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## INVESTIGATING THE DECHLORINATION PATHWAY OF HEXACHLOROBENZENE IN ACETONE THROUGH GAMMA IRRADIATION

Samir KARIMOV<sup>1\*</sup>, Elshad ABDULLAYEV<sup>2</sup>, Muslum GURBANOV<sup>3</sup>, Lala GASIMZADA<sup>1</sup>

<sup>1</sup>French-Azerbaijani University under Azerbaijan State Oil and Industry University,

Baku, Azerbaijan

<sup>2</sup>Sumgait State University,

Sumgait, Azerbaijan

<sup>3</sup>Institute of Radiation Problems,

Baku, Azerbaijan

\*Corresponding author.

E-mail: samir.karimov@ufaz.az (S. Karimov), elshad.abdullayev@sdu.edu.az (E. Abdullayev)

ARTICLE INFO	ABSTRACT
<p>Article history:</p> <p>Received:2024-07-26</p> <p>Received in revised form:2024-09-13</p> <p>Accepted:2024-10-18</p> <p>Available online</p>	<p>Hexachlorobenzene (HCB), a persistent organic pollutant, poses significant environmental and health risks due to its stability and bioaccumulation. This study investigates the degradation of HCB in acetone using gamma irradiation. Gamma radiolysis was performed using a <sup>60</sup>Co source, and the resultant radiolytic products were analyzed through Gas Chromatography-Mass Spectrometry (GC-MS). Mass spectral analysis revealed the formation of various by-products, including lower chlorinated benzenes (CBs) – penta- (PCB), tetra-(TeCB), trichlorobenzene (TCB) – and other chlorinated and non-chlorinated compounds, indicating a complex dechlorination pathway. Detailed investigation of the degradation pathway suggested sequential dechlorination and breakdown of the HCB molecule under gamma irradiation. The effects of different radiation doses on the degradation efficiency were also explored. Results demonstrated significant reduction in HCB concentration, highlighting gamma irradiation as a viable method for the remediation of HCB-contaminated environments.</p>
<p>Keywords:</p> <p>Hexachlorobenzene</p> <p>Radiation chemistry</p> <p>Nuclear energy</p> <p>POPs</p> <p>Environmental remediation</p> <p>JEL CODES: Q53, Q55, Q57, Q65</p>	

## 1. Introduction

HCB is a persistent organic pollutant (POP) known for its environmental persistence, bioaccumulative nature, and toxicity to both human health and ecosystems [1]. Historically used as a fungicide and industrial chemical, HCB has been banned or restricted in many countries due to its hazardous properties including Azerbaijan [2]. Despite these measures, significant amounts of HCB remain in the environment, necessitating effective remediation techniques.

Traditional methods for the degradation of HCB, such as thermal, chemical, and biological treatments are applied [3, 4, 5]. These methods often face limitations in efficiency, cost, and potential secondary pollution [6, 7, 8]. Consequently, alternative approaches are being explored to address these challenges including advanced oxidation processes [9, 10, 11, 12, 13, 14]. One promising technique is gamma radiolysis, which involves the use of high-energy gamma photons from a  $^{60}\text{Co}$  source to induce chemical reactions that break down complex pollutants into simpler, less harmful compounds [15, 16, 17, 18].

Gamma radiolysis has shown potential in the degradation of various chlorinated compounds due to its ability to generate reactive species such as hydroxyl radicals ( $\bullet\text{OH}$ ) and solvated electrons ( $e_{\text{sol}}^-$ ) [19, 19]. These reactive species can effectively cleave carbon-chlorine bonds, leading to the dechlorination of the target pollutants. Previous studies, including our own on the gamma radiolysis of TCB in methanol, ethanol, hexane, and benzene, have demonstrated the efficacy of gamma radiolysis and revealed that the choice of solvent significantly influences the degradation pathway and products formed [16].

This study focuses on the gamma radiolysis of HCB in acetone, a widely used solvent known for its high solubility and moderate reactivity. Acetone's unique properties may affect the stability and reactivity of the intermediates formed during radiolysis, thereby influencing the overall degradation process. By identifying the primary and secondary products of HCB degradation in acetone, this research aims to elucidate the mechanisms involved and assess the potential of gamma radiolysis as a viable method for the remediation of HCB-contaminated environments.

