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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

RADIATION-CHEMICAL TRANSFORMATION PROCESSES OF CHLORINATED DERIVATIVES OF BENZENE IN VARIOUS ORGANIC SOLVENTS UNDER GAMMA IRRADIATION

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Field of science:	Chemistry
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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and degree of development. The interaction of high-energy gamma irradiation with matter leads to the fragmentation of molecular structures of persistent organic pollutants (POPs), thereby positioning ionizing radiation as an effective, promising, and environmentally sustainable remediation technology[1]. Investigating the concentration changes of substances or their solutions under ionizing radiation, along with the study of radiolysis or radiolytic degradation yields, reaction rates, and kinetic constants, has remained one of the main research objectives to date. In particular, the qualitative identification of intermediate and final products formed during these interactions, and the investigation of changes in their kinetic properties, continues to be a pressing research priority.

POPs, especially hexachlorobenzene (HCB), possess a stable structure due to their aromatic ring and show strong resistance to biodegradation[2]. HCB, which exhibits high toxicity, is present in the environment—including in soils, groundwater, and surface waters—and can easily enter the food chain. As a result, HCB has been detected in various animal tissues and accumulates in the human body, creating significant health risks, particularly an increased likelihood of cancer development[3]. Monitoring studies conducted in Azerbaijan have revealed POP contamination along the Caspian Sea coast as well as in agricultural soils. In some cases, the concentrations of these compounds, whether individually or in combination, exceed the maximum permissible limits established by the European Union.

A variety of physico-chemical methods have been employed for

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[1] Trojanowicz M. Removal of persistent organic pollutants (POPs) from waters and wastewaters by the use of ionizing radiation // The Science of the Total Environment. – 2019. – Vol. 718. – Article 134425.

[2] Kumar J. A. Persistent organic pollutants in water resources: fate, occurrence, characterization and risk analysis / J. A. Kumar, M. M. Cabral-Pinto, S. M. S. Oliveira [et al.] // The Science of the Total Environment. – 2022. – Vol. 831. – Article 154808.

[3] Perelló G. Estimation of the daily intake of hexachlorobenzene from food consumption by the population of Catalonia, Spain: health risks / G. Perelló, J. M. Llobet, A. Castell [et al.] // Food Control. – 2011. – Vol. 23, № 1. – P. 198–202.

the degradation or remediation of POPs, particularly HCB. Conventional methods such as adsorption, chemical oxidation, distillation, and bioremediation have been applied with partial success. However, these technologies often present drawbacks, including the formation of additional toxic by-products, high processing costs, and operational complexity, which limit their practical application. Consequently, there is a strong need for the development of more efficient technologies.

Gamma irradiation-based radiolysis is considered a suitable technological approach for addressing the POP problem. The radiolytic degradation process follows a "zero-additive" principle, in which high-energy photons generate solvated electrons ($e^-_{sol.}$), H·, OH·, CH_2OH· radicals, and other reactive species in the liquid phase of organic solvents. These radicals stimulate dechlorination reactions in chlorinated organic molecules. Thus, the process does not require additional chemical reagents and minimizes the spectrum of by-products.

Radiolytic degradation of POPs has been widely studied mainly in aqueous media, largely due to the extensive scale of water pollution with POPs and their severe ecological consequences[4]. However, POP-containing polar and nonpolar organic solvent mixtures typically arise during the treatment of polychlorinated biphenyl (PCB) oils from energy systems. Due to their high toxicity, these solvent systems require the development of novel remediation technologies. Systematic data on radiation-chemical processes in such systems—including radical formation, molecular interaction mechanisms, radiolytic yields, and kinetic parameters—remain very limited.

Organic solvents were selected as reaction media for the γ-radiolytic degradation of HCB and trichlorobenzene (TCB) for two reasons: (i) these hydrophobic pollutants are almost insoluble in water but form homogeneous media in organic phases; (ii) radicals formed from solvents under γ-irradiation (•CH_2OH, •CH_3, •C_3H_7, etc.) act as strong reducing and dechlorinating agents that accelerate C–Cl bond

[4] Искендерова З. И., Курбанов М. А. Радиационно-химическая деградация 1,2,4-трихлорбензола в водной среде // Химическая Безопасность. – 2018. – Т. 2, № 2(4). – С. 112–118

cleavage. Employing different organic solvents allows for comparative analysis of degradation mechanisms.

Object and subject of the research. HCB and 1,2,4-TCB solutions in methanol, ethanol, isopropanol, hexane, benzene, toluene, as well as HCB in acetone, were selected as the objects of investigation. The subject of the study is the systematic examination of the radiolytic degradation of HCB and TCB in selected polar and nonpolar solvents under ionizing gamma irradiation. For this purpose, the dependence of radiation-chemical yields on absorbed dose, the kinetics of dechlorination, the qualitative and quantitative profiles of degradation products, and the variation of free chloride ion (Cl^-) mass balance indicators were investigated. Furthermore, the identification of the mechanism and pathway of dechlorination constitutes an essential part of this research.

Considering the above-mentioned data, the study of the qualitative and quantitative indicators of the transformation process of HCB under the influence of ionizing radiation is of current scientific and practical importance.

Goals and objectives of the dissertation work. The aim of this dissertation is to investigate the kinetics and mechanisms of the dechlorination cycle during the radiolytic degradation of HCB and 1,2,4-TCB solutions in selected polar and nonpolar solvents under gamma irradiation. To achieve this objective, the following tasks were carried out:

– Evaluation of the kinetic parameters of irradiated HCB and TCB samples using Gas Chromatography (GC);

– Qualitative analysis of chlorinated and non-chlorinated radiolysis products of HCB and TCB solutions using Gas Chromatography–Mass Spectrometry (GC–MS);

– Determination of Cl^- ion concentrations in irradiated HCB + methanol samples using Ion Chromatography (IC) with a conductivity-based detector;

– Calculation of radiation-chemical yields and investigation of degradation kinetics within the framework of a pseudo-first-order model;

– Comparative analysis of different solvents in terms of

degradation efficiency, product profiles, and selectivity in the breakdown of HCB and TCB;

– Identification of the degradation mechanism and dechlorination pathway of HCB and TCB based on the research findings.

Research methods. Irradiation of samples has been carried out with gamma rays from a ^{60}Co radioactive isotope in the MRX-γ-25 facility.

The dose rate was determined using Fricke dosimetry, based on the $Fe^{2+} \rightarrow Fe^{3+}$ conversion.

Qualitative and quantitative analyses of radiolysis products were carried out using a Shimadzu QP2010 SE GC–MS system (Japan). Both chromatograms and mass spectra were processed with the PostRun LabSolutions software package.

The concentration of Cl^- ions in irradiated samples was determined using a Shimadzu Ion Chromatograph (Japan) equipped with an anion suppressor system and a conductivity-based detector.

Kinetic calculations were performed using Microsoft Excel. The degradation kinetics were evaluated by pseudo-first-order models, using ln[C] = f(t) plots to determine the effective rate constants (k) and radiation-chemical yields (G).

For visualization of chemical structures of reagents and radiolysis products, as well as proposed degradation mechanisms, ChemSketch (ACD/Labs) and ChemDraw (PerkinElmer) software were employed. The resulting molecular structures and dechlorination pathways were prepared in high-quality formats (TIFF/PNG).

Main provisions submitted for defense:

- Complete degradation of the initial HCB and TCB compounds under the influence of gamma irradiation;
- Modeling of degradation kinetics according to a pseudo-first-order process, including determination of kinetic parameters such as rate constants and radiation-chemical yields;
- Identification of chlorinated benzene derivatives as primary radiolysis products of the initial compounds and assessment of their concentration dependence on absorbed dose;
- Comparative evaluation of other chlorinated and non-

chlorinated by-products formed during the radiolysis process, with emphasis on the selection of the optimal solvent;

- Assessment of the potential risks associated with toxic by-products formed in nonpolar systems;
- Proposed degradation mechanisms and dechlorination pathways of the initial compounds.

Scientific novelties of the research:

- For the first time, the complete degradation of HCB and TCB under gamma irradiation was carried out in various polar and nonpolar organic solvents, and the kinetic features of these processes were investigated;
- Based on mass spectral analysis of radiolytic degradation products of HCB and TCB, the dose dependence of their concentrations was determined;
- A comparative analysis of different polar and nonpolar solvents with respect to by-product profiles was performed, the optimal solvent was identified as methanol, and the overall chlorine balance during the radiolysis of this system was calculated;
- The molecular-level mechanisms and pathways of dechlorination during the radiolytic transformation of HCB and TCB were established.

Theoretical and practical significance of the research. The kinetic regularities and characteristic parameters obtained as a result of this dissertation contribute to clarifying the radiation-chemical degradation processes of TCB and HCB and represent an important stage in the broader field of the radiation chemistry of chlorinated benzenes.

The findings of this study also have direct practical significance for the remediation of industrial effluents, agricultural soils contaminated through pesticide use, and water sources containing chlorinated compounds. Research on the gamma-radiolytic degradation of HCB has demonstrated that radiolysis processes in organic solvents under gamma irradiation provide an effective and scientifically grounded alternative for the detoxification of such pollutants.

