Ionizing Radiation Induced Degradation of Tetrachlorobiphenyl in Transformer Oil

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Complete degradation of 2,2′,6,6′-tetrachlorobiphenyl (PCB-54) in transformer oil is achieved by ionizing radiation without degradation of the oil. γ-Irradiation of transformer oil containing PCB-54 (0.27 mg/g) with a dose of 200 kGy results in complete (>99%) destruction of the PCB. Analysis of samples irradiated with various doses demonstrated gradual degradation of PCB-54 and successive formation and degradation of trichloro-, dichloro-, and monochlorobiphenyl. The final products are mainly biphenyl and inorganic chloride. The mechanism of reductive degradation is studied by pulse radiolysis. The oil contains many aromatic hydrocarbons; the most abundant being biphenyl, fluorene, and phenanthrene. Solvated electrons formed by irradiation of the oil react either with the PCB to lead to dechlorination or with the aromatic hydrocarbons present in the oil to form radical anions. These species are shown to transfer an electron to chlorinated biphenyls relatively rapidly, leading to dechlorination. The rate constants for several such reactions, determined in 2-propanol solutions, are in the range of $10^7–10^8$ L mol^{-1} s^{-1}. These rapid reactions explain why PCB can be dechlorinated in oil despite the presence of aromatic hydrocarbons in the oil and despite the formation of biphenyl as a radiolysis product that reacts rapidly with solvated electrons.

Introduction

The widespread use of polychlorinated biphenyls (PCBs) in various industrial applications presents a major environmental issue due to the toxicity of these compounds and their long lifetime in ambient conditions. The method currently used to destroy most PCB-containing materials is incineration (*1*). This method, however, suffers from two disadvantages: it incinerates the medium along with the PCB, and it converts some of the PCB into more toxic materials, namely, dioxins. Radiolytic degradation of PCBs in organic solvents and in transformer oils may overcome both of these disadvantages. The PCBs may be reduced into inorganic chloride and biphenyl, without formation of any dioxins, while the organic solvent or oil may remain practically

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unchanged and can be recycled. Several recent studies have pointed to this more beneficial outcome (*2−5*). In the present study, we examine the degradation of PCB-54 in transformer oil by ionizing radiation, and we analyze the various intermediate and final products. Furthermore, we investigate the mechanism of radiolytic reduction and determine the rate constants for some relevant reactions by pulse radiolysis.

Experimental Section

Materials. 2,2′,6,6′-Tetrachlorobiphenyl (PCB-54) (*6*) was purchased from AccuStandard (New Haven, CT). Shell Diala AX was used as the transformer oil. The PCB was dissolved in the oil (0.27 mg/g) by stirring and heating to 50 °C.

γ-**Irradiation**. Aliquots of the PCB oil solutions (4 g) were irradiated at room temperature in a Gammacell ^{60}Co source with a dose rate of 2.68 kGy/h (at the National Institute of Standards and Technology). The samples were irradiated in 5-mL glass vials sealed with Teflon-lined caps with doses between 2 and 240 kGy.

Product Analysis. The concentration of PCB-54 in the irradiated samples was determined by capillary gas chromatography (GC) with electron capture detector (ECD) using a 5% phenyl methylpolysiloxane capillary column (60 m × 0.25 mm; 0.25 μm film). Prior to GC/ECD analysis, subsamples of approximately 0.1 g from each irradiated oil sample (four for each dose) were processed through aminopropylsilane solid-phase extraction cartridges (SPEs) to isolate PCB-54 and chlorinated aromatic products from the oil matrix using hexane as the mobile phase. Two subsamples of the nonirradiated oil were also processed to document the initial concentration of PCB-54 and to use as a matrix blank. The SPEs were rinsed once with 20 mL of hexane prior to sample processing, and the samples were eluted with 20 mL of hexane each. The collected eluants were reduced to 0.5 mL under nitrogen, processed again through the SPEs with the same mobile phase, concentrated, transferred to amber vials, sealed with Teflon caps, and stored at −20 °C in the dark until quantification by duplicate GC/ECD analyses. Prior to SPE processing, ^{13}C-2,4,4′-trichlorobiphenyl (PCB-28 (*6*)) was added to each sample for use as an internal standard. In addition, calibration standards of PCB-54 were processed alongside the oil samples to generate a response factor for PCB-54 relative to the internal standard. The ability of the SPE method to isolate PCB-54 from oil was evaluated by determining recoveries of PCB-54 present in unirradiated oil. Three samples of PCB-54 in oil were processed using the method described above, and the concentration of PCB-54 was determined using GC/ECD. The average recovery ($N = 3$) of PCB-54 was 103%, and the standard deviation was 7%. The GC/ECD data were corrected for this average recovery.