## 2. Materials and methods

The similar method applied in our previous investigation has been applied in this study as well [15].

>99% pure HCB was purchased from Merck, while acetone was of gradient grade and obtained from LiChrosolv. All chemicals were used as received without further purification. Standard solutions of HCB were prepared in acetone at a concentration of approximately 0.06 g/L for the gamma irradiation experiments and calibration of GC-MS.

Irradiation was performed using an MRX- $\gamma$ -25 apparatus equipped with a  $^{60}\text{Co}$  source. The solutions were irradiated without degassing to maintain the presence of air. The samples were subjected to various doses to investigate the dose-dependent degradation of HCB.

Post-irradiation, the samples were analyzed using gas chromatography-mass spectrometry (GC-MS) to identify the degradation products of HCB. The GC-MS analysis was conducted using a Shimadzu QP2010 SE instrument equipped with a Rxi-5ms capillary column (30 m  $\times$

0.25 mm, 0.25  $\mu\text{m}$  film thickness). The following conditions were used for the analysis: Helium was used as the carrier gas at a flow rate of 1 mL/min. The injection mode was split with an injection volume of 1  $\mu\text{L}$ . The oven temperature program started at an initial temperature of 30°C (held for 2 minutes), ramped to 320°C (held for 2 minutes) at 10°C/min rate. MS detection was conducted in electron impact ionization (EI) mode at 70 eV, with the mass spectrometer operating in Scan mode to enhance sensitivity and selectivity for the chlorinated products.

### 3. Results and Discussion

The gamma radiolysis of HCB in acetone results in a diverse array of degradation products. Below, we provide a detailed analysis and discussion of the findings, supported by chromatograms, mass spectra, and a summary table of the identified compounds.

#### 3.1. Chromatographic Analysis

The gas chromatograms of the HCB solution before and after, 25.1 kGy gamma irradiation are shown in Figure 1. GC chromatogram of HCB in acetone: A) before gamma irradiation; B) after 25.1 kGy gamma irradiation. A and B respectively.

The pre-irradiation chromatogram displays a single dominant peak corresponding to HCB at a retention time of 17.47 minutes. Post-irradiation, additional peaks appear at different retention times, indicating the formation of degradation products such as dechlorination products of PCB and TeCBs.

