



Radiolytic Decomposition of Polychlorinated Biphenyls in Neutral Aerated Polar and Nonpolar Solvents

by RODNEY E ARBON

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

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MONTANA STATE UNIVERSITY
Bozeman, Montana

November, 1995

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APPROVAL

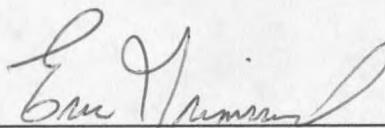
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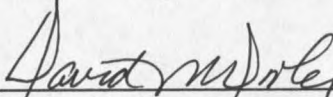


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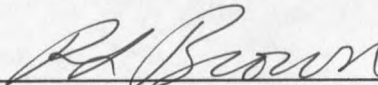


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ACKNOWLEDGEMENT

The support of Dr. Berk Knighton and Bruce Mincher in this project has been invaluable. I would also like to recognize the efforts of Carol Thurston. Finishing this degree would have been nearly impossible without her continued support and good humor.

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ABSTRACT

The radiolytic degradation of twenty-two polychlorinated biphenyl (PCB) congeners from eight homologs, monochlorobiphenyl to octachlorobiphenyl, and complex Aroclor 1260 mixtures was investigated in a variety of polar and nonpolar solvents using spent nuclear fuel as the gamma-ray source. Degradation was found to occur for all of the congeners studied and is conveniently described in terms of a pseudo-first-order rate constant expressed in terms of dose (J kg^{-1}), rather than time, and referred to as a dose constant. Dose constants were found to be dependent on the number and substitution pattern of the chlorines in addition to the solvent used.

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of compounds produced by the direct chlorination of biphenyl with anhydrous chlorine in the presence of iron filings or ferric chloride as catalysts. PCBs have the empirical formula $C_{12}H_{10-n}Cl_n$ ($n=1-10$) with 209 discrete congeners possible (1). PCBs are physically and chemically stable and exhibit many desirable properties such as low vapor pressure, low flammability, high heat capacity, low electrical conductivity, resistance to oxidation, resistance to acids, resistance to bases, and suitable viscosity-temperature relationships. As a result, PCBs were found to have a wide variety of uses in industry. In a 50-year period, approximately 1.4 billion pounds of PCBs were produced and sold as heat transfer fluids, hydraulic fluids, solvent extenders, plasticizers, flame retardants, organic diluents, and dielectric fluids (2). Such widespread use eventually resulted in multiple releases into the environment. Researchers as early as the mid-60s noted spurious peaks in electron capture gas chromatograms of environmental samples that could not be attributed to any known chlorinated pesticides (3). In 1967, Widmark reported mass spectrometric data that provided unambiguous proof that these contaminants were PCBs (4).

It has now been established that PCBs do not readily degrade in the environment and are ubiquitous environmental pollutants occurring in most human and animal adipose tissue, in milk, and in sediment. The persistence of PCBs in the environment, coupled with their apparent toxicity (2), led to the passage of the Toxic Substances Control Act (TSCA) in 1976. This act regulates the use and disposal of PCB-containing materials when the PCB concentration is greater than 50 parts per million (ppm). Tremendous quantities of PCB-contaminated solvents are currently subject to the disposal requirements in the TSCA (1). Two commonly contaminated solvents are transformer and hydraulic oil. For example, it is estimated that somewhere between 300 and 600 million gallons of PCB-contaminated transformer oil fall under the disposal requirements of TSCA (5).

Transformer oil is used in insulating the coils of transformers, both electrically and thermally. Transformer oil is a generic term that encompasses two broad classes: natural and synthetic. Natural transformer oil is a specially refined mineral oil derived from naphthenic base crudes (5). The synthetic types are PCBs, silicon oils, and ester liquids. The most common synthetic oils are neat PCBs sold as complex mixtures known as Aroclors. Over 60 different congeners may be present in a single Aroclor mix.

The major producer, Monsanto Corporation, marketed PCBs under the trade name Aroclor from 1930 to 1977 (1).

The transformer oil evaluated in this study is Aroclor contaminated natural transformer oil. Aroclor contamination of natural transformer oil typically occurred because natural transformer oil-filled transformers and PCB-filled transformers were manufactured and repaired in a common facility. Contamination resulted when trace levels of each type of dielectric found its way into the transformers of the other type. PCB-contaminated hydraulic oil was also investigated. PCB formulations were included in petroleum-based hydraulic fluids and are most often contaminated with Aroclor 1242 (1).

The current TSCA approved destruction methods for both neat PCBs and PCB contaminated solvents employs either high temperature incineration or high efficiency boilers. High temperature incineration, however, is costly. It is estimated that to dispose of 55 gallons (208.45 L) of PCB-contaminated transformer oil using high temperature incineration would cost approximately \$500.00 (6). In addition to the cost, destruction of PCBs by incineration is meeting with increasing public opposition. The public's fear of incomplete incineration and production of highly toxic dibenzofurans and dioxans if the combustion temperature is not held sufficiently high has greatly reduced the general acceptance of this technique. As a

result, the majority of the utility industry are simply storing their contaminated oil.

Natural transformer oil is a valuable product. Current production capacity is estimated to be limited to about 100 million gallons per year (5). Thus, based on the estimated amount of PCB contaminated transformer oil in storage, three to six years' worth of transformer oil is currently regulated to be destroyed. As pointed out by Exner (5), if the PCB fraction could be destroyed or removed, the resulting PCB-free transformer oil could theoretically be placed back into service. In the case of PCB-contaminated hydraulic oil, destroying the PCB fraction could provide a minimum goal of allowing the fluid to be burned for heat. Of obvious need is a solvent-based process that selectively degrades the PCBs, thus allowing the solvent to be recycled.

Significant effort has been directed at the development of solvent-based destruction techniques (7-21). In addition to recycling, solvent-based destruction techniques have several other advantages over incineration. Liquid phase chemical reactions are generally more easily controlled than gas phase reactions such as combustion (5). Therefore, the destruction conditions can be more easily duplicated, resulting in greater reliability. Also, liquid phase processes tend to have only small amounts of gaseous and particulate emissions. Finally, for hazardous waste generators, liquid phase destruction holds the possibility

of onsite treatment. This would give the generator greater control over the processing and handling of its own waste. It would also eliminate the need for and cost of shipping the waste to a fixed incinerator.

The difficulty in designing a solvent-based destruction process is that PCBs are very unreactive. About the only class of chemical reactions known to occur in the condensed phase at low temperatures are electron transfer processes which generally result in dissociation of chloride from the biphenyl ring (5). Because the biological hazard of PCBs increases with the number of chlorines on the biphenyl ring (2), dechlorination reduces the toxicity of a PCB mixture. The final product from stepwise dechlorination would be biphenyl, which TSCA does not include when determining the PCB concentration of a PCB-contaminated solvent (5). Therefore, to decontaminate a PCB solution, it is not necessary to break the biphenyl ring. Although currently not a TSCA approved treatment method, dechlorination could be an alternative to incineration.

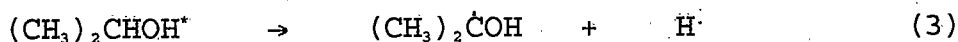
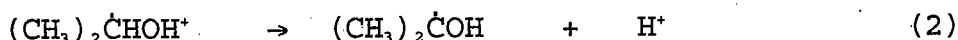
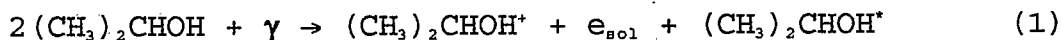
For electron transfer to occur, a suitable source of electrons is needed. Electron donors which have been used in dechlorinating PCBs are typically anion radicals or solvated electrons. These donors can be generated by a variety of methods, including sodium metal, ozonation, photolysis, and radiolysis. The only solvent-based method that has been used on an industrial scale is sodium metal

dechlorination. This technique has been used by Goodyear Tire and Rubber to dechlorinate hydraulic oils contaminated with PCBs in the 100 to 150 ppm range (5). In the process used by Goodyear, a deep green reactive complex of naphthalene and sodium in tetrahydrofuran was prepared. This mixture created naphthalene anion radicals which reacted with the PCBs through charge transfer. A number of variations of this process exist, but all are based on metallic sodium as the initiator. A summary of these methods can be found in reference 5.

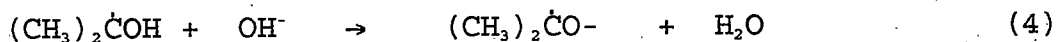
Gamma-ray radiolysis, the method investigated in this thesis, generates both solvated electrons and anion radicals and offers many advantages over other solvent-based processes. Spinks (7) points out that radiolysis offers the possibility of a purer product, since contamination from incomplete removal of catalysts is not a problem. Compared to reactions initiated by UV light, ionizing radiation has the advantage of greater penetrating power so that a more uniform reaction takes place in a larger volume of reactant. Radiation-induced reactions can also be carried out at relatively low temperatures, resulting in lower energy cost, less thermal damage to the system, and reduced danger of fire or explosion (7). Acceptable destruction can be assured by irradiating, sampling to determine if the PCB concentration is at an acceptable level, and, if needed, irradiating again.

A number of studies have explored radiolysis as a method capable of dechlorinating PCBs and other organochlorine materials (8-22). The mechanism by which the dechlorination occurred was found to be dependent on both the nature of the target chlorinated species and the solvent system employed. In general, the radiolytic degradation of PCBs, as well as other halogenated material (14-16), has been conducted in deaerated alkaline isopropanol solutions with cobalt-60 as the gamma-ray source (10-12). The choice of gamma-rays is due to the need for a more penetrating source than alpha or beta sources.

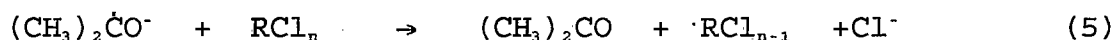
In deaerated alkaline isopropanol, the radiolytic dechlorination occurs *via* a chain reaction. The following key reactions have been proposed (8):



Reactions (1), (2), and (3) show the major products when isopropanol is subjected to high energy gamma-rays. In the presence of alkali, the isopropanol radical undergoes ionic dissociation to produce the acetone radical anion:



This acetone radical anion reacts with the PCBs (RCl_n), through charge transfer, resulting in the loss of chloride anion.



The PCB radical formed upon charge transfer abstracts a hydrogen from the solvent, thus propagating the chain reaction:



This mechanism is discussed in detail in Singh (11). In summary, the work done in alkaline isopropanol has established the following (11):

- 1) chain dechlorination of PCBs;
- 2) stoichiometric equivalence of the production of chloride, acetone, and biphenyl, and the loss of alkali;
- 3) inhibition of the dechlorination by acetone, oxygen, and nitrobenzene;
- 4) stepwise dechlorination of the PCB.

In neutral isopropanol materials such as CCl_4 (17), DDT (18) and hexachloroethane (19) were found to undergo efficient radiolytic dechlorination via a chain reaction involving the α -hydroxyisopropanol radical $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, whereas, for the PCBs, the radiolytic dechlorination in neutral isopropanol has been observed to be less efficient,

with conflicting reports on the identity of the reactive species responsible for initiating the dechlorination (8,10-11). Possibilities include the α -hydroxyisopropanol radical, hydrogen atom, positive ion, and solvated electron.

Even though a demonstrated need for the direct dechlorination of PCBs in oils exists, an exhaustive search of the literature reveals only one study in transformer oil (23) and no radiolysis studies in hydraulic oil. Webber (23) examined the radiolytic decomposition of air-equilibrated Aroclor 1260 in transformer oil and concluded that even at an absorbed dose of 1540 kGy there was no evidence that dechlorination had taken place. This conclusion was based on the absence of chloride ion in the irradiated solution. However, radiolytic degradation of PCBs has been demonstrated to occur in nonpolar cyclohexane and petroleum ether (24,25), but no effort was made to determine the reactive agent responsible. In addition, mass balance information was incomplete.

In a previous study, members of my research group demonstrated that radiolytic degradation of PCBs occurs in neutral aerated isopropanol using spent nuclear fuel as the gamma-ray source (8). However, the identity of the reactive agent or agents was unknown and the mass balance was incomplete. Knowledge of these variables will have important implications in terms of a PCB treatment process. As a result, additional studies were undertaken in

isopropanol with the objective of fully characterizing the reactive species responsible for the observed PCB degradation, the influence of chlorine substitution pattern on degradation efficiency, and providing a complete mass balance. It was believed that determining these parameters in isopropanol would facilitate the successful application of this process to nonpolar solvents. If it could successfully be demonstrated that radiolytic degradation of PCBs in hydraulic oil and transformer oil is possible, the potential benefits are significant. The majority of PCB-contaminated waste is present in these solvents. Moreover, because of the penetrating ability of gamma-rays, *in situ* destruction of PCBs in selected applications may be possible.

Thus, using the knowledge gained in isopropanol, radiolytic studies were performed on a variety of individual PCB congeners and Aroclor 1260 in isooctane, hydraulic oil, and transformer oil. Selected scavenging agents will be used to identify the major reactive agent responsible for the dechlorination of PCBs in the different solvent systems. GC/MS experiments and radiolabelled PCB compounds have been used in an attempt to identify all of the degradation products produced. Accurate determination of the degradation products is of obvious importance. Although there are many similarities, surprising differences were discovered between the two solvents and are illustrated.

Choosing a radiation source depends upon the state and size of the material to be irradiated. Because of its penetrating ability, gamma radiation is generally chosen for liquid or solid samples. Spent nuclear fuel is an excellent source of gamma-rays with an average kinetic energy of approximately 700 keV, and it was chosen as our irradiation source. To my knowledge, this is the first time spent nuclear fuel has been used in this capacity. The use of spent nuclear fuel represents a potential cost effective source, since fuel canals are currently maintained at many locations around the world. This fuel, produced as a by-product of reactor operations, does not require manufacturing or energy investment. Only minor engineering changes are needed to access the gamma-rays for use. Many utility companies that have significant quantities of PCB contaminated oils also have spent nuclear fuel that, as this report will demonstrate, could be used in destroying PCBs. This could convert what is now considered a major liability--spent fuel--into an asset.

THEORY

The basic physical process in radiation chemistry is the transfer of electromagnetic energy to the electrons of the system under study. The electromagnetic energy transfer in radiolysis is fundamentally different than the more familiar electromagnetic energy transfer that occurs in photochemistry and therefore warrants a brief review.

In photochemistry, low energy quanta of light are absorbed in a resonance process that nearly always pertains to the solute molecules. During high energy--often 10^6 eV quantum⁻¹ or greater--gamma irradiation of organic liquids, a nonselective absorption of radiation takes place because the energies used are well in excess of the bond energies of molecules. As a result, the radiation interacts with nearly all bound electrons, irrespective of the atoms to which the electrons belong (20). As gamma-rays pass through liquid, ions and excited molecules (which may be singlet, triplet, or superexcited states) are formed (7). Energy deposition is not uniform. Energy is deposited in highly localized regions called spurs, which are about 5 nm in diameter and from several to thousands of nanometers apart (7). The concentration of free radicals and ions within the spurs is fairly high. It has been estimated to be on the order of 10^{-2} mol L⁻¹ (20). The majority of the ions and radicals

formed undergo geminate recombination prior to spur expansion. Conductivity experiments (20) have shown that only approximately 3% of the ion pairs produced escape the spur to become homogeneously distributed.

The fraction of energy absorbed by any one component is roughly proportional to its concentration (mass fraction or electron fraction). Therefore, in a dilute solution the primary interaction will be the absorption of radiation by the solvent. In contrast is photochemistry, where a solute at a low concentration may still absorb 100% of the total light absorbed by the system. With high-energy radiation the direct action of the radiation on the solute is relatively unimportant (7). The degradation of the solute results from the reactive intermediates produced by the interaction of the radiation with the solvent. Thermal degradation of the solute does not occur because little temperature change occurs when a liquid is irradiated. Spinks (7), for example, estimated the temperature rise of an expanded spur in water to be 1°C above ambient.

Degradation Efficiency --- G Value

The figure of merit typically used when describing the chemical effects from high-energy radiation is the G value. The G value relates the radiation chemical yield to the absorbed dose. Absorbed dose is the amount of energy absorbed per unit mass of irradiated material (the SI unit

is J kg^{-1} or gray (Gy); a more familiar unit is the rad ($1 \text{ rad} = 0.01 \text{ Gy}$). The G value has been arbitrarily chosen to represent the number of molecules changed (starting material Y changed $G(-Y)$ or product X formed $G(X)$) for each 100 eV absorbed (7).

G values were originally used in the radiolysis studies of neat solvents and have been a useful and convenient method to quantitatively describe both molecular products and free ions. However, G values can often be misleading when used in remediation studies because they are frequently concentration dependent. Authors are frequently ambiguous about stating the relationship between concentration and G value. This can lead to difficulty when interpreting results from different investigators. In addition, a variety of methods have been used to calculate G values. Some researchers look for a linear portion of a product dose curve and calculate the G value from that portion. Others simply evaluate the unirradiated point and the first irradiated data point to determine a G value. The resulting degradation or product formation is then given as G_{initial} . However, as the irradiation continues, product degradation or formation often slows. This is not reflected in a G_{initial} value.

G values in our study were calculated using a G_{initial} approach. Knowing the G value does allow us to compare our results with those obtained by others. However, the G value

in our system has limitations in use. G values were found to be concentration dependent, which puts them at a disadvantage when used to compare the results of one study against another where analyte concentrations may vary. For example, a 38 mg L⁻¹ solution of octachlorobiphenyl in isopropanol decomposes with $G_{\text{initial}} = -0.033$ molecules 100 eV⁻¹ while a 150 mg L⁻¹ octachlorobiphenyl solution in isopropanol gives a $G_{\text{initial}} = -0.144$ molecules 100 eV⁻¹. Thus, if one is attempting to determine the effect of a scavenging agent on destruction efficiency, the initial concentrations would need to be equal or the G values obtained would be difficult to interpret. Therefore, a more uniform method for describing radiolytically induced degradation was sought.

