

RADIATION AND CHEMICAL DEGRADATION OF HALOGENATED ORGANIC COMPONENTS POSSIBLY PRESENT IN MIXED WASTE

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ABSTRACT

Chlorinated hydrocarbons are a source of many problems in the environment. Additional difficulties may be encountered if these hydrocarbons are combined with radioactive substances in a mixed waste. Because of these concerns, a technique is necessary to degrade or deposit these substances without harmful consequences for the environment. To dispose of mixed waste safely, many potential hazards must be dealt with beforehand, such as the reactivity of the hazardous waste components under the given storage conditions. Chlorinated compounds can react with the container material or be subject to radical reactions initiated by the radiation effects in the waste.

The purpose of this study was to investigate the radical reactions of five chlorinated hydrocarbons. These radical reactions and their products were studied with two methods. One method involved γ -radiation at doses of $5 \cdot 10^4$ or $5 \cdot 10^5$ Gy. Hexachloroethane, β -hexachlorocyclohexane, γ -hexachlorocyclohexane, hexachlorobenzene, and hexachlorophene were used as model substances. They were irradiated when dry or in the presence of water. The other method used to initiate radical reactions was the addition of peroxide to the model substance. Previous work (1) has shown that the products resulting from the reaction with peroxides were similar to the expected biological degradation products. Hydrogen peroxide or nickel peroxide was added to the model substances, and the mixture was heated at 220°C for a duration of 2 or 24 hours. The reaction products were identified using a GC/MS system.

The results showed that the two methods produced the same major degradation products. The model substances were degraded more thoroughly by peroxides than by irradiation. An exception was hexachloroethane, which yielded more radiation degradation products.

INTRODUCTION

Hydrocarbons in radioactive mixed wastes may become reactive with the matrix or because of the radiation present, which can start a radical reaction in the hydrocarbon. Radical reactions in chlorinated hydrocarbons can also be initiated with the addition of peroxides, heat, or by biological mechanisms. The similarity of the products resulting from the addition of peroxides with heating and those resulting from biological processes has been illustrated in the literature using hexachlorocyclohexane as a model substance. (1) The radical reactions initiated by radiation and the addition of peroxides with heating are studied in this paper by comparing the degradation products of five different chlorinated hydrocarbons.

PURPOSE

The purpose of this experiment was to investigate the radical reactions of five model substances: hexachloroethane, beta-hexachlorocyclohexane, gamma-hexachlorocyclohexane, hexachlorobenzene, and hexachlorophene. Radicals were produced by exposing the model substances to γ -radiation when they were dry or when they were mixed with water. A different technique for radical formation was also used, employing hydrogen and nickel peroxides with heat. The products from the two techniques were compared.

Degradation of the Model Substances

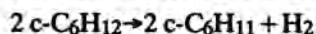
Using γ -Radiation

γ -radiation produces radicals from hydrocarbons as a result of the Compton effect, by which electrons gain energy from a passing photon. One photon possesses enough energy to form many radicals.

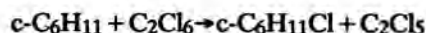
During the radical formation process, the chlorinated hydrocarbons lose chlorine and hydrogen ions. (5) Which ions are lost depends on the reaction temperature and the surrounding matrix. The degradation of C_2Cl_6 in two different solutions are illustrated as examples.

C_2Cl_6 in Cyclohexane

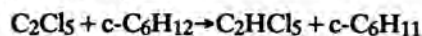
The first step of the reaction is the accumulation of radicals from the solvent molecules.



These radicals then separate a chlorine atom from the C_2Cl_6 .

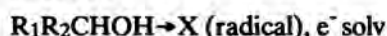


The hydrocarbon radical then either reacts with the solvent to form a new radical or loses another chlorine atom to gain stability.

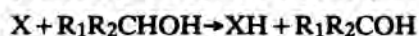
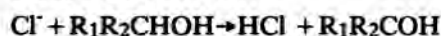
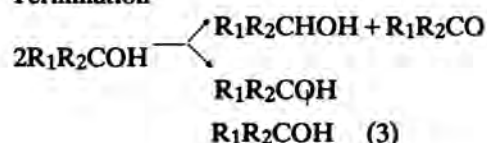


C₂Cl₆ in Alcohols

Again, the first step in the reaction is the accumulation of solvent radicals, which can remove a chlorine atom from the C₂Cl₆. The propagation step continues the production of radicals by removing hydrogen atoms from the solvent. The termination step halts the reaction by either transferring a hydrogen atom from one alcohol radical to another or joining two alcohol radicals.