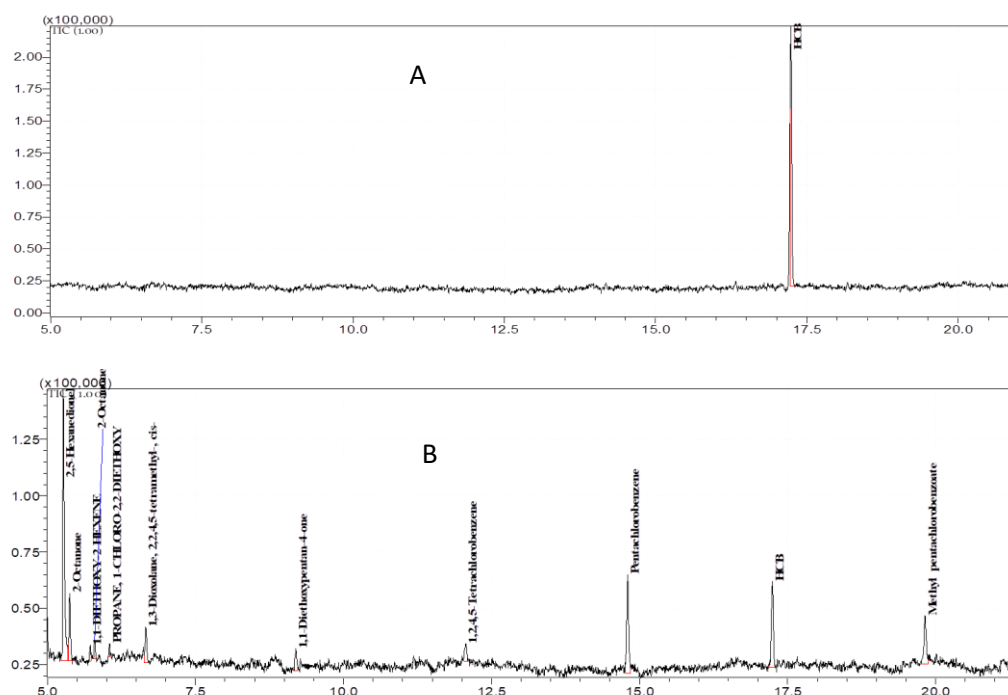


Figure 1. GC chromatogram of HCB in acetone: A) before gamma irradiation; B) after 25.1 kGy gamma irradiation.

#### 3.2. Mass Spectrometric Analysis

Mass spectra for the products were obtained to confirm their identities. For instance, the mass spectrum of pentachlorobenzene (PeCB) (Figure 2 (2)) shows a molecular ion at 250  $m/z$ , with significant fragment ions at  $m/z$  215 and 180, while the mass spectrum of

tetrachlorobenzene (TeCB) (Figure 2) shows a molecular ion at 216 m/z, confirming their identity.

All 20 identified products and HCB at different radiation doses have been numbered according to their respective numbers in

Table 1. The corresponding peak areas of these compounds have also been provided at the relevant absorbed doses. Although it is not the primary aim of this report, information on the quantitative changes can also be inferred from the peak areas of the compounds in the chromatograms given in

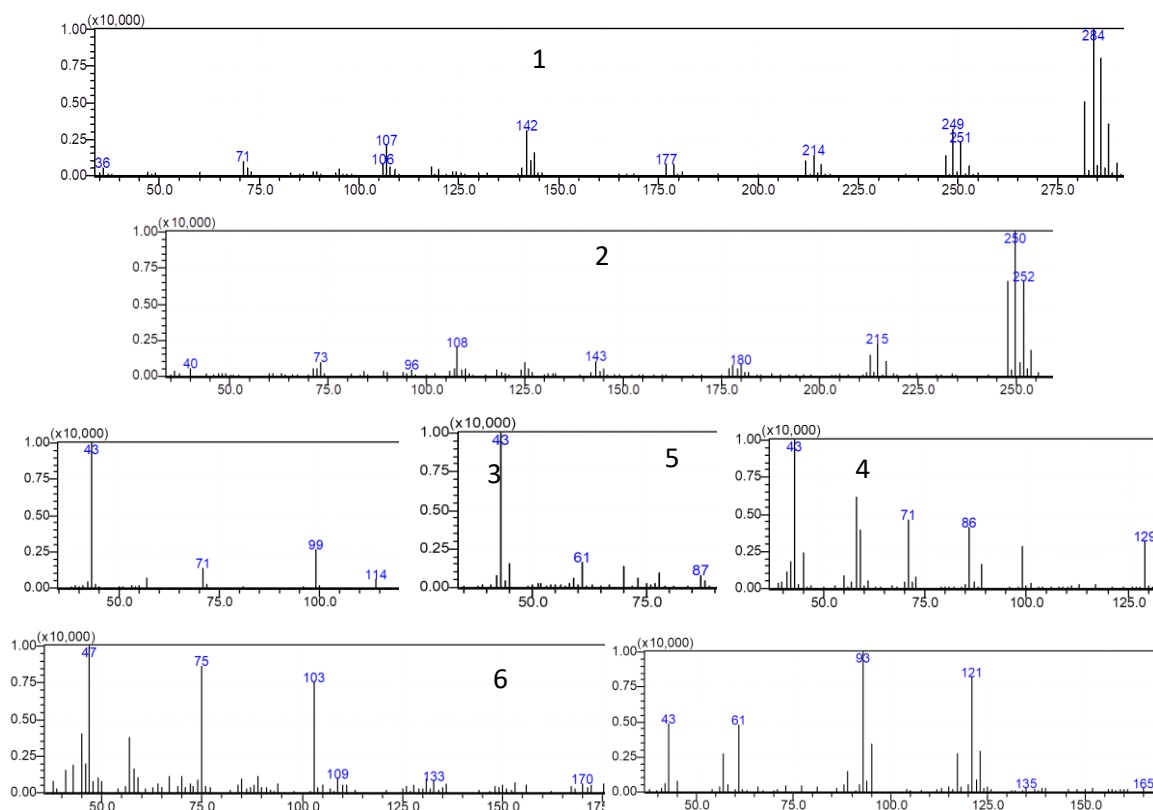
Table 1.