Dose Constants

A method was found that was independent of the initial PCB concentration and thus more versatile. This method, first published by our lab (9,22), adopted the use of a new figure of merit which is referred to as a dose constant. Determination of the dose constant is based on the fact that first order kinetics have been observed in these studies. This is shown in Figure 1 for 2,2',3,3',5,5',6,6' octachlorobiphenyl (Bz 200) where octachlorobiphenyl concentration is plotted against absorbed dose. Exponential decrease in octachlorobiphenyl concentration is observed

with increasing dose. All of the congeners studied exhibited this kinetic behavior in the concentration range used. A discussion of possible reasons why first order kinetics are observed is given in the Results and Discussion section.

Calculation of the dose constant is performed by taking the slope of the line obtained from the plot of the natural logarithm of PCB concentration versus dose, as shown in Figure 2. The slope of this line is a first order rate constant but with the units of dose^{-1} . Just as a first order rate constant is independent of concentration, the dose constant is also independent of concentration and thus proved to be more versatile than the traditional G value. For the example given where the G value varied with octachlorobiphenyl concentration, both solutions decomposed with a dose constant of $0.024 \pm 0.001 \text{ kGy}^{-1}$. Use of the dose constant has allowed us to evaluate changes and trends in degradation efficiency for individual PCB congeners previously unreported.

Modeling

Given the fact that the disappearance of PCB congeners obeys first order kinetics, degradation modeling can be accomplished assuming homogeneous kinetics and using a dose constant, d , in place of a rate constant. For example, the

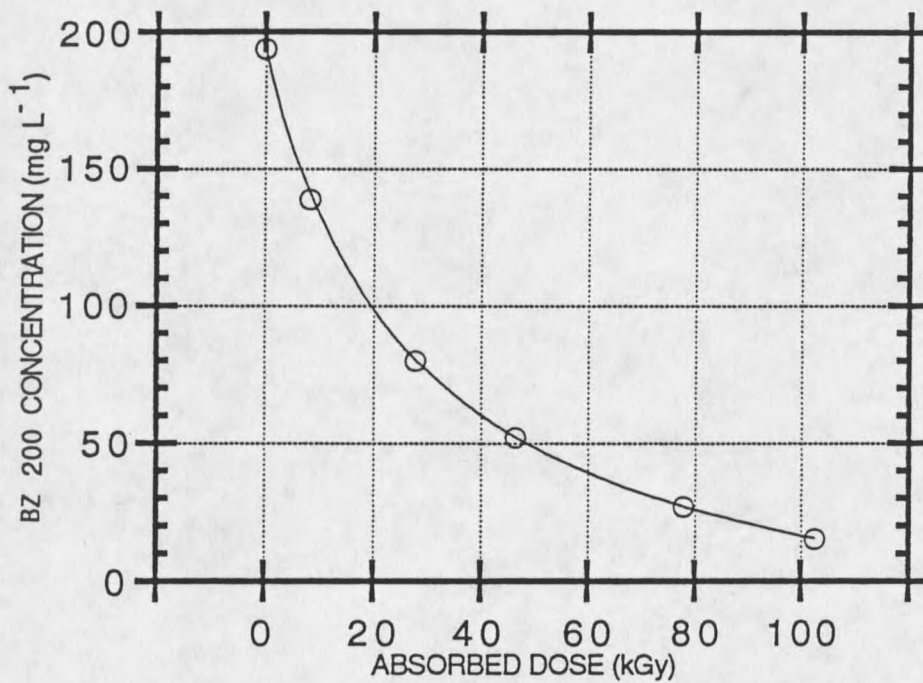


Figure 1. Change in 2,2',3,3',5,5',6,6' octachlorobiphenyl (Bz 200) concentration versus absorbed dose. A steady decrease in Bz 200 concentration with increasing dose is observed. Note the half-life dependency on Bz 200 in relation to absorbed dose.

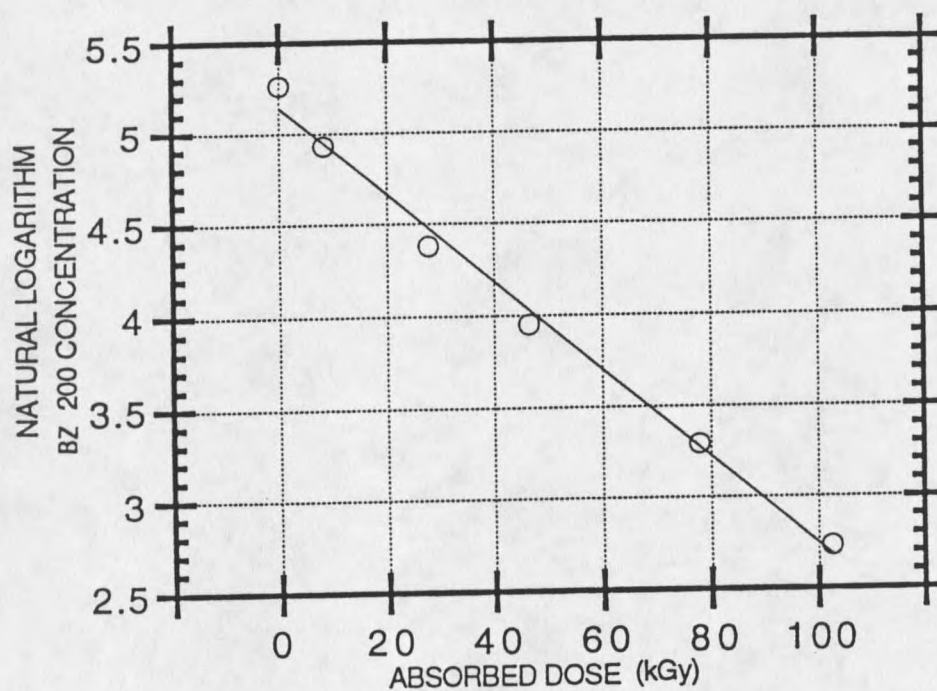


Figure 2. Plot of the natural logarithm of Bz 200 concentration and absorbed dose. The slope of the line provides the dose constant. The correlation coefficient for the above line was 0.996.

disappearance of octachlorobiphenyl is described in differential form as:

$$-d(8CB)/d(\text{dose}) = d_8(8CB) \quad (7)$$

where (8CB) is the concentration of octachlorobiphenyl at the current total absorbed dose and d_8 is the dose constant with units of reciprocal dose. Since the decomposition of octachlorobiphenyl is the only source of the various heptachlorobiphenyls (7CB), and assuming heptachlorobiphenyl decomposes essentially as does octachlorobiphenyl, the appearance and subsequent disappearance of heptachlorobiphenyl can be described as:

$$d(7CB)/d(\text{dose}) = d_8(8CB) - d_7(7CB) \quad (8)$$

where d_8 and d_7 need not have the same value. The form of this relationship would also apply to the lower chlorinated homologs, hexachlorobiphenyl to chlorobiphenyl.

For purposes of graphing the above equations, these differentials can be approximated with a sufficiently small dose increment $\Delta(\text{dose})$ on going from step (i-1) to step (i) to give

$$(8CB)_i = (8CB)_{i-1} - d_8(8CB)_{i-1}\Delta(\text{dose}) \quad (9)$$

for the destruction of octachlorobiphenyl and

$$(7CB)_i = (7CB)_{i-1} + d_8(8CB)_{i-1}\Delta(\text{dose}) - d_7(7CB)_{i-1}\Delta(\text{dose}) \quad (10)$$

for heptachlorobiphenyl. The same type of reasoning is then applied to the rest of the lower chlorinated homologs. In these experiments, the initial concentration of all lower homologs is assumed to be zero.

The above model may then be used to predict the concentration of any homolog during the course of an irradiation. The predicted pattern of less chlorinated homolog growth and destruction is similar to that measured in an irradiated sample, as shown in Figures 3a and 3b. Figure 3b depicts a 190 mg L⁻¹ octachlorobiphenyl solution in isopropanol irradiated to approximately 100 kGy with spent fuel while Figure 3a shows the predicted growth and destruction based on the kinetic model given. The agreement is reasonably good for the first several homologs, after which the model begins to break down.

Several possible reasons exist for this divergence. The number of different congeners capable of being produced is surprising. Starting with 2,2',3,3',4,5',6,6' octachlorobiphenyl, five unique heptachlorobiphenyl congeners theoretically could be produced. The number of hexachlorobiphenyl congeners that can be produced from the above heptachlorobiphenyl congeners would be 25. This trend greatly complicates modeling. For accurate modeling, each dose constant for each congener would need to be known. Therefore, the best that can be done is an estimation.

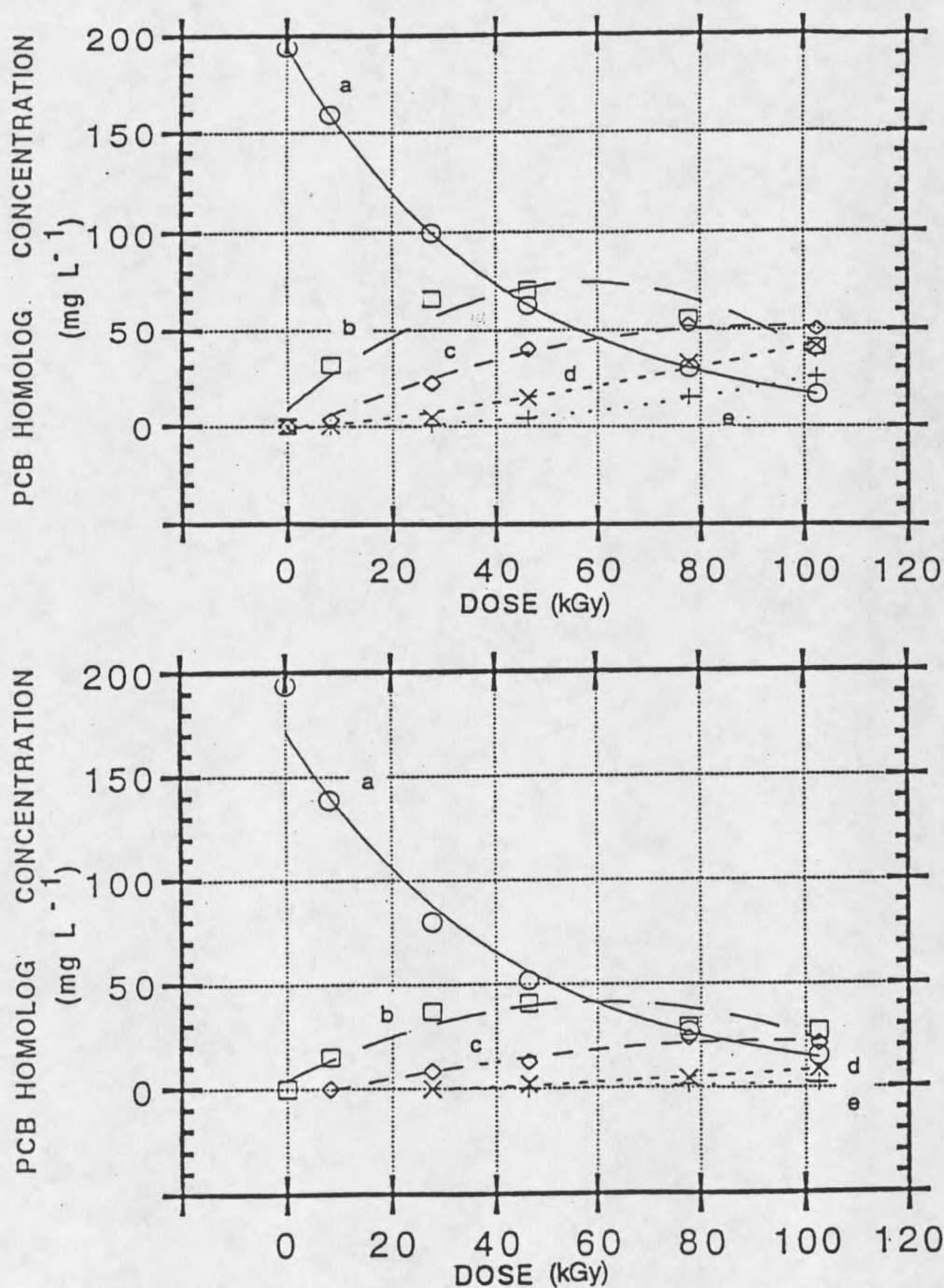


Figure 3. a. The predicted pattern using the kinetic model as described in the text. b. The experimentally determined degradation of octachlorobiphenyl as well as the growth of less chlorinated PCB homologs as a function of absorbed dose. PCB homologs are labeled as follows: (a) octa-; (b) hepta-; (c) hexa-; (d) penta-; and (e) tetrachlorobiphenyl.

Measured congener concentration is another potential source of error. Accurately quantifying the variety of congeners produced is difficult. For quantitative determination, each congener's mass spectrometric response factor must be known. This would require the use of a chromatographic system capable of separating all 209 congeners; however, standards for all 209 congeners are not readily available. Additionally, the model does not include the effect of the formation of PCB solvent adducts which are produced during the irradiation. Identification of the PCB adducts and their impact on mass balance is discussed in detail in Results and Discussion.

The model can be used to estimate the approximate dose needed to reduce a given sample to below 50 mg L⁻¹--the U.S. EPA regulatory limit. For example, if a similar kinetic model analysis is performed starting with 190 mg L⁻¹ tetrachlorobiphenyl with a dose constant of 0.024 kGy⁻¹, the model predicts that 219 kGy would be required to reduce the overall PCB concentration to below 50 mg L⁻¹. Starting with tetrachlorobiphenyl is a more realistic case, since most real world PCB samples do not contain significant concentrations of highly chlorinated congeners. A similar analysis could be done for a commercial Aroclor mixture. If the starting concentration is known, the beginning homolog concentrations could be calculated using published relative abundances of the homologs in an Aroclor mixture. These

concentrations could then be used with the model to determine the approximate dose required to achieve a PCB concentration below the regulatory limit.

EXPERIMENTAL SECTION

Irradiations

Samples were gamma-ray irradiated using spent nuclear fuel at the Advanced Test Reactor at the Idaho National Engineering Laboratory. Depleted fuel elements from the reactor are stored vertically in grids which are under approximately 6.5 meters of water. The fuel elements are then used to surround a dry tube that extends from the surface of the water into the grid. A diagram of the grid and dry tube in position is shown in Figure 4. Samples and dosimetry are placed in a sample capsule (Figure 5) that is placed in the dry tube and inserted into the spent fuel pool. This fuel, produced as a byproduct of nuclear operations, is an excellent source of gamma-rays with an average energy of 700 keV. With this fuel, a dose rate of approximately 25.0 kGy hr⁻¹ is achievable. Proper positioning of the fuel elements around the dry tube allow for the selection of various dose rates. The dose rate can vary from 25.0 to 7.5 kGy hr⁻¹ depending upon the age and position of the fuel. Because few neutrons are present, no neutron activation of the samples occurs. Thus, the samples were radiologically clean following gamma-ray exposure.

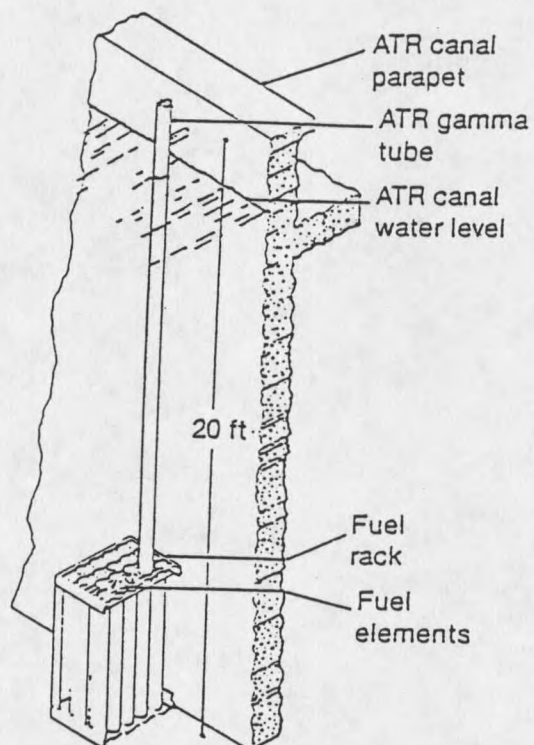


Figure 4. Advanced Test Reactor (ATR) gamma irradiation dry tube.

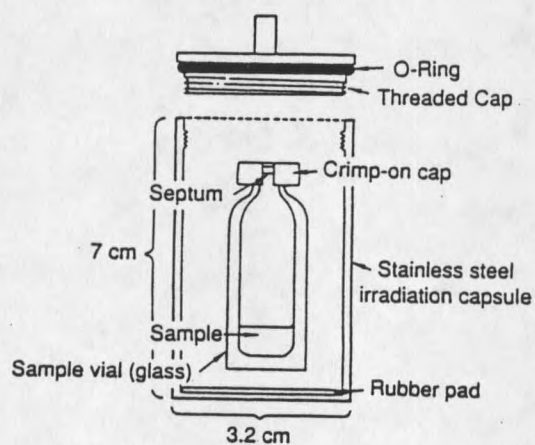


Figure 5. Irradiation vessel used in this study.

For quantitative studies in radiation chemistry the amount of energy transferred from the gamma-rays to the absorbing material, the absorbed dose, needs to be known. The chemical changes observed are generally proportional to the amount of energy transferred from the radiation to the absorbing material (7). Absorbed doses were measured using FWT-60 radiachromic dye dosimeters (Far West Technology, Goleta, CA). The FWT-60 dosimeters are nylon films ($50\text{ }\mu\text{m} \times 1\text{ cm}^2$) impregnated with the colorless cyanide derivative hexahydroxyethylaminotriphenylnitrile (26). When this compound is exposed to ionizing radiation, it undergoes a color change as the cyanide group is cleaved by a gamma-ray producing a colored dye cation. The color change is measured with an optical density reader and is directly proportional to the amount of radiation absorbed. The dosimeters used to establish a calibration curve were calibrated with a 10,000-Ci cobalt-60 source with a known dose rate of 3.633 kGy hr^{-1} .