Initiation

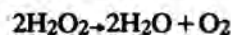
(where R₁ and R₂ are CH₃ or H)

**Propagation****Termination**

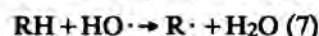
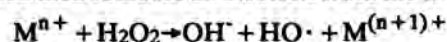
The known products from irradiation of the model substances and the reaction conditions are listed in the following Table.

Degradation of the Model Substances Using Peroxides and Heat

Another way to build radicals is to heat the model substance with a peroxide present. The mechanism by which radicals are produced under the experimental conditions is uncertain and depends upon the matrix. Two mechanisms are known for the formation of radicals using hydrogen peroxide, but they only are recognized under certain conditions. One mechanism assumes that the peroxide removes an electron from the model substance:



The other mechanism assumes that the peroxide takes an electron from trace metals present in the glassware surfaces or within the model substance to produce a radical, which then removes an electron from the model substance:



Investigations of chlorinated hydrocarbon degradation using peroxides have been done by several groups. Table II summarizes their experiments and results.

TABLE I
Irradiation Products From Literature

Substance	Dose	Matrix	Temperature	Products
(2) C ₂ Cl ₆	2.1x10 ¹⁷ eV mL ⁻¹ min ⁻¹	cyclohexane	24-100°C	pentachloroethane chlorocyclohexane tetrachloroethylene HCl
(3) C ₂ Cl ₆	5.25x10 ¹⁷ -2.80x10 ¹⁹ eV/g-h	methanol ethanol 2-propanol	0-50°C	HCl pentachloroethane tetrachloroethane tetrachloroethylene assorted carbonyl compounds
(4) γ-HCH	5x10 ⁵ R/h	2-propanol		tetrachlorocyclohexene pentachlorocyclohexane
(5) γ-HCH	54 Mrad	n-hexane		trichlorobenzene tetrachlorocyclohexadiene tetrachlorobenzene pentachlorocyclohexene hexachlorobenzene heptachlorocyclohexane

TABLE II

Peroxide Products-From Literature

<u>Substance</u>	<u>Matrix</u>	<u>Temperature</u>	<u>Products</u>
(8) α -HCH	30% H ₂ O ₂ solution H ₂ O ₂ , H ₂ O	220°C	assorted PCDD's
(1) α -HCH β -HCH		220°C	chlorobenzene dichlorobenzene trichlorobenzene pentachlorocyclohexene chlorophenol dichlorophenol trichlorophenol
(1) α -HCH β -HCH	NiO ₂	220°C	chlorobenzene dichlorobenzene trichlorobenzene tetrachlorobenzene pentachlorobenzene pentachlorocyclohexene

TABLE III

Biological Products-From Literature

<u>Substance</u>	<u>Matrix</u>	<u>Temperature</u>	<u>Products</u>
(11) γ -HCH	various bacterial cultures	28°C	pentachlorocyclohexene α -tetrachlorocyclohexene β -tetrachlorocyclohexene γ -tetrachlorocyclohexene pentachlorobenzene
(12) γ -HCH	anaerobically incubated in sewage sludge Bowdoin clay loam soil	37°C	γ -tetrachlorocyclohexene benzene
(13) γ -HCH	assay mixtures with cell-free Clostridium sphenoides	30°C	γ -tetrachlorocyclohexene
(14) γ -HCH	various bacterial cultures	25°C	tetrachlorobenzene trichlorobenzene α -hexachlorocyclohexane β -hexachlorocyclohexane
(15) Aroclor 1242 (commercial PCB mixture registered trademark of Monsanto company)	various bacterial cultures	20°C	isohexane isooctane ethylbenzene isohexane isopropylbenzene n-propylbenzene isobutylbenzene n-butylbenzene isononane

