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HIGH ENERGY DECOMPOSITION OF HALOGENATED HYDROCARBONS FY92 FINAL REPORT

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CONTENTS

1	INTRODUCTION	1
2	EXPERIMENTAL METHODS	2
	2.1 Irradiations	2
	2.2 Reagents	3
	2.3 Analytical Methods	3
3	TECHNICAL OBJECTIVES	4
4	RESULTS AND DISCUSSION	4
5	CONCLUSIONS AND PROCESS IMPLICATIONS	7
6	FUTURE WORK	7
7	RELATED FY92 ACCOMPLISHMENTS	8
8	REFERENCES	9

FIGURES

1.	The G Value versus concentration for various PCB congeners in A; methanol, B; isopropanol, and C; transformer oil	10
2.	The radiolytic decomposition of the PCB octachlorobiphenyl in transformer oil for 700 KeV gamma rays and 9 MeV x-rays	10
3.	The suppression of the radiolysis of the PCB octachlorobiphenyl in methanol by the addition of carbon tetrachloride.	11
4.	The suppression of the radiolysis of the PCB octachlorobiphenyl in isopropanol by the addition of carbon tetrachloride	11
5.	The suppression of the radiolysis of the PCB octachlorobiphenyl in transformer oil by the addition of carbon tetrachloride	12
6.	The suppression of octachlorobiphenyl radiolysis by the good electron scavenger nitrobenzene and the partial suppression of radiolysis by the moderate electron scavenger benzene.	12
7.	The radiolysis of octachlorobiphenyl and simultaneous ingrowth of decomposition products.	13
8.	The ingrowth of dechlorination product daughter PCBs from the radiolysis of 200 ng/ul octachlorobiphenyl in isopropanol.	13

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1 INTRODUCTION

This report is a summary of work performed during FY92 for the Office of Technology Development of the U.S. Department of Energy on the program entitled "High Energy Decomposition of Halogenated Hydrocarbons," (TTP ID-0505.RD).

This program is the INEL component of a joint collaborative effort with Lawrence Livermore National Laboratory (LLNL). The purpose of this effort is to demonstrate a viable process for breaking down hazardous halogenated organic wastes to simpler, nonhazardous wastes using high energy ionizing radiation. The INEL effort focuses on the use of spent reactor fuel gamma radiation sources to decompose complex wastes such as PCBs.

Work in FY92 expanded upon that reported for FY91.¹ During FY91 it was reported that PCBs were susceptible to radiolytic decomposition in alcoholic solution, but that only a small percentage of decomposition products could be accounted for. It was shown that decomposition was more efficient in methanol than in isopropanol and that the presence of a copper-zinc couple catalyst did not affect the reaction rate. Major goals of FY92 work were to determine the reaction mechanism, to identify further reaction products, and to select a more appropriate catalyst. Described in this report are the results of mechanism specific experiments, mass balance studies, transformer oil irradiations, the use of hydrogen peroxide as a potential catalyst, and the irradiation of pure PCB crystals in the absence of diluent.

Another goal was the presentation of these results at the Florida Environmental Chemistry Conference, scheduled for October 1992. The results reported here, and at the conference, are the result of a collaborative effort with Montana State University (MSU). The MSU work was directed by Dr. W. B. Knighton.²

2 EXPERIMENTAL METHODS

2.1 Irradiations

The polychlorinated biphenyl (PCB) samples were gamma irradiated with spent fuel at the Advanced Test Reactor of the Idaho National Engineering Laboratory (INEL) as described previously.^{1,3} In addition, some samples were irradiated with machine generated bremsstrahlung to investigate the effects of dose rate and photon energy on the efficiency (G values) of PCB decomposition. These samples were irradiated at Lawrence Livermore National Laboratory (LLNL) using the 9 MeV Linatron linear accelerator at a dose rate of 360 MRad/hr. Samples are generally irradiated as a series of five, each to progressively increasing doses, plus an unirradiated control. This allows the plotting of curves of decomposition versus dose.

Absorbed doses were measured using FWT-60 radiachromic dye dosimeters (Far West Technology, Goleta, CA, U.S.A.).^a The dosimeters are available as a nylon film impregnated with a colorless cyanide derivative of an aminotriphenyl acetonitrile dye. When exposed to ionizing radiation the cyanide group is lost, leaving a colored dye cation. The color change is proportional to the absorbed dose and was measured with the FWT-100 optical density reader from the same vendor. The working range of the dosimetry is 0.05 to 20 MRad.

