



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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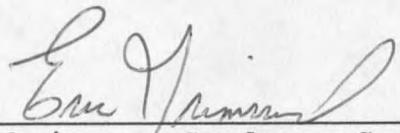
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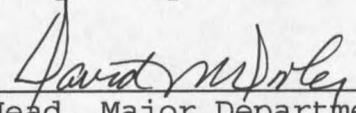
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ACKNOWLEDGEMENT

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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The radiolytic degradation of PCBs in nonpolar isooctane, transformer oil, and hydraulic oil was also investigated. Significant degradation was observed in each solvent studied at moderate absorbed dose. Consistent with neutral isopropanol, scavenging studies also implicate the electron as the primary reactive species responsible for PCB decomposition. However, surprising differences between the radiolytic behavior of PCBs in polar isopropanol and nonpolar isooctane were discovered. PCB degradation was found to be enhanced in isooctane relative to neutral isopropanol. Also, chlorine number and substitution pattern influence degradation efficiency to a lesser extent in isooctane than in isopropanol. Deviations in PCB degradation behavior between isooctane and isopropanol are interpreted in terms of differences in electron behavior between the two solvents. The products of PCB decomposition have not been fully characterized but appear to be in either a semivolatile or nonvolatile form.

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.

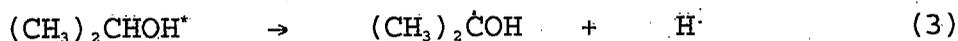
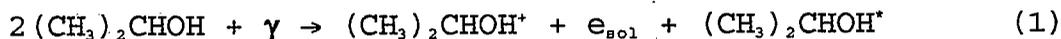
For electron transfer to occur, a suitable source of electrons is needed. Electron donors which have been used in dechlorinating PCBs are typically anion radicals or solvated electrons. These donors can be generated by a variety of methods, including sodium metal, ozonation, photolysis, and radiolysis. 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.

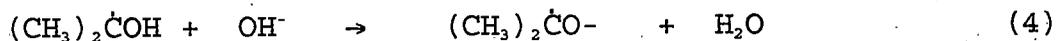
Gamma-ray radiolysis, the method investigated in this thesis, generates both solvated electrons and anion radicals and offers many advantages over other solvent-based processes. Spinks (7) points out that radiolysis offers the possibility of a purer product, since contamination from incomplete removal 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.

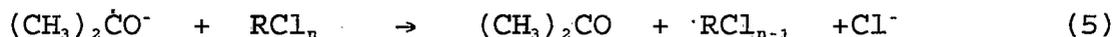
In deaerated alkaline isopropanol, the radiolytic dechlorination occurs *via* a chain reaction. The following key reactions have been proposed (8):



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 rad = 0.01 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

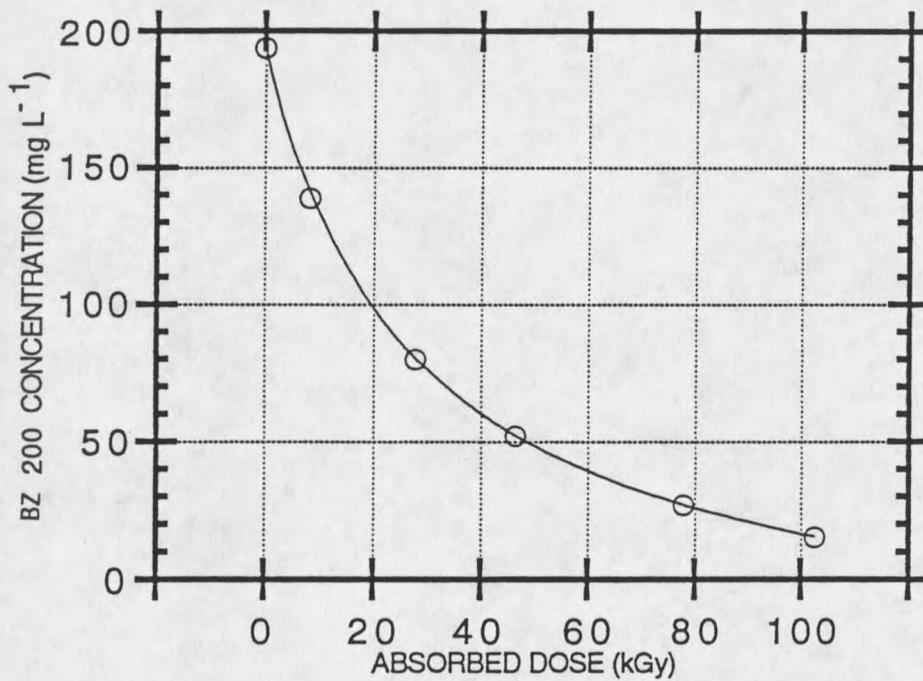


Figure 1. Change in 2,2',3,3',5,5',6,6' octachlorobiphenyl (Bz 200) concentration versus absorbed dose. A steady decrease in Bz 200 concentration with increasing dose is observed. Note the half-life dependency on Bz 200 in relation to absorbed dose.

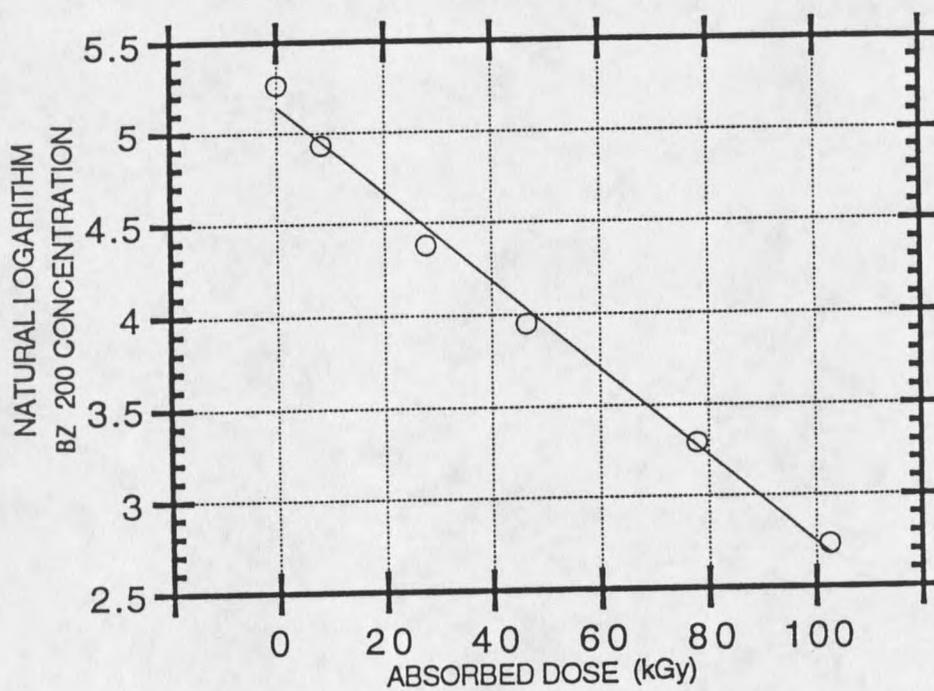


Figure 2. Plot of the natural logarithm of Bz 200 concentration and absorbed dose. The slope of the line provides the dose constant. The correlation coefficient for the above line was 0.996.

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.