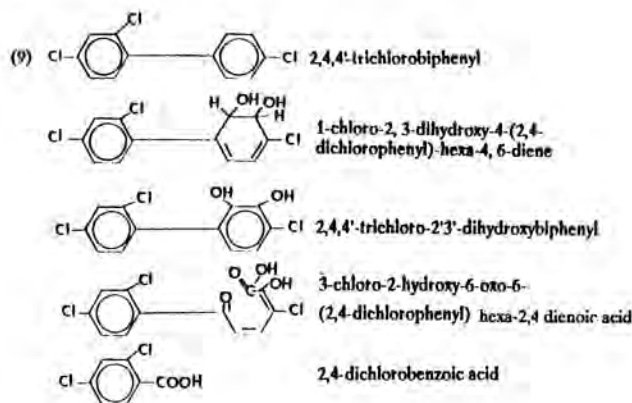
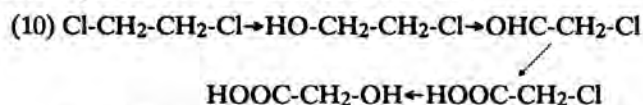


Fig. 1. Biological degradation mechanism of 2,4,4'-trichlorobiphenyl.

Degradation of the Model Substances Using Biological Pathways

Microorganisms can break down chlorinated hydrocarbons into various products. The pathway by which the bacteria *Acinetobacter* sp. P6 metabolizes 2,4,4'-trichlorobiphenyl is illustrated in Fig. 1.

The breakdown of dichloroethane with *Xanthobacter autotrophicus* GJ10 has also been studied:



Several groups have done studies on the microbial degradation of lindane (γ -HCH) and polychlorinated biphenyls (PCBs). Their results are listed in Table III.

Radical Degradation of Chlorinated Hydrocarbons-Procedure

Materials hexachloroethane, hexane, and acetone used were of technical grade. The following chemicals were obtained from Piedad-de Haën AG: β -HCH, 98% pure, hexachlorophene, 99% pure, lindane, technical grade; and hexachlorobenzene, technical grade.

The GC system was the Sichromat I manufactured by Siemens. The MS was an ion trap detector manufactured by Finnegan.

GC program:

starting temperature: 30°C for four minutes

temperature increase rate: 10°C/min to 280°C, 5 min at 280°C

mass range: 50-599 amu

background mass: 45 amu

No.	Substance	Amount (mg)	Dose (Gy)
R1	β -HCH	9.34	5×10^4
R2	β -HCH	8.10	5×10^4
R3	β -HCH	9.59	5×10^5
R4	β -HCH	11.08	5×10^5
R5	C ₂ Cl ₆	9.12	5×10^4
R6	C ₂ Cl ₆	8.57	5×10^4
R7	C ₂ Cl ₆	11.97	5×10^5
R8	C ₂ Cl ₆	9.17	5×10^5
R9	γ -HCH	9.31	5×10^4
R10	γ -HCH	10.67	5×10^4
R11	γ -HCH	8.19	5×10^5
R12	γ -HCH	10.84	5×10^5
R13	HCB	7.95	5×10^4
R14	HCB	8.10	5×10^4
R15	HCB	10.09	5×10^5
R16	HCB	11.10	5×10^5
R17	C ₁₃ H ₆ Cl ₆ O ₂	10.64	5×10^4
R18	C ₁₃ H ₆ Cl ₆ O ₂	11.75	5×10^4
R19	C ₁₃ H ₆ Cl ₆ O ₂	11.44	5×10^5
R20	C ₁₃ H ₆ Cl ₆ O ₂	7.75	5×10^5
R21	C ₂ Cl ₆	7.71	5×10^4
R22	H ₂ O	6.12	
R22	C ₂ Cl ₆	8.49	5×10^4
R22	H ₂ O	8.80	
R23	C ₂ Cl ₆	10.13	5.10^5
R23	H ₂ O	10.02	
R24	C ₂ Cl ₆	7.61	5×10^5
R24	H ₂ O	10.16	
R25	β -HCH	11.56	5×10^4
R25	H ₂ O	9.37	
R26	β -HCH	10.51	5×10^4
R26	H ₂ O	9.74	
R27	β -HCH	10.21	5×10^5
R27	H ₂ O	9.75	
R28	β -HCH	10.23	5×10^5
R28	H ₂ O	10.04	
R29	γ -HCH	9.96	5×10^4
R29	H ₂ O	9.93	
R30	γ -HCH	9.65	5×10^4
R30	H ₂ O	9.85	
R31	γ -HCH	9.13	5×10^5
R31	H ₂ O	10.00	
R32	γ -HCH	11.86	5×10^5
R32	H ₂ O	10.02	
R33	C ₆ Cl ₆	8.56	5×10^4
R33	H ₂ O	9.72	
R34	C ₆ Cl ₆	6.72	5×10^4
R34	H ₂ O	9.91	
R35	C ₆ Cl ₆	10.91	5×10^5

