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HIGH ENERGY DECOMPOSITION OF HALOGENATED
HYDROCARBONS
FY91 FINAL REPORT

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HIGH ENERGY DECOMPOSITION OF HALOGENATED HYDROCARBONS - FY91 FINAL REPORT

INTRODUCTION

This report is a summary of work performed during FY91 for the Office of Technology Development of the U.S. Department of Energy on the program entitled "High Energy Decomposition of Halogenated Hydrocarbons." The goals of the FY91 effort were summarized in Technical Task Plan ID-0505-RD. This was the initial year of funding for this program.

This program is the INEL component of a joint collaborative effort with 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.

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 ATR spent fuel pool. The decomposition rates and products in several solvents are discussed.

This report also summarizes the completion of other FY91 goals associated with the program, including the publication of an article in a technical journal and completion of a Public Acceptance Study for the technology.

EXPERIMENTAL RESULTS

TECHNICAL OBJECTIVES

The INEL's technical objectives as stated in TTP ID-0505-RD for FY91 are as follows:

- Establish GC/MS analysis protocol for PCBs
- Irradiate PCBs in oil and water to establish dose requirements
- Conduct mass balance studies of decomposition products
- Select and study potential reaction catalysts

RESULTS

The GC/MS protocol selected for these studies was EPA Method 680, "Determination of Pesticides and PCBs in Water and Soil/Sediment by GC/MS." The method was modified to provide better resolution in the sample solvents which are specific to this study. The estimated accuracy of this analysis is $\pm 30\%$.

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.

Octachlorobiphenyl was irradiated in different diluent solutions at concentrations of 40-50 ng/ μ l. These solutions were isopropanol, methanol, and transformer oil. Aqueous solutions were not irradiated due to the poor solubility of octachlorobiphenyl in water. Plots of octachlorobiphenyl decomposition versus dose for methanol and isopropanol are shown in Figure 1. 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.⁽¹⁻³⁾ These free radicals have a longer life-time, and hence higher probability of reaction, in a more polar solvent.⁽⁴⁾ This suggests an interesting field of investigation and predicts that decomposition efficiencies may be improved by varying the dielectric constant of the waste matrix.

Presented in Figure 2 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.⁽⁵⁾ When a mass balance analysis is performed only 13% of the original PCB mass can be accounted for following a 100 kGy irradiation. Table 1 shows concentrations of the original octachlorobiphenyl and its decomposition products versus dose. Clearly, reactions other than simple dechlorination are occurring at these doses. Figure 3 shows graphically that the polychlorinated biphenyl decomposition products produced in isopropanol do not account for the octachlorobiphenyl which has been destroyed.

Table 1. Octachlorobiphenyl degradation in isopropanol and ingrowth of product isomers versus applied dose

Homolog	Concentration (ng/ μ l) Initial	Concentration (ng/ μ l) Following Applied Dose Of:				
		10 kGy	30 kGy	50 kGy	80 kGy	100 kGy
OCTACHLOROBIPHENYLS	53.4	34.9	12.6	5.2	1.5	--
HEPTACHLOROBIPHENYLS	--	1.2	1.8	1.3	0.8	0.6
HEXACHLOROBIPHENYLS	--	--	3.1	4.0	3.9	4.2
PENTACHLOROBIPHENYLS	--	--	0.5	0.9	1.3	1.4
TETRACHLOROBIPHENYLS	--	--	--	--	0.1	0.2
TRICHLOROBIPHENYLS	--	--	--	--	0.2	0.4

Table 2 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. Plots of decomposition product ingrowth versus dose for methanol irradiations are shown in Figure 4.

Table 2. Octachlorobiphenyl degradation in methanol and ingrowth of product isomers versus applied dose

Homolog	Concentration (ng/ μ l) Initial	Concentration Following Applied Dose Of:				
		10 kGy	30 kGy	50 kGy	80 kGy	100 kGy
OCTACHLOROBIPHENYLS	36.8	14.9	--	--	--	--
HEPTACHLOROBIPHENYLS	--	1.8	--	--	--	--
HEXACHLOROBIPHENYLS	--	3.0	2.4	0.4	--	--
PENTACHLOROBIPHENYLS	--	--	0.3	--	--	--
TETRACHLOROBIPHENYLS	--	--	0.7	0.7	0.5	0.4
TRICHLOROBIPHENYLS	--	--	0.7	1.5	1.3	1.1
DICHLOROBIPHENYLS	--	--	--	0.2	0.5	0.7

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. 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. Table 3 shows data concerning dichloromethane production versus dose. It should be noted that a collaborative effort at LLNL has shown that dichloromethane itself is susceptible to radiolytic degradation to the point of total mineralization. (6)

Table 3. Dichloromethane production versus dose in solutions containing octachlorobiphenyl

	Concentration (ng/ μ l) Initial	Concentration (ng/ μ l) 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

An initial experiment to measure the rate of octachlorobiphenyl decomposition in transformer oil was irradiated. This preliminary data, shown in Figure 5, clearly demonstrates that PCB's can be decomposed in even a nonpolar solvent such as oil. This experiment further demonstrates that it is possible to decompose PCB's using gamma irradiation in "real world" samples.

