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GAMMA RADIOLYSIS OF CHLORINATED HYDROCARBONS*

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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 waste 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.

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. Among the compounds studied were chloroform, carbon tetrachloride, DDT, lindane and commercial Arocolor mixtures. Aroclor 1221 peaks were shown to nearly disappear when analyzed by gas chromatography following a 50 kGy irradiation.

GC/MS methods were then used during 1990-1991 to identify decomposition products of the PCB 2,2',3,3',4,5',6,6' -octachlorobiphenyl when exposed to kilogray doses. Study of a single congener rather than commercial Arclor mixtures is preferred because of the complexity of Aroclor GC/MS chromatograms. A highly chlorinated congener was selected as a "worst-possible-case" candidate for treatment.

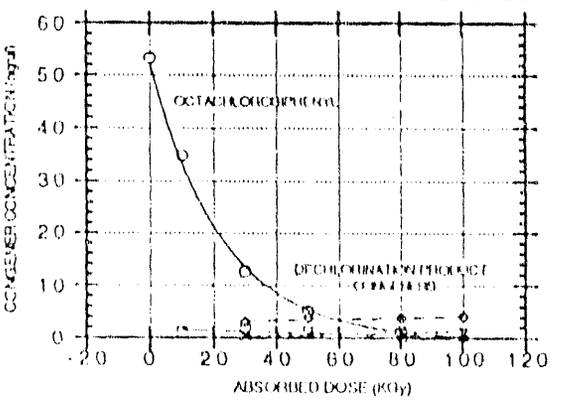
These studies have been performed in collaboration with LLNL since the beginning of FY-91. Our LLNL colleagues are studying chlorinated solvents such as CCl_4 and TCE using accelerator generated radiation. Octachlorobiphenyl has also been irradiated with accelerators at LLNL to compare decomposition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

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.

RESULTS

The congener 2,2',3,3',4,5',6,6'-octachlorobiphenyl was subjected to irradiations of varying length in isopropanol to evaluate the effect of the total absorbed dose on PCB decomposition. Irradiations at five different doses were analyzed and the resultant PCB concentration was plotted versus dose. This plot, shown in Figure 1, shows a steady decrease in octachlorobiphenyl concentration with dose to

FIGURE 1
CONGENER CONCENTRATION VS. DOSE



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100 kGy. Octachlorobiphenyl decomposition products detectable by this method were less chlorinated PCB congeners representing products of a dechlorination reaction. Decomposition product in-growth curves show maxima at specific doses followed by decreasing concentration with dose, indicating that the decomposition products are also susceptible to gamma radiolysis.

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. At 100 kGy 85% of total PCBs was decomposed to compounds not detectable by the method. The uncertainty of these measurements is ±20%. Figure 1 dramatically shows the mass deficit when octachlorobiphenyl and dechlorination product congener concentrations are compared.

In an effort to determine the fate of the missing decomposition product mass a series of irradiated octachlorobiphenyl solutions were subject 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, all of which can be traced to the interaction of radiation with the solvents. Thus, at present, the missing mass has not yet been identified. Future experiments are planned to search for compounds not amenable to gas chromatography using an LC/MS technique. The GC/MS analyses have ruled out thousands of chlorocarbon decomposition products.

Several experiments have been done to explore the mechanism of the decomposition reaction. Many previous authors have postulated free radical chain dechlorinations at gray to decagray doses.[1,2,3] However, at the kilogray doses used in our experiments this is probably not the case. We have measured G values on the order of 0.025 for octachlorobiphenyl decomposition, versus G values as much as five orders of magnitude higher for low dose studies. Our low G values do not appear to be a disadvantage; significant decomposition is possible with easily achievable doses. Our G values show no dependency on dose rate or radiation quality (energy or type). This is illustrated in Figure 2 which shows octachlorobiphenyl decomposition versus dose for samples irradiated with spent fuel at INEL and with 9 MeV bremsstrahlung at LLNL.

The addition of solvated electron scavengers, such as carbon tetrachloride to a solution of octachlorobiphenyl suppresses the decomposition reaction. This is shown in Figure 3. The presence of 1.6M CCl_4 shifted the G value of the octachlorobiphenyl decomposition reaction from 0.026 to 0.000006. This is an indication that solvated electrons are an important part of the decomposition mechanism.

FIGURE 2
OCTACHLOROBIPHENYL DECOMPOSITION VS. DOSE
INEL AND LLNL RADIATION SOURCES

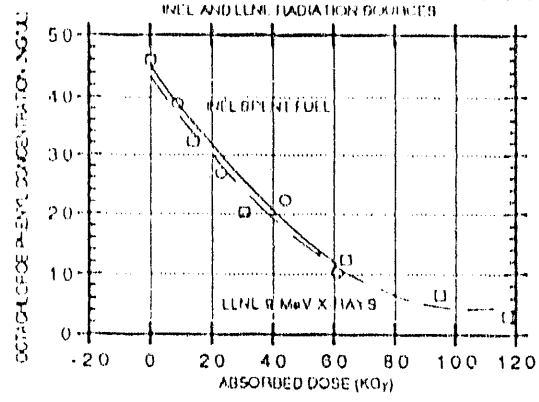


FIGURE 3
OCTACHLOROBIPHENYL CONC. VS. DOSE
ELECTRON SCAVENGER EXPERIMENT

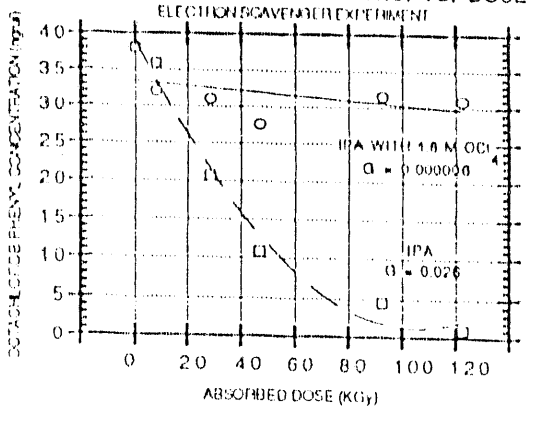
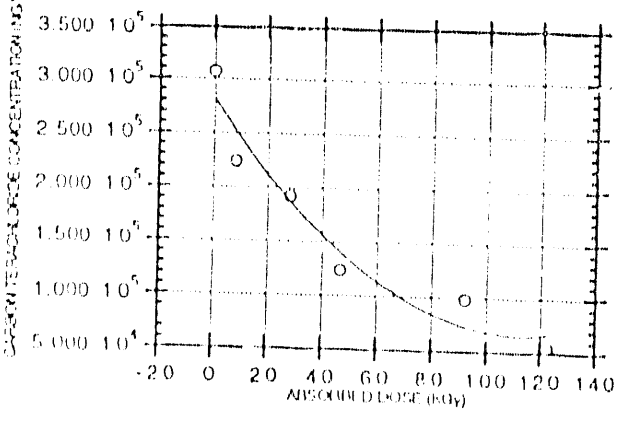


Figure 4 shows the simultaneous decomposition of the carbon tetrachloride. The G value for CCl_4 decomposition was approximately 200.

FIGURE 4
CARBON TETRACHLORIDE CONC. VS. DOSE



FUTURE PLANS

In the future, further experiments to examine the reaction mechanism are planned. Irradiations will be performed to determine if the G value is related to solvent dielectric constant and electron affinity of the target analyte. In addition, the search for missing decomposition products will continue.

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