DATA TABLE C

				No.	Substance	Amount (mg)	Heat Time (hrs)
R37	H ₂ O	10.01					
	C ₁₃ H ₆ Cl ₆ O ₂	9.81	5x10 ⁴				
	H ₂ O	8.48		21	C ₂ Cl ₆	14.20	2
R38	C ₁₃ H ₆ Cl ₆ O ₂	9.97	5x10 ⁴		NiO ₂	15.83	
	H ₂ O	8.81		22	C ₂ Cl ₆	8.42	2
R39	C ₁₃ H ₆ Cl ₆ O ₂	7.75	5x10 ⁵		NiO ₂	12.97	
	H ₂ O	6.67		23	C ₂ Cl ₆	10.27	24
R40	C ₁₃ H ₆ Cl ₆ O ₂	10.04	5x10 ⁵		NiO ₂	10.63	

DATA TABLE B

No.	Substance	Amount (mg)	Heat Time (hrs)	No.	Substance	Amount (mg)	Heat Time (hrs)
1	C ₂ Cl ₆	8.14	2	25	β-HCH	10.60	2
	H ₂ O ₂	11.21		26	NiO ₂	15.08	
2	C ₂ Cl ₆	9.31	2	27	β-HCH	10.01	2
	H ₂ O ₂	11.31		28	NiO ₂	15.91	
3	C ₂ Cl ₆	11.43	24	29	β-HCH	11.71	24
	H ₂ O ₂	11.58		30	NiO ₂	12.80	
4	C ₂ Cl ₆	11.00	24	31	β-HCH	17.79	24
	H ₂ O ₂	11.56		32	NiO ₂	21.43	
5	β-HCH	9.64	2	33	γ-HCH	8.13	2
	H ₂ O ₂	12.22		34	NiO ₂	11.37	
6	β-HCH	11.06	2	35	γ-HCH	8.73	2
	H ₂ O ₂	10.05		36	NiO ₂	23.83	
7	β-HCH	10.10	24	37	γ-HCH	10.99	24
	H ₂ O ₂	12.21		38	NiO ₂	11.28	
8	β-HCH	8.79	24	39	γ-HCH	9.04	24
	H ₂ O ₂	12.26		40	NiO ₂	10.11	
9	γ-HCH	9.85	2		HCb	13.55	2
	H ₂ O ₂	11.88			NiO ₂	14.48	
10	γ-HCH	8.21	2		HCb	9.33	2
	H ₂ O ₂	12.14			NiO ₂	16.54	
11	γ-HCH	9.77	24		HCb	9.66	24
	H ₂ O ₂	12.25			NiO ₂	11.43	
12	γ-HCH	8.80	24		HCb	10.79	24
	H ₂ O ₂	12.26			NiO ₂	13.61	
13	C ₆ Cl ₆	7.18	2		C ₁₃ H ₆ Cl ₆ O ₂	11.62	2
	H ₂ O ₂	12.14			NiO ₂	12.58	
14	C ₆ Cl ₆	8.53	2		C ₁₃ H ₆ Cl ₆ O ₂	11.91	2
	H ₂ O ₂	12.01			NiO ₂	14.58	
15	C ₆ Cl ₆	11.04	24		C ₁₃ H ₆ Cl ₆ O ₂	10.79	24
	H ₂ O ₂	13.33			NiO ₂	12.18	
16	C ₆ Cl ₆	7.91	24		C ₁₃ H ₆ Cl ₆ O ₂	12.30	24
	H ₂ O ₂	11.42			NiO ₂	13.15	
17	C ₁₃ H ₆ Cl ₆ O ₂	8.57	2				
	H ₂ O ₂	12.48					
18	C ₁₃ H ₆ Cl ₆ O ₂	9.67	2				
	H ₂ O ₂	12.16					
19	C ₁₃ H ₆ Cl ₆ O ₂	8.32	24				
	H ₂ O ₂	12.03					
20	C ₁₃ H ₆ Cl ₆ O ₂	10.35	24				
	H ₂ O ₂	11.68					

split injection: 15 mL/min
sample volume: 1 μ L
GC-column: HT5/25m
film thickness-0.1 μ m
0.33-ID
manufactured by J.E.W.
mass detect: 60 mmu
carrier gas: helium
carrier gas pressure: 0.8 bar
open coupling

RADICAL DEGRADATION OF CHLORINATED HYDROCARBONS-PROCEDURE

Formation of Radicals with Gamma-Irradiation

Approximately ten mg of model substance was placed in a capillary tube. The capillary tube was then sealed by melting the open end until it closed. These samples were then irradiated with gamma radiation.

