.; Zell, M. *Fresenius Z. Anal. Chem.* **1980**, *302*, 20–31.
- (36) Rosen, M. J. In *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley & Sons: New York, 1989; pp 326–329.
- (37) Wallace, S. C.; Thomas, J. K. *Radiat. Res.* **1973**, *54*, 49–62.
- (38) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133–138.
- (39) Henglein, A.; Grätzel, M. In *Electron transfer in heterogeneous photochemical reactions, Solar Power and Fuels*; Bolton, J. R., Ed.; Academic Press, Inc.: New York, 1977; pp 53–73.
- (40) Mertens, R.; von Sonntag, C. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1262–1264.
- (41) Fang, X.; Mertens, R.; von Sonntag, C. *J. Chem. Soc. Perkin Trans. 2* **1995**, 1033–1036.
- (42) Atkinson, R. *Environ. Sci. Technol.* **1987**, *21*, 305–307.
- (43) Shugg, W. T. In *Handbook of Electrical and Electronic Insulating Materials*; Van Nostrand Reinhold: New York, 1986; pp 471–494.
- (44) Allen, A. O. *Yields of Free Ions Formed in Liquids by Radiation*; NSRDS-NBS 57; National Bureau of Standards: Gaithersburg, MD, 1976.
- (45) von Sonntag, C.; Schuchmann, H. P. In *Peroxy Radicals*; Alfassi, A. B., Ed.; Wiley: London, 1997; pp 173–234.
- (46) Bothe, E.; Schulte-Frohlinde, D. *Z. Naturforsch.* **1978**, *33N*, 786–788.

Received for review May 27, 1997. Revised manuscript received October 1, 1997. Accepted October 12, 1997.*

ES9704601

* Abstract published in *Advance ACS Abstracts*, November 15, 1997.