EGG-M-91495

Conf-9110277--1

EGG-M--91495

DE92 003319

GAMMA-RAY DECOMPOSITION OF PCBs*

B. J. Mincher, D. H. Meikrantz
Physics & Mathematics Group

R. E. Arbon, R. J. Murphy
Chemical Sciences Group

Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, ID 83415

Presented at
FLORIDA ENVIRONMENTAL CHEMISTRY CONFERENCE
Palm Coast, Florida
October 30 - November 1, 1991

*Work performed under contract to the U.S. Department of Energy, Office of Technical Development, under contract number DE-AC07-76ID01570.

ABSTRACT

This program is the Idaho National Engineering Laboratory (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, non-hazardous 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. At LLNL, halogenated solvents such as carbon tetrachloride and trichloroethylene are being studied using accelerator radiation sources.

The INEL irradiation experiments concentrated on a single PCB congener so that a limited set of decomposition reactions could be studied. The congener 2, 2′, 3, 3′, 4, 5′, 6, 6′-octachlorobiphenyl was examined following exposure to various gamma doses at the Advanced Test Reactor (ATR) spent fuel pool. The decomposition rates and products in several solvents are discussed.

A. INTRODUCTION

Work at INEL during 1988-1989 demonstrated that many compounds were susceptible to decomposition by exposure to gamma-rays at the ATR spent fuel pool.[1] Among the compounds studied were chloroform, carbon tetrachloride, DDT, lindane and commercial Aroclor mixtures. A Varian 2740 GC using either OV-101 or OV-210 packed columns in conjunction with an FID was used to compare before and after chromatograms for samples exposed to megarad (kilogray) radiation doses. Aroclor 1221 peaks were shown to nearly disappear following a 50 kGy irradiation. This is shown in Slide 1.[1] A schematic of the sample irradiation capsules is shown in Slide 2.

It was then decided to employ GC/MS methods to identify decomposition products. The PCB 2,2'3,3'4,5'6,6'-octachlorobiphenyl is the sole congener which has been investigated in these studies. Study of a single congener rather than commercial Aroclor mixtures is preferred because the complexity of Aroclor GC/MS chromatograms precludes meaningful interpretation. A highly chlorinated congener was selected as a "worst-possible-case" candidate for treatment.

These studies have been performed in collaboration with LLNL since the beginning of FY-91. Our LLNL colleagues are studying chlorinated solvents such as CCl_4 and TCE using accelerator generated radiation. Octachlorobiphenyl has also been irradiated with accelerators at LLNL to compare decomposition efficiencies for different gamma-ray energies. These samples are currently being analyzed.

The LLNL contact for these experiments is Dr. Steve Matthews, Lawrence Livermore National Laboratory, P. O. Box 808, Mail Code L-629, Livermore, CA 94550.

B. OCTACHLOROBIPHENYL EXPERIMENTS

The congener 2,2',3,3',4,5',6,6'-octachlorobiphenyl in isopropanol was subjected to irradiations of varying length to evaluate the effect of total applied dose on PCB decomposition. Duplicate irradiations at five different applied doses were analyzed and the resultant PCB concentrations were plotted versus dose. This plot, shown in Slide 3, shows a steady decrease in octachlorobiphenyl concentration with dose to 100 kGy. At 100 kGy the octachlorobiphenyl is present at only three times the detection limit of approximately 1% by GC/MS. The concentrations shown are based upon the ratio of the peak areas to the known starting concentration (42 ppm) of the original isomer. The GC/MS protocol in use at this time was

EPA Method 827[illegible] (semivolatile organics) and thus was not specifically calibrated for PCBs. The uncertainty of these measurements is ±30%. Octachlorobiphenyl decomposition products detectable by this method were less chlorinated PCB congeners representing products of a dechlorination reaction. Slides 4-6 show decomposition product in-growth curves versus dose. These data may be reviewed in detail in (2).

Upon mass balance analysis of the various PCB congeners in these curves it can be seen that production of total dechlorination products is nonstoichiometric. Ninety-seven percent of the octachlorobiphenyl was decomposed at 100 kGy yet the appearance of dechlorination congeners accounts for only 12% of the missing PCB. This indicated decomposition of octachlorobiphenyl to compounds lighter than phenol which are not detectable by the GC/MS method used in this study. At 100 kGy 85% of total PCBs was decomposed to compounds not detectable by the method.

In the most recent experiments octachlorobiphenyl was irradiated in three different diluent solutions at concentrations of 40-50 ng/μl. These solutions were isopropanol, methanol and transformer oil. Plots of octachlorobiphenyl decomposition versus dose for methanol and isopropanol are shown in Slide 7. Note that the decomposition reaction in methanol appears to be more dose efficient than that in isopropanol. This may be due to the higher dielectric constant of methanol. The decomposition reaction is a dechlorination and is known to be catalyzed by free radicals produced by irradiation of the solvent.[3-5] These free radicals have a longer life-time, and hence higher probability of reaction, in a more polar solvent.[6] This suggests an interesting field of investigation and suggests that analyte decomposition efficiencies may be improved by raising the dielectric constant of the matrix.

Results for these measurements are shown in terms of concentration since the EPA Method 680 (PCBs and Pesticides) specific to PCB analysis is now being used. The uncertainty of these measurements is ±30%.

Presented in Slide 8 is a plot of decomposition products detectable by GC/MS versus dose for isopropanol. These are the products of the dechlorination reaction and are less chlorinated PCB homologs. These curves are in agreement with those generated in previous work.[2] When a mass balance analysis is performed only 13% of the original PCB mass can be accounted for following a 100 kGy irradiation. Clearly, reactions other than simple dechlorination are occurring at these doses. Slide 9 shows graphically that the polychlorinated biphenyl decomposition products produced in isopropanol do not account for the octachlorobiphenyl which has been destroyed.

Slide 10 shows analogous data for octachlorobiphenyl irradiations in methanol. Only 6% of the original octachlorobiphenyl mass can be accounted for by PCB decomposition products detectable by GC/MS.