The decay of PCB-54 in irradiated oil was also determined by a second analytical technique, namely, GC with mass spectrometry (MS) using the same capillary column described above, with the intent to also identify and quantify PCB congeners formed as products of irradiation. However, due to the complexity of the oil matrix, the sample preparation method used for GC/ECD analyses was not sufficient for GC/MS. For example, a chromatogram obtained from the GC/MS analysis of a PCB-54 in oil sample prepared for GC/ECD is shown in Figure 1A. The high background results from the complex oil matrix and eliminated the possibility of accurately quantifying the PCB congeners. This complicated background can be virtually eliminated by selective extraction of the aromatic components with dimethyl sulfoxide (DMSO). Larsen et al. (*7*) demonstrated that this method, also described by Orazio et al. (*8*) for the determi-
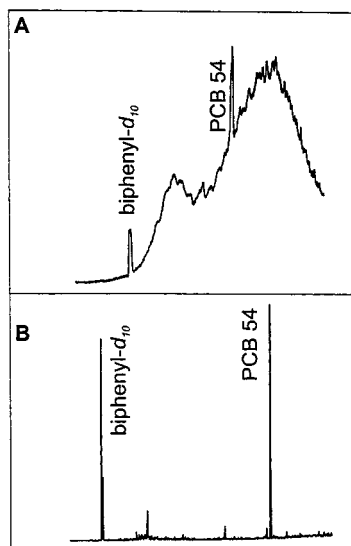
FIGURE 1. Chromatograms from the GC/MS analysis of transformer oil containing biphenyl-d_{10} and PCB-54 without (A) and with (B) DMSO cleanup. The y axis is Ge/MS response and the x axis is time.
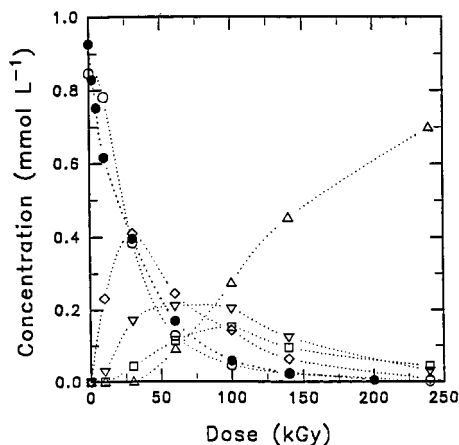

FIGURE 2. Concentration of PCB-54 and its radiation products in transformer oil as a function of irradiation dose. The concentrations of PCB-54 were determined by GC/ECD (○) and by GC/MS (●). The concentrations of the radiation products were determined by GC/MS: 2,2',6-trichlorobiphenyl (◇), 2,2'-dichlorobiphenyl (▽), 2-chlorobiphenyl (□), and biphenyl (△). The initial concentration of PCB-54 was 0.27 mg/g oil.