In conclusion, this research substantiates gamma radiolysis as a

technology adaptable to diverse environmental conditions, contributing substantially to global pollution reduction efforts. As a robust and environmentally attractive alternative to existing technologies, this approach offers wide application prospects in both scientific and industrial contexts.

Approval and implementation of work. The results of the dissertation have been presented and discussed at international conferences, and published in their proceedings:

VII International Scientific Conference of Young Researchers, 28–29 April 2023, Khirdalan, Azerbaijan;

5th International Conference on Natural and Applied Science and Engineering, 26–28 May 2023, Ürgüp-Nevşehir, Türkiye (online);

Scientific-Technical Conference dedicated to the 100th anniversary of National Leader Heydar Aliyev, on Radiation Technologies and Their Applications, 5 May 2023, Baku, Azerbaijan;

XIII International Scientific-Practical Conference "Science and Technologies", 20 September 2024, Almaty, Kazakhstan;

XI International Scientific-Practical Conference "Science and Technologies", 25 May 2024, Almaty, Kazakhstan.

Publications: The findings of the research have been reflected in **11 scientific papers** (7 articles and 4 conference papers) published in both international and local scientific journals and conference proceedings. In addition, 1 scientific work has been presented online in conference (without publication).

Name of the organization the dissertation work was performed: The dissertation was carried out between 2019 and 2025 at the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan and at the Azerbaijan-French University operating under the Azerbaijan State Oil and Industry University.

Structure of the Dissertation. The present dissertation consists of an introduction (30091 characters), five chapters (Chapter I – 54847 characters; Chapter II – 21560 characters; Chapter III – 32842 characters; Chapter IV – 31152 characters; Chapter V – 19478 characters), and conclusions (3,134 characters). In total, the

dissertation comprises 193104 characters (excluding tables, figures, and references).

The dissertation is 165 pages in length, including 81 pages of main text, 35 figures and graphs, and 20 tables.

Author's Personal Contribution:

- Development of the research concept and systematic review of the literature on the subject;
- Preparation of the experimental methodology and determination of protocols;
- Preparation of standards and execution of radiolysis experiments;
- Optimization of analytical methods (GC–MS, IC, pH-metry, spectral analysis, etc.) and performance of analyses;
- Investigation of degradation kinetics, execution and processing of calculations;
- Visualization of molecular mechanisms and interpretation of results;
- Preparation of the dissertation text and compilation of the scientific presentation of the research.

MAIN CONTENT OF THE RESEARCH:

In the **Introduction**, the relevance of the dissertation research, the defined objectives and main tasks, the scientific novelty achieved, the theoretical and practical significance, the research methods employed, the principal theses submitted for defense, the approbation of the work, the author's personal contribution, and a brief summary of the chapters are presented.

In **Chapter I**, radiolysis procedures carried out by gamma irradiation and their role in the degradation of POPs are thoroughly discussed. The formation mechanisms of free radicals, solvated electrons, and ions in the selected polar and nonpolar solvents within the scope of this dissertation are explained, and the advantages of this approach compared to conventional technologies are highlighted. The chemical structures, ecotoxicological properties, and global

distribution[5] mechanisms of POPs are presented, while the main groups—such as PCBs, dioxins, furans, pesticides (e.g., DDT, Aldrin, Dieldrin), and polycyclic aromatic hydrocarbons (PAHs)—are classified in terms of environmental persistence and bioaccumulation potential[6].

For the remediation of POPs, chemical oxidation methods (Fenton's reagent, ozonation), Advanced Oxidation Processes (AOPs), bioremediation, phytoremediation, and soil washing are comparatively analyzed with respect to energy demand, operational parameters, and the risk of forming toxic by-products.

The literature review at the end of the chapter demonstrates that radiolysis in organic solvents under gamma irradiation represents a promising and scalable technology for the efficient and environmentally justified detoxification of POPs, particularly HCB.

In **Chapter II**, the experimental design and methodological principles of the present research are comprehensively summarized. This section provides a detailed description of the preparation and purification of standard solutions of HCB and TCB, the protocols of gamma irradiation applied to liquid samples, the operating principles of the analytical instruments, the calibration methods used to ensure accuracy, as well as the software packages employed for the processing and interpretation of data. The overall objective of this part of the study is to obtain both quantitative and qualitative parameters of the radiolysis processes of the selected persistent organic pollutants with maximum precision and reproducibility.

Standard solutions of the target compounds were prepared in a variety of solvents, including methanol, ethanol, isopropanol, acetone (for HCB), hexane, benzene, and toluene, thereby allowing comparative evaluation of solvent effects. For this purpose, exact quantities of highly pure HCB and TCB crystals were weighed using

[5] Bailey R. E. Global hexachlorobenzene emissions // Chemosphere. – 2001. – Vol. 43, № 2. – p. 167–182.

[6] Islam R. Bioaccumulation and adverse effects of persistent organic pollutants (POPs) on ecosystems and human exposure: a review study on Bangladesh perspectives / R. Islam, S. Kumar, J. Karmoker [et al.] // Environmental Technology & Innovation. – 2018. – Vol. 12. – P. 115–131.

a precision analytical balance (“Mettler Toledo,” sensitivity ±0.0001 g). Solutions were prepared in the concentration ranges of 0.044–0.055 g/L for HCB and 1.4–2.0 g/L for TCB, ensuring solubility and stability. To obtain homogeneous systems, all prepared solutions were subjected to ultrasonic treatment in a bath (“Branson,” 40 kHz) for 5 minutes. To avoid photodegradation and solvent evaporation, the vials were tightly sealed with Teflon caps and stored at 4 °C under dark conditions until irradiation.

Figure 1. Shimadzu GC–MS system

Gamma irradiation experiments were conducted at 25 °C and under atmospheric pressure using the MRX-γ-25 gamma facility located at the High Technology Park of the National Academy of Sciences. Dosimetry was carried out with two complementary techniques: the classical Fricke method, based on the $Fe^{2+} \rightarrow Fe^{3+}$ redox transition, and the alanine-tablet dosimeter method, both of which ensured traceable dose measurements. During the studies conducted on HCB and TCB, the dose rates were 1.74 Gy/s and 1.67 Gy/s, respectively. The absorbed dose range was 0–456.9 kGy for TCB and 0–169.5 kGy for HCB, with three independent replicates irradiated at each dose level to guarantee statistical reliability.

The identification and quantification of radiolysis products were performed on a Shimadzu QP2010 SE GC–MS system (Figure 1) equipped with an Rxi-5 ms capillary column. Analyses were carried out under electron ionization conditions (70 eV), in both SIM and full-scan modes, with helium as the carrier gas (1.0 mL/min).

Injections of 1 µL were introduced in split mode (20:1). A temperature program of 40 → 250 °C with a linear heating rate of 10 °C/min was applied, enabling separation and identification of volatile degradation products with high sensitivity and reproducibility.

The determination of Cl^- ion concentrations released into the irradiated solutions was carried out using a Shimadzu Ion Chromatograph. The system operated under $Na_2CO_3/NaHCO_3$ (2.0/4.0 mM) mobile phase conditions, with a flow rate of 0.8 mL/min, column temperature of 45 °C, and system pressure of 25 MPa. Calibration curves were established using certified reference standards, meeting the requirement of $R^2 > 0.99$. Figure 2 presents representative chromatograms of methanolic solutions of HCB and TCB irradiated at ~12 kGy, showing clearly separated peaks corresponding to chloride ions.

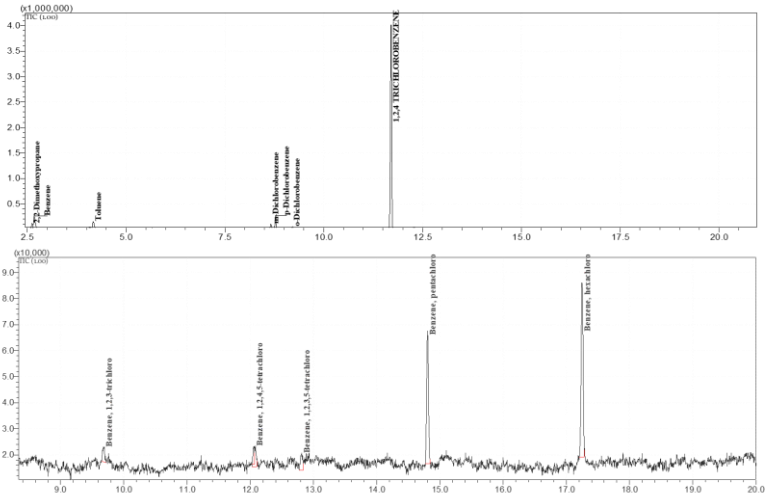

Figure 2. Chromatograms of HCB and TCB methanolic solutions irradiated at a dose of ~12 kGy

The pH changes of irradiated TCB solutions were measured with a Hanna Instruments Edge pH-meter (HI2002-01), calibrated using a three-point buffer system (pH = 4.01, 7.01, 10.01). Based on these measurements, dose-dependent variations in solution acidity

were determined and correlated with the release of hydrogen chloride and other acidic by-products.