### 3.3. Mechanistic Insights of product formations

The gamma radiolysis of HCB in acetone leads to the formation of a wide variety of products through several distinct mechanisms:

1. Dechlorination: Dechlorination of HCB results in compounds such as PCB, 1,2,4,5-TeCB and 1,2,4-TCB. These intermediates suggest a stepwise removal of chlorine atoms facilitated by the high-energy gamma photons. These products indicate interactions between hydrogen radicals – forms from the radiolysis of acetone – and HCB.

2. Oxidation: The radiolytic conditions favor oxidation reactions, producing ketones, including: 2,5-hexanedione; 3,4-dihydroxy-3,4-dimethyl-hexan-2,5-dione; 2-octanone; 1,1-diethoxypentan-4-one; 4-methyl-pent-4-en-2-one and 2-hexanone, 6-(acetoxy). The formation of carboxylic acid - 2-ethyl-butanoic acid further highlights the oxidative pathways. Those products are expected to form due to interaction between oxygen and other compounds available in irradiated systems.



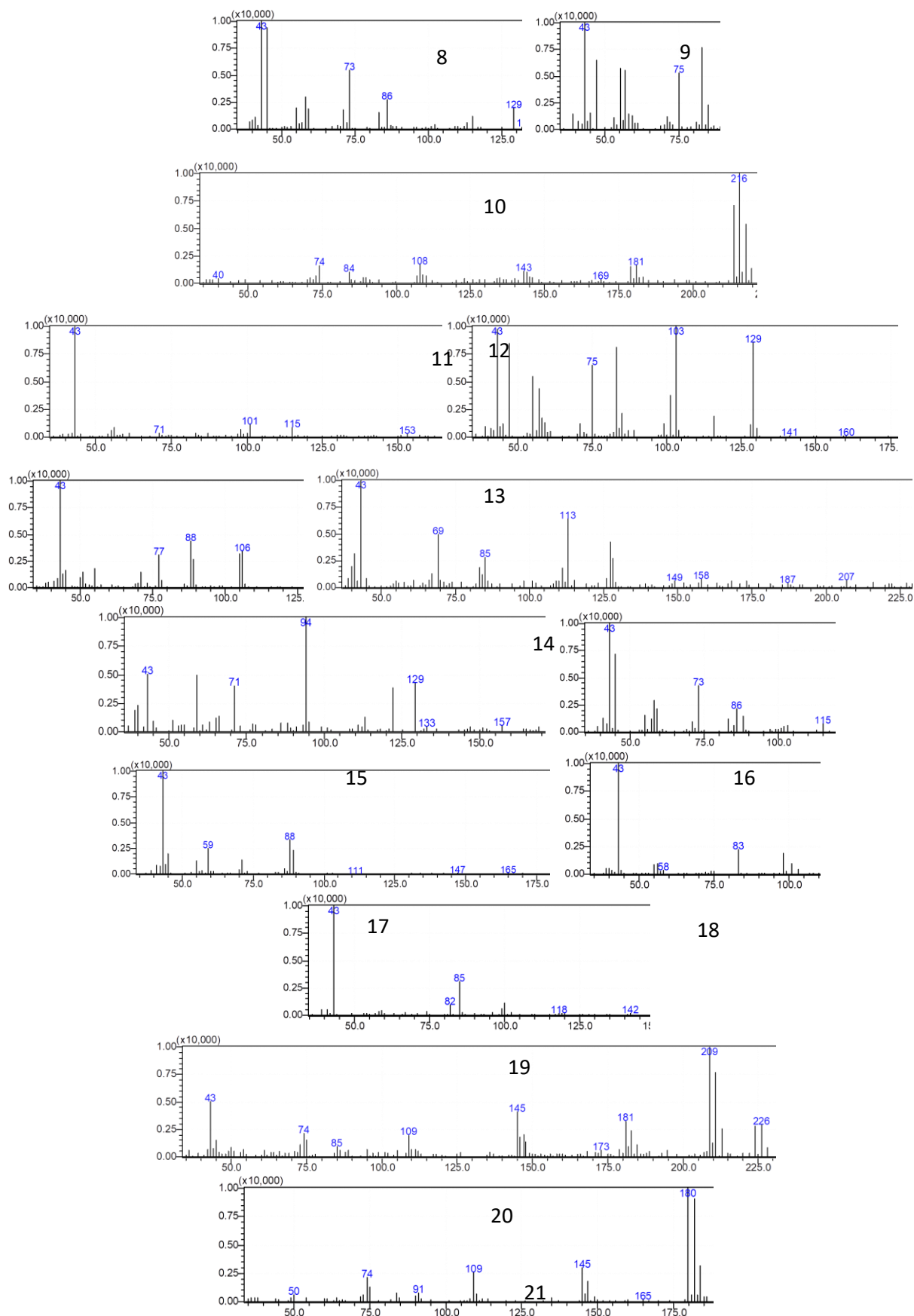


Figure 2. Mass spectra and appropriate structures of identified products post-irradiation.

3. Substitution and Esterification: The formation of methyl pentachlorobenzoate; ethyl acetate; pentanoic acid 3-hydroxy-5,5-dimethoxy-3-methyl-,ethyl ester; phenyl butyrate; acetic acid 1-methyl-3-oxo-but-1-enyl ester points to substitution and esterification reactions. These products indicate interactions between the reactive species – primary products of radiolysis of acetone – and acetone itself.

4. Formation of Ethers and Acetals: Compounds 1,1-diethoxy-hexen-2; 1-chloro-2,2-diethoxy-propane demonstrate the incorporation of ethoxy groups, indicating the formation of ether and acetal structures.