In an effort to determine the fate of the missing decomposition product mass a series of irradiated isopropanol and methanol solutions of octachlorobiphenyl were subjected to Volatile Organics Analysis (VOA). This analysis is designed to detect and quantify decomposition products with masses too low to be seen by the GC/MS PCB protocol. Numerous reaction products appeared in these analyses of which the majority can be traced to the interaction of radiation with the solvents. As an example, Slide 11 shows the production of 2-methoxypropane and acetaldehyde in isopropanol solutions versus dose. While these reactions are not directly related to PCB decomposition they may provide information concerning free radical production and thus information concerning possible PCB decomposition mechanisms. The only chlorinated volatile organic product detected in either irradiated methanol or irradiated isopropanol octachlorobiphenyl solutions was dichloromethane (methylene chloride). This product appeared consistently but without trend. It is unknown whether this product is due to direct decomposition of PCB or due to chlorine recombination with other products. Slide 12 shows data concerning dichloromethane production versus dose. It should be noted that the collaborative effort at LLNL has shown that dichloromethane itself is susceptible to radiolytic degradation to the point of total mineralization.(7)

The previous results clearly demonstrate the viability of PCB decomposition is alcoholic solvents. However, PCBs in "real-world" samples are generally found dissolved in oil. The 2, 2′, 3, 3′, 4, 5′, 6, 6′-octachlorobiphenyl was therefore irradiated at various applied doses in transformer oil. These preliminary results are shown in Slide 13. Clearly, the process is capable of decomposing octachlorobiphenyl in oil. A dose of 100 KGy decreased octachlorobiphenyl concentration by a factor of ten.

C. CONCLUSIONS AND FUTURE WORK

Irradiation experiments performed in FY91 have confirmed initial results presented in (2) which demonstrated the radiolytic PCB decomposition concept. Further, the new data suggests that decomposition is more efficient in more polar solvents. A series of samples in various solvents has been prepared for irradiation at a single dose to demonstrate this effect. Should this experiment be successful it would suggest that a PCB contaminated solvent (such as oil) of low dielectric constant may be treated at lower doses simply by mixing with a high dielectric constant solvent. Irradiations will be performed to verify this.

The fate of much of the octachlorobiphenyl mass following irradiation is still unknown. The only chlorinated product discovered by VOA was dichloromethane. It occurs at low concentrations. The lack of an identifiable trend in dichloromethane production is of concern. These experiments will be repeated with better control over headspace volume in the samples.

Some advantages of using ionizing radiation as a waste treatment tool are summarized in Slide 14.

REFERENCES

1. Meikrantz, D. H., and Mincher, B. J., Unpublished results, 1988.

2. Mincher, B. J., Meikrantz, D. H., Murphy, R. J., Gresham, G. L., and Connolly, M. J., Applied Radiat. Isot., in press.

3. Evans, R., Nesyto, E., Radlowski, C., and Sherman, V. W., (1971), J. Phys. Chem., 75, 2762.

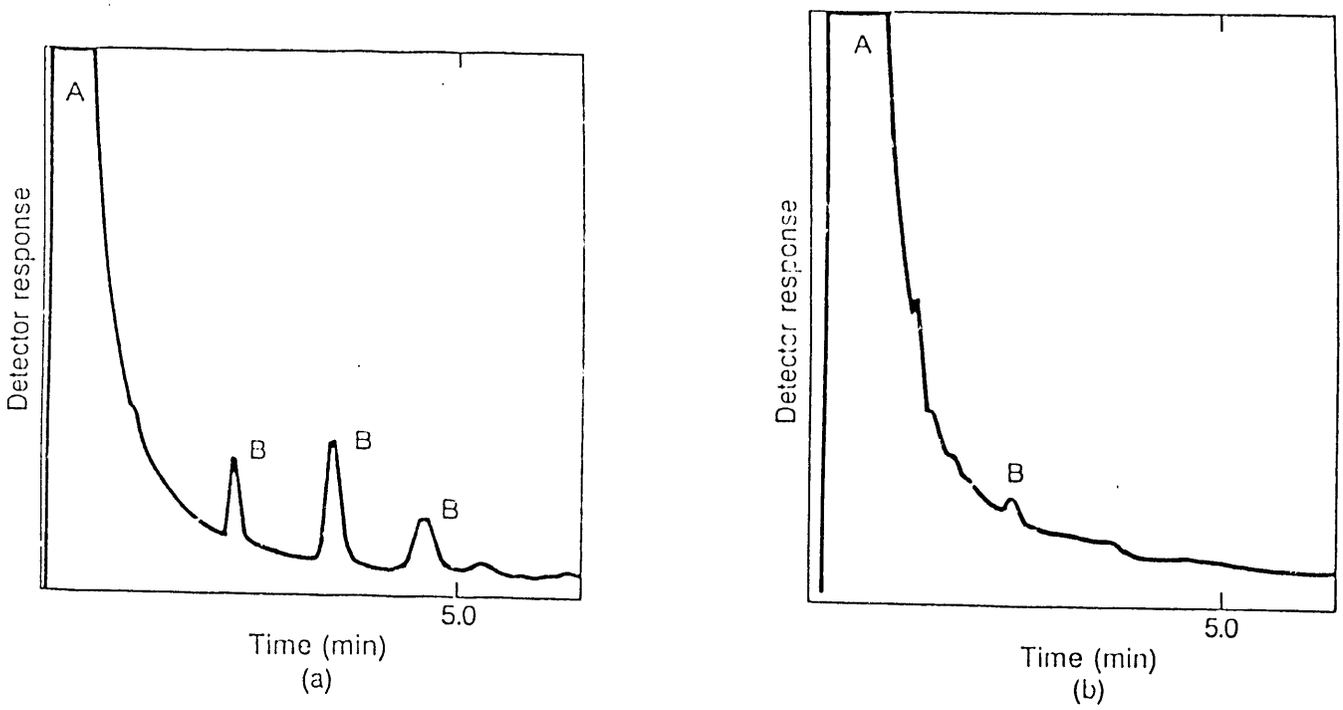
4. Sherman, V. W., Evans, R., Nesyto, E., and Radlowski, C., (1971), Nature, 232, 118.