The degradation kinetics of HCB and TCB were analyzed within the framework of a pseudo-first-order model, applying ln[C] versus absorbed dose plots processed in Microsoft Excel. From these linear correlations, effective rate constants (k) were derived. In addition, radiation-chemical yields (G-values) were calculated with high precision, enabling comparative evaluation of the degradation efficiency in different solvents.

Finally, the molecular structures of the identified degradation products, the underlying mechanisms of radical-induced reactions, and the predicted dechlorination pathways were visualized and schematically represented using ChemDraw and ChemSketch software packages. These graphical representations allowed clearer understanding of the progressive breakdown of chlorinated benzene molecules under ionizing radiation and the formation of less chlorinated, less toxic intermediates.

In **Chapter III**, the kinetic analyses were carried out based on the changes in the initial concentrations of the samples depending on the absorbed γ-irradiation dose. Figure 3 presents the dose–response curves for the concentrations of HCB and TCB.

As can be seen from the graphs, in the selected organic solvent systems, complete (100%) degradation of the initial compound was achieved for all polar solutions of HCB and, among the non-polar solvents, only in the hexane system under γ-irradiation. For TCB, however, a reduction of up to 100% was observed in all cases at the maximum applied absorbed dose of 456.9 kGy.

The kinetic curves were interpreted according to a pseudo-first-order reaction model and expressed by the equation $[-ln\,C = kt + (-ln\,C^0)]$ (Figure 4). In the graphs, the slope of the line corresponds to the rate constant (k), while the intercept with the y-axis corresponds to the initial concentration (C_0). Mathematical data processing and analysis were carried out using Microsoft Excel. The equations provided in the graphs are consistent with the corresponding solvent systems.

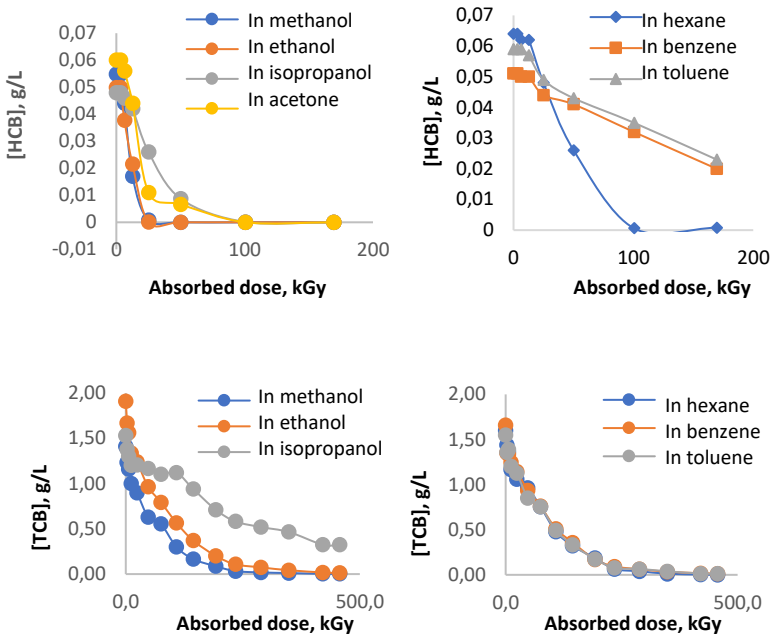

Figure 3. Dependence curves of HCB and TCB concentrations on the absorbed dose of gamma irradiation

According to the results, in all cases the radiolytic degradation of both HCB and TCB in the selected solvents exhibited linear dependencies characteristic of first-order kinetics, where the slope (k) of the functions corresponds to the effective rate constants. The highest values were observed in methanol among the polar systems and in hexane among the nonpolar systems for both HCB and TCB. The determined values were as follows: for HCB and TCB respectively — in methanol, 5×10^{-3} s^{-1} and 9×10^{-2} h^{-1}; in ethanol, 2×10^{-3} s^{-1} and 7×10^{-2} h^{-1}; in isopropanol, 4×10^{-5} s^{-1} and 2×10^{-2} h^{-1}; in acetone (for HCB), 9×10^{-5} s^{-1}; in hexane, 3×10^{-4} s^{-1} and 9×10^{-2} h^{-1}; in benzene, 6×10^{-5} s^{-1} and 6×10^{-2} h^{-1}; in toluene, 6×10^{-5} s^{-1} and 6×10^{-2} h^{-1}. The observed differences are directly related to the dielectric constant of the solvent, its proton-donating ability, and the strength of its interactions with intermediate products.

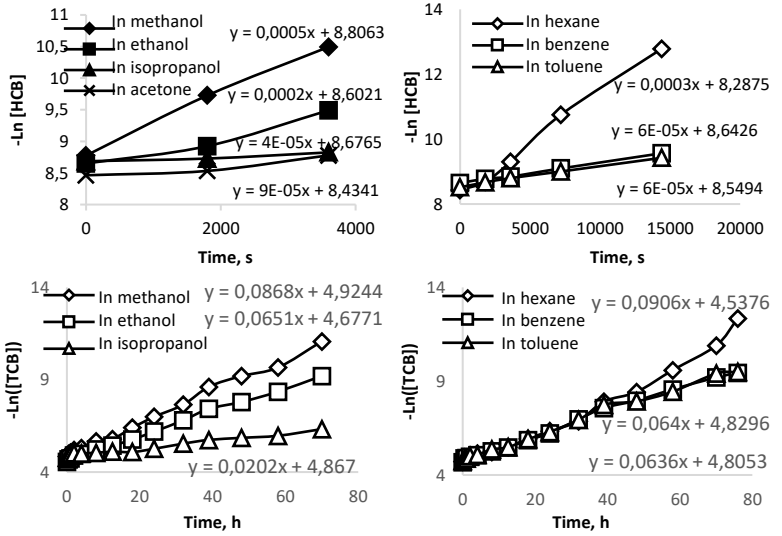

Figure 4. Determination of the rate constants for HCB and TCB based on the linear dependence $[-ln\,C = k\,t + ln\,C_0]$

In addition, the linear trend derived from the relationship between −log (v_i) and −log (C) (instantaneous rate – concentration), presented in **Figure 5**, provides the mathematical indicator of the reaction order. In all cases, the reaction order was found to lie between 1 and 2, showing that while the radiolytic degradation of both HCB and TCB corresponds to a second-order reaction, it is observed in practice as a first-order process. This can be explained by the fact that the concentration of the solvent involved in the reactions remains virtually unchanged during the process.

In the chromatograms, the peak areas of the initial HCB and TCB compounds as well as their by-products were processed in both automated and manual modes using the LabSolutions v5.92 software, forming the basis of the quantitative analysis. The obtained spectra were compared with corresponding spectra available in the NIST database, and structural identifications were confirmed. Furthermore, the compiled chromatogram collection allowed not only the evaluation of the concentrations of initial and final products but also the dose-dependent profiles of intermediate products and derivative compounds.

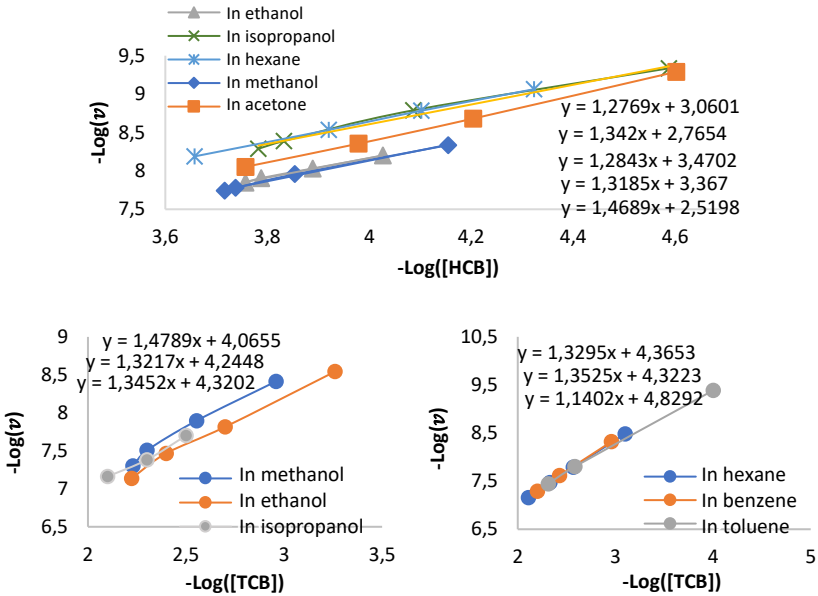

Figure 5. Plot of –log(rate) versus –log(concentration) used to determine the reaction order of the gamma-radiolytic degradation of HCB and TCB

The radiation-chemical yields of HCB were calculated for different solvents. Among them, the polar solvents (methanol, ethanol) demonstrated the highest kinetic and radiation-chemical efficiency for HCB degradation, with complete decomposition achieved at comparatively lower doses.

The radiation-chemical yields were calculated using the following equation:

$$G = (\Delta C \cdot N_a)/(D \cdot 6.2 \times 10^{15}\, eV/q)$$

Here, ΔC is the change in concentration (mol/L), N_a is Avogadro's constant, and D is the absorbed dose (Gy). The G values represent the number of molecules decomposed per 100 eV of absorbed energy, and this parameter provides a quantitative basis for comparing the efficiency of different solvents. For visual comparison, the corresponding diagrams are presented in Figure 6.

