Research article

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

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ABSTRACT

This study investigates the degradation of TCB in methanol, ethanol, hexane, and benzene solutions using gamma radiolysis. Kinetic properties of TCB dechlorination and its pathway are examined, with TCB selected as a representative chlorinated organic compound. Chromatograms of irradiated samples and mass spectra of liquid-phase products are presented. The change in concentration of TCB, dichlorobenzenes (DCB), chlorobenzene (MCB), and benzene with absorbed doses are observed. The radiation-chemical yield (G values) of TCB in the solvents are calculated as 1.83, 2.56, 1.93, and 1.84 $100eV^{-1}$ in methanol, ethanol, hexane, and benzene solutions, respectively. 100 % degradation of TCB by gamma irradiation is found to be efficient in polar solvents but leads to a wide variety of byproducts in low polar solvents, particularly the formation of polychlorinated biphenyls in TCB + benzene solutions, making benzene an incompatible medium. The main dechlorination pathway of TCB involves the formation of 1,4-DCB, MCB, and benzene.

Environmental Implication.

The gamma irradiation of chlorinated organic compounds, focusing on TCB as a model compound, was investigated due to its status as a hazardous material for the environment and living organisms. TCB is a byproduct of the dechlorination of certain chlorinated pesticides listed under the Stockholm Convention's Persistent Organic Pollutants (POPs) list, which prohibits their production and use. Gamma irradiation was found to be an effective method for the degradation of chlorinated compounds, achieving 100 % degradation during irradiation. The study underscores the potential of gamma irradiation as a viable approach for the treatment of chlorinated compounds, particularly in addressing environmental and health concerns associated with TCB and related compounds.

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1. Introduction

Hexachlorobenzene (HCB) is one of the most toxic and POPs-listed compounds in Stockholm Convention [1]. The degradation byproduct of HCB and hexachlorocyclohexane [2,3], the TCB, also has its safety considerations. TCB is hazardous compound designated as air pollutant in the frame of Clean Air Act regulated by Environmental Protection Agency in USA [4], and subjected to export notification procedure in the frame of EU regulations [5]. Humans can be exposed to TCB in the workplaces, via inhalation in air or during the use of consumer products [6,7]. There are several health risks of TCB to animals' organs, such as rats, rabbits, guinea pigs [8].

There are some studies covering the research on organochlorine compounds removal from air, aqueous environments, and soil, or involve its degradation. Incineration, oxidation, biological oxidation, or reduction, chemical and catalytic, electrochemical and electrocatalytic treatment are some of those removal methods applied in industry. Conventional methods such as incineration, oxidative and biological techniques have some limitations to degrade hazardous materials, particularly requirement to high amount of energy in incineration and oxidative methods [9]. During biodegradation of these materials requires to create the most appropriate environment for growing of microorganisms and this method may take long time and would be effective not on the whole toxic background, but only on specific toxic compounds [10]. Nanoscale zero valent Fe particles supported on chitosan and silica has been studied [11], however it has some drawbacks, such as low reactivity, low selectivity, metal precipitation, narrow working pH ranges [12]. Photochemical and photocatalytic degradation of TCB has been reported [13,14]. Pure semiconductors are not suggested to be used in photocatalytic degradation because of significant band gap magnitude and the elevated recombination of rate of charge carrier species. Complete MCB degradation has been achieved in the reported study, in turn of 1,2,4-TCB, however, degradation has not had the same efficacy [15]. To reduce the process duration and increase the degree of TCB conversion, naphthalene has been used as media for TCB in electrochemical system [16]. The investigation has revealed degradation of TCB; however, because it necessitates a notably positive potential and exhibits low current efficiency, this technique is not advisable for the advancement of CB removal [17]. The technology of non-thermal plasma has been applied and found that water could play a significant role in decomposition of TCB in low % content and TCB degradation decreases by increasing of oxygen content in the plasma system [18]. Mechanochemical treatment is based on the degradation in the presence of some additives, such as the use SiC for accelerating the reaction [19]. Mechanochemical degradation methods are accompanied by certain limitations. These encompass the necessity for specialized equipment, the potential formation of undesired byproducts, restricted applicability to specific materials, and difficulties in precisely controlling reaction parameters to ensure consistent outcomes.

The removal of POPs by γ-irradiation is promising method could be applied in industrial scale. In the published patent No: CN1277755C in China, HCB utilization and technical scheme have been shown. Some scientific studies have been conducted on the degradation of CBs through γ-irradiation [20,21,22,23]. In the study of [23] TCB has been irradiated in the transformer oil without any additive and >99 % conversion of TCB has been achieved. Some kinetic properties of TCB degradation in deoxygenated 2-propanol and the conversion pathway results have been reported [21]. The degradation of 1,3-DCB was investigated in water-based solutions in the absence of oxygen, with the addition of N_2O or N_2O along with potassium ferrocyanide, $K_3Fe(CN)_6$, as described in the study [20]. Reported that, 1,3-DCB's degradation is dependent on the absorbed dose.