nation of polychlorinated dibenzo-p-dioxins and dibenzofurans in waste oil, effectively isolates PCB congeners and all aromatic compounds from oil without discrimination due to the chlorine substitution pattern. Figure 1B shows the chromatogram of PCB-54 in oil after DMSO "cleanup". To prepare each irradiated oil sample and two unirradiated oil samples for GC/MS analyses, aliquots from each oil sample were SPE processed once using the method described above, and the resulting hexane was partitioned with DMSO. The DMSO phase was back-extracted with hexane and deionized water. The DMSO/water phase was saved and partitioned with hexane to remove traces of aromatic compounds that may have solubilized in the water. This hexane phase was combined with the previous one, concentrated under nitrogen, and processed through a silica SPE to remove possible traces of water that may have solubilized in the hexane during the liquid−liquid partitioning step. The processed samples were concentrated 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 duplicate GC/MS analyses. Prior to the sample preparation, biphenyl-d_{10} was added to each sample for use as an internal standard. In addition, calibration standards of PCB-54 were processed alongside the oil samples to generate a response factor for PCB-54 relative to the internal standard. The ability of the DMSO method to isolate PCB-54 from oil was evaluated by determining recoveries of PCB-54 present in unirradiated oil. Specifically, two samples of PCB-54 in oil were processed using the method described above, and the concentration of PCB-54 was determined using GC/MS. The two recoveries of PCB-54 were 102% and 112%.

Pulse Radiolysis Studies. The spectra of the intermediate species produced by the radiation and the kinetics of their reactions were investigated by pulse radiolysis, by using the 2 MeV Febetron-based apparatus at NIST (9). The dose per pulse was varied from 15 to 30 Gy. All solutions for these studies were deoxygenated by bubbling with ultra-high-purity Ar for 20 min prior to irradiation and were irradiated at room temperature.

Results and Discussion

Product Analysis. The concentration of PCB-54 remaining after γ-irradiation was determined both by GC/ECD and by GC/MS, and the values were found to be in very good

agreement. The remaining concentration as a function of dose is shown in Figure 2. From these data, we determined the concentration of biphenyl and the chlorinated biphenyls and found the resulting sum to be independent of dose. The results also show that a dose of 200 kGy destroys practically all (>99%) of the PCB.

To identify and quantify the intermediate and final products of the irradiated PCB-54 in oil, the extracted samples and PCB congener calibration mixtures (AccuStandard C-CSQ-SET) were analyzed by GC/MS. The products were determined by using the retention time of each congener and their response factor relative to the internal standard. The results shown in Figure 2 demonstrate that the initial product observed after short irradiations is 2,2',6-trichlorobiphenyl; subsequently, this is degraded to 2,2'-dichlorobiphenyl and then to 2-chlorobiphenyl. Finally all the chlorinated compounds are dechlorinated, and the remaining product is biphenyl.

Mechanism and Kinetics. The transformer oil used in these experiments is reported by the supplier to contain mostly saturated hydrocarbons in the range of $C_{15}-C_{23}$, with varying amounts of aromatic hydrocarbons. Solvated electrons formed upon irradiation of this oil can be scavenged by the aromatic hydrocarbons to produce the corresponding radical anions. If PCB is also present in the oil, the electrons can be partially scavenged by the PCB. Since all polycyclic aromatics and PCBs react with solvated electrons with similar diffusion-controlled rate constants (10), the competition between the various components depends directly on their relative concentrations. Moreover, as the irradiation proceeds to convert some of the PCB into biphenyl, the fraction of solvated electrons reacting with the PCB correspondingly decreases. However, the radical anions formed by reaction of the electron with biphenyl and with other aromatic hydrocarbons may transfer an electron to PCB and lead to dechlorination. It has been shown before that aromatic radical anions can transfer an electron to alkyl iodides relatively rapidly and to alkyl bromides more slowly (11, 12). On the basis of those results, we expect to be able to measure the rate constants for electron transfer to PCB-54. To validate the above mechanistic assumptions and to measure the relevant rate constants, we carried out pulse radiolysis experiments with oil alone and with solutions of some aromatic hydrocarbons and PCB-54 in 2-propanol.