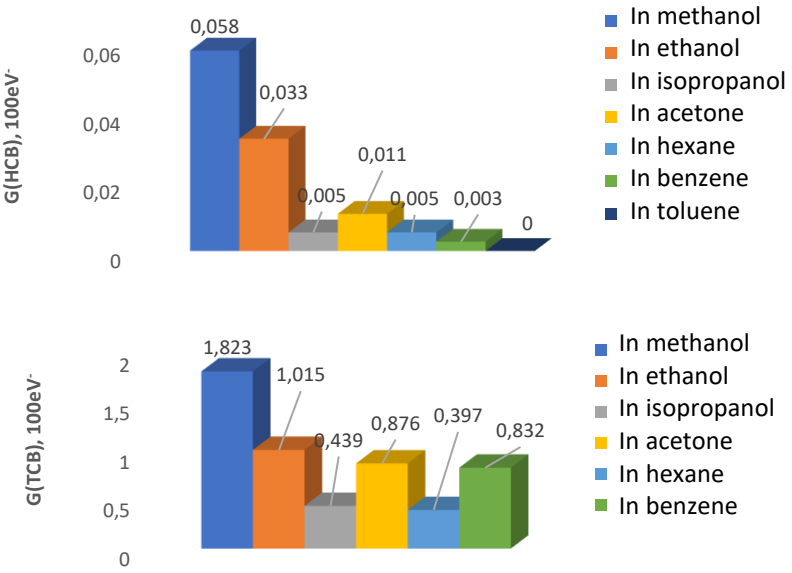

Figure 6. Comparative radiation chemical yields of HCB and TCB at ~12 kGy

According to the diagrams, methanol exhibited the highest radiation-chemical yield for both HCB and TCB across the studied dose ranges (~0.058 and 1.82 molecules/100 eV, respectively). In contrast, less polar solvents (hexane, benzene, toluene) showed weaker kinetic profiles and lower G values, indicating slower reaction rates. For HCB, these values ranged between 0–0.0055 molecules/100 eV, while for TCB they varied between 0.40–0.88 molecules/100 eV.

pH variations play an additional role in clarifying the reaction mechanism (Figure 7). In polar solvent solutions of TCB (primarily

methanol and ethanol), an increase in absorbed dose led to a decrease in pH from the range of 6.5–7.3 down to 4.0–4.2. This indicates the formation of HCl and other protonated intermediate products at certain concentrations. In less polar systems, however, the pH changes were less pronounced, decreasing from 7.2–7.6 to 5.4–6.1. This suggests the occurrence of buffering-type stabilization processes in the medium and that the dechlorination mechanism proceeds more gradually.

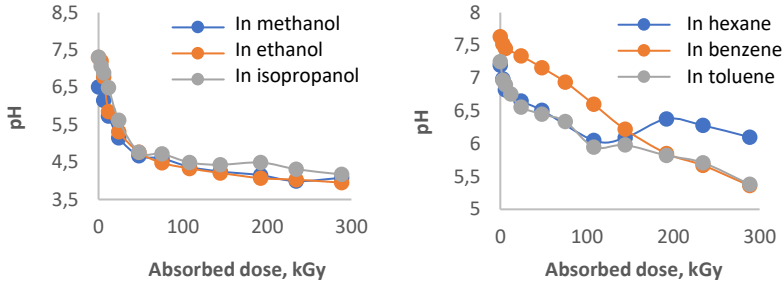

Figure 7. Variation of pH in irradiated TCB solutions as a function of absorbed dose.

Polar solvents serve as favorable media that accelerate the degradation process while reducing the risk of toxic by-product formation.

Thus, the systematic kinetic studies carried out in Chapter III have established a fundamental knowledge base for the detoxification of persistent organic pollutants by gamma irradiation, clarified the prospects for methodological optimization, and highlighted the technological application potential. These findings form the basis for emphasizing the scientific novelty, practical significance, and detailed kinetic insights of the study.

In **Chapter IV**, the qualitative results complement the overall picture of spectral and chromatographic analyses of products formed in HCB and TCB systems through radiolytic degradation. This chapter systematically investigates the diversity, structures, and formation sequences of chlorinated and non-chlorinated compounds generated in different solvent media, depending on the composition of the solution.

Table 1 presents the radiolysis products of HCB in methanolic solution, along with the dose intervals in which they were identified and their molecular ions in the mass spectra.

In the initial stages of HCB radiolysis in methanol (0–25.1 kGy dose interval), pentachlorobenzene (PeCB) was identified. At 12.6–50.2 kGy, an increase in the amount of less chlorinated aromatic compounds such as 1,2,3,5- and 1,2,4,5-tetrachlorobenzene (TeCB), and 1,2,3- and 1,2,4-trichlorobenzene (TCB)—was observed.

Table 1

Radiolysis products of HCB in methanol, their identified dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	1,2-Dichlorobenzene	50.25–100.5	146
2	1,4-Dichlorobenzene	50.25–100.5	146
3	1,2,3-Trichlorobenzene	12.56–50.25	178
4	1,2,4-Trichlorobenzene	12.56–50.25	178
5	1,2,4,5-Tetrachlorobenzene	12.56–50.25	222
6	1,2,3,5-Tetrachlorobenzene	12.56–50.25	222
7	Pentachlorobenzene	3.14–25.13	250
8	*n*-Dodecane	100.5–169.5	170

Within the 50.2–100.5 kGy dose range, the main products were 1,2- and 1,4-dichlorobenzene (DCB).

At higher absorbed doses (100.5–169.5 kGy), the formation of *n*-dodecane, a long-chain aliphatic hydrocarbon, was recorded, indicating that deep radical and condensation reactions associated with aromatic ring cleavage had occurred.

The dynamics of peak areas of the radiolytic products support a stepwise dechlorination pathway. The mass spectra of the chlorinated benzenes obtained in the process are presented in Figure 8. These compounds were identified as radiolytic degradation products across all of the investigated systems.

The ethanol system differs from methanol not only in the type and number of products formed but also in the stepwise progression of the degradation mechanism (Table 2). In the initial stages, PeCB (3.1–25.1 kGy) and TeCB isomers (1,2,4,5- and 1,2,3,5-TeCB at 12.5–50.2 kGy) predominate in the system; however, at 25.1–50.2 kGy their concentrations begin to decrease. At this stage, less chlorinated aromatic compounds such as 1,2,4-TCB and the dichlorobenzene isomers 1,3-DCB and 1,4-DCB (dominant in the 50.2–100.5 kGy range) become prevalent in the system.

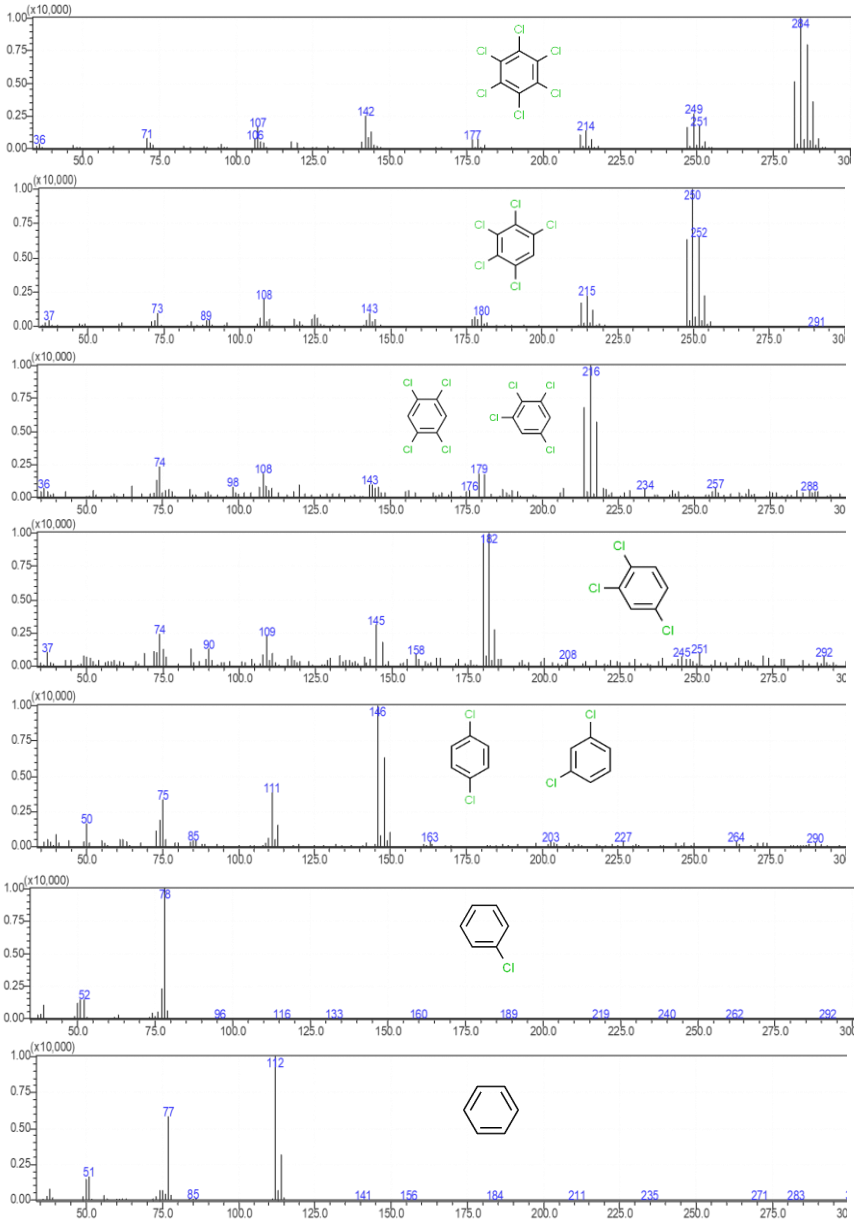

Figure 8. Mass spectra and molecular structures of chlorinated benzene derivatives identified as the principal products