5. Sawai, T., Shimokawa, T., and Shinozake, Y., (1974), Bull. Chem. Soc. Jpn., 47, (8), 1889.

6. Butler, J., Land, E. J., and Swallow, A. J., (1984), Radiat. Phys. Chem., 24, (1/4), 273.

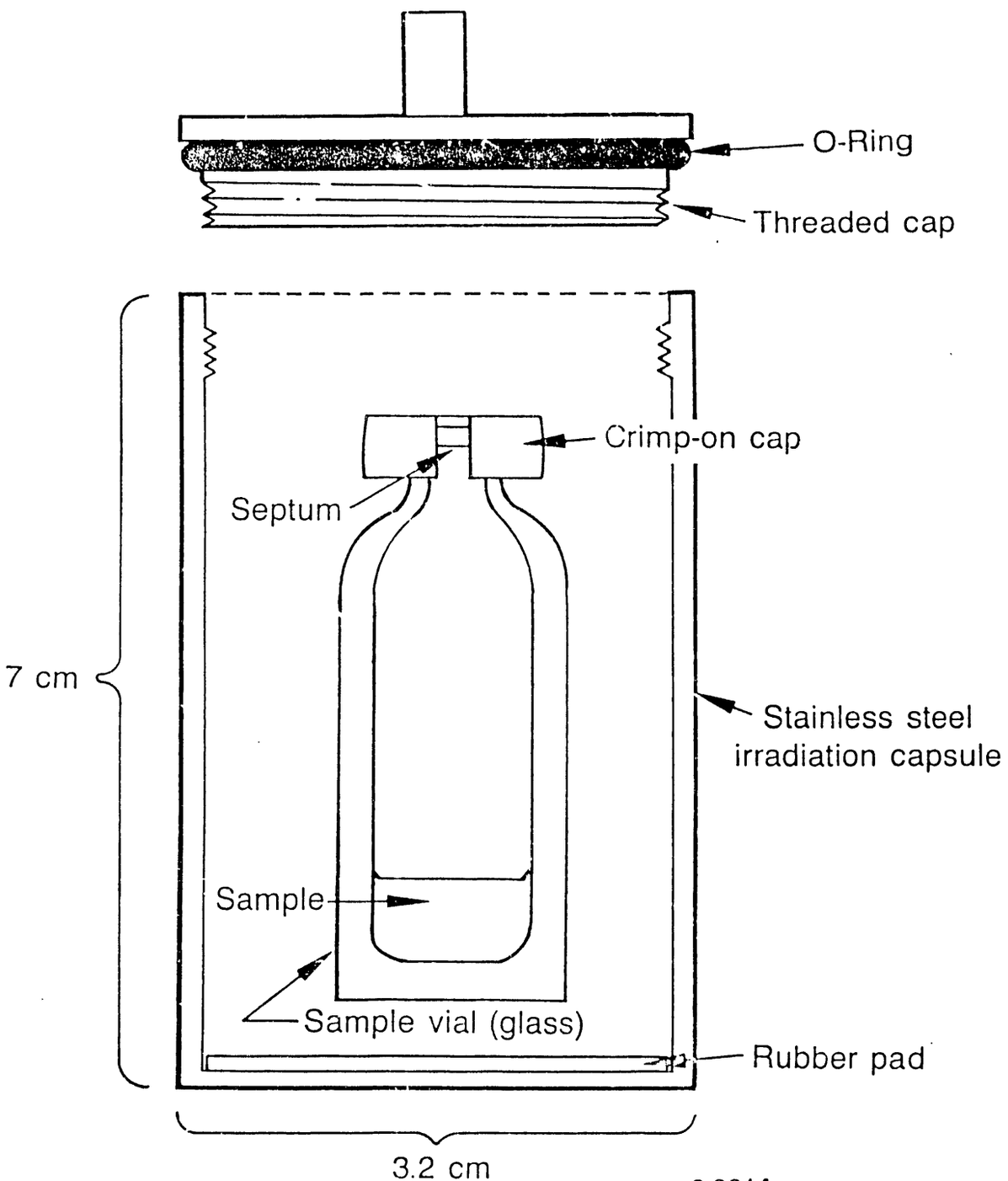
7. Matthews, S. M., Boegel, A. J., Eccles, S. F., Homann, S. G., Rice, D. W., Loftis, J. A., Jovanovich, M. C., Caufield, R. A., Mincher, B. J., Meikrantz, D. H., Murphy, R. J., Gresham, G. L., and Connolly, M. J., High Energy Irradiation of Chlorinated Hydrocarbons, American Nuclear Society International Topical Conference, Methods and Applications of Radioanlaytical Chemistry II, Kona, HI, April 21-27, 1991.

SLIDE 1



AROCLOR 1221 DECOMPOSITION IN HEXANE
a) before irradiation, b) following 50 kGy.