To accurately measure the absorbed dose of the samples the dosimeters were prepared to simulate the samples as closely as possible. Dosimeters could not be immersed directly into the sample solution because of the possibility of leaching the dye from the nylon film. Instead the dosimeters were placed between layers of lucite, so that the resulting sandwich was the same thickness as a sample vial. These were positioned adjacent to the sample vials during an irradiation. This is discussed in detail by Mincher and Zaidi.⁴ The dosimeters were calibrated using the 10,000 Ci Co-60 source at a dose rate of 0.3633 MRad/hr at the Radiological and Environmental Sciences Laboratory (RESL) of the INEL.

The efficiency of radiolytic decomposition reactions is commonly reported in terms of G values. The G value allows for comparison of experimental results and optimization of irradiation conditions. The G values were calculated as the number of molecules/ml decomposed per 100 eV/g of energy deposited. Measured absorbed doses were converted to eV per gram using the relationship $6.24E13$ eV/g/Rad.⁵ Density corrections were made as appropriate for the specific solvents. The calculation of G is performed by plotting the natural logarithm of the PCB concentration (in molecules per ml) versus the absorbed dose (in eV/g). The plot is linear with a slope representing the rate constant k' . The y intercept of this plot is the natural logarithm of

^aMention of specific products and/or manufacturers in this document implies neither endorsement or preference nor disapproval by the U.S. Government, any of its agencies, or EG&G Idaho, Inc., of the use of a specific product for any purpose.

the initial PCB concentration. Thus, the product of the rate constant and the initial PCB concentration is the number of molecules decomposed per eV absorbed. This value is multiplied by 100 to conform to convention.

$$G = k' \cdot (\text{PCB})^\circ \cdot 100$$

2.2 Reagents

Polychlorinated biphenyl standards were purchased from AccuStandard (New Haven, Ct., U.S.A.) and were greater than 99% pure. Other reagents such as solvents and analytical reagents were all purchased as reagent grade.

2.3 Analytical Methods

Polychlorinated biphenyl measurements were performed using a Hewlett Packard 5995 Gas Chromatography/Mass Spectrometer operated in positive ion mode. A db5-625, 30 m column was used with helium carrier gas at a flow rate of 32 ml/min. Samples were injected onto the column at 80°C, held one minute and then the temperature was ramped at 3°C per minute to 310°C.

The quality control measures used were based on USEPA Method 680. A five point calibration curve containing nine PCB congeners (chlorobiphenyl through octachlorobiphenyl and decachlorobiphenyl) was constructed. Relative response factors were then calculated for each analyte of the five standards. The percent relative standard deviation of the relative response factor over the five points was calculated and was required to be less than 20% for a calibration curve to be considered valid. Prior to an actual sample analysis, the calibration curve was verified by analyzing the midpoint calibration standard and comparing it to the initial curve. A percent difference of less than twenty was considered valid and samples were then quantitatively analyzed by comparison to two internal standards; chrysene-d12 and phenanthrene-d10. The two internal standards were added to the samples following irradiation and were used to evaluate potential changes in detector response and sample matrix effects.

The free chloride ion produced by sample irradiations 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 ten with 18 Mohm water and directly injected onto the sample loop. The chlorides were then eluted from the analytical column with a 0.002M sodium carbonate/0.00075M sodium bicarbonate eluent at a flow rate of 2 ml per minute and a pressure of 1000 to 1050 psi. A suppressor column eluted with 0.025M sulfuric acid was used to minimize contributions of the carbonate/bicarbonate eluent conductivity to the sample signal. This is a standard Dionex protocol for analysis of inorganic anions. The chloride ion eluted at a retention time of about 2.2 minutes, free of interferences.

3 TECHNICAL OBJECTIVES

The INEL's technical objectives for FY92 were as follows:

- Determine the mechanism of the PCB radiolysis reaction
- Determine feasibility of PCB transformer oil irradiations
- Determine feasibility of neat PCB radiolysis
- Investigate potential reaction catalysts
- Complete a mass balance of the reaction products.