Table 2

Radiolysis products of HCB in ethaol, their identified dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	Glycolaldehyde diethyl acetal	25.1–169.5	75
2	Triethyl formate	50.2–169.5	75
3	2,5-Hexanediol	100.5–169.5	90
4	1,3-Dichlorobenzene	50.2–100.5	146
5	1,4-Dichlorobenzene	50.2–100.5	146
6	Limonene	50.2–100.5	136
7	1-Phenylethanol	169.5	122
8	2-Ethoxybenzoin	50.2–100.5	166
9	1-(4-Chlorophenyl)ethanol	50.2–169.5	156
10	1,2,4-Trichlorobenzene	25.1–50.2	178
11	1,2,4,5-Tetrachlorobenzene	12.5–50.2	222
12	1,2,3,5-Tetrachlorobenzene	12.5–50.2	222
13	Pentachlorobenzene	3.1–25.1	250
14	Tetraethyl-dichlorobenzene	100.5	270
15	Methylpentachlorobenzoate	12.5–25.1	318

In parallel, oxidation products of ethanol—particularly glycolaldehyde diethyl acetal (25.1–169.5 kGy), triethyl formate (50.2–169.5 kGy), and 2,5-hexanediol (100.5–169.5 kGy)—were identified with high intensity.

In isopropanol, the spectral diversity of products is more complex. Within the 3.1–25.1 kGy dose range, one of the main chlorinated products identified was PeCB (0–50.2 kGy). In the 50.1–100.5 kGy range, isomers such as 1,2,3-TCB, 1,3,5-TCB, and 1,2,4,5-TeCB (at 100.5 kGy) were formed. At higher doses (100.5–169.5 kGy), pentachlorobenzene again appeared as one of the dominant chlorinated products.

At the same time, other products of isopropanol were also detected, including 2-methyl-2,4-pentanediol (25.1–169.5 kGy), tetrahydro-2,2-dimethyl-5-(1-methylethyl) furan (100.5–169.5 kGy), and propanone (acetone, 3.1–50.2 kGy) (Table 3).

Table 3

Radiolysis products of HCB in isopropanol solution, their identified dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	Acetone	3.1–25.1	58
2	*n*-Dodecane	3.1–12.5	170
3	*n*-Tetradecane	3.1–169.1	198
4	*n*-Pentadecane	3.1–12.5	212
5	Pentachlorobenzene	6.3–50.1	250
6	2-Methyl-2,4-pentanediol	25.1–169.1	118
7	Limonene	50.1–100.2	136
8	1,2,3-Trichlorobenzene	50.1	181
9	Propyl acrylate	100.2	128
10	cis-3-Hexenyl butyrate	100.2	170
11	2,6-Dimethyl-6-hepten-2-ol	100.2–169.1	142
12	1,3,5-Trichlorobenzene	100.2	181
13	1,2,4,5-Tetrachlorobenzene	100.2	216
14	2,5-Dimethyl-2,5-hexanediol	100.2–169.1	146
15	Tetrahydro-2,2-dimethyl-5-(1-methylethyl)furan	100.2–169.1	154
16	Ethyl isobutyrate	169.1	116
17	(1S,2R)-2-(2′-Hydroxy-2′-methyl-ethyl)cy.hexanol	169.1	172
18	3-Methoxy-6,7,8,9-tetrahydrodibenzofuran-2-ol	169.1	218
19	2,5-Hexanediol	169.1	118

In the acetone solution of HCB, a wide spectrum of carbonyl and ester group–containing products was observed (Table 4). Condensation and esterification products - 2,5-hexanedione (12.5–169.5 kGy), 2-octanone (25.1 kGy), 1,1-diethoxy-2-hexene (25.1 kGy), 1,1-diethoxypentan-4-one (25.1–100.5 kGy), and the 1-methyl-3-oxo-but-1-enyl acetate ester (169.5 kGy) were identified.

These results demonstrate not only the efficient degradation of chlorinated benzenes under the influence of ionizing radiation, but also reveal the complex chemical interactions that occur

simultaneously with this process. In particular, the data indicate that the target compounds are capable of reacting with a variety of intermediate species that are formed during the radiolysis of the surrounding solvent.

Table 4

Radiolysis products of HCB in acetone, their identified dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	Pentachlorobenzene	6.3–100.5	250
2	2,5-Hexanedione	12.5–169.5	114
3	Ethyl acetate	12.5	88
4	1,1-Diethoxy-2-hexene	25.1	158
5	1,1-Diethoxypentan-4-one	25.1–100.5	130
6	1,2,4,5-Tetrachlorobenzene	25.1–100.5	315
7	1,3-Dioxolane, 2,2,4,5-tetramethyl-, *cis*-isomer	25.1–169.5	114
8	1-Ethoxy-2-heptanone	25.1	158
9	2-Octanone	25.1	142
10	1-Chloro-2,2-diethoxypropane	25.1	134
11	Methylpentachlorobenzoate	25.1–50.2	288
12	6-(Acetyloxy)-2-hexanone	50.2–100.5	158
13	Triethyl formate	50.2–169.5	102
14	1,2,4-Trichlorobenzene	100.5	181
15	1-Propoxy-2-propanol	100.5–169.5	102
16	2-Ethylbutanoic acid	100.5	130
17	Ethyl-3-hydroxy-5,5-dimethoxy-3-methylpentanoate	100.5	216
18	Phenylbutyrate	100.5	164
19	2-Hydroxy-6-hexanone acetate	100.5	158
20	2-Hydroxy-2-methylpropanal	169.5	102
21	2,2-Dimethyl-4,4′-bis-1,3-dioxolane	169.5	156
22	4-Methylpent-4-en-2-one	169.5	110
23	1-Methyl-3-oxo-but-1-enyl acetate ester	169.5	144
24	2-Hexyl acetate	169.5	172
25	1-(2,4,5-Trichlorophenyl)ethanol	169.5	208

The detection of intermediates with carbonyl–alcohol groups (e.g., 2-hexanol acetate, 169.5 kGy), carbonyl–ester groups (triethyl formate, 50.2–169.5 kGy), and diols (2-hydroxy-2-methylpropanal, 169.5 kGy) indicates that resonant radical mechanisms operate in parallel within the system.

During the process in hexane, aliphatic and oxygenated intermediate products were formed - 3-isopropoxypivaldehyde (12.5–169.5 kGy), 2,6-dimethyl-2-octanol (6.3–169.5 kGy), 3-octanone (100.5 kGy), and 2,5-dimethyl-2-hexanol (100.5 kGy) (Table 5). Stepwise decrease in the concentrations of chlorinated components such as HCB (0–169.5 kGy) and PeCB (6.3–169.5 kGy) was observed, indicating progressive dechlorination.

Table 5

Radiolysis products of HCB in hexane, their dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	5,6-Dimethyldecane	12.5–169.5	170
2	Hexachlorobenzene	0–169.5	284
3	2-Hexyloxyethane	25.1–169.5	146
4	4,5-Diethyloctane	6.3–169.5	170
5	5-Methylundecane	25.1–169.5	170
6	3-Methyl-2-heptanol	100.5	130
7	3,4-Dimethyl-2-hexanol	3.1–12.5	130
8	2,3-Dimethylundecane	25.1–169.5	184
9	Limonene	3.1–169.5	136
10	5-Methylnonane	12.5–169.5	142
11	1,1-Diethoxyhexane	25.1–169.5	174
12	2,5-Dimethyl-2-hexanol	100.5	130
13	Methyl-3-methyl-2-butyl ether	25.1–100.5	116
14	*n*-Dodecane	6.3–169.5	170
15	3-Isopropoxypivaldehyde	12.5–169.5	–
16	4-Ethyloctane	50.2–100.5	142
17	Pentachlorobenzene	6.3–169.5	266
18	2,6-Dimethyl-2-octanol	6.3–169.5	158
19	3-Octanone	100.5	128