The absorbed dose that a dosimeter receives is easily measured. However, does this absorbed dose accurately reflect the absorbed dose received by the sample? The dose absorbed by the dosimeter may be used to estimate the dose absorbed by a sample by correcting the measured dose with the mass energy absorption coefficients of the absorbing material, averaged over the estimated photon energies (7). The problem is that many of the mass energy absorption

coefficients are not known and have to be estimated based upon elemental compositions. Both regularly changing solvents and the constantly changing gamma-ray dose rate of decaying fuel make estimating the absorbed dose the sample receives complex.

These problems can be minimized by surrounding the dosimeter with solvent so that the electron equilibrium associated with the sample is also seen by the dosimeter (27). If the nylon dosimeters used in this study are placed in 2-propanol or oil, the cyanide derivative is leached from the film, rendering the dosimeter useless. To achieve an equivalent electron equilibrium, the dosimeters were sandwiched between layers of lucite and placed into the sample irradiation capsule. Lucite has approximately the same carbon/hydrogen/oxygen ratio as typical organic solvents and therefore has similar mass energy absorption coefficients. Thus, the dosimeter experiences irradiation conditions similar to the sample, and the absorbed doses reported should closely reflect those actually received.

Analytical Measurements and Reagents

Polychlorinated biphenyl congener measurements were performed using a Hewlett-Packard 5995 Gas Chromatograph/Mass Spectrometer (GC/MS) operated in the electron impact mode. A db5-625, 30m column (J&W Scientific) was used with a helium carrier gas at a flow of 2 mL min⁻¹.

Samples were injected onto the column at an initial temperature of 80°C, held one minute, ramped at a rate of 30°C per minute to 160°C, and then ramped 3°C per minute to 310°C.

To assure the integrity of the quantitative data generated, strict quality control measures were followed. The quality control measures used were based on the U.S. Environmental Protection Agency's Method 680: Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry. A five-point calibration curve, typically bracketing the PCB concentration under study, containing eight PCB isomers (chlorobiphenyl through octachlorobiphenyl) was constructed using each isomer's calculated response factor. Response factors (RF) are calculated as follows: $RF = A_x Q_{is} / A_{is} Q_x$ where A_x is the integrated abundance of the quantitation ion (typically the most abundant ion in the mass spectra) for each PCB congener. A_{is} is the integrated abundance for m/z 188, the quantitation ion used for the internal standard phenanthrene- d_{10} . Q_{is} is the injected quantity of phenanthrene- d_{10} and Q_x is the injected quantity of the PCB congener.

To be considered as a valid calibration curve, the percent relative standard deviation of the response factors over the five calibration points was required to be less than 20%. Prior to sample analysis, the calibration curve

was verified on a daily basis by analyzing the midpoint calibration standard. A percent difference of less than 20, between the average response factor for the initial calibration and the midpoint standard, was required before samples were quantitatively analyzed. The internal standard was added to the sample following irradiation and was used in the calculation of the response factor. It was also used to evaluate potential changes in detector response or injection anomalies during analysis.

Aroclor 1260 samples in transformer and hydraulic oil were analyzed using a Hewlett-Packard 5890 Series II Gas Chromatograph with electron capture detection. A DB-1701, 30 m column was used with a carrier flow of 7.5 mL min^{-1} and a 5% argon methane makeup gas at 45 mL min^{-1} . A one to ten dilution was performed on the samples prior to analysis. Injections were made using a 7673 Hewlett-Packard automatic sampler onto the column at an initial temperature of 60°C , ramped at a rate of $10.0^{\circ}\text{C min}^{-1}$ to 180°C , held 6.00 minutes, and then ramped at $5^{\circ}\text{C min}^{-1}$ to a final temperature of 250°C . Free chloride ion produced in the irradiated samples was measured by ion chromatography using a Dionex 2010i ion chromatograph and a AS4A separator column with conductivity detection. Irradiated alcohol samples were diluted by a factor of 10 with 18 M ohm water and injected directly onto the column. The chloride ion was then eluted with a 0.002 M sodium carbonate/0.00075 M sodium

bicarbonate eluent at a rate of 2 mL per minute and a pressure of 1000 psi. A suppressor column eluted with 0.025 M sulfuric acid was used to minimize contribution of the carbonate/bicarbonate eluent conductivity to the sample signal. The chloride ion eluted at a retention time of about 1.6 minutes, free of interferences.

Carbon-14 measurements were made using a model 2250CA Packard Tricarb liquid scintillation counter and Ecolume scintillation cocktail. Using calibration standards purchased from Amersham International (U.K.), the counting efficiency was determined to be 43% for the carbon-14 beta, which has an endpoint energy of 156 keV. A carbon-14 labelled tetrachlorobiphenyl was purchased from Sigma Chemicals (St. Louis, MO, USA) and was labelled in all 12 positions. The radio-PCB was diluted with stable tetrachlorobiphenyl carrier (Ultra Scientific) and isopropanol and was irradiated in the same manner as the other experiments in this study. Following irradiation, the liquid was counted for carbon-14 and compared to the original unirradiated solution.

Polychlorinated biphenyl solutions were purchased from Ultra Scientific and were greater than 99% pure. Reagent grade solvents were used as received. When discussing PCB congeners in this report, the use of the full chemical name was found to be cumbersome. As a result, the numbering system proposed by Ballschmiter (28) has been adopted. The exact

chemical composition and Ballschmiter number (Bz) for each PCB congener used in this study are given in Table 3.

RESULTS AND DISCUSSION

This chapter is divided into two sections. The first contains the radiolytic studies that were conducted in polar solvents, while the second section describes the radiolytic studies conducted in nonpolar solvents.

Radiolysis of PCBs in Polar Solvents

General Radiolytic Characterization

The initial aspect of this study involved further characterizing the radiolysis of PCBs in neutral aerated isopropanol with spent nuclear fuel. Individual congeners rather than complex Aroclor mixtures were used in order to facilitate the characterization process. The highly chlorinated congener 2,2',3,3',4,5',6,6'-octachlorobiphenyl, or Bz 200, was the congener originally chosen for study as a "worst case" candidate. Aerated solutions were chosen to minimize sample preparation. In a process situation it is generally desirable to limit the number of additives and steps required to achieve a desired result.

When Bz 200 was irradiated with spent fuel to doses of 10-100 kGy, significant degradation occurred. Figure 1, a plot of Bz 200 in neutral aerated 2-propanol versus absorbed dose, shows a steady decrease in Bz 200 concentration with

increasing dose. Concurrent with the destruction of Bz 200 is the growth and destruction of less chlorinated homologs (Figure 3b curves a,b,c,d, and e). This pattern is typical for all of the congeners studied. The rise in free chloride (Figure 6) occurs simultaneously to the production of less chlorinated PCBs.

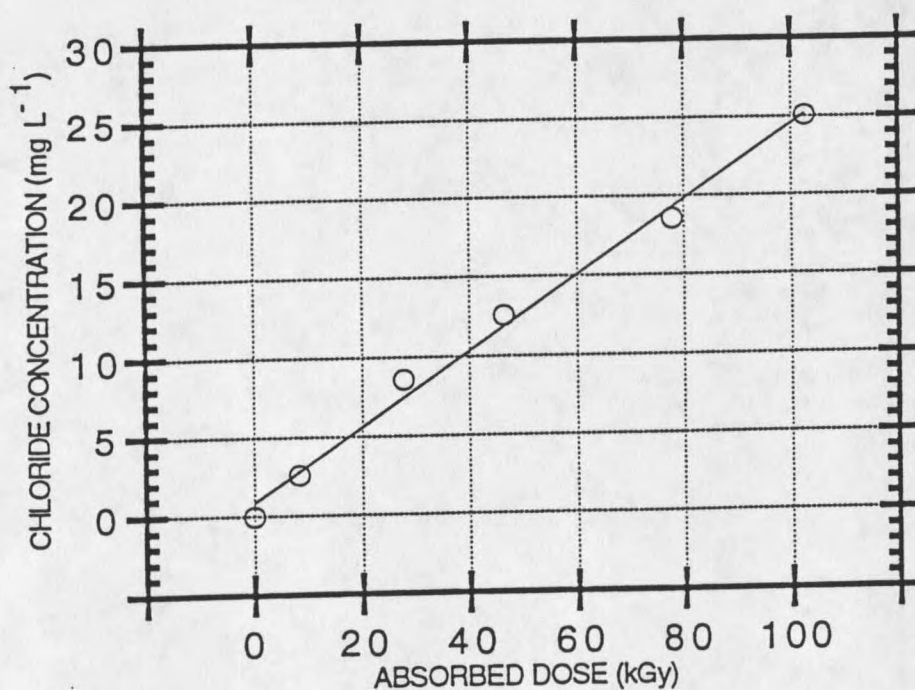


Figure 6. Simultaneous to the production of less chlorinated PCBs is the increase in free chloride concentration.

Mechanistic Studies

Conflicting reports exist concerning the identity of the reactive agent responsible for PCB dechlorination in neutral aerated isopropanol (8,10-11). Possibilities include the isopropanol radical, hydrogen atom, positive ion and the solvated electron. Sawai and Shinozaki (10) concluded that solvated electrons were not important in the radiolytic dechlorination of PCBs in neutral isopropanol, based on the observation that neither O_2 or H_2O_2 impacted the decomposition efficiency. In the presence of oxygen or hydrogen peroxide, solvated electrons were expected to be scavenged. The difficulty in identifying the reactive species responsible for PCB dechlorination in neutral isopropanol may be a result of the difficulties in interpreting the scavenging experiments. It could also reflect potential differences in the dechlorination mechanism. As a result, experiments were undertaken to definitively identify the reactive species.

Direct Gamma-ray Interaction

Could the observed degradation be the result of direct gamma-ray interaction with the PCBs themselves? Direct action can be easily discounted. If direct action were solely responsible for the observed destruction, the maximum obtainable G value would be 0.0021, based on the mass

fraction of 1 mL of a 50 mg L⁻¹ solution of octachlorobiphenyl in isopropanol.

Mass of solvent:

$$1 \text{ mL} * 0.785 \text{ g/mL} = 0.785 \text{ g}$$

Mass of octachlorobiphenyl:

$$50 \text{ mg/L} * 10^{-3} \text{ L} = 0.050 \text{ mg} = 5.0 \times 10^{-5} \text{ g}$$

The fraction of gamma-rays absorbed by any one component is dependent upon its mass fraction. Assuming a bond strength of 3.05 eV bond⁻¹, each 100 eV of absorbed energy could break up to 32.7 bonds. Therefore, the maximum obtainable G value would be:

$$5 \times 10^{-5} / 0.785 * 32.7 = 0.0021$$

However, measured G values were approximately 0.1, which is approximately two orders of magnitude larger than the calculated maximum G value. This estimate demonstrates that direct action is insufficient to explain the observed destruction. It further illustrates that the majority of the gamma-ray energy is deposited to the solvent; therefore, the PCB degradation observed must be initiated from a species formed upon radiolysis of the solvent.

Reactive Species

Radiolysis produces a wide variety of reactive species that may be involved in the observed dechlorination. Of

main concern are those species that escape from the tracks and spurs to become free radicals. The radiolysis chemistry of 2-propanol has been well documented (29). The primary reactive species that escape from the spurs in 2-propanol are positive ions, hydrogen atoms, solvated electrons, and the α -hydroxyisopropanol radical (29). Based on experimental yields and theoretical considerations, Freeman and Russell (29) estimated the free ion yields, expressed in terms of G values, to be 0.8 for the hydrogen atom and 2-propanol radical and 1.2 for the solvated electron and positive ions. It is at least conceivable that any of these may be involved in the dechlorination of Bz 200. With the addition of a judiciously chosen solute--a scavenger--that reacts rapidly with a particular reactive species the identification of that reactive agents role in the radiation-induced mechanism should be possible (30). Each reactive specie will be addressed and the evidence for or against its participation in degrading PCBs is presented.

Scavenging Experiments

Table 1 shows the effects of various scavenging agents on the dose constant for Bz 200 when added to a 160 ppm solution of Bz 200 in 2-propanol. The dose constant was unchanged with the addition of benzene and cyclopropane, while nitrobenzene reduced the dose constant by approximately half. Addition of 1.6 M carbon tetrachloride eliminated degradation completely, while sparging with SF₆.

Table 1. Dose Constant Obtained for Bz 200 in Isopropanol Under Various Conditions of Irradiations using Spent Fuel.

Dose Constant (kGy ⁻¹)	Condition
0.024 ± 0.002	unadulterated
0.025 ± 0.005	Cyclopropane Sparged
0.023 ± 0.005	160 mg L ⁻¹ Benzene
0.013 ± 0.004	160 mg L ⁻¹ Nitrobenzene
No destruction	1.6 M CCl ₄
0.005 ± 0.002	SF ₆ Sparged

reduced the dose constant approximately 95%. Interpretation of these results in relation to the reactive species present is given below.

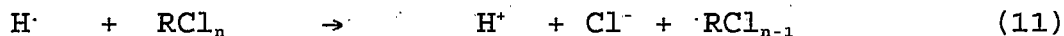
Positive Ions

It has been observed that certain solutes are capable of reacting with positive ions (31). However, the addition of cyclopropane produces a set of very unreactive positive ions (31). When a solution of octachlorobiphenyl was sparged with cyclopropane, no reduction in the dose constant was obtained. Therefore, positive-ion PCB reactions, if they occur, do not appear to be responsible for the degradation observed.

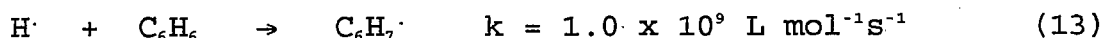
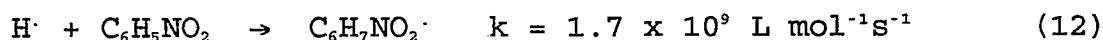
Hydrogen Radical

The hydrogen atom has a standard reduction potential of -2.3 V (30) and readily reduces inorganic ions having a more positive reduction potential. With this relatively large reduction potential (just slightly lower than a solvated

electron), one can envision the hydrogen atom participating in a generalized dechlorination process shown in equation 11.

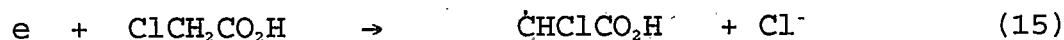


Scavenging experiments can be utilized to determine whether the $\text{H}\cdot$ is participating in the reduction of Bz 200. This is demonstrated by its second-order rate constants with nitrobenzene and benzene (30).



The rate constant for nitrobenzene scavenging the hydrogen atom is 70% greater than benzene. With nitrobenzene present the dose constant was reduced about 43%, which could suggest that $\text{H}\cdot$ may have been involved.

However, the chemistry of the hydrogen atom can be somewhat surprising. This can be illustrated by observing the difference between a hydrogen atom and the solvated electron reacting with chloroacetic acid (eqs. 14 & 15).



Given the above behavior, it is probable that the hydrogen atom in our system is abstracting a hydrogen from the solvent rather than reducing Bz 200. Confirmation of this

is given by the work performed by Simic and Neta (32).

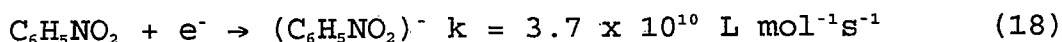
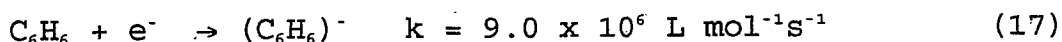
Simic and Neta reported that hydrogen atoms react rapidly with 2-propanol to form the alpha hydroxyisopropanol radical shown in equation 16.



Given this, the hydrogen atom's contribution to PCB decomposition in relatively dilute solutions is negligible.

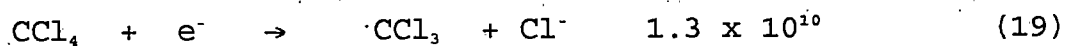
Solvated Electron

With a standard reduction potential of -2.9 V, the solvated electron reacts very rapidly with compounds having a larger reduction potential (30). Its mode of reaction may be represented as a one-electron transfer process. The solvated electron behaves as a nucleophile with organic molecules. Its reactivity is greatly enhanced by the presence of electron-withdrawing substituents attached to aromatic rings (30), which is exactly the case with PCBs. Based on scavenging experiments, the solvated electron appears to be the major reactive species responsible for the observed dechlorination. This is demonstrated by observing the second-order rate constants for benzene and nitrobenzene with a solvated electron (30).



There is a four orders of magnitude difference in the rate constant for benzene and nitrobenzene with the solvated electron. With a rate constant of 3.7×10^{10} , a significant fraction of the electrons are expected to be scavenged by nitrobenzene when present with Bz 200, assuming the rate constant for Bz 200 is similar to nitrobenzene. The assumption that Bz 200 captures electrons at a rate similar to nitrobenzene is based upon the rate constants observed with other chlorinated organics (16). With nitrobenzene competing with Bz 200 for the available electrons, the dose constant is reduced by half. This result is consistent with nitrobenzene and Bz 200 having approximately the same rate constant, since the concentration of nitrobenzene and Bz 200 are approximately equal. In the case of Bz 200 with benzene as the additive, no change in the dose constant was observed. This is what one would expect if Bz 200 captures electrons significantly faster than benzene.

Carbon tetrachloride is known to capture electrons very rapidly, as shown in reaction 19 (30).

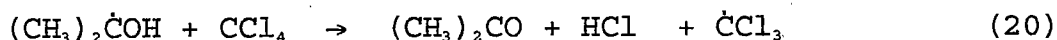


When carbon tetrachloride is added at 1.6 M, no PCB decomposition reaction is observed. With carbon tetrachloride present at 1.6 M and Bz 200 at 160 ppm, a four orders of magnitude difference exists in the concentrations. With such a large concentration difference, one can assume that all of the electrons produced are scavenged by the

carbon tetrachloride. With no solvated electrons available for Bz 200 no reaction would be expected.