4 RESULTS AND DISCUSSION

The G values for the radiolysis of many combinations of PCBs and solvents have been measured. These results confirm our original hypothesis that the reaction is most efficient in high dielectric constant solvents. Figure 1 shows a comparison of G values versus PCB concentration for methanol, isopropanol and transformer oil. It can be seen that the efficiency of decomposition is highest in high dielectric constant solvents. This observation suggests that a charged species is an important active intermediate in the radiolysis mechanism. Charged species have longer lifetimes in more polar solvents. While the decomposition of PCBs in transformer oil is less efficient than in alcohols it can be seen in Figure 2 that it is still feasible at easily achievable doses. This figure also compares the irradiation of PCBs in oil using the ATR spent fuel source and an irradiation at LLNL using the 9 MeV Linatron linear accelerator. It can be seen that the decomposition curves for the two sources are statistically identical. Thus the photon energy and dose rate are not important to the radiolysis reaction, rather only the total absorbed dose. This suggests that the reactive intermediate is produced in excess by either source. If this is the case, pseudo-first order kinetics would be expected for the radiolysis reaction, with dependence only on PCB concentration. This is what is actually observed.

One possible reactive intermediate, which is a charged species likely to be produced in excess during gamma irradiations, is the free, thermalized electron. The source of these thermal electrons would be the photoelectric and Compton effects which result from gamma ray interactions with matter (in this case the solvent). These high energy free electrons would be expected to be thermalized in about 10^{-7} seconds.⁶ They would then be expected to have lifetimes dependent on the ability of the medium to solvate them, which is in turn dependent upon the solvent's dielectric constant.

An understanding of the mechanism of PCB radiolysis is important to designing an efficient PCB treatment process. To determine the nature of the reactive intermediate (and thus the mechanism) of the PCB radiolysis reaction, a number of thermal electron scavenger experiments were conducted. In the first experiment, 1.6M carbon tetrachloride was added to the solutions of

octachlorobiphenyl in methanol, isopropanol and transformer oil. The presence of carbon tetrachloride, a known electron scavenger, suppressed the decomposition of the PCB in all solvents. This effect is shown in Figures 3, 4 and 5 for methanol, isopropanol and transformer oil, respectively. It suggests that thermal electrons are an important active intermediate, consistent with what is observed when solvent dielectric strength is varied. In an additional experiment nitrobenzene was chosen for its high affinity for thermal electrons and lower affinity for other radicals. Benzene exhibits the reverse behavior. These affinities, referred to as capture coefficients, are given in Table 1.⁶

Table 1. Aqueous capture coefficients for scavenging agents for thermalized electrons and hydroxyl radicals ($l \text{ mol}^{-1} \text{ sec}^{-1}$).

<u>Agent</u>	<u>e^{-1} Capture</u>	<u>$\bullet\text{OH}$ Capture</u>
Carbon Tetrachloride	1.6E10	1E6
Nitrobenzene	3.7E10	3.9E9
Benzene	9E6	7.8E9

While the values tabulated are for aqueous solution, rather than alcohol or oil, the relative differences are believed to remain unchanged by solvent substitution. The effect of these additives on octachlorobiphenyl in isopropanol are shown in Figure 6. Nitrobenzene, with an electron capture rate 4000 times higher than that of benzene completely suppresses the reaction, while benzene suppresses the reaction by about a factor of 2. This suggests that thermal electrons are the reactive intermediate in the radiolysis reaction, and predicts that the principal decomposition mechanism is one of reductive dechlorination. In fact, as previously reported, important decomposition products of radiolysis are dechlorination congeners.^{1,3} Other evidence supporting this theory is that this reactive intermediate is one which would be produced in any of the three solvents examined. It is difficult to conceive of a charged free radical other than the electron which would be common to both alcohol and oil solvents.

The possibility of superoxide radical anion as an active agent in the decomposition of PCBs has been eliminated by the irradiation of a nitrogen sparged sample. This deaerated series of samples was decomposed with the same efficiency as a normal aerated control series.

A series of irradiations was also performed with hydrogen peroxide as an additive. Hydrogen peroxide is a common catalyst in organic degradation studies. It was thought that it may be useful in radiolysis as a source of hydroxyl radicals. However, analysis of these irradiated samples indicated that no increase in decomposition efficiency resulted.

Finally, an experiment to determine the susceptibility of pure PCB crystals to radiolytic decomposition was performed. Approximately 1 mg of neat octachlorobiphenyl was irradiated to 8 MRad, then dissolved in isopropanol for analysis. No dechlorination products were observed. This experiment suggests that either little or no degradation occurs without solvent present.