In this work, methanol, ethanol, hexane and benzene have been chosen for gamma-irradiation of 1,2,4-TCB as media. The selection of these solvents for gamma radiolysis in this study was motivated by several factors. These solvents were chosen due to their diverse polarities and chemical properties, which can significantly influence the degradation pathways and efficiency of gamma radiolysis for TCB. Methanol and ethanol are polar solvents, while benzene and hexane are nonpolar solvents, allowing for an investigation into how solvent polarity affects the degradation process. Additionally, the choice of these solvents enables a comparative study to be conducted, evaluating the degradation efficiency and byproduct formation of TCB under different conditions. Furthermore, these solvents are relevant to environmental settings or industrial applications, where POPs contamination may occur, making the study findings potentially applicable to remediation strategies in these contexts. Finally, the selection of these solvents also addresses a gap in the existing literature, as there is limited research on the gamma radiolysis of TCB in organic solvents compared to water.

2. Materials and methods

2.1. Sample preparation

TCB 1,2-, 1,3-, 1,4-DCBs, and MCB were purchased from MERCK, while gradient grade methanol, ethanol, n-hexane (hexane), and benzene were obtained from LiChrosolv. Standard solutions of TCB, DCB isomers, and MCB at concentrations of 1.4–2 g/L in methanol, ethanol, hexane, and benzene were prepared for calibration and γ-irradiation experiments. These solutions were crucial for tracking the byproducts, their concentrations, and determining the TCB-benzene pathway.

2.2. -γirradiation

For γ-irradiation, 1 mL of each TCB + solvent mixture was irradiated in a 2 mL glass bottle with a Teflon screw cap. Irradiation was conducted at room temperature and atmospheric pressure without degassing the solutions. The irradiation was performed using an MRX-γ-25 apparatus with ^{60}Co as the radiation source. Fricke dosimetry [24] with ferrous sulphate was employed to determine the dose rate, which was measured at 1.67 kGy s^{-1}. Complete conversion of TCB was achieved at doses ranging from 0 to 457 kGy, requiring two irradiation processes for each TCB + solvent system.
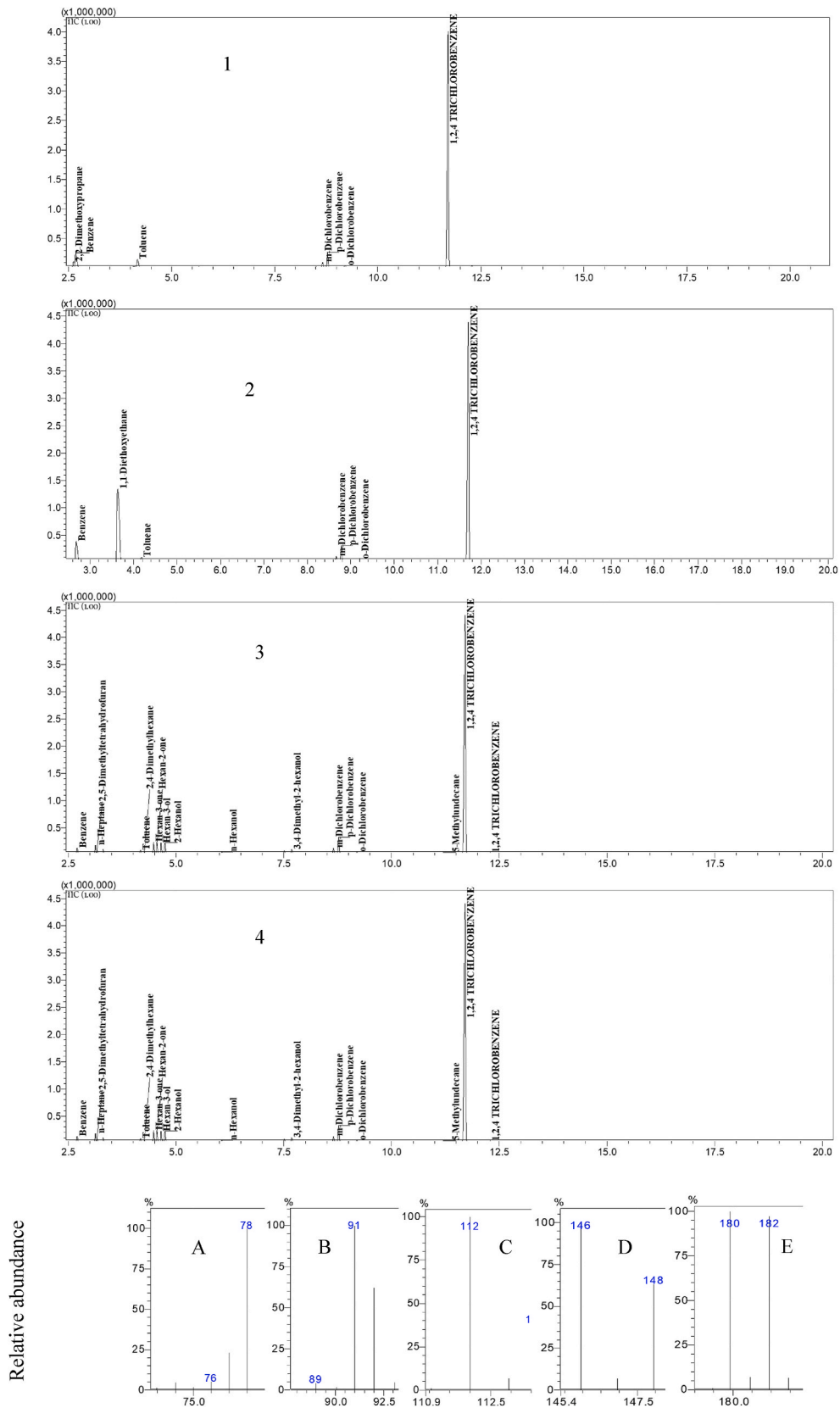
(caption on next page)