Isopropanol Radical

As mentioned in the Introduction, reaction 20 is known to occur.



Could a similar reaction occur for PCBs? Nitrobenzene has a fast rate of reaction with the alpha hydroxy isopropanol radical, 2×10^9 , (37) and the dose constant was reduced by the presence of nitrobenzene. The reaction rate for this alcohol radical with benzene is unknown. Therefore, the benzene-nitrobenzene experiment is insufficient to permit a choice between the solvated electron and the alcohol radical as the primary agent responsible for PCB decomposition. Since the above scavenging experiments were inconclusive, experiments were performed with sulfur hexafluoride and nitrous oxide.

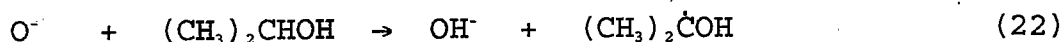
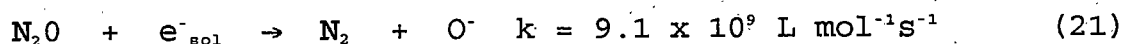
Sulphur Hexafluoride

Sulfur hexafluoride is known to have a high rate of reaction with electrons and is thought to be unreactive toward the isopropanol radical. Johnson and Salmon observed that the rate that nitrobenzene reacted with the methanol radical (produced by the radiolysis of methanol) was five orders of magnitude greater than that of sulfur hexafluoride

with the methanol radical (38). Assuming a similar trend in isopropanol, the rate of reaction of sulfur hexafluoride with the alcohol radical should be negligible. Irradiation of sulfur hexafluoride-sparged solutions showed a reduction of the dose constant by approximately 95%. This indicates that the solvated electron is primarily responsible for the observed dechlorination. However, dechlorination is still observed in the absence of solvated electrons and is thought to occur either by the alcohol radical or from the PCBs successfully competing with sulfur hexafluoride for the solvated electrons. An experiment to examine alcohol radical participation in the decomposition mechanism was desired.

Nitrous Oxide Sparging

The role of the alcohol radicals was investigated further by the addition of nitrous oxide to the radiolysis mixture. With nitrous oxide, the following reaction sequence is proposed to occur (39) during the radiolysis of 2-propanol:



The nitrous oxide reacts with solvated electrons, converting them into the oxygen radicals. The oxygen radical then reacts with the solvent, creating hydroxide and the

reacts with the solvent, creating hydroxide and the corresponding solvent radical. When nitrous oxide was sparged into samples containing Bz 200, the dose constant was suppressed by a factor of 2 from 0.024 to 0.011 kGy⁻¹. This result may be interpreted in two ways. In the absence of solvated electrons, the alcohol radical may cause reductive dechlorination of the PCBs by electron transfer. If this is the case, in our system it occurs on a limited basis as compared to that seen by Radlowski and Sherman (17). The low G values obtained indicate that the alcohol radical does not participate in a chain reaction.

Another explanation is that the PCBs are able to compete with nitrous oxide for the available solvated electrons. In an attempt to resolve this issue, the nitrous oxide scavenging experiments were repeated in t-butanol. The radicals formed by t-butanol radiolysis are generally considered to be inert toward reductive dehalogenation (39). When this was done the dose constant was reduced by a factor of two as observed in 2-propanol. This further indicates that solvated electrons are primarily responsible for PCB degradation.

Effect of Dielectric Constant on the Dose Constant

A significant amount of data exists on the variation of free ion yield, production of an electron and a positive ion with the static dielectric constant in the radiolysis of liquids (33,34,35). Of the parameters that influence the

process of free ion-pair formation in irradiated liquids, the static dielectric constant appears to be of primary importance (36). The influence of dielectric constant on the dose constant obtained for Bz 200 and the free ion yield for three alcoholic solvents is shown in Table 2.

Table 2. Dose Constant - kGy^{-1} for Bz 200, Free Ion Yield-G (e^-), and Dielectric Constant as a Function of Solvent.

Solvent	kGy^{-1}	G(e^-)	Dielectric Constant
2-propanol	0.024 ± 0.002	1.2	18.3
ethanol	0.080 ± 0.004	1.7	24.3
methanol	0.108 ± 0.006	2.0	32.6

The above dose constants are in qualitative agreement with the production of solvated electrons. Given the above information, as well as the scavenging experiments, it is reasonable to suggest that the solvated electron is a major reactive species in the observed dechlorination process.

Oxygen Sparging

The finding that the solvated electron is the principal agent of radiolytic PCB destruction suggests that in the absence of oxygen, a known free radical scavenger, the decomposition rate may be higher. In alkaline conditions the presence of oxygen eliminated the chain reaction. Oxygen was thought to accept the electron from the acetone anion but not transfer it to PCBs. Because of this, the

majority of the radiolysis studies have been performed in deaerated solutions (15). When Bz 202 was sparged with oxygen in our system, the dose constant was indeed suppressed by approximately 25%, from $0.019 \pm 0.002 \text{ kGy}^{-1}$ to $0.014 \pm 0.001 \text{ kGy}^{-1}$. These results indicate that high concentrations of oxygen do suppress the decomposition of PCBs in isopropanol, probably by electron capture.

When solutions of Bz 200 were irradiated in nitrogen sparged, neutral isopropanol no observable change in the dose constant occurred, given the uncertainties at the 90% confidence interval. The dose constant obtained was 0.024 ± 0.006 . In air-equilibrated solutions the dose constant was 0.024 ± 0.002 . Similarly, the nitrogen sparged Bz 202 sample decomposed with a dose constant of $0.021 \pm 0.003 \text{ kGy}^{-1}$, and the unsparged Bz 202 sample decomposed with a dose constant of $0.019 \pm 0.002 \text{ kGy}^{-1}$. These results may be due to the possibility of electron transfer. When O_2 captures an electron to become O_2^- , it may react with PCBs through charge transfer at a lower rate. The superoxide ion is suspected to dehalogenate chlorinated benzenes (40). Although the lifetime of the superoxide in alcoholic solvents is unknown, it is probably quite short and its contribution to PCB degradation is probably limited.

Another explanation for these results is the possibility that the dissolved oxygen is depleted in the early stages of irradiation. It is known that approximately 1 kGy is required to consume dissolved oxygen completely in

aqueous solution, after which solvated electrons are free to participate in other reactions (7). This is consistent with the experimental results we obtained. Our destruction curves appeared to include an induction period--that is, the second data point appeared to be slightly higher than what would have been predicted. The remaining points then follow exponential decay.

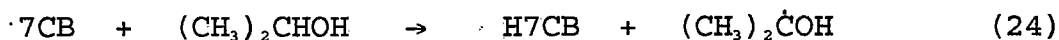
Partial Mechanism

Based on the scavenging results obtained, a partial mechanism can now be proposed in neutral aerated isopropanol. Radiolysis of the alcohol proceeds as previously described in reactions (1-3) yielding isopropanol radicals, solvated electrons, and hydrogen atoms. The hydrogen atoms react rapidly with the alpha hydrogen of the solvent, reaction 16, yielding H_2 and additional isopropanol radicals.

Starting with octachlorobiphenyl, represented as 8CB, the solvated electrons react with PCBs to produce free chloride and a heptachlorobiphenyl radical.



The heptachlorobiphenyl radical created stabilizes by abstracting a hydrogen from the solvent, producing heptachlorobiphenyl (7CB).

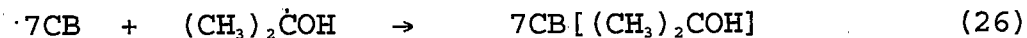


Both heptachlorobiphenyl and free chloride ion are measured products. Heptachlorobiphenyl then captures an electron and produces the hexachlorobiphenyl radical, which can then repeat the process. This process could repeat until biphenyl is reached.

Reductive dechlorination by the α -hydroxyisopropanol radical is an additional pathway which is consistent with the observed dechlorination.



If reaction 24 is slow, then with the existence of PCB radicals and isopropanol radicals one might expect radical-radical recombination to occur, resulting in an isopropanol-PCB adduct as shown in reaction 26.



Isopropanol-PCB adducts have been observed indicating that reaction 26 is occurring. The identification of adducts as well as their contribution to the overall mass balance is discussed in detail in the Mass Balance section. A more complete discussion of the mechanism and the observed kinetics is given in the section entitled Reaction Mechanism and Kinetics.

Chlorine Substitution Pattern and Dose Constant

To determine how chlorine number and chlorine position affect radiolytic degradation, 25 individual PCB congeners were irradiated. Not all PCB congeners found in an Aroclor mixture exhibit the same biological and toxic activity. Congeners that are non-ortho substituted and are substituted in both para positions and at least two meta positions are the most biochemically active, as well as the most toxic (2). Congeners that meet the above requirements are the planar or co-planar PCBs and were included in the 25 congeners studied. The radiolytic degradation efficiency or dose constants for these 25 congeners are reported in Table 3. If dose constant is plotted against chlorine number, as shown in Figure 7, a general increase in the dose constant is observed as the number of chlorine atoms on the molecule increases. Within a homolog series, as shown in Figure 7, considerable variability exists, demonstrating that the positions of the chlorine atoms also have a significant impact on the observed dose constant. For example, if the dose constants obtained for the hexachlorobiphenyl congeners are evaluated, it can be seen that the dose constant for Bz 169 is over 2.5 times larger than that obtained for Bz 155. Careful review of Table 3 shows that those compounds found to have the largest dose constants for their respective homologs are para/meta

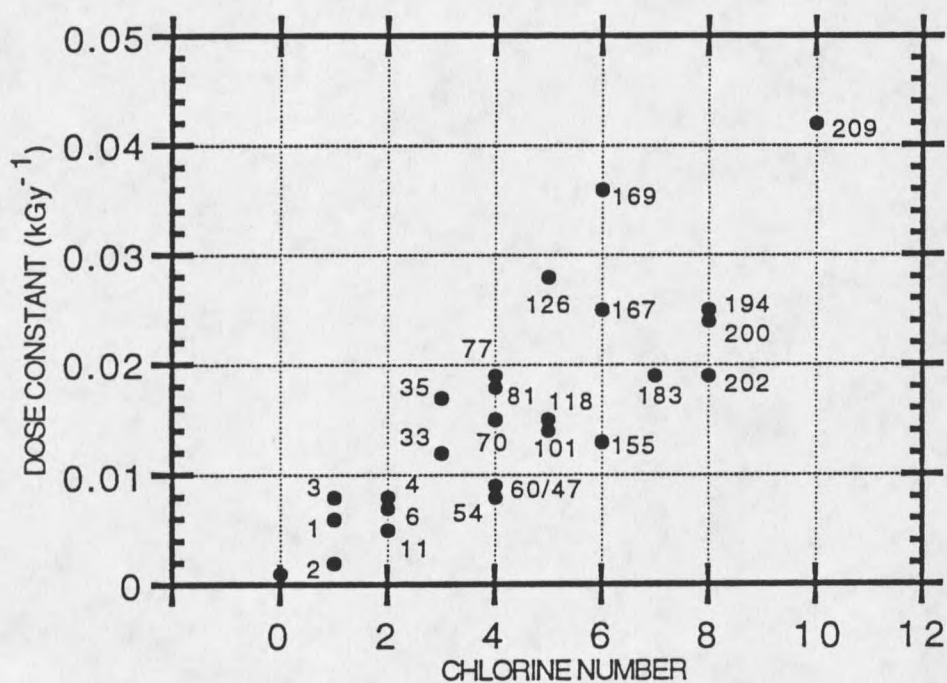


Figure 7. Observed dose constant as a function of chlorines on the biphenyl ring. Specific congeners can be identified by their Ballschmider number given in Table 3.

Table 3. Ballschmider Numbers, Observed Dose Constants (kGy^{-1}), and Structure of PCBs

Bz No.	Structure	(kGy^{-1}) in Isopropanol	Type	Bz No.	Structure	(kGy^{-1}) in Isopropanol	Type
Monochlorobiphenyl				Pentachlorobiphenyl			
1	2	0.006 ± 0.001	M	101	2,2',4,5,5'	0.014 ± 0.002	D
2	3	0.003 ± 0.002		118	2,3',4,4',5	0.015 ± 0.002	M
3	4	0.008 ± 0.002		126	3,3',4,4',5	0.028 ± 0.003	P*
Dichlorobiphenyl				Hexachlorobiphenyl			
4	2,2'	0.009 ± 0.001	D	155	2,2',4,4',6,6'	0.014 ± 0.002	T
6	2,3'	0.007 ± 0.002	M	167	2,3',4,4',5,5'	0.025 ± 0.002	M
11	3,3'	0.005 ± 0.001		169	3,3',4,4',5,5'	0.036 ± 0.004	P*
Trichlorobiphenyl				Heptachlorobiphenyl			
33	2',3,4	0.010 ± 0.003	M	183	2,2',3,4,4',5',6	0.019 ± 0.002	Tr
35	3,3',4	0.017 ± 0.001					
Tetrachlorobiphenyl				Octachlorobiphenyl			
47	2,2',4,4'	0.009 ± 0.002	D	194	2,2',3,3',4,4',5,5'	0.025 ± 0.002	D
54	2,2',6,6'	0.008 ± 0.001	T	200	2,2',3,3',4,5',6,6'	0.024 ± 0.002	T
60	2,3,4,4'	0.009 ± 0.001	M	202	2,2',3,3',5,5',6,6'	0.019 ± 0.002	T
70	2,3',4',5	0.015 ± 0.003	M				
77	3,3',4,4'	0.019 ± 0.002	P*		Decachlorobiphenyl		
81	3,4,4',5	0.018 ± 0.004	P	209		0.042 ± 0.007	

P = planar, M - mono-ortho, D = di-ortho, Tr - tri-ortho, T - tetra-ortho.

* = biochemically most active. The uncertainties shown in Table 3 are at the 90% confidence level and were calculated according to Noggle (53).

substituted only. It appears that chlorine substitution in the ortho position decreases the dose constant.

Based on the scavenging results, PCB degradation was proposed to occur by a reductive electron capture process. It is well known that, upon electron capture, the captured electron resides in the lowest unoccupied molecular orbital (LUMO) (41). Thus, a correlation between the observed dose constants and the energy level or availability of the LUMO may exist. LUMO energies for all 209 PCB congeners have been estimated by Greaves (42-43) using a semiempirical general molecular orbital program referred to as MOPAC (the data generated by Greaves was based on *in vacuo* conditions and at 0 K). When the dose constants are plotted against LUMO energy, as shown in Figure 8, a strong correlation exists. Further inspection of Figure 8 reveals that a decrease in the energy level of the LUMO corresponds to an increase in the dose constant.

A more complete understanding of the trends shown in Figure 7 is now possible by considering the energy of the PCB LUMOs. Calculations performed by Greaves (42) showed a general decrease in the energy of the LUMO with increasing chlorine content. Organic compounds with positive electron affinities possess conjugated bonds (41) which lead to a relatively low-lying LUMO. The presence of electron withdrawing groups such as chlorine lead to additional lowering of the LUMO. Thus, as the number of chlorines increases, a concomitant increase in the electron affinity

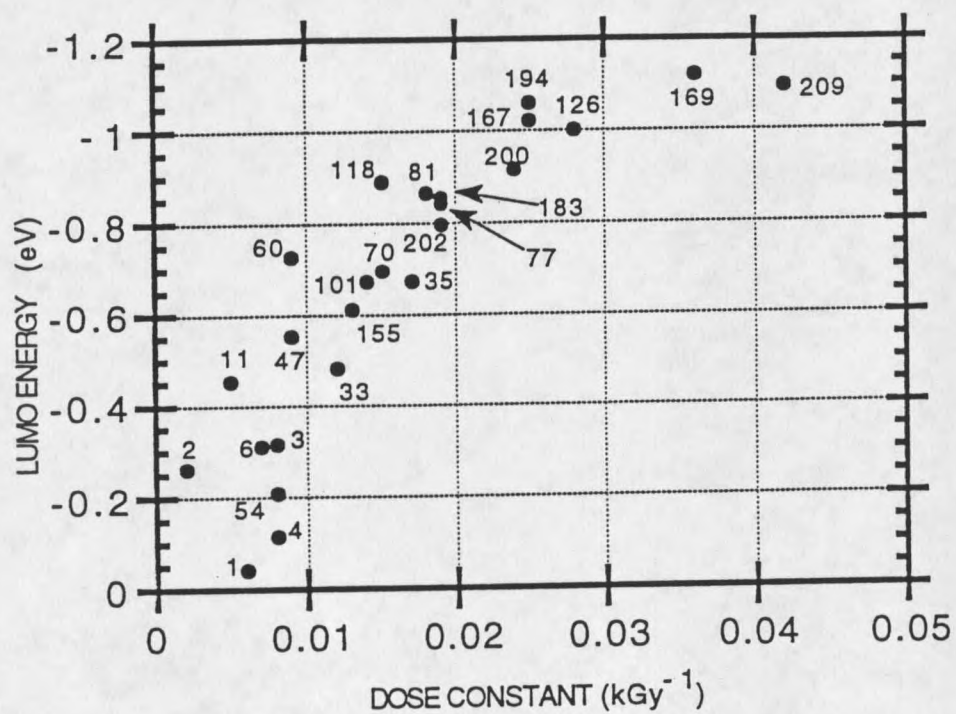


Figure 8. Calculated LUMO energy versus observed dose constants. Ballschmiter numbers are also given.

(or lowering of the LUMO) results and is reflected experimentally in the form of a larger dose constant.

Congeners that are para/meta substituted only, or the planar PCBs, were observed to have the largest dose constant within their respective homolog series as shown in Table 3. Calculated LUMO energy was also found to be lowest for the planar congeners within a homolog series (42). In the planar configuration, conjugation can extend between the two phenyl rings resulting in an increase in electron affinity and thus the dose constant.