As of this date only one reaction catalyst, copper-zinc couple powder, has been tested. In a single experiment the powder was added to an octachlorobiphenyl in isopropanol solution. No change in the decomposition rate was seen. Other potential catalysts have been selected and will be tested.

The chemical literature reports decomposition of analytes⁽⁷⁾ (or production of their decomposition products) in terms of G-values. The G-value is defined as numbers of molecules destroyed, (or created) per 100 eV of energy absorbed. In order to compare this work with other investigators' results, it is necessary to accurately determine the dose absorbed by a sample. The G-value is important in determining the final cost of a waste processing facility as molecules/eV translates into dollars/mass of waste treated in a process system. Toward this end, a radiochromic dosimetry system was purchased. The system chosen was the FWT-100 from Far West Technology, Inc., (Goleta, CA). The system has been installed and calibrated. Initial sample irradiations containing dosimetry are currently in progress.

Additional samples of octachlorobiphenyl in transformer oil are currently awaiting irradiation at ATR. A series of octachlorobiphenyl samples in isopropanol and another in transformer oil have been sent to LLNL for irradiation by accelerator bremsstrahlung. They will be returned to INEL for analysis. This will allow comparison of decomposition efficiencies of two different radiation sources and energies.

CONCLUSIONS AND FUTURE WORK

Irradiation experiments performed in FY91 have confirmed initial results presented in (5) which demonstrated the radiolytic PCB decomposition concept. Further, it has been shown that significant PCB decomposition can be effected in transformer oil. The new data suggests that decomposition is more efficient in polar solvents. A series of samples in various solvents with differing dielectric constants, 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 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.

OTHER TTP GOALS

One of the FY91 milestones of TTP ID-0505-RD was the completion and presentation of a technical paper summarizing halogenated hydrocarbon decomposition studies completed previous to FY91. These studies were supported by in-house funding. A paper entitled "High Energy Irradiation

of Chlorinated Hydrocarbons" was presented in collaboration with LLNL at the American Nuclear Society Second International Conference on Methods and Applications of Radioanalytical Chemistry, April 21-27, 1991 in Kona, Hawaii.⁽⁶⁾ Both poster and oral presentations were made. Proceedings of this conference will be published. Additionally, a more detailed manuscript entitled "Gamma-Ray Induced Degradation of PCBs and Pesticides Using Spent Reactor Fuel" profiling the INEL portion of this research was accepted for publication by the journal, "Applied Radiation and Isotopes." This issue is currently in press.⁽⁵⁾

An invitation has been received to present the results of the current PCB irradiation studies at the Florida Environmental Chemistry Conference, October 30-November 1, 1991 in Palm Coast, Florida.

The final goal for FY91 was the preparation of a paper assessing the likelihood of public acceptance of hazardous waste irradiation technology. In support of this goal an author of that paper attended a school on Systematic Development of Informed Consent in Boulder, Colorado on June 18-21, 1991. The school teaches methods of encouraging public understanding and support of new technologies and these methods are addressed in the Public Acceptance Study which was completed and submitted in August 1991. This paper is entitled, "Public Acceptability of The Use of Gamma Radiation as a Hazardous Waste Treatment Process."

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FIGURE 1. Octachlorobiphenyl decomposition versus dose for isopropanol and methanol. Error bars are 30%.

INGROWTH OF DECHLORINATION PRODUCTS IN ISOPROPANOL

FIGURE 2. Ingrowth of dechlorination products. 1; Hexachlorobiphenyls, 2; Pentachlorobiphenyls, 3; Heptachlorobiphenyls, 4 Trichlorobiphenyls, 5; Tetrachlorobiphenyls.

OCTACHLOROBIPHENYL DECOMPOSITION AND DECHLORINATION PRODUCT INGROWTH VERSUS DOSE

FIGURE 3. Ingrowth of dechlorination products can not account for disappearance of octachlorobiphenyl. 1: Octachlorobiphenyl curve, 2: product curves.

FIGURE 4. Ingrowth of dechlorination products. 1; Heptachlorobiphenyls, 2; Hexachlorobiphenyls, 3; Pentachlorobiphenyls, 4; Trichlorobiphenyls, 5; Dichlorobiphenyls, 6; Tetrachlorobiphenyls.

FIGURE 5.
Preliminary data concerning Octachlorobiphenyl decomposition
in transformer oil. Error bars are 30%.

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