During FY92 an exhaustive search for decomposition products other than dechlorination congeners was conducted. Using EPA approved GC/MS analyses approximately 79,000 volatile and semivolatile compounds have been ruled out. This list includes regulated compounds such as phenols, chlorophenols and chlorobenzenes, as well as most chloroalkanes. The absence of hydroxylated chlorobiphenyls is evidence against the oxidative decomposition of PCBs by hydroxyl radicals.⁷ Ion chromatography was performed on alcoholic PCB solutions to determine the free chloride content of the irradiated material. This is shown in Figure 7 for the irradiation of octachlorobiphenyl in isopropanol. The free chloride concentration increases linearly with dose. The amount of chloride produced however is not stoichiometric with that being lost from PCBs. This is shown in Table 2 where free chloride production, chloride as PCB and their difference (the chloride deficit) are shown. Figure 7 also shows the ingrowth of daughter PCBs and a total accountable mass curve. The total accountable mass curve is the sum of the daughter PCBs, free chloride and the original residual octachlorobiphenyl. The difference between this curve and the PCB concentration in the unirradiated sample is the unidentified decomposition mass and represents about 50% of the mass at 10 MRad for this irradiation. This is a significant improvement in the mass balance over that of our previous studies. The ingrowth of the individual daughter products is shown in Figure 8.

Table 2. Chloride fate upon radiolytic dechlorination of 194 ppm octachlorobiphenyl in isopropanol.

Absorbed Dose (Mrad)	Cl ⁻ as Octa- (ppm)	Cl ⁻ as Daughters (ppm)	Free Cl ⁻ (ppm)	Deficit %
0	128	0	0	0
0.836	91.7	9.6	2.6	19
2.77	52.8	28.3	8.6	30
4.64	34.3	34.3	12.6	37
7.78	17.8	35.5	18.6	44
10.26	10.2	34.5	25.1	45

Recently, in samples of 400 ppm octachlorobiphenyl irradiated to 19 MRad in isopropanol, a series of peaks eluting from the gas chromatograph later than the PCBs was discovered. These compounds have been tentatively identified as the product of an addition reaction between dechlorination product PCBs and isopropyl radicals. It is not known at this time whether the product compound has a saturated phenyl ring following isopropyl radical substitution or if this is the beginning of the ring splitting process.

Either result has important mechanism implications. Further, this intermediate compound may account for as much as 25% of the decomposition product mass in irradiations at this dose.

When congeners other than octachlorobiphenyl are irradiated the same kinetics are observed. This effect has been demonstrated for biphenyl, tetrachlorobiphenyl and decachlorobiphenyl. The fact that nonchlorinated biphenyl is also susceptible to radiolytic degradation proves that decomposition other than simple dechlorination can occur. Many decomposition products, perhaps all at vanishingly small concentrations, may be possible.

5 CONCLUSIONS AND PROCESS IMPLICATIONS

Scavenger experiment evidence exists to support the theory that the thermal electron is the principal active agent of PCB decomposition in irradiated, aerated solvents of widely varying dielectric constant. This is the only solvent radiolysis product which is a charged radical common to alcoholic and oil solvents. It is an extremely powerful reducing agent certainly capable of dechlorination, and probably capable of phenyl ring decomposition. This also explains the absence of hydroxylated reaction products which are usually detected in the effluents of processes using hydroxyl radical oxidation reactions.

It has been demonstrated that the reaction does occur in transformer oil, although with lower efficiency. This is believed to be due to the shorter lifetime of the thermal electron in nonpolar solvents. This lowered efficiency does not preclude a viable process as the required doses are still easily achieved.

The presence of a solvent appears to be required for measurable amounts of decomposition to occur. An irradiation of neat PCB crystals did not produce any measurable dechlorination products. This too supports the thermal electron hypothesis, which requires the presence of a solvent as both a source of electrons and as a medium to thermalize and stabilize them.

About 50 to 75% of the radiolytic degradation products have been identified. Although some work remains to be done this represents a significant addition to the FY91 level of knowledge. The products identified are dechlorination congeners, free chloride, and some newly identified compounds produced by the addition of isopropyl radicals to the PCBs. These are probably intermediates, and may be the key to phenyl ring splitting reactions.