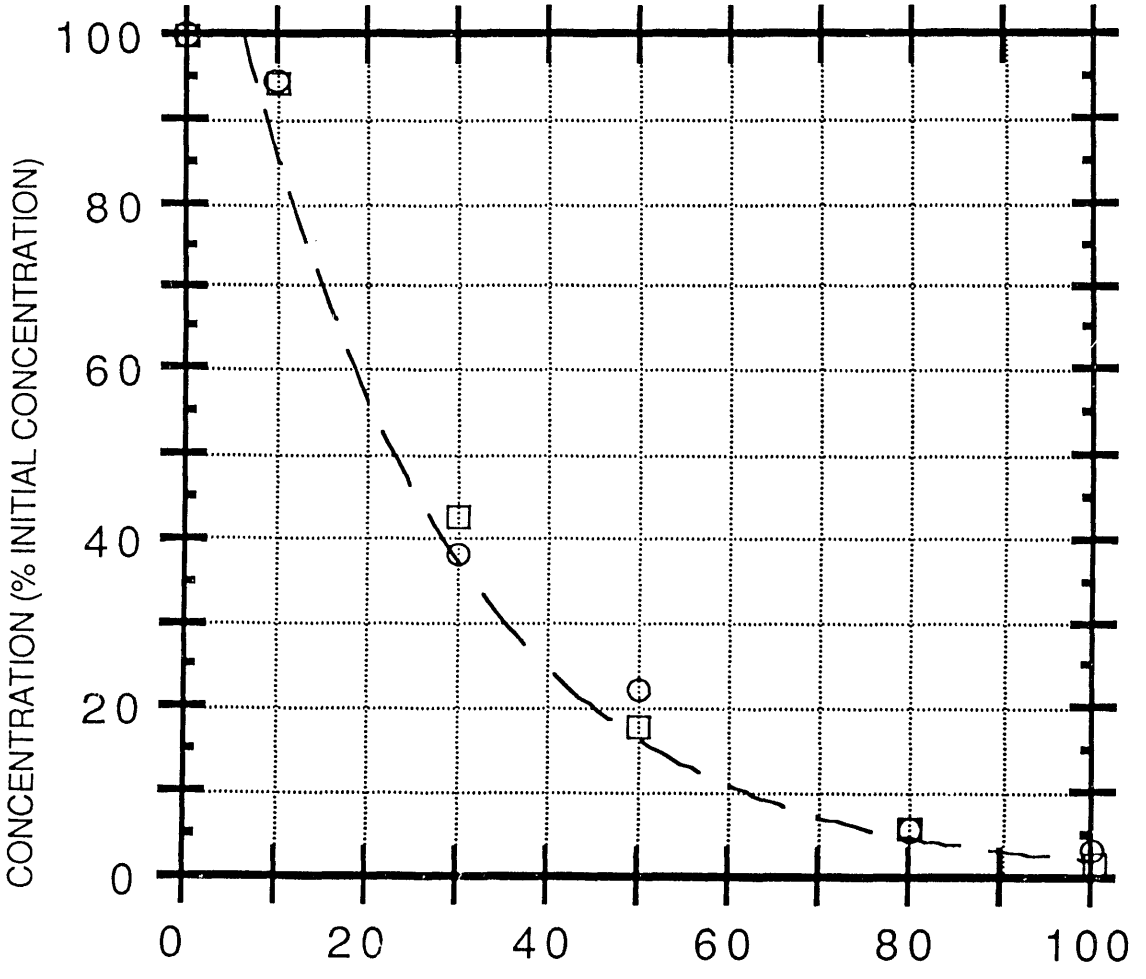
SLIDE 2



8-9014

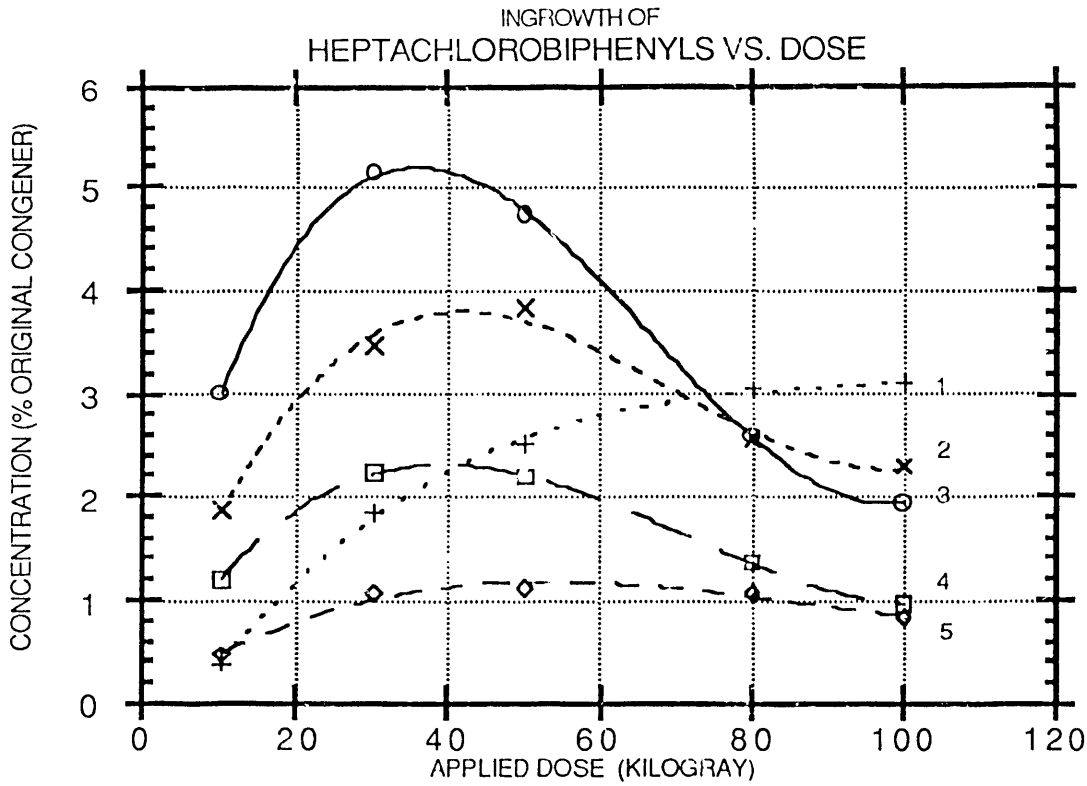
SLIDE 3

OCTACHLOROBIPHENYL DECOMPOSITION VS. DOSE



Replicate trials using 2,2',3,3',4,5',6,6'-octachlorobiphenyl

SLIDE 4

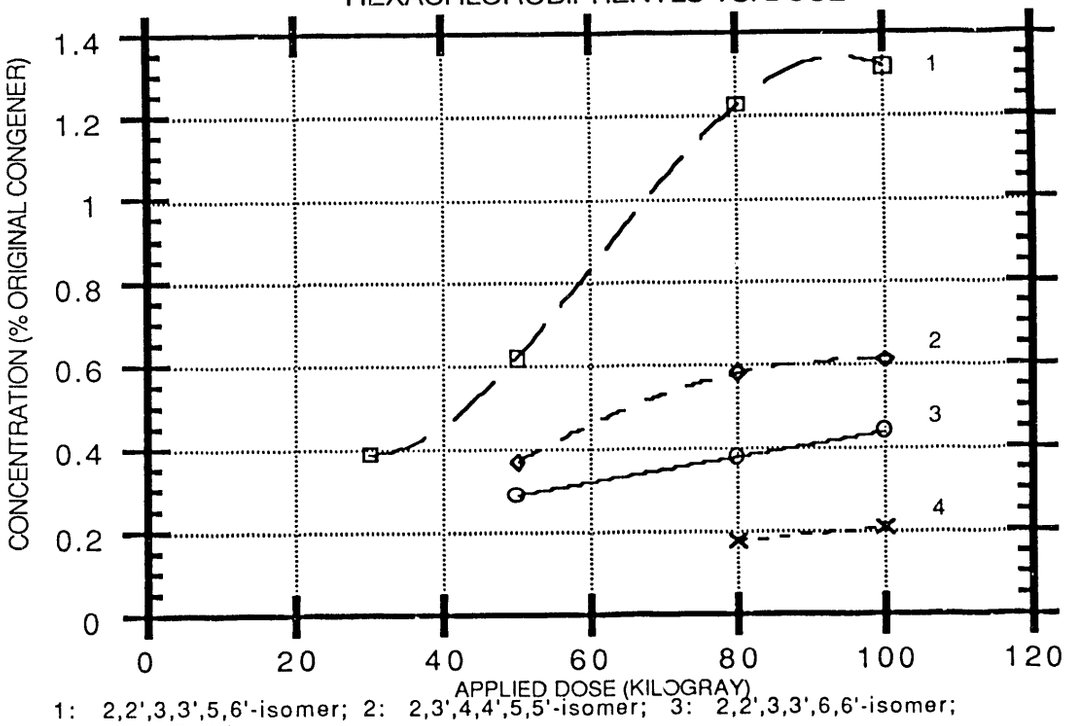


1. Unidentified isomer;2: 2,3,3',4,4',5,5'-isomer; 3: 2,2',3,4,5,5',6-isomer ; 4: 2,2',3,3',4,4',6- isomer ; 5: 2,3,3',4',5,5',6-isomer