Formation of Radicals with Hydrogen Peroxide

Approximately 10 mg of model substance and 10 μ L H₂O₂ were placed in a capillary tube. The samples were heated for either two or 24 hours at 220°C. The sample contents are listed in Data Table B.

Formation of Radicals with Nickel Peroxide

The open end of a micropipette was melted until it closed. Approximately 10 mg of model substance and 10 mg of nickel peroxide were placed in the micropipette's tube. The tube was separated from the rest of the micropipette by melting it in the middle and pulling it apart into two sections, one section containing sample and the other empty. The sections containing sample were heated at 220°C for either two or 24 hours. The sample contents are listed in Data Table C.

Preparation of Samples to be Analyzed

After the irradiation or heating was completed, the capillary tube was placed in a test tube that contained 100 μ L hexane or acetone. The capillary tube was crushed with a glass stick against the walls of the test tube, and the solution was mixed. The liquid was pipetted from the crushed glass and could be analyzed with GCMS without further sample preparation.

RESULTS

Tables IV-VIII list the degradation products obtained from each sample. Table IX provides the key for the product numbers.

Contamination with hexachlorocyclohexane and hexachlorobenzene was found in most of the samples. The contamination was due to performing experimental work in a glove box, which was impossible to keep free from trace contamination.

The hexachloroethane samples (Table IV) contains hexachlorocyclo-hexane and hexachlorobenzene, but this is probably due to contamination as explained above. Hexachlorobutadiene and hexachloropropene were also found, along with pentachloroethane.

The β -hexachlorocyclohexane samples (Table V) contains hexachloroethane due to contamination. The samples treated with peroxides produced various chlorinated benzenes, phenols, and traces of trichloro- and tetrachlorobiphenyls. Those samples treated with radiation produced hexachlorobenzene, trichlorobenzene, and traces of tetrachlorobenzene. Those samples that were mixed with water before irradiation also produced chlorophenol, dichlorophenol, and trichlorophenol.

Both the peroxide treatment and the irradiation produced chlorinated benzenes from γ -hexachlorocyclohexane (Table VI). Chlorinated phenols were produced after peroxide treatment and in irradiated samples that had water present. The hexachloroethane found in sample R31 was due to contamination. A substance that could not be identified was found at a base peak of 253 amu possessing four to six chlorine atoms.

Hexachlorobenzene (Table VII) did not give many degradation products. It was inert to radiation, and peroxide treatment produced only trichlorobenzene and pentachlorobenzene. The hexachlorocyclohexane found was due to contamination.

The hexachlorophene samples (Table VIII) also did not degrade when it was irradiated. The peroxide treatment produced chlorinated phenols. The hexachloroethane, hexachlorocyclohexane, and the hexachlorobenzene present were due to contamination.

In the samples containing the model substances hexachloroethane, β -hexachlorocyclohexane, and hexachlorophene, an additional substance was found. It had a base peak of about 464 amu and a typical pattern for a chlorinated molecule with eight or nine chlorine atoms. A standard solution of C₁₃H₆Cl₆O₂ injected into the GC also produced this substance; therefore, the substance was probably built inside the GC injector.

TABLE IV
C₂Cl₆

Degradation Product	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	
Sample No.	↓																					
1	*	*					*															
3	*	*					*															
21	*	*					*					*										
23	*	*					*					*										
R5	*	*					*															*
R7	*	*					*											*				
R21	*	*					*					*						*		*	*	
R23	*	*					*					*						*		*	*	

TABLE V
β-HCH

Degradation Product	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	
Sample No.	↓																					
5		*		*	*	*	*	T		*												
7		*	T	*	*	*	*	T		*												
25		*	*	*	*	*	*	*	*	*		*		T	T							
27		*	*	*	*	*	*	*	*	*		*		T	T							
R1		*					*															
R3		*		*			*															T
R25	*	*		T	*		*	*	*	*		*										
R27	*	*		*	T		*	*	*	*		*										