6 FUTURE WORK

A major objective of FY93 work will be to examine the decomposition of PCBs in oil in detail. This includes investigation of hydrocarbon (hydraulic oils) and aromatic oil (transformer oils). Commercial PCB mixtures (Aroclors) will be irradiated and analyzed by GC as an investigation of "real world" samples.

Several additional scavenger experiments are planned to verify the proposed mechanism. Some of these irradiations (including Ni⁺⁺ ion electron scavenging and iodine labeling of radicals) have already been completed and are currently being analyzed.

The completion of the mass balance is still an important item of concern. It is desirable to identify as many of the reaction products as possible to ensure a nonhazardous process effluent. There are several possibilities still to be investigated. Among them are the generation of molecular gases, such as chlorine or methane; production of polymeric products; production of organic acids; and production of large numbers of compounds, all at less than analytical detection limits. Experiments have been designed to study the first three possibilities. It should be noted that radiolysis studies seldom achieve 100% mass balance, especially if the fourth possibility plays a significant role.

It is also of interest to examine the applicability of this process to other hazardous organics, including nonhalogenated compounds. Many polyaromatic hydrocarbons have low electron affinities. If they are amenable to treatment, even at lowered efficiencies, it may indicate that gamma radiolysis is a process capable of decomposing many organic compounds.

7 RELATED FY92 ACCOMPLISHMENTS

This program resulted in the presentation of four conference papers^{4,8,9,10} during FY92. Additionally, the program is a vehicle by which the DOE Office of Technology Development will co-sponsor the Florida Environmental Chemistry Conference in October 1992. A patent record has been filed for a conceptual process for the in-situ destruction of PCBs in transformer oil and transformers.

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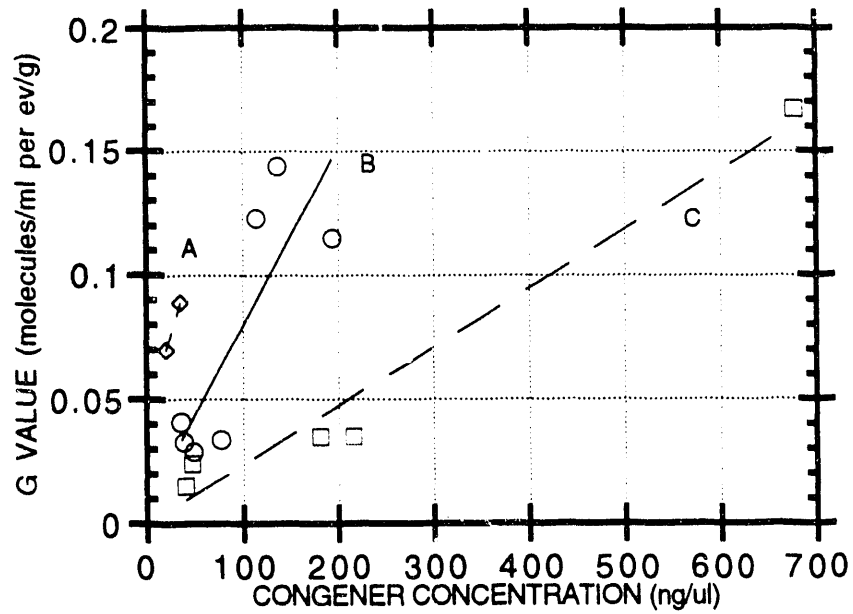


Figure 1. The G Value versus concentration for various PCB congeners in: A; methanol, B; isopropanol, and C; transformer oil.