SLIDE 5

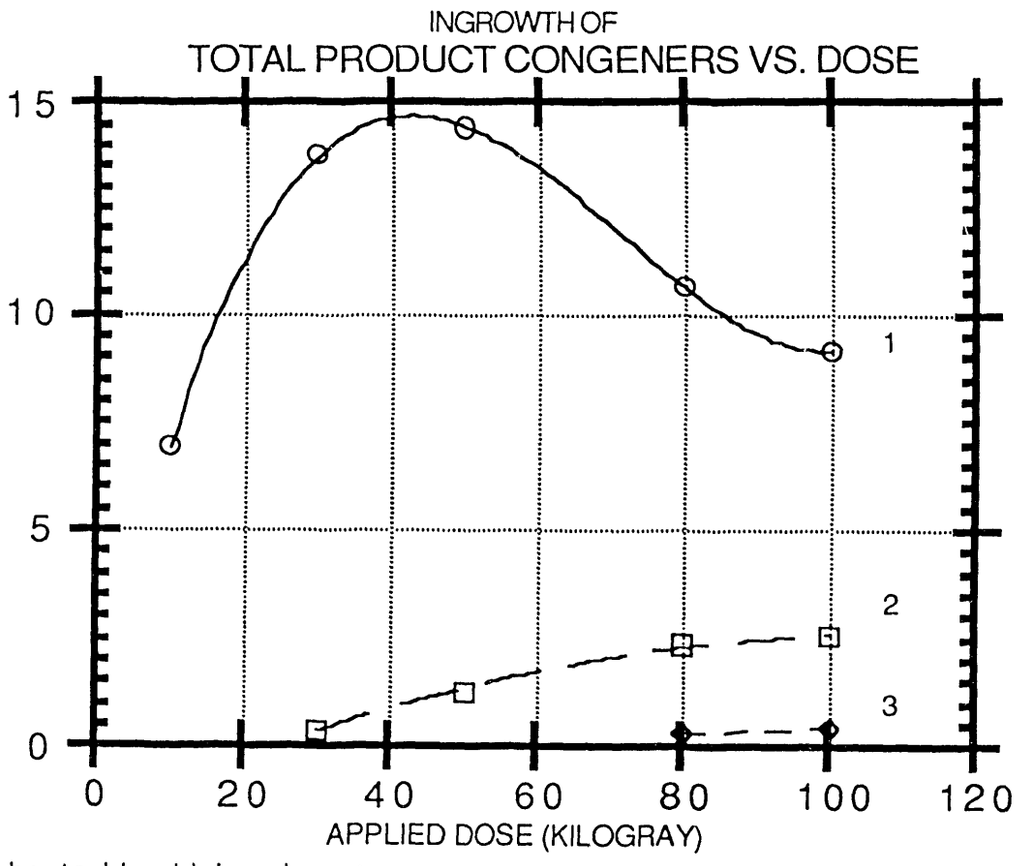
INGROWTH OF

HEXACHLOROBIPHENYLS VS. DOSE



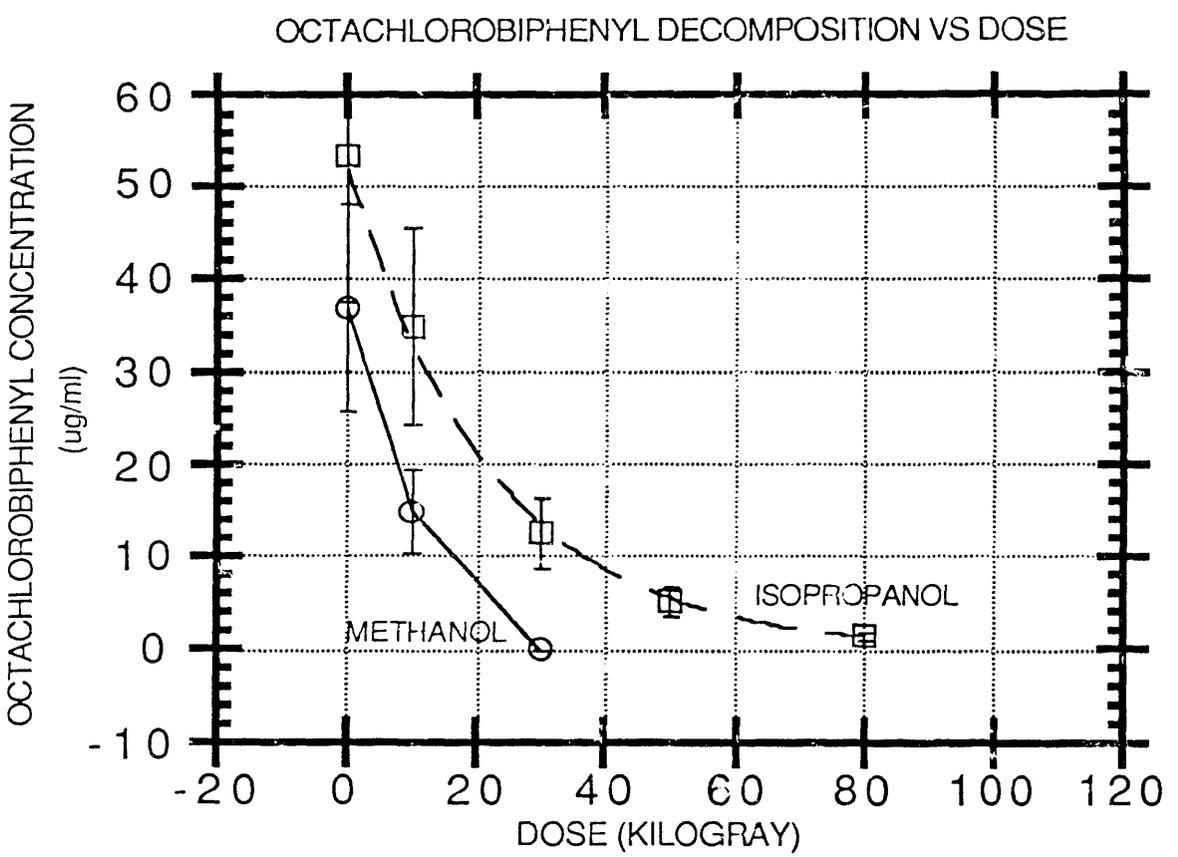
1: 2,2',3,3',5,6'-isomer; 2: 2,3',4,4',5,5'-isomer; 3: 2,2',3,3',6,6'-isomer;
4: unidentified isomer.