Table 6

Radiolysis products of HCB in benzene, their identified dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	Ethyl phenyl ether	3.1–169.5	122
2	1,1′-Biphenyl	3.1–169.5	154
3	1,4-Diphenylbenzene	50.2	154
4	1-Phenylethanol	100.5–169.5	122
5	2,4,5,3′,4′-Pentachlorobiphenyl	12.5–25.1	314
6	Benzaldehyde	50.2	106
7	Phenol	6.3–169.5	94
8	3-Phenyl-1,4-cyclohexadiene	6.3–169.5	118
9	2,4-Dimethylfuran	12.5–169.5	96
10	Methyl-(tricyclo[3.1.0.0(2,6)]hex-3-yl) ether	12.5–25.2	138
11	7,8-Benzobicyclo[2.2.2]octa-2,5-diene	6.3–169.5	142
12	Butyl phthalate	12.5–25.2	278
13	Pentachlorobenzene	12.5–169.5	266
14	2-Chlorobicyclo[4.1.0]heptane	50.2	122
15	3-(2-Propenyl) methyl ester of cycloprop-2-ene-carboxylic acid	50.2	168
16	Ethoxytoluene	50.2–169.5	136
17	2,5-Cyclohexadiene-1,4-diol	50.2	112
18	Methylcyclopenta-1,3-diene	50.2–169.5	82
19	2,5-Etheno[4.2.2]propella-3,7,9-triene	50.2	132
20	3-Methylbicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carboxylic acid	50.2–169.5	216
21	(−)-(3aR,6aS)-3,3a,6,6a-Tetrahydro-2H-cyclopenta[b]furan-2-one	6.3–100.5	138
22	1-Phenyl-2-propanol (2-Phenyl-2-propanol)	100.5–169.5	136
23	trans-(1,3-Butadienyl)cyclobutane	100.5–169.5	110
24	2-Oxabicyclo[3.3.0]oct-7-en-3-one	169.5	136
25	*o*-Cresyl ethyl ether	169.5	150
26	3-Cyclopropyl-1,2-butadiene	100.5	108
27	2-Phenyl-2-propanol	100.5–169.5	136

In the hexane system, the formation of long-chain alcohols and ethers, such as 2-hexyloxyethane (25.1–169.5 kGy), 5-methylundecane (25.1–169.5 kGy), 2,3-dimethylundecane (25.1–169.5 kGy), and methyl-3-methyl-2-butyl ether (50.2–100.5 kGy)—indicates that specific condensation and radical recombination reactions occur. The presence of saturated alkanes (e.g., 4,5-diethyloctane and 5,6-dimethyldecane, both at 12.5–169.5 kGy) further reflects the involvement of complex molecular mechanisms in the system.

In benzene, radiolytic transformation of HCB resulted in the formation of PeCB (12.5–169.5 kGy), 2,4,5,3′,4′-pentachlorobiphenyl (12.5–25.1 kGy), and 2-chlorobicyclo[4.1.0]heptane (50.2 kGy) (Table 6).

Alongside chlorinated structures, non-chlorinated aromatic compounds such as 2,4-dimethylfuran (12.5–169.5 kGy), 7,8-benzobicyclo[2.2.2]octa-2,5-diene (6.3–169.5 kGy), and ethoxytoluene (50.2–169.5 kGy) demonstrate the intensity of radical recombination and condensation reactions in the system.

In addition, 1,1′-biphenyl (3.1–169.5 kGy), 1,4-diphenylbenzene (50.2 kGy), and other polyaromatic derivatives were also identified. Benzyl alcohol derivatives such as 1-phenyl-2-propanol (100.5–169.5 kGy) and 2-phenyl-2-propanol (100.5–169.5 kGy) confirm that the system undergoes reactions involving aromatic ring cleavage and alkyl radical participation. These complex processes demonstrate that in benzene, HCB is subjected to multi-step radiation-chemical transformations.

In toluene, γ-irradiation produced structures similar to those observed in benzene, but with an overall broader and structurally richer profile (Table 7). Starting from as low as 3.1 kGy, aromatic products such as benzaldehyde, benzyl alcohol, cresol isomers, ethoxytoluene, biphenyl, and diphenylmethane derivatives appeared.

At higher irradiation doses (100.5–169.5 kGy), the intensity of heterocyclic and polyaromatic compounds increased, including spiro-dimers, 3-oxabicyclic structures, dimethylbiphenyl, and various cyclohexene derivatives. These products reflect not only the degradation of HCB but also the methylation of toluene, condensation of aromatic cycles, and enhanced radical interactions.

Table 7

Radiolysis products of HCB in toluene, their dose intervals, and molecular ions in the mass spectra

№	Product name	Dose interval (kGy)	Molecular ion, *m/z*
1	Benzaldehyde	3.1	106
2	Benzyl alcohol	3.1–169.5	108
3	Cresol (total)	3.1–169.5	94
4	Cresyl ethyl ether	3.1–25.1	150
5	Ethoxytoluene	3.1–169.5	136
6	Dibenzyl	6.3–169.5	182
7	Benzyl ether	25.1–169.5	198
8	Dimethylbiphenyl (and isomers)	12.1–169.5	182
9	2- and 4-Methyldiphenylmethane	6.3–169.5	196
10	1,2-Diphenylethanol	100.5–169.5	198
11	Hydrobenzoin	100.5–169.5	214
12	Phenylacetone	100.5–169.5	134
13	α-Methylbenzyl alcohol	100.5–169.5	136
14	Dimethylbenzylcarbinol	100.5–169.5	136
15	2-Ethoxybenzoin	100.5–169.5	166
16	1,2-Dimethyl-4-methylene-3-phenylcyclopentene	100.5–169.5	184
17	1,5,5-Trimethyl-4-phenylcyclopenta-1,3-diene	100.5–169.5	188
18	Spiroheptadiene dimer	25.1–169.5	154
19	3-Carbomethoxy-5-methylene-cyclohex-1-ene	25.1–169.5	192
20	3-Ethylidenecyclohexene	100.5–169.5	138
21	3-Oxabicyclo[3.3.0]octan-2-one, 6-methylene-7-methyl	100.5–169.5	154
22	3-Methyl-trans-1,4,6-heptatriene	100.5–1	

For TCB + solvent systems with higher initial concentrations, higher doses were applied to achieve the goal of complete decomposition of TCB.

In Chapter IV, the main intermediate and final products obtained in all six TCB systems are presented in tables within the dissertation.

Due to the extensive qualitative composition of these products, the radiolytic degradation products of TCB + solvent systems are not included in the abstract.

In addition to the complete degradation of chlorobenzenes, particularly in nonpolar solvent systems, the formation of numerous complex compounds was also recorded.

In this context, methanol stands out as the most selective system with the simplest product profile. In the methanol medium, oxygenated and chlorinated aromatic/aliphatic products were identified, including 1,2-, 1,3-, and 1,4-DCB isomers as radiolysis products of TCB, as well as compounds such as benzyl alcohol and dihydroxyacetone. In ethanol, however, the number of identified products was significantly higher.

In isopropanol, an even greater diversity of components was detected. These included not only DCB isomers formed from the radiolysis of 1,2,4-TCB, but also isopropanol-derived radiolysis products such as isopropoxymethane and diisopropoxymethane, which contain isopropyl fragments.

The qualitative results of TCB in hexane, benzene, and toluene solutions were considerably more complex. In these nonpolar systems, the process exhibited a more intricate character, producing also certain compounds with toxic potential.

The hexane solution, at different doses, yielded dozens of products, further complicating the process. Although TCB degradation in hexane was effective, the simultaneous radiolytic decomposition of hexane generated numerous aliphatic hydrocarbons and other oxygenated and non-oxygenated products. This makes hexane unsuitable as a solvent for practical gamma radiolytic dechlorination.

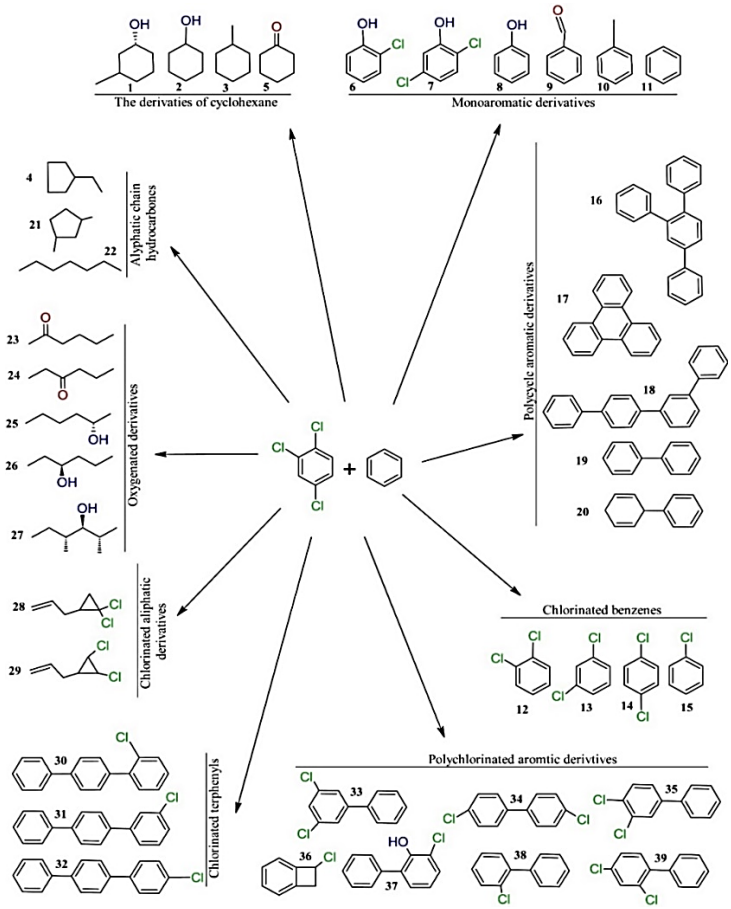

Figure 9. **Radiolysis products identified in the benzene solution of 1,2,4-TCB**

In benzene and toluene, the identification of similarly complex compounds also suggests their unsuitability as solvents. In particular, benzene promoted the formation of polycyclic aromatic compounds, along with other POPs such as polychlorinated biphenyls (PCBs) and more complex chlorinated terphenyls. This limits the potential of benzene and toluene as solvent systems (Figure 9). In all three nonpolar solvents, the presence of high radical profiles emphasizes the occurrence of numerous recombination reactions.