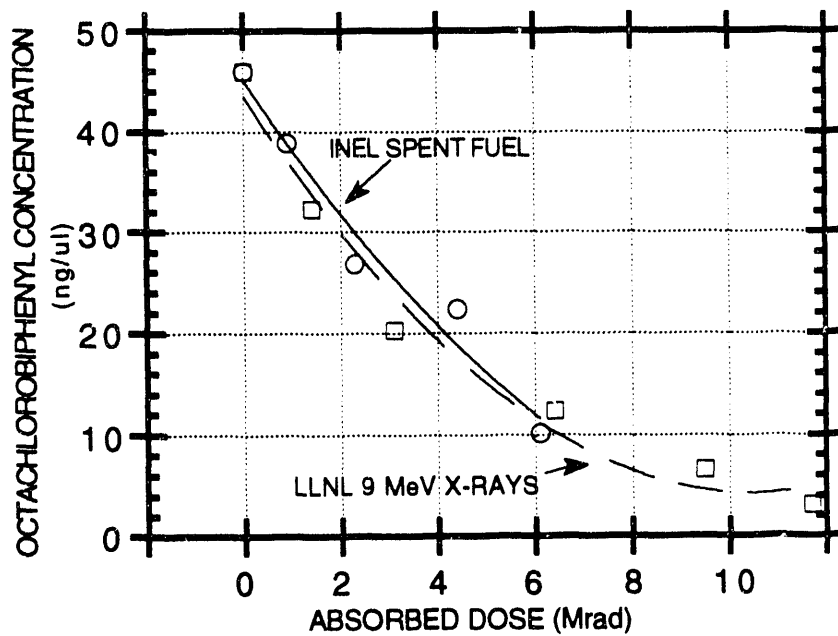


Figure 2. The radiolytic decomposition of the PCB octachlorobiphenyl in transformer oil for 700 KeV gamma rays and 9 MeV X-rays.

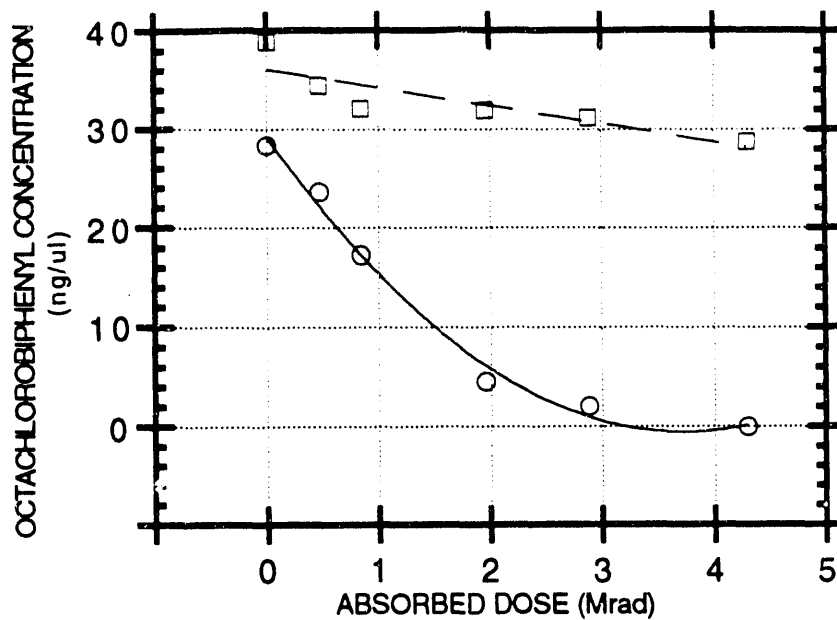


Figure 3. The suppression of the radiolysis of the PCB octachlorobiphenyl in methanol by the addition of carbon tetrachloride.

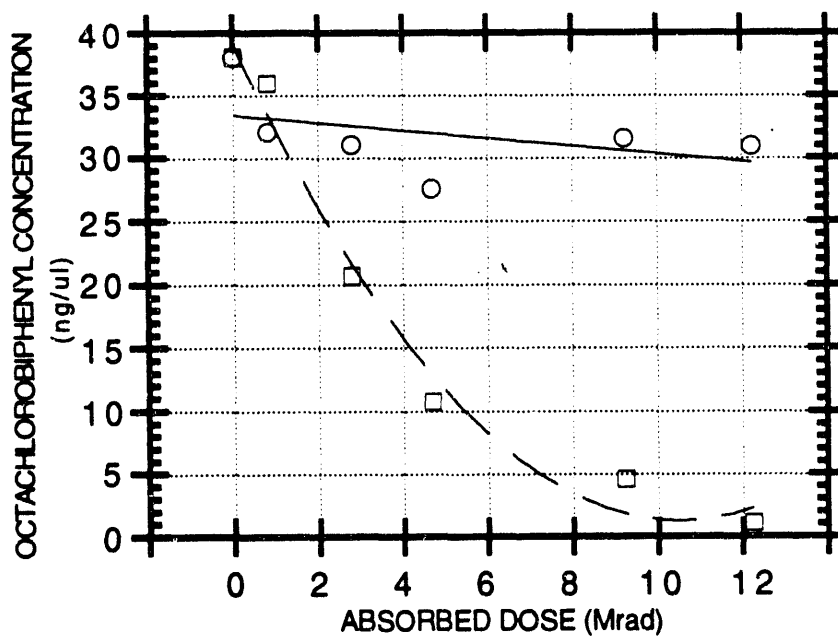


Figure 4. The suppression of the radiolysis of the PCB octachlorobiphenyl in isopropanol by the addition of carbon tetrachloride.