5. Reduction: The presence of alcohols – 1-(2,4,5-trichlorophenyl)-ethanol and 1-propoxy-2-propanol suggests reduction reactions are also occurring, reducing the chlorinated intermediates to their corresponding alcohols.

These results illustrate the complex interplay of radiolytic reactions occurring during the gamma irradiation of HCB in acetone. The identification of diverse products underscores the versatility of gamma radiolysis in degrading POPs. This study's findings provide a comprehensive understanding of the degradation pathways and highlight the potential of gamma irradiation for environmental remediation applications.

**Table 1.** Identified products from gamma irradiated acetone solutions of HCB

No.	Name of products	Dose, kGy							
		0	3.1	6.3	12.6	25.1	50.2	100.5	169.5
		Area of the peaks							
1	HCB	351385	404961	358657	89111	43369	0	0	0
2	PCB	0	0	27165	82967	99272	76092	22069	0
3	2,5-hexanedione	0	0	0	116593	229362	277026	401050	865129
4	Ethyl acetate	0	0	0	19967	0	0	0	0
5	2-octanone	0	0	0	0	49594	9883	26850	0
6	1,1-diethoxy-2-hexene	0	0	0	0	8342	13266	-	30405
7	Propane, -1-chloro-2,2-diethoxy	0	0	0	0	8082	0	0	0
8	1,3-dioxolane, 2,2,4,5-tetramethyl-, cis-	0	0	0	0	30860	0	0	28090
9	1,1-diethoxypentan-4-one	0	0	0	0	20935	53370	139574	0
10	1,2,4,5-TeCB	0	0	0	0	19720	50262	31735	0
11	Methyl pentachloro benzoate	0	0	0	0	61106	38570	0	0
12	2-hexanone, 6-(acetoxyl)	0	0	0	0	0	11872	31985	12639
13	2-ethylbutanoic acid	0	0	0	0	0	0	24869	0
14	Pentanoic acid, 3-hydroxy-5,5-dimethoxy-3-methyl-,ethyl ester	0	0	0	0	0	0	10109	0
15	Phenyl butyrate	0	0	0	0	0	0	20474	0
16	1-propoxy-2-propanol	0	0	0	0	0	0	43389	81081
17	3,4-dihydroxy-3,4-dimethyl-hexan-2,5-dione	0	0	0	0	0	0	0	33877
18	4-methyl-pent-4-en-2-one	0	0	0	0	0	0	0	20624
19	Acetic acid 1-methyl-3-oxo-but-1-enyl ester	0	0	0	0	0	0	0	12639
20	1-(2,4,5-trichlorophenyl) ethanol	0	0	0	0	0	0	0	15015
21	1,2,4-Trichlorobenzene	0	0	0	0	0	0	14015	0