In **Chapter V**, the mechanisms of radiolytic transformation

processes occurring in the studied systems are discussed based on kinetic and qualitative parameters, with particular emphasis on the dechlorination pathways of HCB and TCB.

The γ-radiolysis of solvents proceeds through five principal mechanisms: excitation/ionization, excitation/fragmentation, radical cation reactions, formation of solvated (free) electrons and their participation in transformations, and radical recombination. It should be noted that the formation of solvated electrons does not occur in nonpolar solvents. In such systems, the electrons generated remain free in the medium for a certain period before subsequently entering into reactions. Table 8 presents the main primary active species formed during the radiation-chemical transformation of selected solvents, along with their corresponding radiation-chemical yields[7].

Table 8

Primary active species formed during solvent radiolysis and their corresponding radiation-chemical yields

Solvent	**Products (G values, 100eV^{-})**
Methanol	$e^-_{sol.}$ (3.1); ·H (2.02); CH_2O· (1.44); ·CH_2OH (2.7); ·CH_3(1);
Ethanol	$e^-_{sol.}$ (1.7); ·H (2.6); CH_3CHO (1.7); ·CH_3(0.4); and heavy ions
Hexane	·H (3.16); ·CH_3(0.92); C_2H_5(0.92); C_3H_7(0.92); and heavy ions
Benzene	·H (0.72); ·C_6H_5(0.72); and heavy ions
Isopropanol	$e^-_{sol.}$ (2.9); ·H (0.8);·CH_3, ·CH_2OH (~2.7–3.5); acetone (~0.5–1.0);
Acetone	$e^-_{sol.}$ (0.8); ·H (0.5); ·CH_3, CO, ·$COCH_3$, H_2 (~1.5–3.0);
Toluene	·H (0.5); ·$C_6H_5CH_2$, ·CH_3 (~0.7–1.5); and heavy ions

[7] LaVerne J. A., Araos M. S. Heavy ion radiolysis of liquid benzene // Journal of Physical Chemistry A. – 2002. – Vol. 106, № 46. – P. 11408–11413. Middeldorp P., Enrichment and properties of a 1,2,4-trichlorobenzene-dechlorinating methanogenic microbial consortium / P. Middeldorp, J. De Wolf, A. J. B. Zehnder [et al.] // Applied and Environmental Microbiology. – 1997. – Vol. 63, № 4. – P. 1225–1229. Pan X. Alumina-mediated photocatalytic degradation of hexachlorobenzene in aqueous system: kinetics and mechanism / X. Pan, J. Wei, R. Qu [et al.] // Chemosphere. – 2020. – Vol. 257. – Article 127256.

The γ-radiolysis of the selected systems was carried out under air-saturated conditions, which allowed interactions between the primary products formed during solvent radiolysis—including solvated oxygen—and the existing molecules in the medium. The rate constants of possible reactions for the active species ·H and $e^-_{sol.}$ is presented in Table 9[8]. It should be noted that no literature data were found regarding the reaction rate constants of TCB with ·H and $e^-_{sol.}$ particles. Therefore, assuming that dechlorination occurs in the aromatic ring of TCB, the rate constants of benzene with ·H and $e^-_{sol.}$ were used as reference values.

Table 9 shows that both ·H and $e^-_{sol.}$ species are scavenged to varying extents by solvent, oxygen, and TCB molecules. To clarify the relative scavenging capacity of each active species, the following formulas were applied:

$$\alpha = \frac{k_n[R_1][R_2]}{k_n[R_1][R_2] + k_m[R_1][R_3] + k_p[R_1][R_4]}$$

$$Relative\ G = \alpha * G(ref.)$$

$$\%\ of\ particle = \frac{Relative\ G}{G(ref.)} * 100\%$$

(1) – Average reaction rate;
(2) – Relative G values;
(3) – Percentage of active species subjected to chemical interaction.

[8] Buxton G. V. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O⁻) in aqueous solution / G. V. Buxton, C. Greenstock, W. P. Helman [et al.] // Journal of Physical and Chemical Reference Data. – 1988. – Vol. 17, № 2. – P. 513–886. Freeman G. R.; Radiation Chemistry Data Center, Radiation Laboratory, University of Notre Dame. Radiation chemistry of ethanol: a review of data on yields, reaction rate parameters, and spectral properties of transients. – Washington, D.C.: U.S. Government Printing Office; National Bureau of Standards, U.S. Department of Commerce, 1974. – 48 p.

Table 9

The rate constants of •H and $e^-_{sol.}$ with some species available in selected systems

	·H INVOLVING REACTIONS AND G VALUES	**$e^-_{sol.}$ INVOLVING REACTIONS AND G VALUES**
SPECIES	rate constant, L/ (mol x s)	rate constant, L/ (mol x s)
CH_3OH	1.7×10^6	10^4
C_2H_5OH	1.7×10^7	1.7×10^5
C_6H_{14}	1.4×10^8	-
C_6H_6	9.1×10^8	9×10^6
O_2	2.1×10^{10}	1.9×10^{10}
TCB	9.1×10^8	9.1×10^6

The values of the rate constants (k) were taken from Table 9. Here, R_1 represents the active species ·H and $e^-_{sol.}$, while R_2, R_3, and R_4 correspond to solvent, oxygen, and TCB reactants, respectively. All calculated parameters are presented in Table 10**.**

As shown in Table 10, the relative G values calculated for all systems were much smaller compared to the experimental results. This indicates that TCB is not primarily consumed in the initial reactions with active species, but rather participates in molecular-level reactions. However, according to the calculations, the proportion of ·H radicals entering into reduction reactions with TCB in methanol, ethanol, hexane, and benzene solutions amounted to 22.86%, 14.57%, 6.01%, and 0.78%, respectively. These findings demonstrate the conversion of TCB into less chlorinated compounds.

In the benzene system, the very low participation of ·H radicals (0.78%) correlates with the formation of chlorinated biphenyls identified in irradiated TCB + benzene solutions

The results presented in Chapter V provide the key ideas regarding the stepwise mechanisms of the reactions. Depending on the structure of the solvents, their degree of polarity, and the dose applied, the observed qualitative changes also enabled a quantitative evaluation of the products.

Table 10

Calculated relative G values and percentage participation of active species in primary reactions with solvent, oxygen, and TCB molecules, along with experimental G values of TCB obtained under γ-irradiation in the selected systems

In methanol (calculated)					Exp.	In hexane (calculated)					Exp.
	$e^-_{sol.}$		·H		100eV$^-$		$e^-_{sol.}$		·H		100eV$^-$
	Relative G	%	Relative G	%			Relative G	%	Relative G	%	
Methanol	4.3×10^{-3}	0.14	2.74×10^{-1}	13.55		**Hexane**	-	-	2.55	80.59	
Oxygen	3.1	99.86	1.28	63.58		**Oxygen**	-	-	4.23×10^{-1}	13.4	
TCB	1.2×10^{-3}	0.14	4.62×10^{-1}	22.86	**1.83**	**TCB**	-	-	1.9×10^{-1}	6.01	**1.93**
In ethanol (calculated)						**In benzene (calculated)**					
Ethanol	3.4×10^{-2}	2	1.44	55.41		**Benzene**	8.59×10^{-1}	85.85	7.13×10^{-1}	99.04	
Oxygen	1.67	97.95	7.81×10^{-1}	30.02		**Oxygen**	1.41×10^{-1}	14.08	1.28×10^{-3}	0.18	
TCB	8.8×10^{-4}	0.05	3.79×10^{-1}	14.57	**2.56**	**TCB**	6.75×10^{-4}	0.07	5.6×10^{-3}	0.78	**1.84**

Taking these findings into account, it was demonstrated that solvent selection plays a crucial role in carrying out the radiolysis processes of HCB and TCB. Based on kinetic parameters, and in terms of quantitative efficiency and product selectivity, methanol was determined to be the most effective solvent.

33

Furthermore, on the basis of the results obtained, the radiolytic transformation mechanisms of the solvents were presented, and the overall pathways of complete dechlorination were proposed and visually illustrated for both compounds below.

The scheme in Figure 10 demonstrates the γ-radiolytic dechlorination pathway of HCB**,** showing its progressive transformation through intermediate chlorobenzenes until the formation of benzene. The process initiates with the conversion of HCB → PCB, which then undergoes further dechlorination to different TeCB isomers. Subsequent stepwise chlorine elimination produces various TCB isomers, followed by DCB, then MCB, and ultimately benzene.