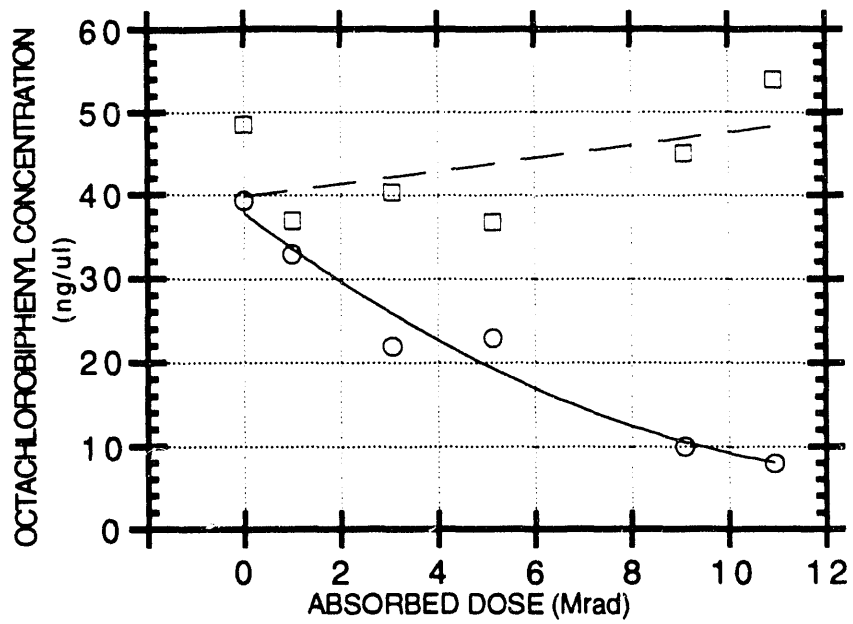


Figure 5. The suppression of the radiolysis of the PCB octachlorobiphenyl in transformer oil by the addition of carbon tetrachloride.

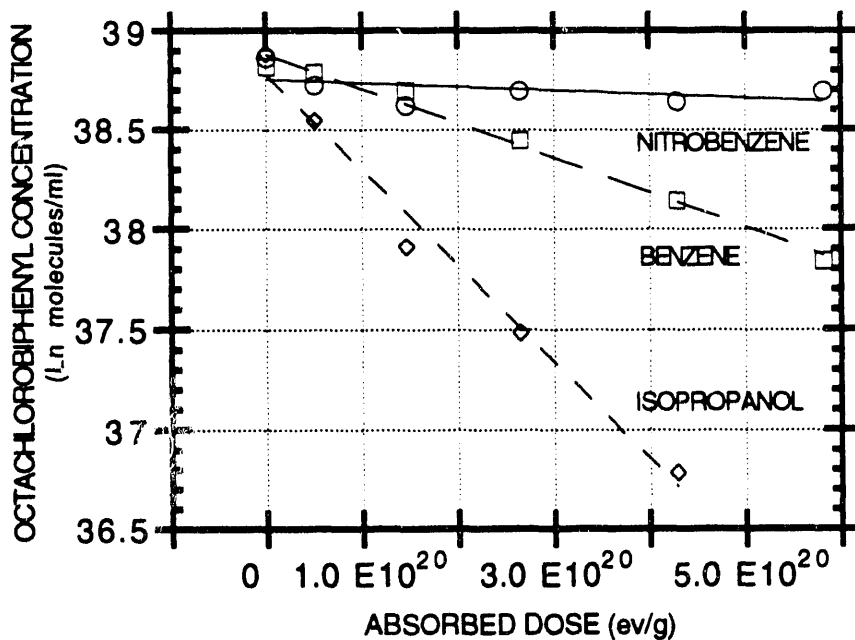


Figure 6. The suppression of octachlorobiphenyl radiolysis by the good electron scavenger nitrobenzene and the partial suppression of radiolysis by the moderate electron scavenger benzene.