### 3.4. Analysis of Degradation Patterns Under Gamma Radiation

The observed changes in the peak areas of various compounds subjected to increasing doses of gamma radiation illustrate distinct degradation and formation patterns as shown in Figure 3 as well.

Initially, HCB displays a high peak area at 0 kGy, which gradually decreases with increasing dose, becoming 0 by 25.1 kGy. This trend indicates that HCB undergoes extensive degradation as the radiation dose increases.

PCB is not detected at lower doses but emerges at 6.3 kGy, with its peak area increasing up to 25.1 kGy before diminishing at higher doses. This suggests that PCB is a by-product of HCB degradation and itself undergoes further degradation with higher radiation exposure.

The compound 2,5-hexanedione appears at 12.6 kGy, with its peak area steadily

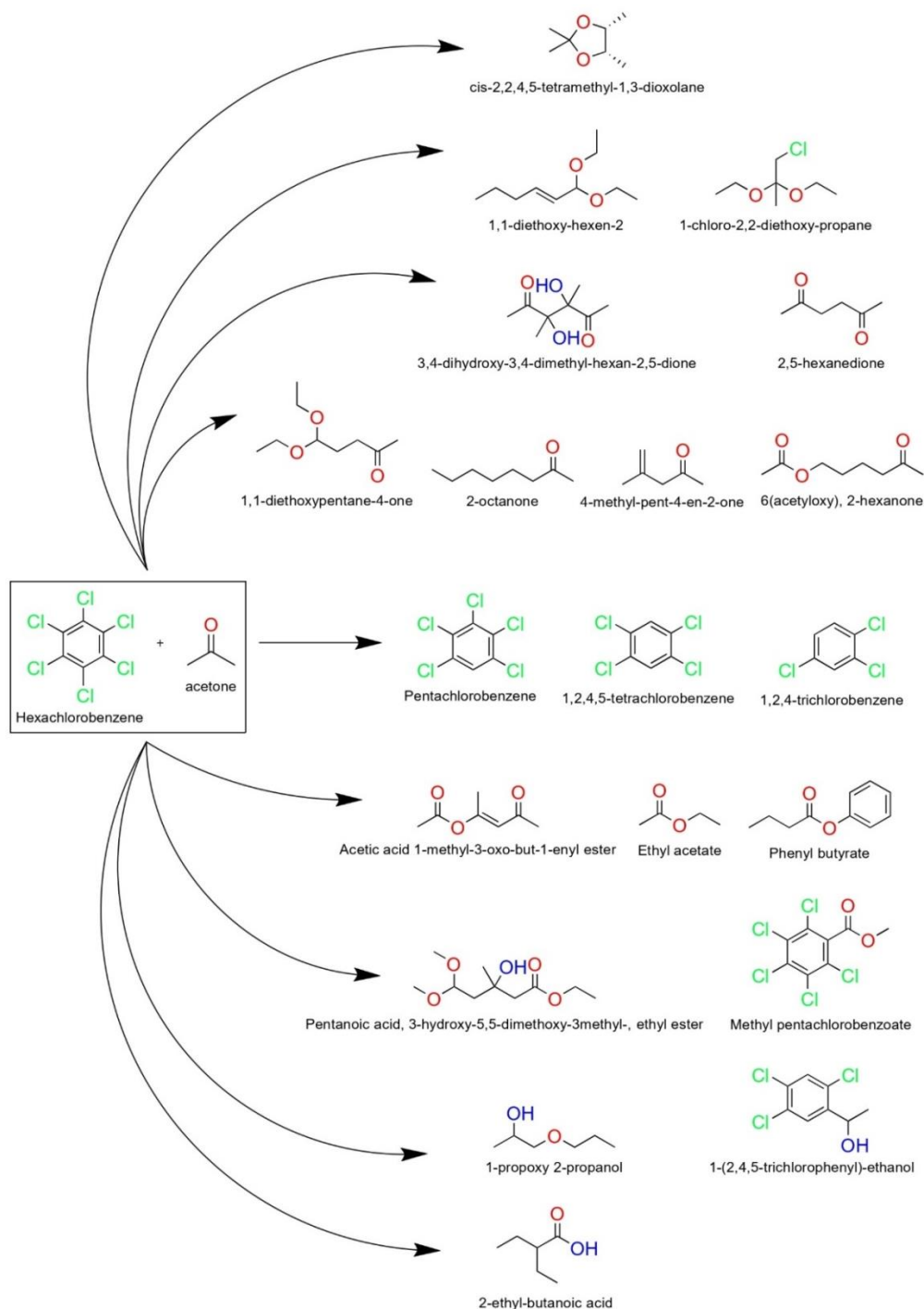


Figure 3. Overall pathways of HCB + acetone irradiation under gamma rays

increasing up to 169.5 kGy, indicating it is a stable by-product formed at higher doses. Ethyl acetate is detected only at 12.6 kGy, suggesting transient formation and instability at higher doses. Similarly, 2-octanone appears at 25.1 kGy, increases at 50.2 kGy, but is not present at higher doses, indicating formation at intermediate doses followed by degradation or volatility.

The presence of 1,1-diethoxy-2-hexene is first detected at 50.2 kGy, with its peak area increasing at 100.5 kGy before slightly diminishing, indicating late formation and some stability under high radiation. Propane-1-chloro-2,2-diethoxy is only present at 50.2 kGy, suggesting specific formation conditions that do not persist at higher doses. Similarly, 1,3-dioxolane, 2,2,4,5-tetramethyl-, cis- appears at 50.2 kGy but not at higher doses, indicating formation under specific conditions and instability at higher radiation levels.

The compound 1,1-diethoxypentan-4-one appears at 50.2 kGy and significantly increases at 100.5 kGy, suggesting formation at higher doses and stability. 1,2,4,5-TeCB is detected from 50.2 kGy, with its peak area increasing and stabilizing at 100.5 kGy, indicating it is a stable degradation by-product.