TABLE VI
γ-HCH

Degradation Product	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	
Sample No.	↓																					
10		*	T	*	T		*		*	*												
11		*	T	*	T		*		*	*	*											
29		*	*	*	*	*	*		*	*												
31		*	*	*	*	*	*	*	*	*	T			T	T	T						
R9		*	*	*	*		T															*
R11		*	*	*	*	*	*															*
R29		*	*	*	*	T	*															*
R31	*	*	*	*	*	*	*															*

TABLE VII
HCB

Degradation Product	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Sample No.	↓																				
13		*		*			*														
15		*					*														
33		*		*		*	*														
35		*				*	*														
R13		*					*														
R15		*					*														
R33		*					*														
R35		*					*														

TABLE VIII
C₁₃H₆Cl₆O₂

Degradation Product	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Sample No.	↓																				
17		*								*	T									*	
19		*					*			*	T									*	
37		*					*		*	*										*	
39		*					*		*	*										*	
R17		*					*													*	
R19		*					*			T										*	
R37		*					*													*	
R39	*	*					*													*	

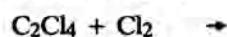
TABLE IX

- | | |
|--------------------------|---------------------------------------|
| 1. Hexachloroethane | 12. Hexachlorobutadiene |
| 2. Hexachlorocyclohexane | 13. Tetrachloroethane |
| 3. Dichlorobenzene | 14. Trichlorobiphenyl |
| 4. Trichlorobenzene | 15. Tetrachlorobiphenyl |
| 5. Tetrachlorobenzene | 16. Hexachlorobiphenyl |
| 6. Pentachlorobenzene | 17. Hexachloropropene |
| 7. Hexachlorobenzene | 18. Heptachlorocyclohexane |
| 8. Chlorophenol | 19. Pentachloroethane |
| 9. Dichlorophenol | 20. Unknown with base peak at 464 amu |
| 10. Trichlorophenol | 21. Unknown with base peak at 253 amu |
| 11. Tetrachlorophenol | |

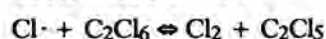
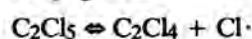
DISCUSSION AND CONCLUSIONS

A comparison can now be made between the products of the different methods. Hexachloroethane yielded the same main degradation product, hexachlorobutadiene, when heated with NiO₂ for 24 hours and when irradiated in the presence of water. Irradiation also yielded hexachloropropene and pentachloroethane. Pentachloroethane was probably formed by the following mechanism:

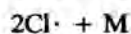
Primary initiation



Propagation



Termination



β -hexachlorocyclohexane degraded to the same products if NiO₂ and irradiation in the presence of water were used. H₂O₂ also degraded β -hexachlorocyclohexane to some of the same products as the aforementioned methods.

γ -hexachlorocyclohexane yielded the same major benzene products whether it was treated with peroxides or radiation. The peroxide method also produced dichloro- and trichlorophenol, which weren't produced by radiation.

Irradiation did not degrade hexachlorobenzene at all, but the NiO₂ caused some dechlorination, producing pentachlorobenzene. Hexachlorophene also was inert to radiation, but H₂O₂ and NiO₂ built small amounts of chlorinated phenols.

Looking only at the major degradation products, it can be seen that the irradiation and the peroxide degradation produced nearly the same products. In the cases of the model substances β - and γ -hexachlorocyclohexane, hexachlorobenzene, and hexachlorophene, the peroxide degradation produced more products in addition to those produced by the irradiation. This shows that the model substances are much more reactive with the peroxides than the radiation. A γ -radiation dose higher than 5×10^5 Gy would probably produce the same results as the peroxide degradation.

The case of hexachloroethane was different from the other model substances. There were more degradation

products in the irradiated samples than in those mixed with peroxide. The additional products were pentachloroethane and hexachloropropene. The reason for this difference is that hexachloroethane is not cyclic. Aromatic substances are more stable than alkanes against irradiation (17), as shown in this paper by radiations' inability to degrade hexachlorobenzene and hexachlorophene. Hexachlorocyclohexane degraded mainly to aromatic hydrocarbons. Since hexachloroethane is an alkane, it was possible for it to degrade into more products than the other model substances.

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