Chlorine substitution in the ortho position was found to decrease the dose constant. PCB congeners that contain ortho chlorine substituents are restricted from free rotation about the central phenyl-phenyl bond, and the planar configuration cannot be easily adopted. This ortho effect can be explained by observing the twist angles between the biphenyl rings as a function of the number of ortho chlorines. The twist angle measured in degrees between phenyl rings has been calculated (42). With no ortho chlorine atom the calculated twist angle was approximately 41° . With the addition of one ortho chlorine the angle was increased to 56° . Successive additions of ortho chlorine atoms increased bond angles to 76° , 86° , and 87° for two, three, and four chlorine atoms, respectively. Using MOPAC calculations (42), the LUMO was the orbital whose energy was most affected by increasing the number of ortho chlorine atoms. As a general rule, shown in Table 3,

increasing the number of ortho substituents did decrease the observed dose constants.

Given the above considerations, an unexpected result was obtained when the dose constants were compared to LUMO energy for di and mono substituted congeners. A reversal of this ortho effect appears to have occurred when PCB congeners contain two chlorine atoms or less. Ortho substituted monochlorobiphenyl and dichlorobiphenyl congeners did not have the lowest dose constant for their respective homologs. Reference to Table 3 shows that the dose constant obtained for the ortho-substituted congeners were higher than for meta-substituted congeners. Consistent with other ortho-substituted congeners, calculated LUMO energies are higher than for meta-substituted congeners. This would have predicted a reversal in the observed dose constants. It is currently not understood why this occurs, but this trend has also been observed in the gas phase electron capture responses by mono- and dichlorobiphenyls. The relative electron capture response has been determined empirically for a variety of PCB congeners in the gas phase (2) by measuring the response of individual PCB congeners in an electron capture detector. Table 4 gives the variation in the relative molar electron capture response observed for individual PCB congeners and their relative dose constants. The trend is qualitatively the same. Consistent with our dose constants, ortho-substituted congeners responded better in an ECD than meta-substituted congeners.

Table 4. Relative PCB Response in an Electron Capture Detector and Dose Constant.

<u>Chlorobiphenyl</u>	<u>Relative Response</u>	
	<u>Electron Capture</u>	<u>Dose Constant</u>
2-	1.0	1.0
3-	0.20	0.5
4-	1.10	1.3
3,3'-	6.1	0.83
2,2'-	5.16	1.5

Toxicity and Dose Constant

As reported by De Voogt et al. (44), the adverse effects of PCBs, particularly the planar PCBs, on wildlife have been documented for 20 years. Some of the more common biological effects, typically expressed in terrestrial animals, include hepatic damage, dermal disorders, reproductive toxicity, body weight loss, and teratogenicity (45-46). Demonstrating that these toxic planar PCBs are susceptible to radiolytic degradation is of obvious importance. PCB congeners 77, 81, 126, and 169 are the so-called planar or co-planar PCBs. It has been estimated that the planar PCBs, taken in conjunction with the trace levels of polychlorodibenzo-p-dioxins and polychlorodibenzofurans typically present, account for most of the observed toxicity of commercial Aroclor mixtures (44).

As mentioned, planar PCBs each exhibit the largest dose constant for their respective homolog series. In terms of a

treatment process, these high dose constants for planar PCBs are fortunate. Less dose is needed to achieve significant levels of destruction. For example, the dose needed to reduce a given congener concentration in half is readily calculated using the relationship:

$$\text{dose} = 0.693 / \text{dose constant} \quad (27)$$

Planar pentachlorobiphenyl Bz 126 has a dose constant of 0.028 kGy^{-1} , while ortho-substituted pentachlorobiphenyl Bz 101 has a dose constant of 0.014 kGy^{-1} . The dose needed to reduce the concentration of these congeners in half would be 24.75 kGy for Bz 126 and for Bz 101 exactly twice that dose, or 49.5 kGy.

Many of the mono-ortho substituted PCBs and some of the di-ortho substituted PCBs exhibit biochemical activities comparable to that of the planar congeners (44).

Destruction of these compounds is also possible. Dose constants for mono-ortho congeners are, as a rule, slightly higher than di-ortho PCBs but lower than meta- and para-substituted congeners. Although the dose constants are lowest for PCBs with three chlorines or less, these congeners are unable to meet the basic requirements for a toxic, planar molecule: non-ortho substituted and substituted in both para positions and in at least two meta positions. It should be pointed out that Bz 118, a mono-ortho congener, is the most widely measured congener in the environment that can adopt an almost planar structure (44).

Its dose constant is also high, being only slightly lower than that of Bz 126.

Mass Balance Studies

In any treatment process, identifying the degradation products is essential. Exhaustive studies were undertaken to determine the degradation products produced and to provide an accurate carbon and chlorine mass balance. The expected products, assuming dissociative electron capture, would be less chlorinated homologs and free chloride ion. As amply demonstrated, in fact, these products are observed. Figure 9 shows an electron impact (EI) total ion chromatogram for a solution of BZ 200, labeled OCB, in neutral 2-propanol after receiving a 120 kGy dose. The envelope of peaks having retention times shorter than Bz 200 are due to less chlorinated congeners ranging from heptachlorobiphenyl to trichlorobiphenyl. The peaks having a retention time larger than that of Bz 200 are due to the presence of a series of solvent-altered PCB congeners. Solvent altered congeners were also observed for congeners containing six, five, four, three, and two chlorines. These PCB-solvent adducts were identified by a combination of mass spectrometric measurements and derivatization techniques.

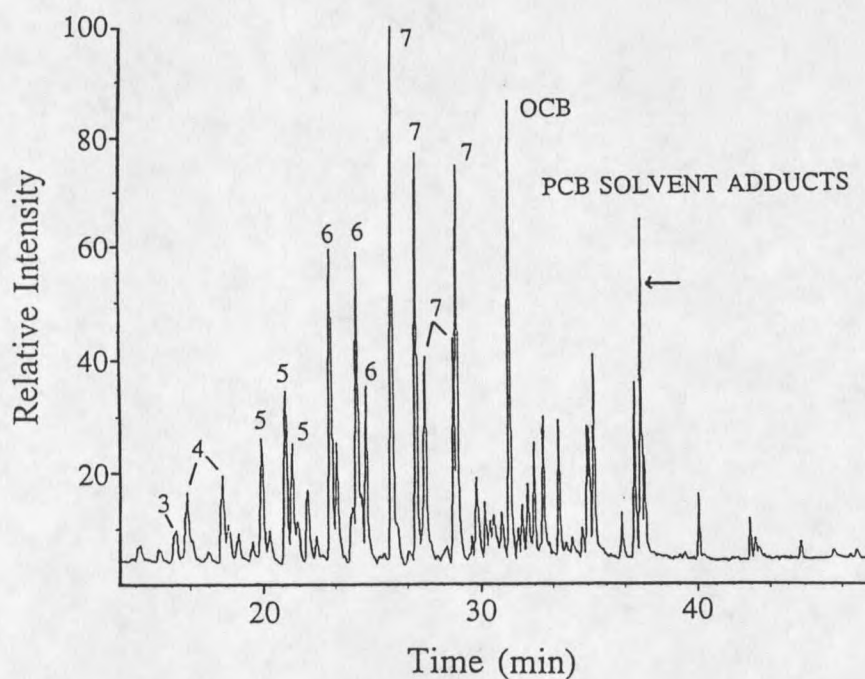


Figure 9. Electron impact total ion chromatogram for a solution initially containing Bz 200 (OCB) after receiving a dose of 120 kGy. Peaks are labelled to indicate the level of chlorination on the biphenyl ring. Peaks with retention times longer than Bz 200 are solvent altered congeners. The mass spectrum for the adduct identified with the arrow is given in Figure 10.

Adduct Identification

The generalized structure of this PCB-solvent adduct is shown as an insert in Figure 10. This conclusion was based in part by the mass spectra obtained (Figure 10).

Inspection of Figure 10 reveals the two major fragment ions: m/z 59 and an isotopic cluster starting at m/z 435-443. Low ion intensity is observed for masses corresponding to the molecular ion where a weak molecular cluster at m/z 450-458 was observed. This spectrum is consistent with the proposed structure. Confirmation that the isopropanol group is attached to the biphenyl ring via the alpha carbon as shown in Figure 10 was verified by chemical derivatization with N,O-bis(trimethylsilyl)acetimide (BSA). An aliquot of irradiated sample was blown dry and then reconstituted in pyridine. A small amount of BSA was added and refluxed for 10 minutes. BSA converts free alcohol groups to their corresponding trimethylsilyl (TMS) derivatives. Figure 11 shows a partial mass spectrum of the compound shown in Figure 10 after derivatization. The formation of the TMS derivative is confirmed by the presence of the isotopic cluster starting at m/z 507 which corresponds to the loss of a methyl group from the TMS derivative. TMS derivatives were observed for all of the adducts identified.

If a mass balance is performed on Figure 9, not all of the beginning carbon and chlorine can be accounted for as free chloride, less chlorinated homologs and PCB solvent

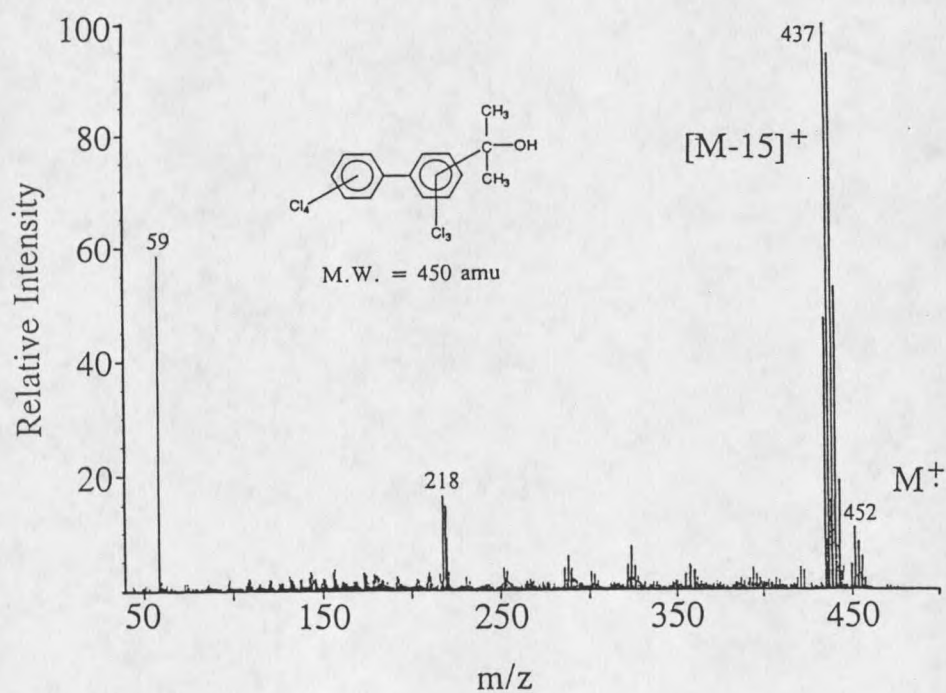


Figure 10.

Electron impact mass spectrum from solvent altered Bz 200. Insert shows the proposed structure of the PCB-solvent adduct assigned to the mass spectrum.

adducts. Approximately 60% of the beginning carbon and chlorine can be accounted for as either less chlorinated homologs or as free chloride. Accurate quantitation of the observed PCB adducts is not currently possible because of the lack of standards. However, if typical response factors obtained from the PCBs themselves are used, it has been estimated that the adducts could account for no more than 10% of the missing carbon or chlorine.

Missing Carbon and Chloride Mass

Mass balance results for 19 PCB congeners when 50% percent of the original material has been destroyed appears to vary from congener to congener. An excellent example of this variability is demonstrated by PCB 3 and PCB 1, both monochlorobiphenyl congeners. The percentage of carbon and chlorine recovered is shown in Table 5. Approximately 95% of the carbon and chlorine is recovered as residual parent PCB, biphenyl, or free chloride for Bz 3, while approximately eighty percent can be recovered for Bz 1. The amount of recoverable mass does not appear to related directly to absorbed dose but appears to be a function of the individual chemistry of each congener. The majority of the percent recoveries for carbon and chlorine are within one to five percentage points of each other. This is an indication that the unidentified material contains both the carbon and the chlorine.

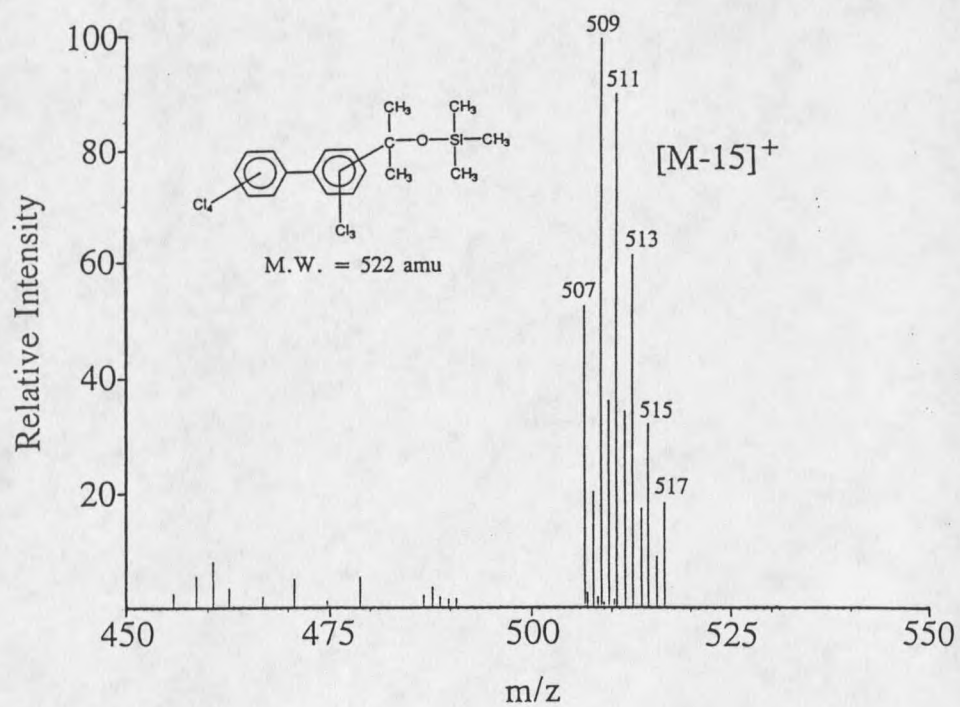


Figure 11. TMS derivatized mass spectrum of Figure 10.

Table 5. Carbon and Chlorine Mass Balance when Fifty Percent of the Beginning Material is Destroyed. Also Presented is the Dose Needed to Achieve Fifty Percent Destruction.

Bz No.	Dose kGy ⁻¹	% Carbon Rec.	% Chlor. Rec.	Bz No.	Dose kGy ⁻¹	% Carbon Rec.	% Chlor. Rec.
Monochlorobiphenyl				Pentachlorobiphenyl			
1	115.5	88	80	101	49.5	96	100
2	231.0	101		118	46.2	95	98
3	86.6	99	95	126	24.8	88	80
Dichlorobiphenyl				Hexachlorobiphenyl			
4	77.0	111		155	49.5	93	95
6	99.0	111	91	167	27.7	95	93
Trichlorobiphenyl				169	19.3	93	92
33	69.3	94	90				
35	40.8	106	99				
Tetrachlorobiphenyl				Heptachlorobiphenyl			
54	86.6	84	89	183	36.5	97	101
60	77.0	100	96				
77	36.5	83	81	Octachlorobiphenyl			
81	38.5	80	81	194	27.7	82	92

Carbon 14 Labeled Tetrachlorobiphenyl

For those congeners which had the poorest recovery of starting material, a variety of mass spectrometric techniques such as GC/MS and LC/MS in positive and negative chemical ionization modes were used to search for the missing mass. Volatile, semivolatile, and nonvolatile fractions were each evaluated in an unsuccessful attempt to identify the missing mass. Finally, a carbon-14 labeled tetrachlorobiphenyl congener Bz 47 was irradiated. Following a series of absorbed doses with a maximum of 149 kGy, 100% of the activity was determined to be in the

bulk irradiated solution. This is in contrast to what was found using mass spectrometric techniques where only 78% of the original material could be identified as original parent material, less chlorinated congeners, PCB-solvent adducts, and biphenyl. The identity of the missing mass is unknown, and its detection may be hindered by the fact that products which are many steps down a chain of reactions are often present in very small concentrations. To further define the fraction in which the carbon-14 labelled product resides, an aliquot was distilled at 93°C. No activity was removed at that temperature. Thus, the unidentified material appears to be in a semivolatile or nonvolatile fraction yet to be identified. Since the experiments using carbon-14 suggest that the degradation products could be present in the semivolatile fraction, samples were analyzed by EPA Method 8270 for semivolatile analytes. No EPA regulated 8270 compounds, such as chlorinated benzenes, were identified. While this is negative evidence, it is significant in that the degradation products formed are not EPA regulated compounds. Also, it should be pointed out that no evidence of chlorinated dioxans or dibenzofurans was found. Based on the results that we have obtained, the most likely location of the missing mass is in solvent based adducts which have not yet been identified. This was confirmed by eliminating the adducts. This work is discussed below.

Adduct Elimination

With the addition of 160 mg L⁻¹ nitrobenzene to a 160 mg L⁻¹ solution of octachlorobiphenyl adduct formation was eliminated as shown in Figure 12. Figure 12 contains extracted ion chromatogram for mass 59 for Bz 200, Bz 200 with benzene, and Bz 200 with nitrobenzene after receiving a dose of 60 kGy. Mass 59 is a common fragment ion for all of the PCB adducts observed. As can be seen, a significant fraction of adducts are present in the solutions of Bz 200 and Bz 200 with benzene. However, with the addition of nitrobenzene, mass 59 is eliminated, indicating the absence of PCB solvent adducts. In the absence of adducts, carbon and chlorine mass balance is significantly improved. When 70% of the octachlorobiphenyl was destroyed in the presence of nitrobenzene, approximately 97% of the beginning carbon and chloride was identified as octachlorobiphenyl, less chlorinated congeners, and free chloride. In the absence of nitrobenzene, when 70% of the beginning octachlorobiphenyl was destroyed, only 72% of the beginning carbon and chloride could be identified.