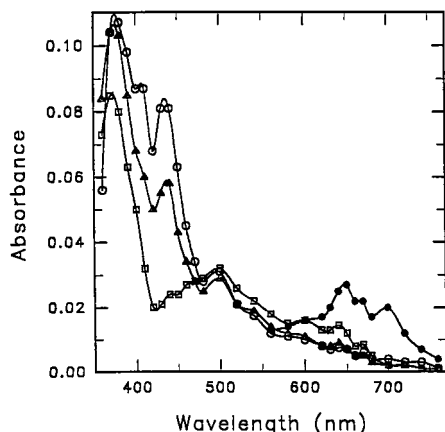First, we analyzed our oil sample to determine the concentrations of the various aromatic compounds (by GC/

FIGURE 3. Transient absorption spectra recorded by pulse radiolysis of the transformer oil used in the present study. The oil, containing 10% TEA, was deoxygenated by bubbling with ultra-high-purity Ar and was irradiated with a dose of 25 Gy/pulse. The spectra were recorded 0.3 (●), 1 (○), 3 (▲), and 20 μs (□) after the pulse.

MS after processing as described in the Experimental Section). We detected more than 50 aromatic compounds. The most abundant constituents are biphenyl (0.19 mmol/kg), fluorene (0.09 mmol/kg), and phenathrene (0.22 mmol/kg). Minor constituents include various methylated naphthalenes, phenanthrenes, and pyrenes. The same compounds were detected in oil irradiated with 240 kGy, although the composition varied somewhat.

Pulse radiolysis of the oil, thoroughly deoxygenated by bubbling with pure Ar, showed transient spectra composed of various peaks that were formed and decayed with different time profiles. Considerable luminescence was seen at the low wavelength range (λ < 500 nm), which prevented the observation of short-lived species in this range. Addition of 10% (volume) triethylamine was found to quench much of the luminescence and to increase the yield of the radical anions, in accord with previous results (13). The triethylamine is also expected to scavenge any remaining radical cations. Transient optical absorption spectra were monitored at different times after the pulse: 0.3, 1, 3, and 20 μs (Figure 3). The spectrum at 0.3 μs after the pulse was recorded only at λ > 500 nm (because of remaining luminescence) and is found to exhibit peaks at 700 and 650 nm that decay very rapidly. The spectrum recorded at 1 μs after the pulse has only remnants of these peaks but has strong absorptions at 440 and 380 nm. At 3 μs after the pulse, the 650 nm peak decayed completely while the other peaks have decayed only partially. At 20 μs after the pulse, the main peaks remaining are at 500 and 370 nm. These peaks decay at longer times. The main peaks observed at short times can be ascribed to the radical anions of biphenyl (650 nm), fluorene (700 nm), and phenanthrene (450 nm) (14). The radical anions of biphenyl and fluorene decay very rapidly, possibly via protonation by some protic contaminants in the oil (such as alcohols) (15) and/or via electron transfer to phenanthrene and pyrene and to more electron-affinic compounds. Previous studies (16) have demonstrated such electron-transfer reactions in alcohol solutions and measured very high rate constants for the electron transfer from the biphenyl radical anion to phenanthrene and pyrene.

The aromatic radical anions formed in irradiated oil may be expected to transfer an electron to PCB-54 and lead to dechlorination. The rate constants for such reactions could not be measured directly in the irradiated PCB/oil mixtures because of the complexity of this system. Therefore, kinetic measurements were carried out in 2-propanol solutions, where rate constants for individual electron-transfer reactions
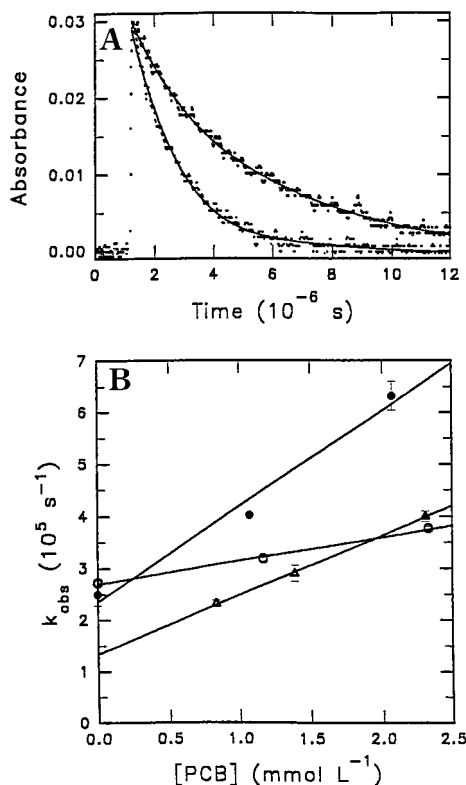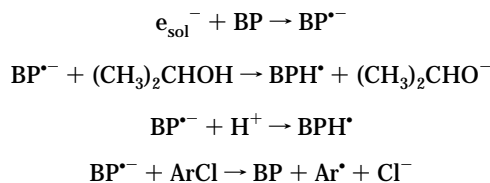