Methyl pentachloro benzoate appears at 50.2 kGy, with significant peaks at 100.5 kGy, indicating formation and stability at high radiation doses. The compound 2-hexanone, 6-(acetoxo) appears at 100.5 kGy, maintaining a stable peak at 169.5 kGy, suggesting formation and stability at high doses. 2-ethylbutanoic acid and pentanoic acid, 3-hydroxy-5,5-dimethoxy-3-methyl-,ethyl ester are both detected at 100.5 kGy, indicating formation under specific high-dose conditions.

Phenyl butyrate, present at 100.5 kGy, and 1-propoxy-2-propanol, which increases from 100.5 kGy to 169.5 kGy, further indicate formation and stability at high doses. The compound 3,4-dihydroxy-3,4-dimethyl-hexan-2,5-dione is only detected at 169.5 kGy, along with 4-methyl-pent-4-en-2-one and acetic acid 1-methyl-3-oxo-but-1-enyl ester, indicating formation under very high radiation doses. Lastly, 1-(2,4,5-trichlorophenyl)ethanol and 1,2,4-trichlorobenzene (TCB) are present at 169.5 kGy, indicating they are degradation products formed at high doses.

#### **4. Conclusion**

The study demonstrates the effective degradation of HCB in the presence of acetone under gamma irradiation. As the radiation dose increases, HCB significantly degrades, showing the efficacy of gamma rays in breaking down this compound. The process leads to the formation of various by-products, which appear at different stages of irradiation. Intermediate products such as PCB and TeCB emerge at lower doses and either stabilize or degrade further at higher doses into compounds like TCB. The formation of specific compounds at high doses indicates complex degradation pathways and secondary product formation. Overall, the results highlight the potential of gamma irradiation for environmental remediation, providing insights into the mechanisms of radiolytic degradation and the stability of the resulting by-products.



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