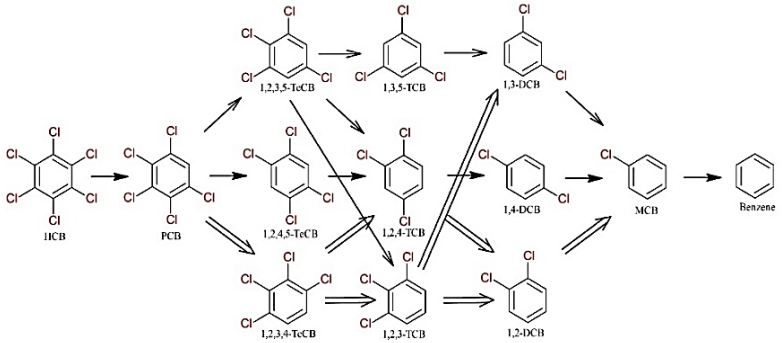

Figure 10. Proposed gamma-radiolytic dechlorination pathway of HCB molecules

Among the multiple transformation directions, the middle pathway (HCB → PCB → TeCB → TCB → DCB → MCB → benzene) is considered the main dechlorination route. This dominance is explained by the higher stability and prevalence of the intermediate isomers (particularly TeCB and TCB) under γ-irradiation, as consistently verified by chromatographic analyses.

The alternative branches leading through other TeCB or TCB isomers exist but play a secondary role, representing minor parallel reactions that occur alongside the primary track. Thus, the figure highlights that the central sequence of progressive chlorine elimination

is the main and most efficient pathway, eventually ensuring almost complete dechlorination of HCB to benzene.

The scheme in Figure 11 represents the γ-radiolytic dechlorination pathway of TCB isomers. Dechlorination proceeds through the sequential removal of chlorine atoms accompanied by hydrogen substitution, ultimately yielding benzene.

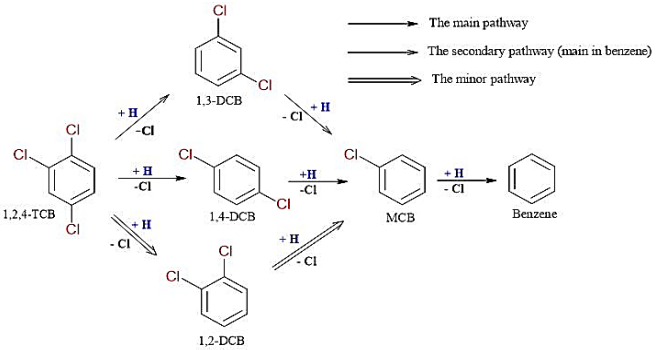

Figure 11. Proposed gamma-radiolytic dechlorination pathway of TCB molecules

According to the figure, the main pathway is observed along the sequence TCB → 1,4-DCB → MCB → benzene, which dominates due to the relative stability of the 1,4-DCB intermediate and its higher frequency of detection during analysis. The secondary pathway, involving 1,3-DCB formation, also leads efficiently toward MCB and finally benzene but occurs to a somewhat lesser extent. In addition, a minor pathway through 1,2-DCB is present, although it contributes insignificantly to the overall transformation.

This distribution clearly emphasizes that while multiple routes exist, the central sequence via 1,4-DCB is the predominant degradation route for TCB, ensuring effective progression toward complete dechlorination into benzene.

MAIN CONCLUSION

1. It was observed that the initial concentrations of HCB (0.044–0.066 g/L) and TCB (1.4–2.0 g/L) decreased by up to 100%. Complete

degradation of HCB and TCB occurred in protic alcohols—methanol and ethanol—at doses of 25.1 kGy and 348.7 kGy, respectively; in acetone and isopropanol at 100.5 kGy and 456.9 kGy, respectively; and in the nonpolar solvent hexane at 169.5 kGy and 456.9 kGy, respectively. At a dose of 169.5 kGy in benzene and toluene, HCB degraded only up to 36%, whereas TCB showed 100% degradation at 456.9 kGy [1, 2, 5, 6, 9, 10].

2. Kinetic analyses demonstrated that the degradation of both HCB and TCB followed pseudo-first-order behavior in all systems. Despite the involvement of solvent radiolysis products, the solvent concentration was assumed to remain essentially unchanged during the analysis of kinetic features. The highest reaction rates were achieved in methanol and ethanol, while among the nonpolar solvents, hexane showed relatively higher kinetic efficiency. In contrast, the aromatic solvents exhibited the lowest degradation rates. The effective rate constants were determined as follows for HCB and TCB, respectively: methanol—5×10^{-3} s^{-1} and 9×10^{-2} h^{-1}; ethanol—2×10^{-3} s^{-1} and 7×10^{-2} h^{-1}; isopropanol—4×10^{-5} s^{-1} and 2×10^{-2} h^{-1}; acetone (for HCB)—9×10^{-5} s^{-1}; hexane—3×10^{-4} s^{-1} and 9×10^{-2} h^{-1}; benzene—6×10^{-5} s^{-1} and 6×10^{-2} h^{-1}; toluene—6×10^{-5} s^{-1} and 6×10^{-2} h^{-1}. These results confirm that methanol provides the most effective degradation pathway for both chlorinated derivatives of benzene [1, 2, 3, 4, 5, 6, 7].

3. Solvent polarity plays a critical role in the selective and complete dechlorination of chlorinated benzene derivatives under γ-irradiation. Although all systems displayed certain levels of efficiency, methanol was consistently confirmed to be superior across all parameters. Based on GC–MS analyses, only chlorobenzene isomers were identified in methanol solutions, and in the HCB + methanol system, no oxygenated or non-oxygenated by-products were detected. This demonstrates that methanol is the most selective solvent, and its use is proposed for the practical implementation of dechlorination by γ-irradiation [1, 2, 3, 4].

4. The results also reveal that the variety of intermediate products formed in all solvent systems is highly complex, which increases the requirement for additional purification stages and elevates the risk of toxic by-product formation. In hexane, the degradation mechanism

involved multiple radical pathways, producing the largest number of by-products. In benzene and toluene, polycyclic aromatic hydrocarbons, biphenyls, terphenyls, and toxic polychlorinated biphenyls (PCBs) were identified [1, 4].

5. According to the proposed complete dechlorination scheme, HCB and TCB decompose through analogous pathways in their respective solvents. In polar solvents, the degradation of HCB proceeds via PeCB, 1,2,4,5-TeCB, 1,2,4-TCB, 1,4-DCB, and monochlorobenzene (MCB), while TCB yields 1,4-DCB, MCB, and benzene. In nonpolar solvents—particularly benzene—the degradation pathway for HCB involves PeCB, 1,2,3,5-TeCB, 1,3,5-TCB, 1,3-DCB, MCB, and benzene, whereas for TCB it proceeds through 1,3-DCB, MCB, and benzene [1, 2, 3, 4, 8].

LIST OF SCIENTIFIC PUBLICATIONS RELATED TO THE DISSERTATION

1. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A., Millet M. Radiolytic degradation of 1,2,4-trichlorobenzene (TCB) in some organic solvents by gamma rays: The kinetic properties of complete dechlorination of TCB and its pathway // Heliyon – 2024, vol. 10, № 10, e31547.
2. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A., Gasimzada L. K., Feyziyeva S. S. Gamma Irradiation-Induced Degradation of Hexachlorobenzene in Methanol: Kinetics, Mechanism and Dehalogenation Pathway // Radiation Physics and Chemistry – 2024, vol. 226, 8 pp.
3. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A., Gasimzada L. K. The role of gamma irradiation in the remediation of hexachlorobenzene: A study in 2-propanol // Key Engineering Materials, Switzerland – 2024, vol. 1003, p. 87–99.
4. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A. Byproduct Analysis from Gamma Radiolysis of 1,2,4-Trichlorobenzene in Benzene // Chemical Safety Science, Russia – 2024, vol. 8, № 2, p. 140–153.
5. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A. Gamma

radiation effects on the pH of 1,2,4-trichlorobenzene in diverse solvent systems // Azerbaijan Journal of Chemical News, Azerbaijan – 2024, vol. 6, № 2, p. 4–15.

6. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A., Gasimzada L. K. The kinetic properties of radiolysis of HCB in selected organic solvents // Scientific News, Azerbaijan – 2024, vol. 24, № 2, p. 24–29.
7. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A., Gasimzada L. K. Investigating the Dechlorination Pathway of Hexachlorobenzene in Acetone through Gamma Irradiation // Advances in Chemistry and Chemical Engineering, Azerbaijan – 2024, vol. 8, № 1, p. 13–22.
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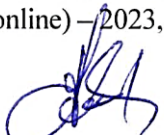
11. **Karimov S. A.**, Abdullayev E. T., Gurbanov M. A. The Study of γ-Radiolysis of 1,2,4-Trichlorobenzene in Methanol Solution // VII International Scientific Conference of Young Researchers, Azerbaijan – 2023, p. 180–182.
12. **Karimov S. A.**, Abdullayev E. T., Qurbanov M. A. The Effect of Gamma Rays on Hexachlorobenzene in Methanol Solutions // 5th International Conference on Natural and Applied Science and Engineering, Türkiye (online) – 2023, Online.



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