SLIDE 6

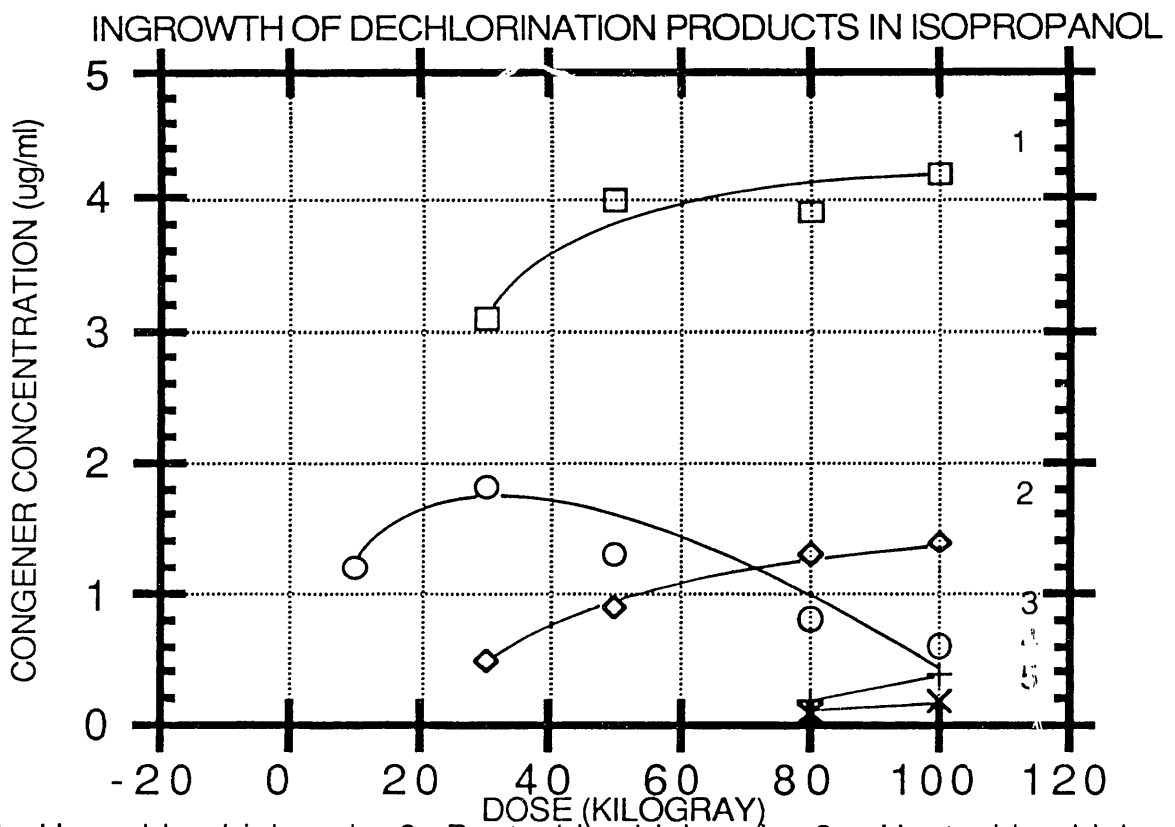


1; heptachlorobiphenyl; 2: hexachlorobiphenyl, 3: pentachlorobiphenyl.

SLIDE 7


OCTACHLOROBIPHENYL DECOMPOSITION VS DOSE
OCTACHLOROBIPHENYL CONCENTRATION
(ug/ml)
60
50
40
30
20
10
0
-10
-20
0
20
40
60
80
100
120
DOSE (KILOGRAY)
METHANOL
ISOPROPANOL