Biphenyl

The final product from the stepwise dechlorination of polychlorinated biphenyls would be biphenyl. Shown in Figure 13 is a graph showing the production of biphenyl as a function of chlorine loss from 4-chlorobiphenyl. Biphenyl

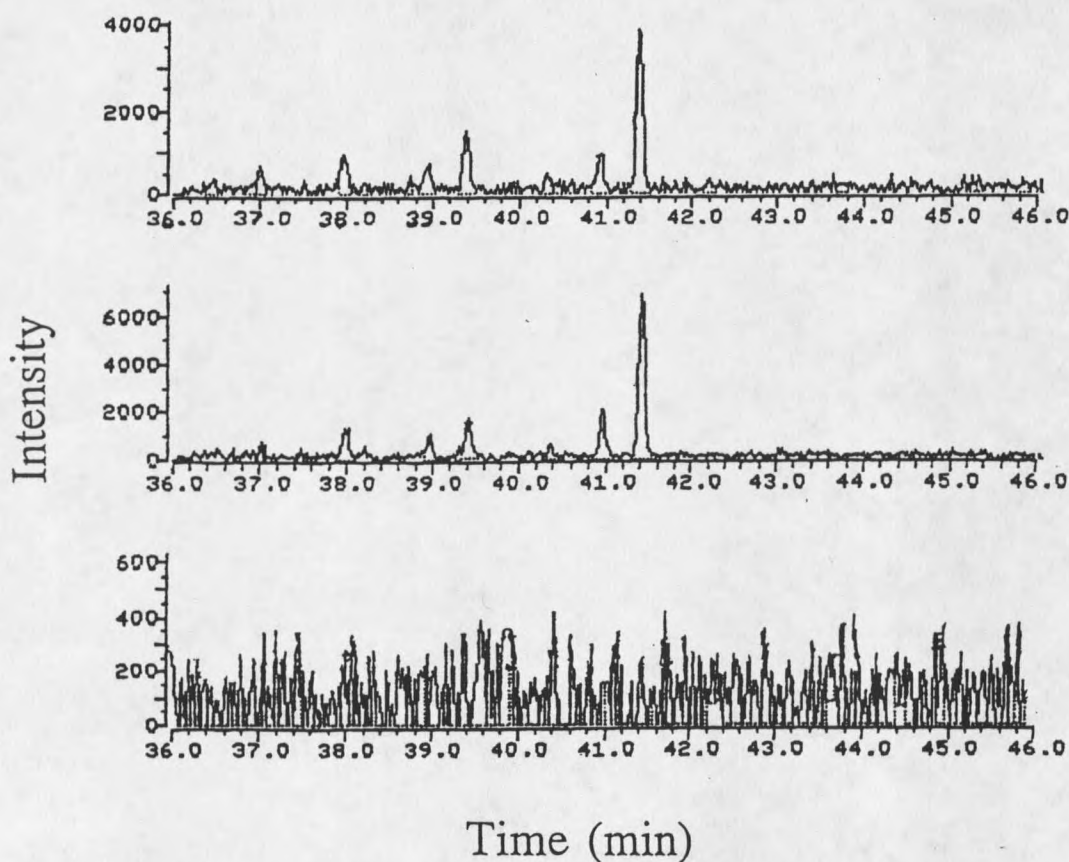


Figure 12.

Extracted ion chromatogram for m/z 59 a common ion for all of the adducts under three conditions. The top extracted ion chromatogram (EIC) is for a solution of Bz 200 while the middle EIC is Bz 200 and benzene and the bottom EIC is Bz 200 and nitrobenzene. Note the abundance scale. Adducts are eliminated in the presence of nitrobenzene.

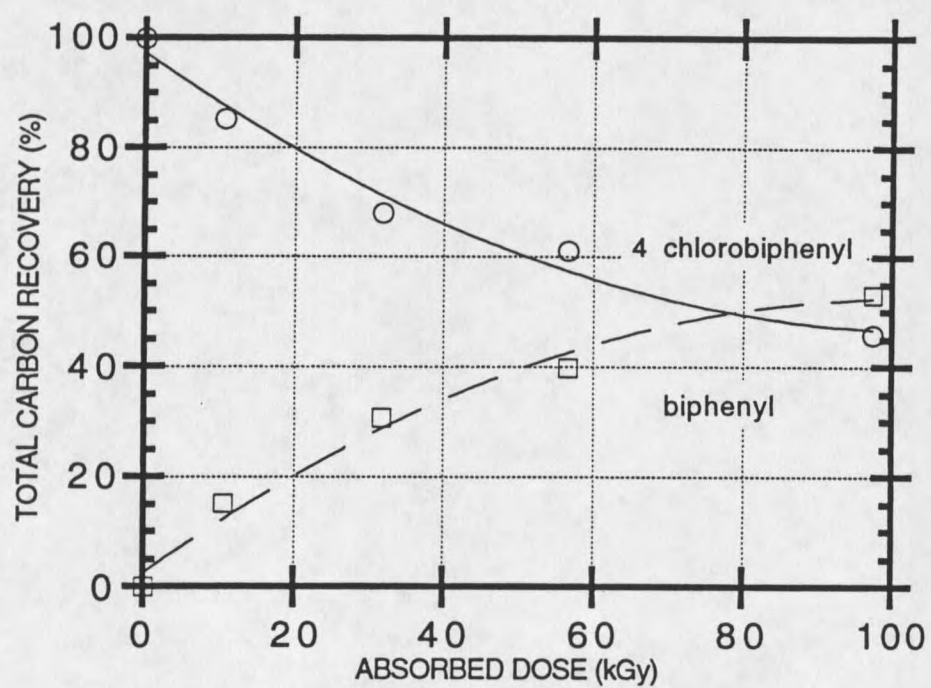


Figure 13. Production of biphenyl from 4-chlorobiphenyl.

itself was irradiated and its concentration was measured as a function of dose (Figure 14). As shown, there was no change in biphenyl concentration. Biphenyl is particularly resistant to radiation damage and has been suggested for use in nuclear reactors as a coolant (7).

It is not necessary to break the biphenyl ring (3) in order to chemically destroy PCBs. In fact, biphenyl is not regulated by TSCA and is not included in the quantification of a PCB sample. This is fortunate because cleavage of the aromatic biphenyl requires a high energy of activation that can be accomplished most readily using some form of combustion (5).

PCB Degradation in Nonpolar Solvents

Three nonpolar solvents were studied, transformer oil, hydraulic oil and isooctane. Isooctane is more amenable to mass spectrometric analysis than transformer and hydraulic oil, which require extensive cleanup to remove high molecular weight hydrocarbons from the PCB elution window. Thus, the majority of this work was performed in isooctane, which greatly facilitated mass spectrometric identification of the degradation products. Significant differences between the radiolytic behavior of PCBs in nonpolar isooctane and polar 2-propanol were discovered and are illustrated.

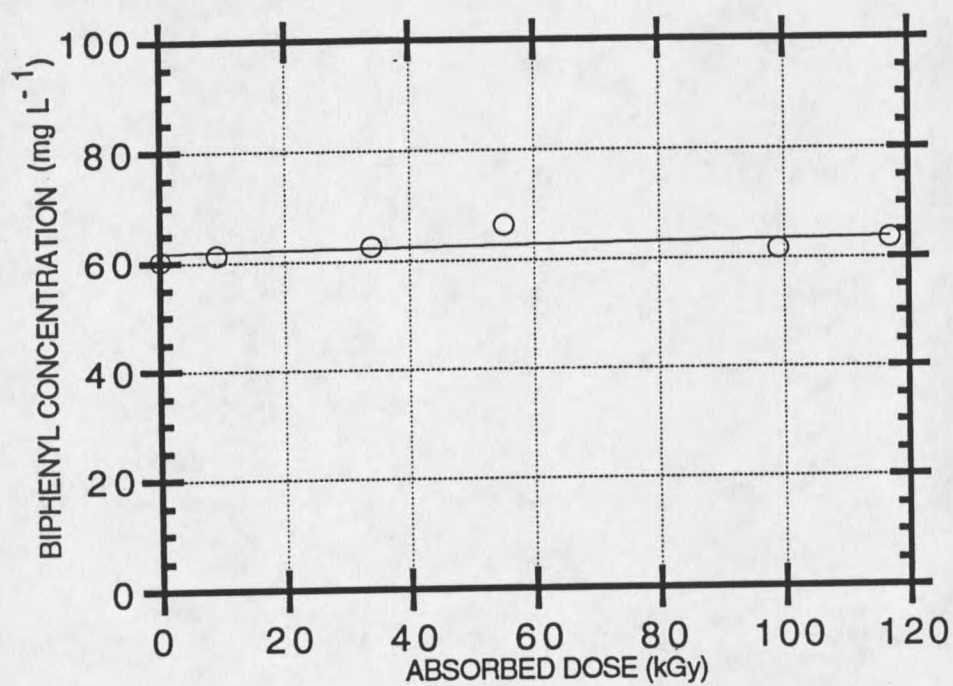


Figure 14.

Concentration of biphenyl as a function of absorbed dose.

PCB Radiolysis in Isooctane

Figure 15 shows a plot of Bz 200 in isooctane as a function of absorbed dose. As shown, the octachlorobiphenyl concentration steadily decreases with increasing dose. The degradation of octachlorobiphenyl is accompanied by the simultaneous growth and destruction of hepta, hexa, penta, tetra, tri, and dichlorobiphenyl, as shown in Figure 16. At the maximum absorbed dose in Figure 16, negligible amounts of monochlorobiphenyl and biphenyl were observed. This degradation pattern was observed with all of the congeners studied in isooctane, transformer oil, and hydraulic oil, and is similar to that obtained in isopropanol (22). In an attempt to understand the radiolytic dechlorination mechanism in these solvents, scavenging experiments were undertaken. However, before discussing these results, the use of the dose constant as measure of degradation needs to be reexamined. The dose constant in isooctane was found to be concentration dependent.

Determination of Degradation Efficiency

In isooctane individual congener degradation exhibits apparent first-order kinetics analogous to what was observed in isopropanol. In contrast to isopropanol, the dose constant in isooctane was observed to vary with initial PCB concentration. This phenomenon was investigated further by preparing a series Bz 155 solutions at approximately 1800,

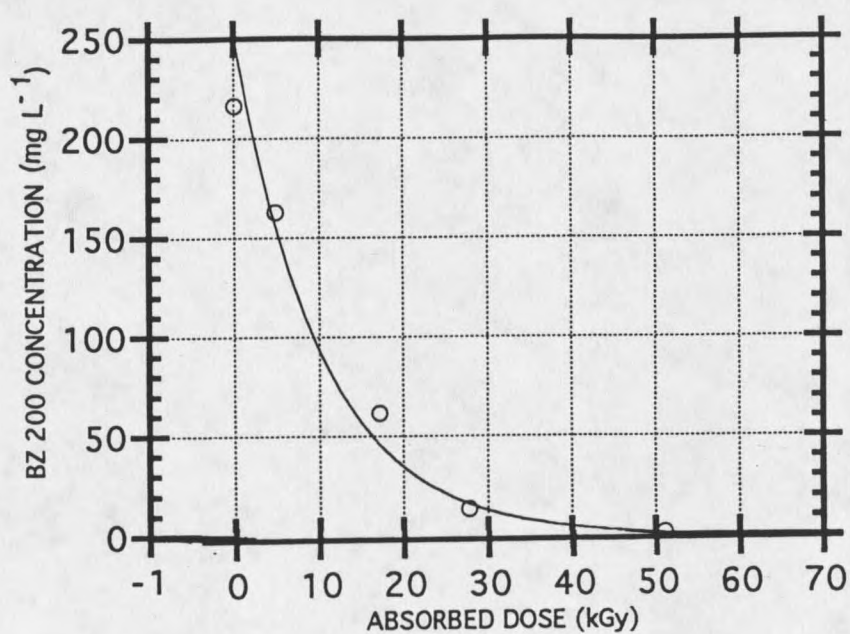


Figure 15.

Observed destruction from the irradiation of BZ 200 in isooctane. Note the exponential decay of Bz 200 in relation to absorbed dose.

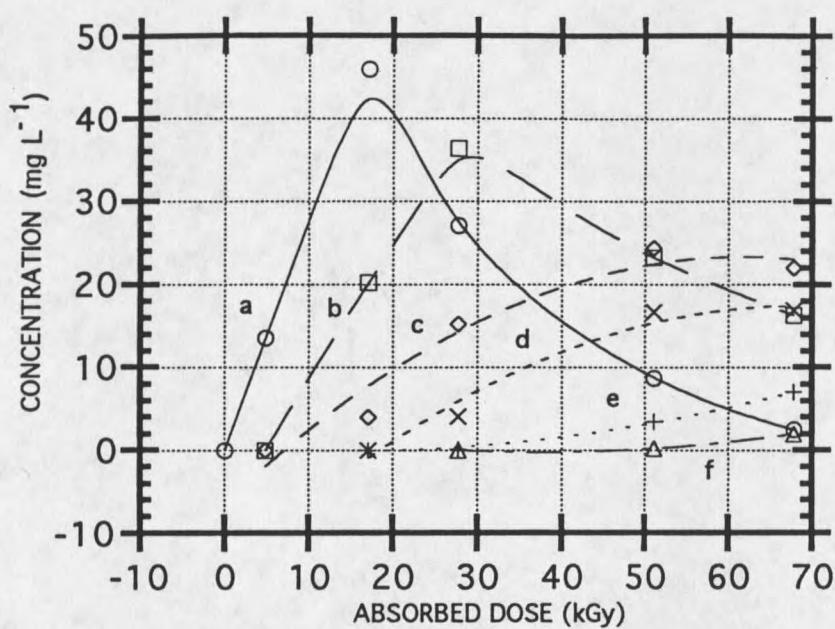


Figure 16.

Degradation products produced from Bz 200. Curves a-e correspond to hepta-, hexa-, penta-, tetra-, tri-, and dichlorobiphenyl, respectively.

750, 250 and 125 mg L⁻¹. Other factors, such as dose rate or solvent purity, could result in varying dose constants. Therefore, to ensure that the variation in dose constant was due solely to differences in PCB concentrations, the above samples were prepared with the same solvent and irradiated at the same dose rate. The results of this study are shown in Figure 17. A concentration dependence is clearly shown, which complicates the comparison of congeners under various conditions. A discussion of the concentration dependence and dose constant is given on page 95.

The use of G_{initial} values does not provide any significant improvement over the use of dose constants. For G_{initial} values, the dose each sample receives should be identical because, as shown, degradation is exponential with absorbed dose. Using spent nuclear fuel with its constantly changing dose rate led to poor reproducibility in delivering precise amounts of dose. G values are also concentration dependent where increasing solute concentration increases the G value.

Despite its concentration dependence, the dose constant was ultimately chosen as our figure of merit because it eliminated the precise dose requirements necessary for use with the G value. However, to allow for congener degradation comparison, the beginning PCB concentrations was kept approximately equal.

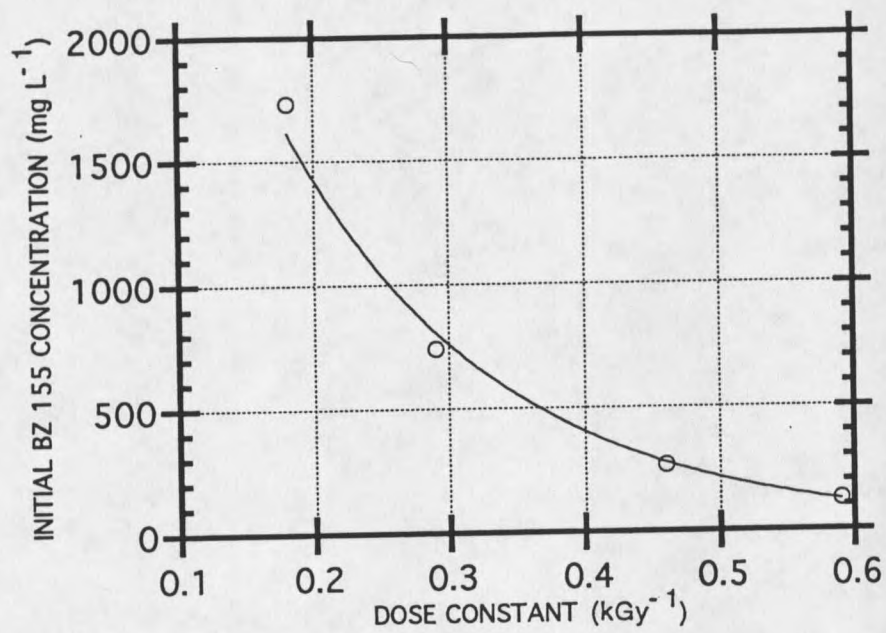


Figure 17. Beginning PCB concentration versus the dose constants obtained.

Reactive Species

The yield and identity of the radicals produced when hydrocarbons are irradiated has been studied extensively (31,38,47). The major radicals produced are hydrogen atoms, various alkane radicals, positive ions, and solvated electrons (38). It is known that the total free ion yield varies little with increasing chain length (38). Thus, the radicals discussed above should predominate in transformer oil, hydraulic oil, and isooctane with approximately the same free ion yield. It is conceivable that any of the above reactive agents could be responsible for PCB degradation. Determining the reactive agent responsible should be possible by the addition of judiciously chosen scavenging agents.