FIGURE 4. Reaction of aromatic radical anions with chlorinated biphenyls. (A) Decay of the biphenyl radical anion absorption at 630 nm in the absence (a) and presence (b) of 1 mmol L^{-1} PCB-54. (B) Observed first-order rate constants for the decay of biphenyl (630 nm) and phenanthrene (450 nm) radical anions as a function of PCB concentration. The three lines are for the reactions: (biphenyl)$^{\bullet-}$ + tetrachlorobiphenyl (●), (biphenyl)$^{\bullet-}$ + dichlorobiphenyl (△), and (phenanthrene)$^{\bullet-}$ + tetrachlorobiphenyl (○).

can be accurately determined. It should be noted, however, that the change in solvent may affect the rate constants for these electron-transfer reactions by up to an order of magnitude (17), but this will not affect the conclusions drawn below.

The rate constant for electron transfer from the biphenyl radical anion to PCB-54 was measured in deoxygenated 2-propanol solutions containing 18 mmol L^{-1} biphenyl and between 0 and 2.3 mmol L^{-1} PCB-54. The decay of the biphenyl radical anion was monitored at 630 nm (Figure 4). From the slope of the linear plot of k_{obs} vs PCB concentration, the second-order rate constant was calculated to be $(1.8 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1}. The decay in the absence of PCB is due to protonation of the biphenyl radical anion (15). The formation and decay of the biphenyl radical anion in these solutions can be summarized by the following reactions:

$$e_{sol}^- + BP \rightarrow BP^{\bullet-}$$

$$BP^{\bullet-} + (CH_3)_2CHOH \rightarrow BPH^{\bullet} + (CH_3)_2CHO^-$$

$$BP^{\bullet-} + H^+ \rightarrow BPH^{\bullet}$$

$$BP^{\bullet-} + ArCl \rightarrow BP + Ar^{\bullet} + Cl^-$$

Similarly, the rate constant for the reaction of the biphenyl radical anion with dichlorobiphenyl was determined to be $(1.4 \pm 0.2) \times 10^8$ L mol^{-1} s^{-1}. The rate constant for electron transfer from the phenanthrene radical anion to PCB-54 was also determined in 2-propanol solutions and found to be $(4.5 \pm 0.7) \times 10^7$ L mol^{-1} s^{-1}. The phenanthrene radical anion

reacts more slowly with PCB-54 than the biphenyl radical anion because the reduction potential of phenanthrene is less negative than that of biphenyl (*18*). For the same reason, the pyrene radical anion is expected to react even more slowly. These reactions are also expected to take place more slowly with the monochlorobiphenyl than with the dichloro and tetrachloro derivatives, because of the differences in reduction potential. It should be noted, however, that even when the electron transfer to the PCB is slow and thermodynamically unfavorable, the reaction does take place because it involves an irreversible elimination of chloride ion. The representative rate constants measured in these experiments indicate that electron transfer to PCBs is relatively rapid and can lead to complete dechlorination.

It is noteworthy that the initial slope of the decrease in PCB-54 concentration with dose (Figure 2) leads to an initial radiation yield for the dechlorination of PCB-54 of 0.03 μmol J^{-1}; this is larger than the yield of free electrons in linear alkanes ($\sim$0.01 μmol J^{-1}) (*19*). Thus, the results indicate that the aromatic components of the oil convert a fraction of the geminate electrons formed in the oil ($\sim$0.4 μmol J^{-1}) (*20*) into an effective dechlorination agent.

Acknowledgments

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