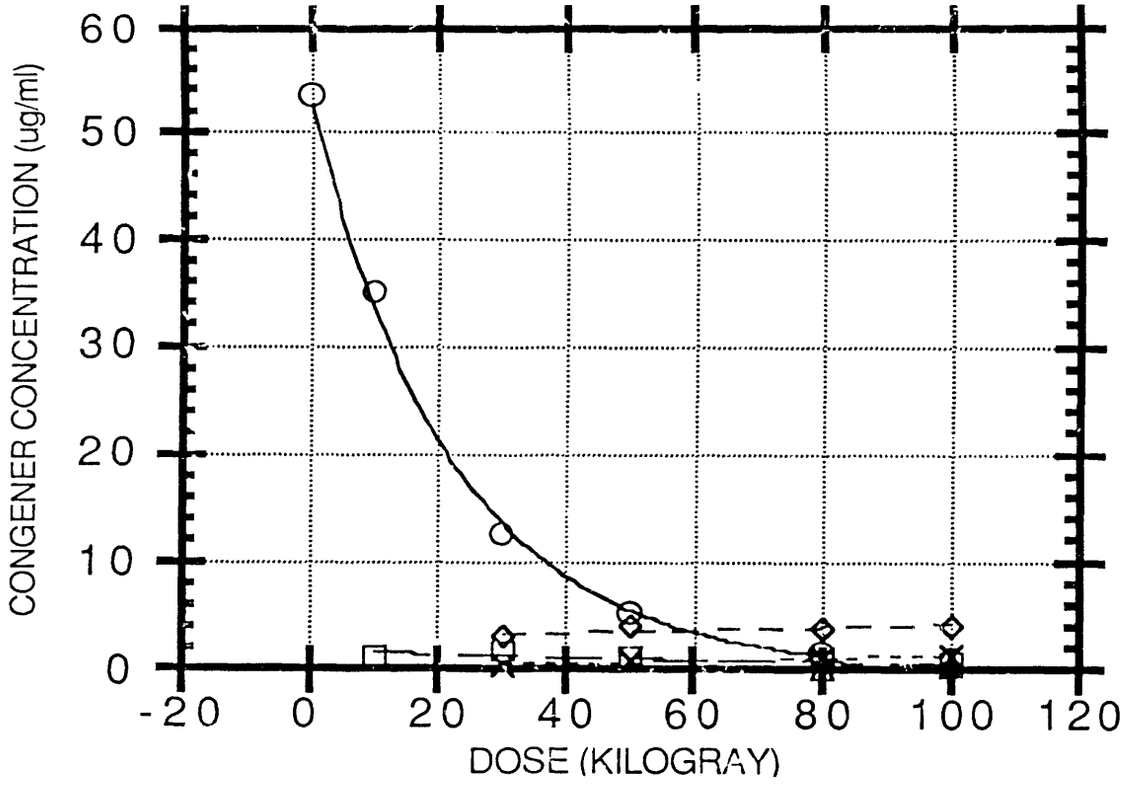
SLIDE 8



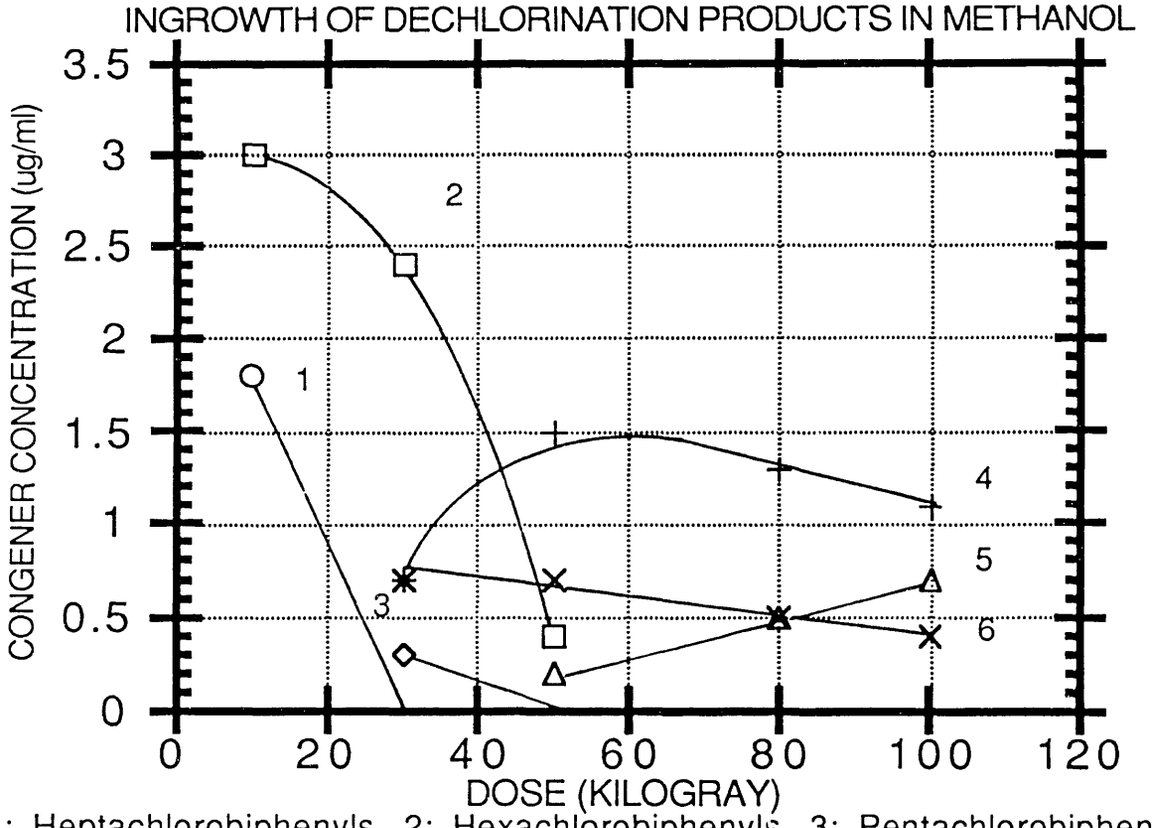
1; Hexachlorobiphenyls, 2; Pentachlorobiphenyls, 3; Heptachlorobiphenyls, 4; Trichlorobiphenyls, 5; Tetrachlorobiphenyls.