Scavenging Experiments

The effect various scavenging agents have on the dose constants obtained for Bz 1 and 200 in isooctane is shown in Table 6. The data are expressed as relative values with the scavenger free congener having been assigned a value of one. Normalizing the dose constants allows for easy comparison of scavenging agent effects. The addition of nitrobenzene significantly reduced the degradation of Bz 200 and Bz 1, while benzene had no effect. Nitrobenzene has a diffusion controlled rate of reaction with aqueous electrons, while benzene has a reaction rate with aqueous electrons that is

Table 6. Relative Destruction for a 250 mg L⁻¹ Solution of Bz 1 and Bz 200 in Isooctane With and Without the Addition of Radical Scavengers.

PCB Bz#	Relative Destruction Rate	Condition
200	1	No additive
200	1	400 mg L ⁻¹ Benzene
200	0.18	400 mg L ⁻¹ Nitrobenzene
200	0.052	SF ₆ Sparged
200	0.72	Cyclopropane Sparged
1	1	No additive
1	1	400 mg L ⁻¹ Benzene
1	0.19	400 mg L ⁻¹ Nitrobenzene
1	0.081	SF ₆ Sparged
1	1	Cyclopropane Sparged
1	1.3	N ₂ Sparged

over three orders of magnitude smaller (22). Both benzene and nitrobenzene have similar reaction rates with hydrogen atoms (22). Given this, it is reasonable to conclude that hydrogen atoms do not contribute to PCB degradation in isooctane.

The above experiment is not definitive towards solvated electrons because nitrobenzene is also known to scavenge alkane radicals (31). However, sulfur hexafluoride, known to have a high rate of reaction with electrons, is believed

to have a reaction rate significantly less for alkane and hydrogen radicals. This conclusion is based upon work performed by Johnson and Salmon (38). Johnson and Salmon found that the rate of nitrobenzene reacting with a methanol radical was five orders of magnitude greater than was the rate for sulfur hexafluoride. Assuming a similar trend with other radicals, the reaction of alkane radicals with sulfur hexafluoride should be negligible. When samples were sparged with sulfur hexafluoride, the dose constants were greatly reduced, implicating the solvated electron as a major reactive species. The effect dissolved oxygen has on degradation also implicates solvated electrons. Oxygen is a known free radical scavenger capable of efficiently scavenging solvated electrons (7). In the absence of oxygen, degradation should be enhanced. As shown in Table 6, sparging a solution of Bz 1 with nitrogen increased degradation while sparging with oxygen reduced Bz 1 degradation.

Radiolysis literature identifies cyclopropane as an efficient positive ion scavenger (31). A modest reduction in degradation was observed for Bz 200 when sparged with cyclopropane, while no reduction in degradation for Bz 1 was observed. This result required further investigation. PCB congeners 169, 155, and 77 were evaluated with and without cyclopropane. No observable reduction in degradation due to the presence of cyclopropane occurred. Positive-ion PCB reactions, if they occur, do not appear to be significant.

Consequently, it is reasonable to conclude that dissociative electron capture is responsible for the degradation pattern shown in Figure 16. This conclusion is supported by work performed by Warman, Asmus, and Schuler (31). In their study, chlorinated and brominated hydrocarbons were found to efficiently capture electrons in nonpolar cyclohexane. In fact, dissociative electron capture was found to be the major pathway for dechlorination. These results are also consistent with the scavenging experiments in isopropanol conducted by our lab (9) in which the solvated electron was the primary reactive species. At the concentration of sulfur hexafluoride and nitrobenzene used, PCBs are capable of competing with these scavengers for the available electrons, and thus neither completely eliminated degradation.

Degradation Efficiency

To quantitate the destruction efficiency, dose constants were evaluated for individual congeners in isooctane where the initial PCB congener concentration was approximately 250 mg L⁻¹. The larger the dose constant the greater the susceptibility toward radiolytic degradation. Dose constants for 18 PCB congeners obtained in isooctane, as well as those previously measured in isopropanol, are given in Table 7. All of the congeners studied were found to have 1.4 to 9 times larger dose constants in isooctane than the corresponding dose constant in isopropanol. Given

Table 7. Ballschmider Numbers and Structure, Dose Constants (kGy⁻¹) in Isooctane and Isopropanol

Bz No.	Structure	(kGy ⁻¹) in Isooctane	(kGy ⁻¹) in Isopropanol	Bz No.	Structure	(kGy ⁻¹) in Isooctane	(kGy ⁻¹) in Isopropanol
				Monochlorobiphenyl			
1	2	0.034 ± 0.004	0.006 ± 0.001	101	2,2',4,5,5'	0.060 ± 0.016	0.014 ± 0.002
3	4	0.036 ± 0.008	0.008 ± 0.002	118	2,3',4,4',5	0.066 ± 0.003	0.015 ± 0.002
				126*	3,3',4,4',5	0.073 ± 0.003	0.028 ± 0.003
				Dichlorobiphenyl			
4	2,2'	0.042 ± 0.001	0.009 ± 0.001	155	2,2',4,4',6,6'	0.046 ± 0.018	0.014 ± 0.002
11	3,3'	0.007 ± 0.001	0.005 ± 0.002	167*	2,3',4,4',5,5'	0.043 ± 0.004	0.025 ± 0.002
				169*	3,3',4,4',5,5'	0.085 ± 0.003	0.036 ± 0.004
				Trichlorobiphenyl			
33	2',3,4	0.056 ± 0.003	0.012 ± 0.003	Heptachlorobiphenyl			
35	3,3',4	0.066 ± 0.015	0.017 ± 0.001	183	2,2',3,4,4',5',6	0.11 ± 0.010	0.019 ± 0.002
				Tetrachlorobiphenyl			
47	2,2',4,4'	0.065 ± 0.004	0.009 ± 0.002	Octachlorobiphenyl			
54	2,2',6,6'	0.041 ± 0.004	0.008 ± 0.001	194	2,2',3,3',4,4',5,5'	0.12 ± 0.014	0.025 ± 0.002
77*	3,3',4,4'	0.068 ± 0.005	0.019 ± 0.002	200	2,2',3,3',4,5',6,6'	0.10 ± 0.014	0.024 ± 0.002

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* Planar or almost planar. The uncertainties shown are at the 90% confidence level and were calculated according to Nogge (53).

that electrons are the primary reactive species in both solvent systems, the extent of degradation in isooctane was initially surprising. In nonpolar solvents such as isooctane, the majority of electrons formed are expected to undergo geminate recombination with their parent ion; thus, the free ion electron yield available for reaction is quite small--approximately 0.1 electrons 100 eV^{-1} (47). This value is over an order of magnitude less than the free electron yield in isopropanol of 1.4 (7).

How can these results be reconciled if the free ion yield is an order of magnitude greater in isopropanol than in isooctane? Free ion yield does not necessarily reflect the total electron yield available for reaction with the PCBs. Because isopropanol has a measurable electron capture rate, the amount of electrons available to react in this solvent is reduced. The electron attachment rate constant for isopropanol is $1.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (48) which, when taken in conjunction with its high concentration of 13.1 M, leads to a pseudo-first-order rate constant of $2 \times 10^7 \text{ s}^{-1}$. This may be compared to the pseudo-first-order rate constant for a 200 mg L^{-1} solution of Bz 200 of $8 \times 10^6 \text{ s}^{-1}$, based on a PCB molar concentration of $4 \times 10^{-4} \text{ M}$ and a very fast electron attachment rate of $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This shows that, at best, only 30% of the electrons will be scavenged by the PCB molecules in 2-propanol. This figure will be even lower if the PCB concentration or the electron attachment rate constant is smaller.

In isooctane, the solvent and the PCBs do not directly compete for electrons because the solvent does not capture electrons. In fact, PCB molecules are able to scavenge electrons which normally would undergo geminate recombination. This is confirmed by evaluating G_{initial} values obtained for Bz 155, which varied from 0.37 to 2.4 molecules 100 eV^{-1} depending upon beginning Bz 155 concentration. These G values all significantly exceed the free ion yield of 0.1. In fact, a G value of 2.4 is approaching the theoretical yield of both free electrons and geminate electrons (31). Thus, the conclusion that the recombination reaction is less efficient than PCB electron capture appears to be justified. The net effect is that more electrons are available for reaction with the PCB molecules in isooctane than in isopropanol, which is reflected by the higher dose constants observed.

The practical significance of these high dose constants is that less dose is needed to achieve significant levels of destruction in isooctane than in neutral isopropanol. This can be demonstrated by observing the dose needed to reduce the concentration of a given PCB congener by 90%. This dose can be calculated using the relationship:

$$\text{dose} = \text{dose constant}^{-1} * \ln 10 \quad (28)$$

A dose constant of 0.10 kGy^{-1} was obtained for PCB 200 in isooctane. The dose needed to reduce its concentration 90% would be 23.0 kGy. For PCB 200 in isopropanol, the dose

constant obtained was 0.024 kGy^{-1} (22). The dose needed to reduce its concentration 90% would be 95.9 kGy.

Congener Substitution and Degradation

Figure 18 shows a plot of dose constant as a function of chlorine number in isooctane. In general, the dose constant increases with increasing chlorine content. Careful review of Table 7 shows that the overall difference in homolog dose constants is smaller in isooctane relative to that in isopropanol. The notable exception is Bz 11 where the dose constant is essentially identical in both isooctane and isopropanol. As demonstrated by the variability shown in Figure 18 and Table 7, chlorine position within a homolog also influences the dose constants obtained in isooctane, but again to a lesser extent than isopropanol. If the high and low dose constant obtained for each homolog are evaluated, greater variability exists in isopropanol than isooctane. Once more Bz 11 is the exception. The behavior of Bz 11 is currently not understood. Excluding Bz 11, congener degradation appears to be less dependent upon chlorine number and substitution in isooctane than in isopropanol.

In isopropanol, a strong correlation was found to exist between the dose constant and the energy of the lowest

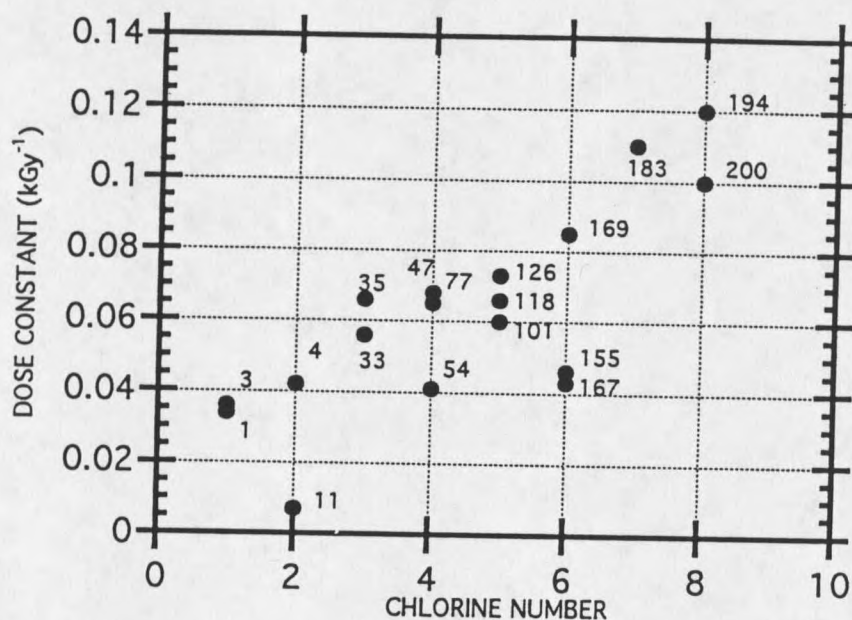


Figure 18.

Plot of observed dose constant in isooctane as a function of chlorine content on the biphenyl ring. Specific congeners can be identified by their Bz numbers.

unoccupied molecular orbital (LUMO) of the congener (8). Decreasing LUMO energy resulted in larger dose constants with the planar or almost planar congeners having the largest dose constants. If the dose constants obtained in isooctane are plotted against isopropanol dose constants, Figure 19, a reasonably linear agreement exists, with the exception of planar or almost planar Bz 169, 167, 126 congeners. Thus, a general correlation also exists between LUMO energy and the dose constants for PCB congeners in isooctane. Because solvated electrons are responsible for PCB degradation in isopropanol and isooctane, it was expected that dose constant behaviors in the two solvents would be analogous. However, the compression of the dose constants and the behavior of the planar or almost planar congeners show that they are not entirely analogous.

The available reaction rate data for electron scavenging solutes in nonpolar solvents indicates a complex chemistry for the electron (49-52). In contrast to polar solvents, reactions of electrons in nonpolar liquids can bear a similarity to the reactions of electrons in the gas phase, where the rates of reaction may depend upon the kinetic energy of the electron. In nonpolar liquids, the kinetic energy of the electron varies with the choice of the solvent. In a study performed by Allen, Gangwer, and Holroyd (49), electron scavengers such as sulfur hexafluoride, carbon tetrachloride, ethylbromide and trichloroethylene exhibited maxima in their measured rate

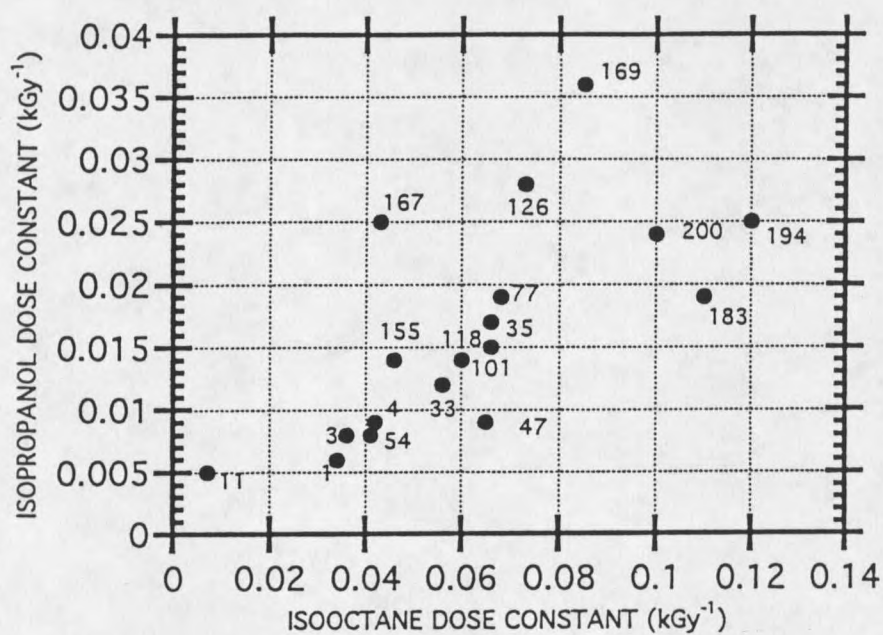


Figure 19.

Plot of dose constants obtained in isooctane against the dose constants obtained in isopropanol. Congeners can be identified by their Bz numbers.

constants at characteristic energy levels of the electrons. Holroyd et. al. (49) also determined that low electron affinity solutes exhibit a greater dependence upon the energy of the electron than compounds with high electron affinity. This work could help in interpreting the results obtained in isooctane.

It is well known that considerable differences in electron affinity exist among PCB congeners within a homolog series, particularly between the planar and nonplanar congeners. Even greater differences in electron affinity are found between homologs. It is conceivable that the lower electron affinity PCBs exhibit a maxima in their electron attachment cross section at a different energy than the high electron affinity PCBs. Thus, if the energy of the electron in isooctane occurs at or near the maxima in the electron attachment cross section for the lower electron affinity PCBs such as mono- and dichlorobiphenyl then the dose constant obtained for these compounds would be increased relative to the higher electron affinity PCBs. The high electron affinity planar or almost planar congeners would not experience a proportional increase in dose constants as would low electron affinity compounds. The result would be a relative compression of the dose constants and could also help to explain the outlying congeners in Figure 19. For example, in Figure 19 congeners 126, 167, and 169 appear as though their dose constants should have been larger. To determine definitively if this effect is

operative, experiments designed to probe the dependence of reaction rate on electron energetics should be performed.