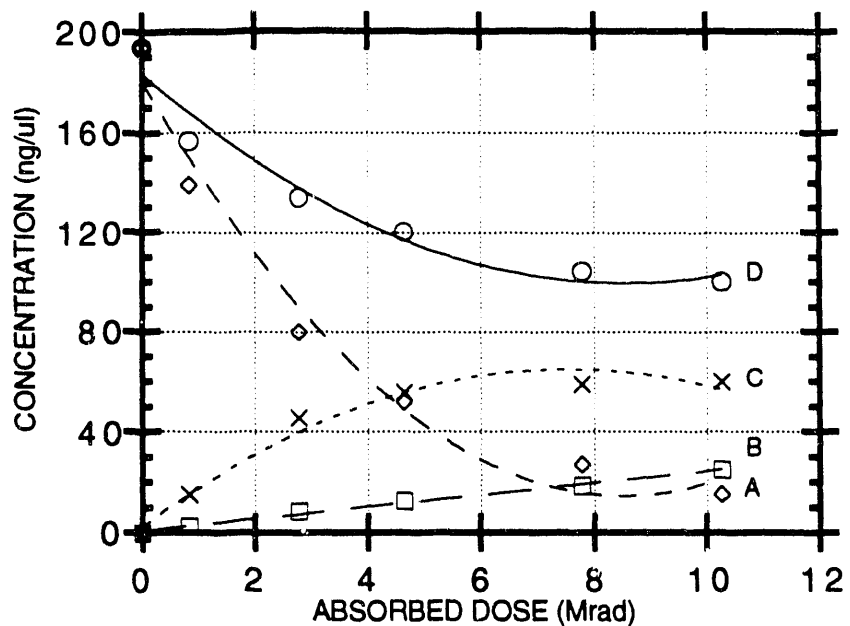


Figure 7. The radiolysis of octachlorobiphenyl and simultaneous ingrowth of decomposition products. A; residual octachlorobiphenyl, B; free chloride, C; daughter PCBs produced by dechlorination, and D; the sum of all identified products.

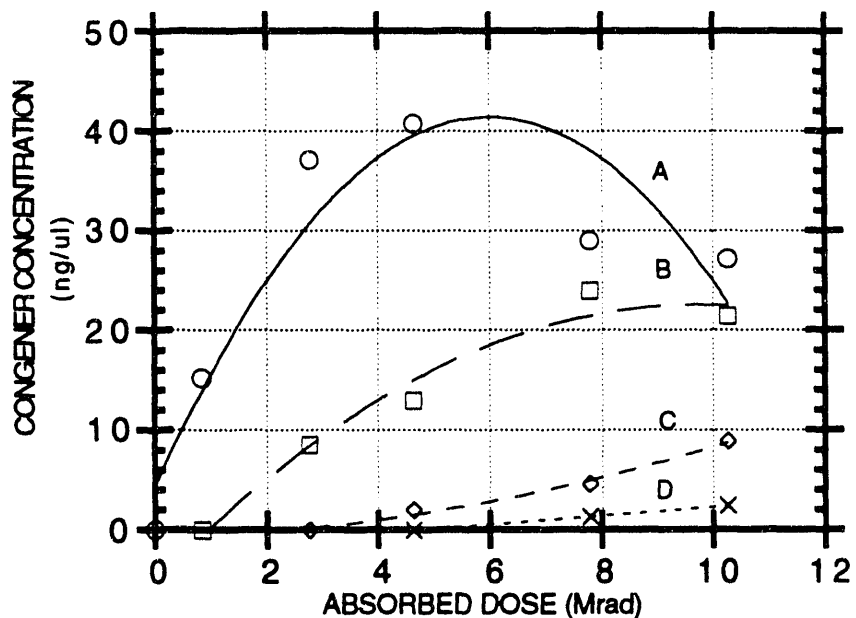


Figure 8. The ingrowth of dechlorination product daughter PCBs from the radiolysis of 200 ng/ul octachlorobiphenyl in isopropanol. A; sum of heptachlorobiphenyls, B; hexachlorobiphenyls, C; pentachlorobiphenyls, and D; tetrachlorobiphenyls.

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