SLIDE 9

OCTACHLOROBIPHENYL DECOMPOSITION AND DECHLORINATION
PRODUCT INGROWTH VERSUS DOSE



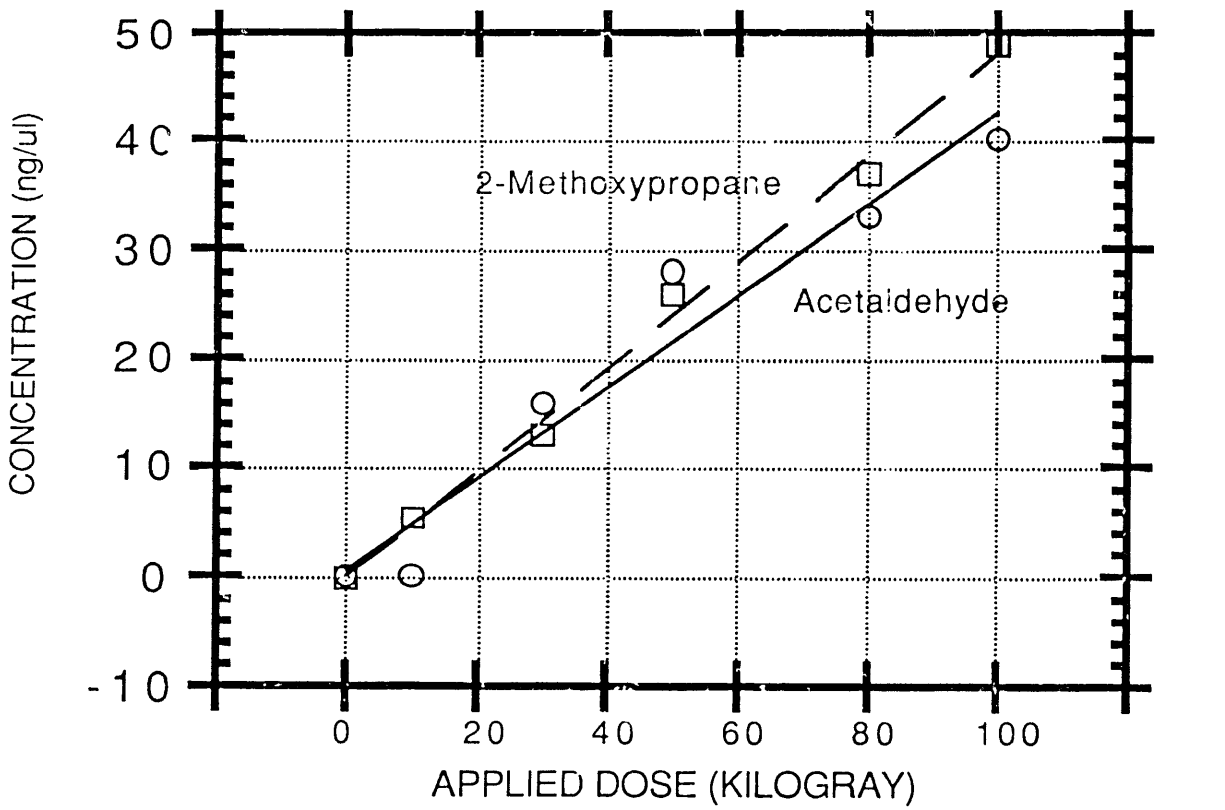
SLIDE 10



1; Heptachlorobiphenyls, 2; Hexachlorobiphenyls, 3; Pentachlorobiphenyls, 4; Trichlorobiphenyls, 5; Dichlorobiphenyls, 6; Tetrachlorobiphenyls.

SLIDE 11

FORMATION OF ISOPROPANOL RADIOLYSIS PRODUCTS VERSUS DOSE

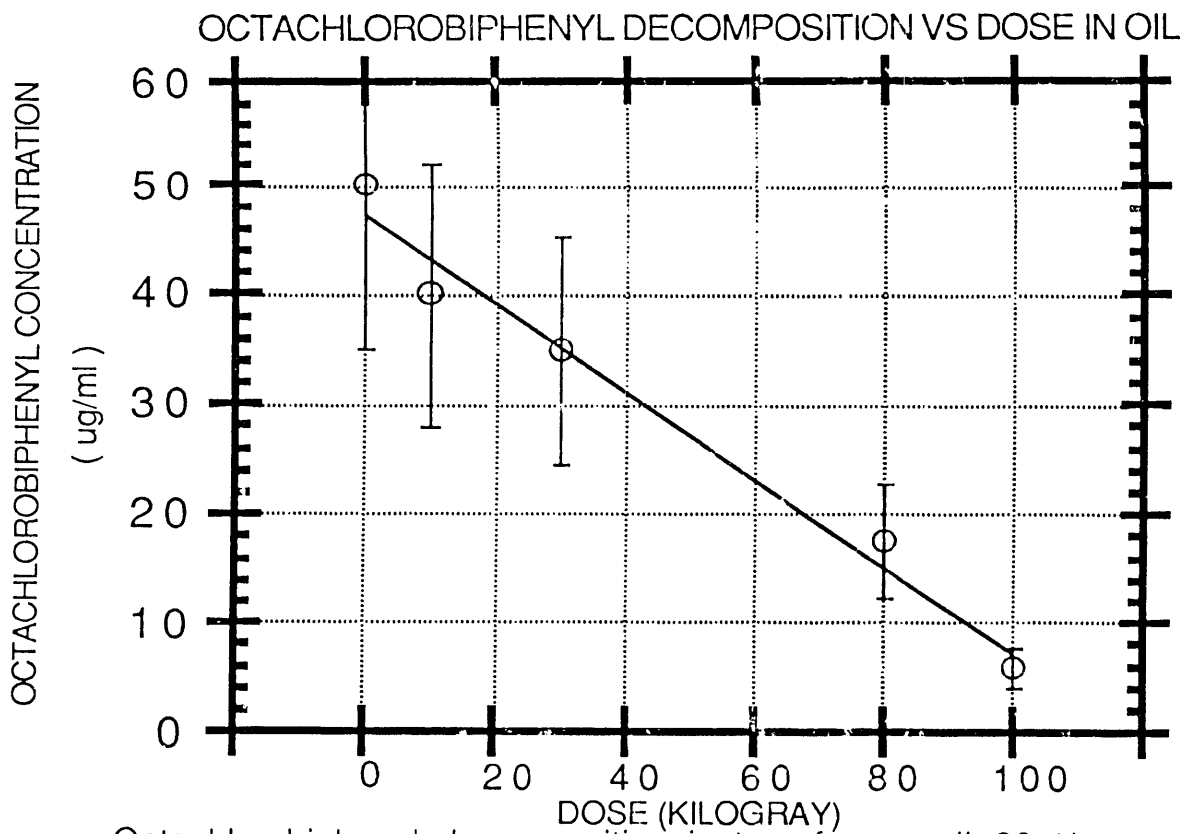


SLIDE 12

DICHLOROMETHANE PRODUCTION VERSUS DOSE IN SOLUTIONS CONTAINING OCTACHLOROBIPHENYL

	Concentration (ng/μL) Initial	Concentration (ng/μL) Following Applied Dose Of: 10 kGy	30 kGy	50 kGy	80 kGy	100 kGy
METHANOL	0.1	0.7	4.0	0.6	1.5	7.4
ISOPROPANOL	0.5	1.1	1.4	17.4	1.8	4.4

SLIDE 13



Octachlorobiphenyl decomposition in transformer oil; 30 % error bars.
(Preliminary Data)

Advantages of Ionizing Radiation Decomposition

1. Ionizing Radiation can Treat a wide range of halogenated Wastes from TCE to PCBs.

2. Process is inherently Selective to reactive Compounds.

3. Process (dose) is easily controlled.

4. Process minimizes gaseous and particulate effluents.

5. In-Situ destruction possible in many Waste Situations.

6. Existing Technology employed for Sources of Ionizing Radiation via two methods

    A. Accelerators where spent fuel is not available or practical.

    B. Spent Fuel

END

DATE
FILMED
1/16/92