Aroclor 1260 Degradation in Transformer Oil

Given the results obtained in isooctane, radiolytic degradation of PCBs in transformer oil was believed to be possible with much lower doses than predicted by Webber (23). Figure 20 shows the effect of increasing dose on the degradation of gamma irradiated Aroclor 1260 chromatograms obtained with an electron capture detector in transformer oil. The dose each sample received is shown as an insert on the chromatogram. A significant change in the Aroclor 1260 fingerprint occurs with increasing dose. The original peaks have been reduced, with the simultaneous appearance of smaller peaks at shorter retention times which are taken to be less chlorinated PCBs. The Aroclor 1260 concentration has been reduced from approximately 5000 mg L^{-1} to 1800 mg L^{-1} at an absorbed dose of 229 kGy . To our knowledge, this is the first time that radiolytic degradation of Aroclor 1260 has been demonstrated to occur at these moderate absorbed doses in air equilibrated, unadulterated transformer oil. To confirm the reactive agent in transformer oil, individual congeners were sparged with sulfur hexafluoride. As was observed in isooctane, the presence of SF_6 significantly retarded the radiolytic degradation efficiency. A reasonable conclusion is that electrons are responsible for the radiolytically induced

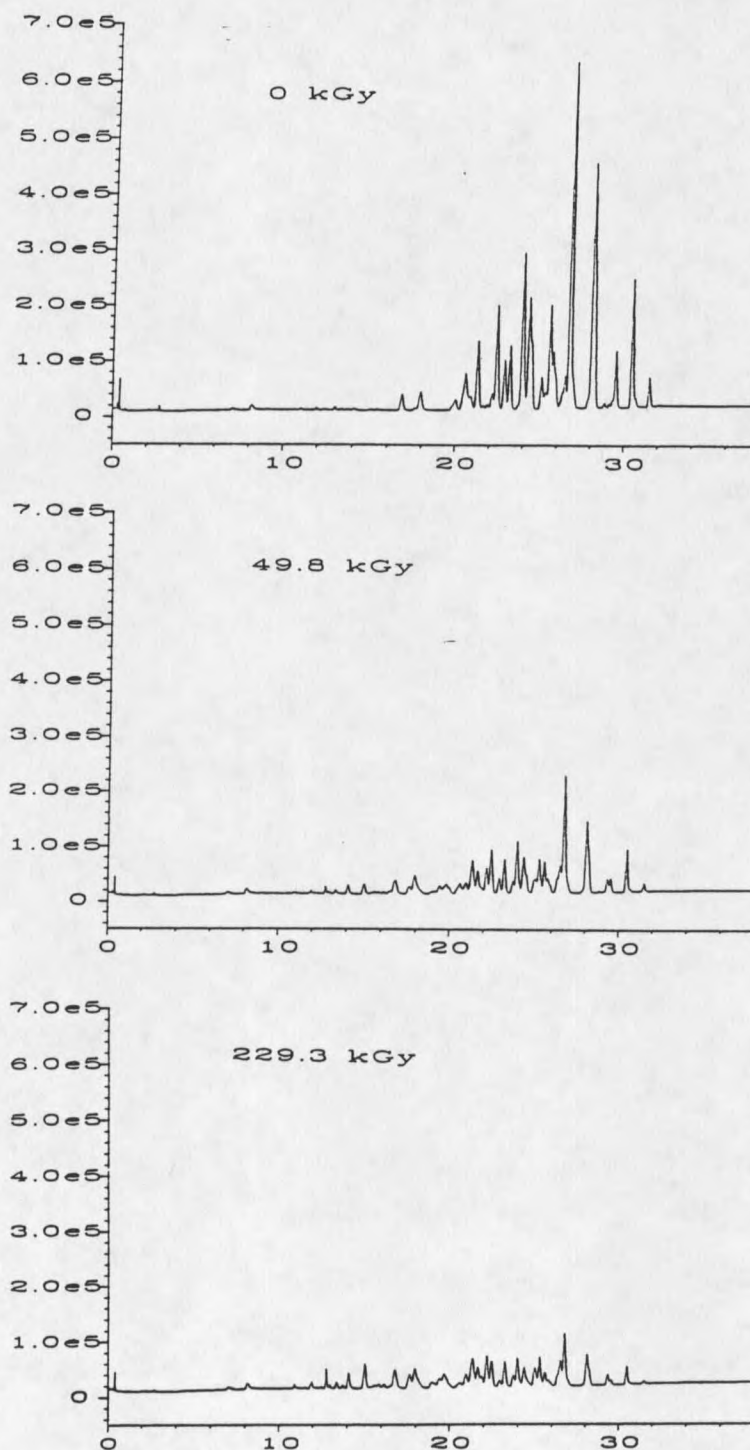


Figure 20.

Aroclor 1260 in transformer oil as a function of absorbed dose. Aroclor 1260 concentration steadily decreases with increasing dose. The Aroclor 1260 concentration has been reduced from 5000 mg L⁻¹ to 1800 mg L⁻¹.

degradation of PCBs in transformer oil. A 230 mg L^{-1} solution of Aroclor 1260 was also irradiated and at an absorbed dose of 500 kGy, the concentration of the PCBs remaining was less than 2 mg L^{-1} which is below the EPA requirement for a PCB treatment process (3).

PCB Contaminated Hydraulic Oil

Interest in PCB destruction in hydraulic oil was generated by the fact that a significant amount of radioactively contaminated and Aroclor 1260 contaminated hydraulic oil exists at the Idaho National Engineering Laboratory. When a solvent contains both a radioactive and an EPA regulated compound, it is referred to as "mixed waste." Mixed waste is currently very difficult to dispose of because of the many regulations. Existing degradation techniques cannot be used because of potential radiological contamination of the destroying equipment. The only identified treatment process for TSCA regulated mixed waste is the TSCA mixed waste incinerator at Oak Ridge National Laboratories in Tennessee. The capacity for this incinerator is rather limited. To dispose of the mixed PCB waste already in existence is estimated to require over 15 years. Further, PCB mixed waste is being generated at three times the incinerator's capacity.

If radiolytic degradation of nonradioactive Aroclor samples in hydraulic oil could be demonstrated, then the mixed PCB waste should also be amenable to treatment.

Removal of the EPA component would be a major step forward in the final disposition of this waste. After the removal of the TSCA regulated component, the radioactive waste could then be dealt with using existing hot waste technologies. The radiolytic degradation of Aroclor 1260 in hydraulic oil is shown in Figure 21. The trend observed in transformer oil is also seen in hydraulic oil; however, the degradation obtained in hydraulic oil is more efficient than the degradation observed in transformer oil. In hydraulic oil, the concentration of Aroclor 1260 was reduced from approximately 5000 to 520 mg L⁻¹ at an absorbed dose of 229 kGy. The final concentration obtained in hydraulic oil is over a factor of three smaller than what was obtained in transformer oil. To confirm the reactive agent in hydraulic oil, individual congeners were sparged with sulfur hexafluoride with reductions in degradation similar to that observed in isooctane. A reasonable conclusion is that electrons are responsible for PCB degradation in both hydraulic oil and transformer oil.

Mass Balance in Isooctane

To quantify the degradation products, experiments were conducted using individual PCB congeners in isooctane. When a mass balance analysis is performed on the data shown in Figure 15 about 43% of the original carbon and chlorine could be identified as residual Bz 200 and less chlorinated PCB congeners. This leaves a significant fraction of both

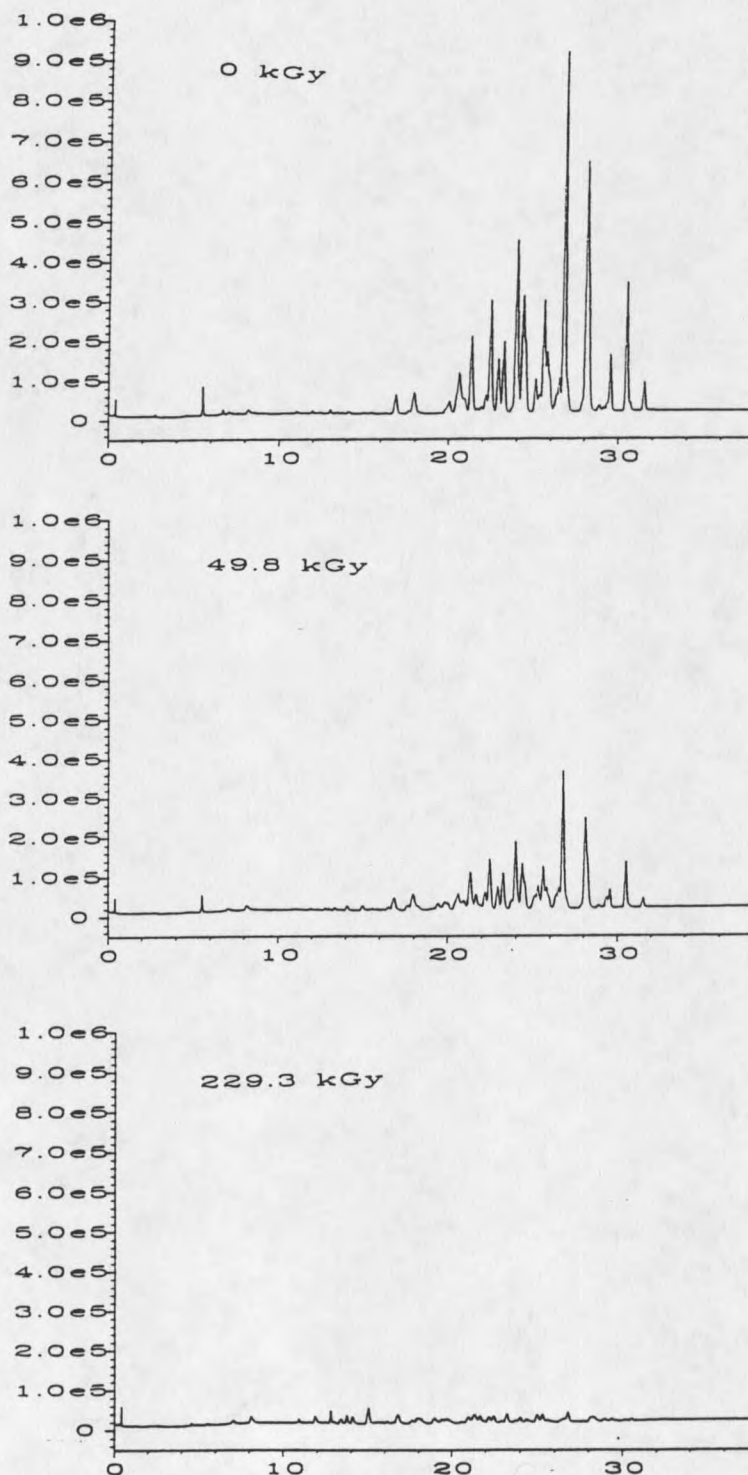


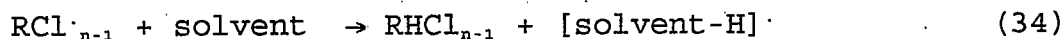
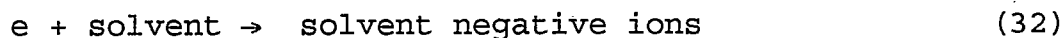
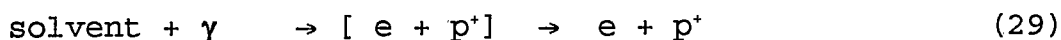
Figure 21. Aroclor 1260 as a function of absorbed dose in hydraulic oil. Aroclor 1260 concentration steadily decreases with increasing dose. The Aroclor 1260 concentration has been reduced from 5000 mg L^{-1} to 520 mg L^{-1} .

the carbon and chlorine missing. Ion chromatography was performed in an attempt to locate the missing chlorine as chloride. The chloride ion concentration was far from stoichiometric. Volatile analysis failed to locate the missing mass as recombination products. In an attempt to identify the missing mass, a ^{14}C -labeled Bz 47 was irradiated. The irradiation was run in a series of doses, as done previously for dose constant measurements, to a maximum dose of 89 kGy. Following irradiation, liquid scintillation counting of sample aliquots revealed that the activity level was the same as the unirradiated solution at all absorbed doses. No activity was deposited on the walls of the glass sample vials. To determine in which fraction the ^{14}C -labelled products reside, aliquots were nitrogen sparged at room temperature with no reduction in activity. Aliquots were also distilled at 100°C and 150°C . No activity was removed at either temperature. This is significant evidence that the degradation products are present in either semivolatile or nonvolatile fractions. When analyzed with electron impact GC/MS only 40% of the original carbon could be identified as PCBs. While apparently still in solution the identity of the missing mass is unknown.

Reaction Mechanism and Kinetics

Scavenging experiments indicated solvated electrons as the major reactive species responsible for the observed

degradation of PCBs in isooctane and isopropanol; therefore, only reactions involving the production and loss of electrons are illustrated in the mechanism. Reactions other than those listed below involve PCBs but are not important under low absorbed dose conditions and thus are not included here. The following simplified reaction sequence is proposed to explain the observed degradation of PCBs at low absorbed doses.



Irradiation of the solvent--reaction 29--produces ion pairs which are concentrated in spurs and tracks along the path of the gamma-ray. The majority of these ion pairs undergo geminate recombination--reaction 30--but a small fraction diffuse out of the spurs to become free or solvated ions/electrons as shown in the second part of reaction 29. The production of free electrons, represented as P, is given by the product of the free ion yield and the absorbed dose rate. These free electrons are then available to participate in the reactions shown: recombination with free positive ions (reaction 31), electron capture by the solvent

(reaction 32), electron capture by the PCBs and their resulting destruction (reactions 33-35). As shown, the products of the radiolytic induced decomposition of the parent PCBs are less chlorinated PCBs. Dechlorination is believed to occur in a stepwise fashion and is thought to be the major process responsible for the production of less chlorinated PCBs. At any given time during the course of the irradiation, the initial molar PCB concentration, as shown in equation 36, is equal to the sum of the various homologs.

$$[\text{PCB}]_0 = [\text{octachlorobiphenyl}] + [\text{heptachlorobiphenyl}] + \quad (36) \\ [\text{hexachlorobiphenyl}] + \dots$$

The radiolytic degradation for the parent PCB, RCl_n , is observed to follow first-order kinetics in both isopropanol and isooctane even though the rate expression, based on equation 33, is clearly bimolecular.

$$-d[\text{RCl}_n]/dt = k[\text{RCl}_n][e] \quad (37)$$

For pseudo-first-order kinetics to be observed, the electron concentration must remain essentially constant during the radiolysis. In order to examine how this condition can arise, it is instructive to examine the rate equation for the electron concentration.

$$d[e]/dt = P - [\alpha[+][e] + k_{\text{solv}}[e][\text{solv}] + k[e][\text{RCl}_n] + \quad (38) \\ k[e][\text{RCl}_{n-1}]]$$

Inspection of equation 38 shows that the electron concentration will remain constant during the radiolysis experiment if the electron attachment rate constant for reaction 33 and 35 are approximately equal. While the electron capture rate constants for the individual PCBs are not all equal, the differences between the various rate constants are relatively small. This conclusion is based upon the difference between the measured rate constants for biphenyl and carbon tetrachloride in aqueous solutions with the hydrated electron. Buxton reported a second-order rate constant for the reaction of biphenyl with a hydrated electron of 9.5×10^9 and for carbon tetrachloride of 1.6×10^{10} . It is reasonable to assume that all of the PCBs will have rate constants within this range. However, the expected difference between a parent PCB congener and its degradation product is probably smaller.

Initial PCB Concentration and Measured Dose Constant

Interpretation of equation 38 indicates that, as the concentration of the PCBs increases, the fraction of electrons lost through this pathway should also increase. Thus, the observed dose constant is expected to be concentration dependent up to the point where virtually all of the electrons are lost to the PCBs. A concentration dependence is observed in isooctane but not in isopropanol. The isopropanol results can be explained, via equation 38, based on competition with the solvent--that is,

$k_{[\text{solv}]} > k_{[\text{octa}]}$, which effectively controls the concentration of the electrons. This occurs because of the large concentration of solvent and the limited PCB solubility in isopropanol. For the highly chlorinated congeners, concentrations higher than 300 to 400 mg L⁻¹ were difficult to achieve. If concentrations approaching those utilized in isooctane were achievable, a dose constant concentration dependence may have also been observed in isopropanol. In isooctane, the electron capture loss rate exceeds the free ion/electron production rate, P indicating that geminate electrons are being scavenged. This is confirmed by comparing the free ion yield of 0.1 molecules 100 eV⁻¹ for isooctane to the measured degradation G values which varied from 0.37 to 2.4 molecules 100 eV⁻¹ for Bz 155 depending upon the beginning PCB concentration with G values increasing with increasing solute concentration. The measured G values in isooctane significantly exceed the free ion yield, demonstrating that the amount of electrons capable of being scavenged is dependent on the amount of scavenger added and not on the free ion yield. Warman (31) observed this for chlorinated hydrocarbons in nonpolar solvents where his G value exceeded the free ion yield. Given this, a concentration dependence in isooctane up to the point where all the electrons, both geminate and free, are lost to the PCBs is reasonable.

SUMMARY

The radiolytic degradation of 25 PCB congeners in neutral isopropanol using spent nuclear fuel has been investigated. Radiolytic degradation efficiency is conveniently described in terms of a pseudo-first-order rate constant expressed in terms of dose rather than time and is referred to as a dose constant. Radiolytic PCB degradation was suppressed by the addition of compounds capable of scavenging electrons, but not by the addition of hydrogen atom or solvent radical scavengers. In neutral aerated isopropanol, the solvated electron appears to be the primary species responsible for PCB degradation.

Destruction efficiency in isopropanol was found to be dependent on both the number and position of the chlorine atoms on the PCBs. Those compounds that are para/meta substituted only are capable of adopting a planar configuration and were found to have the largest dose constants for their respective homologs. This is attributed to the extended conjugation between the phenyl rings in the planar configuration which results in an increase in their electron affinity and thus the dose constant. Substitution in the ortho position decreases the dose constant. The differences in congener susceptibility to destruction has been explained in terms of the energy level of the LUMO that

can accept an electron. Given the above findings, destruction efficiencies or dose constants could be estimated reasonably well for any of 209 PCB congeners of interest. This would be useful in the practical application of a treatment process. A new class of radiolytically generated compounds has been definitively identified to be an isopropanol substituted polychlorinated biphenyl. Mass balance information is incomplete for some PCB congeners. Carbon-14 labeled experiments were conducted and demonstrated that the missing mass remains in solution but no EPA regulated compounds have been identified.

Radiolytic degradation of PCBs has also been shown to occur in nonpolar isooctane. Scavenging experiments also implicate the solvated electron as the primary reactive species in this solvent. Degradation was observed to be more efficient in nonpolar solvents than in polar isopropanol. Chlorine substitution pattern and chlorine content were found to influence degradation efficiency to a lesser extent in isooctane than in isopropanol. A potential correlation between electron energetics and electron affinity has been pointed out as a possible explanation for this observation. Mass balance is incomplete. However, based on the results obtained, the degradation products appear to still be in solution in either semivolatile or nonvolatile fractions.

Radiolytic degradation of Aroclor mixtures in transformer and hydraulic oil has also been demonstrated.

Aroclor degradation to below 2 mg L⁻¹ using moderate (0.5-229) kGy doses is achievable in both transformer and hydraulic oil. Degrading Aroclor 1260 samples to below 2 mg L⁻¹ was determined to be achievable. No sample preparation was necessary to achieve this degradation. This is significant; limiting the number of steps in a process situation is generally desirable because of reduced cost. Because of the penetrating ability of gamma-rays, PCB contaminated transformer oil could theoretically be remediated *in-situ*, allowing the oil to be placed back into service. In the case of hydraulic oil, after the destruction of the PCBs, the resulting solution could be burned for heat. Many of the utility companies that have significant quantities of PCB-contaminated transformer oils also have spent nuclear fuel that could be used as a radiation source for destroying PCBs. Another potentially useful application of this process would be the radiolytic remediation of radioactively contaminated PCB waste. Currently, the options available for treating such wastes are extremely limited.

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