Fig. 1. The chromatograms 1, 2, 3 and 4 are the chromatograms of 6 kGy irradiated samples of TCB + methanol, ethanol, hexane and benzene respectively and mass spectra of identified molecules, including benzene (A), Toluene (B), MCB (C), 1,2-, 1,3- and 1,4-DCBs (D), TCB (E).

2.3. GC-MS analysis

A GC-MS (Shimadzu QP2010 SE) equipped with Shimadzu auto injector (AOC-20i) has been used for analysis. Molecules were separated on a Rxi-5ms (Crossbond®), low polarity phase, diphenyl dimethyl polysiloxane capillary column (30 m × 0.25 mm I.D, 0.25 μm film thickness) by using a temperature gradient from 40 °C (2 min) to 250 °C (2 min) at 10 °C/min. Helium was used as mobile phase at 1 mL min⁻ flow rate. The injection was done using a split/splitless injector maintained at 280 °C in split mode (1 min). Detection and quantification were done by electron impact mass spectrometry (single quadrupole) in the Single Ion Monitoring (SIM) mode (EI mode). Masses used for the SIM were: 74 m/z, 109 m/z, and 145 m/z for TCB, 74 m/z, 111 m/z, and 146 m/z for DCBs. The temperatures of the source and transfer line were 210 °C and 280 °C, respectively.

With this method, separation of TCB, chlorinated and non-chlorinated radiolysis products have been achieved in 27 min.

3. Results

3.1. GC-MS analysis of irradiated samples

The samples of the TCB + organic solvent systems were subjected to γ-irradiation and subsequently analyzed using GC-MS. Fig. 1 shows the chromatograms of samples irradiated at 6 kGy from mixtures of TCB with methanol, ethanol, hexane, and benzene and main byproducts' mass spectra.

The chromatograms of 6 kGy irradiated samples from different systems illustrate the increasing complexity of byproducts in methanol, ethanol, hexane, and benzene media. This complexity indicates the diverse range of degradation products generated during the irradiation process.

3.1.1. The samples of TCB in methanol and ethanol
Fig. 2 illustrates the change in concentration and degree of TCB in the irradiated samples. Complete degradation of TCB, corresponding to 100 % conversion, was achieved at 420.8 kGy and 456.9 kGy in methanol and ethanol solutions, respectively.

3.1.2. The samples of TCB in hexane and benzene
In Fig. 3, the change in concentration and conversion degree of TCB in low-polarity solvents is presented. TCB reaches maximum degradation at the maximum applied dose of 456.9 kGy in hexane and benzene, with conversion degrees of 100 % and 99.1 %, respectively. Both figures show that all curves start to decrease sharply, continuing until 48.1 kGy in polar solvents and 108.2 kGy in low-polarity solvents. This reduction in changes after the mentioned doses is attributed to the low concentration of TCB remaining in the solutions, which continues until complete dechlorination of TCB is achieved.

3.1.3. CB products
The first and the main CB product of TCB degradation in all the systems is 1,4-DCB, except in benzene. The dependence of CB products' concentration on absorbed doses has been given in Fig. 4. After reaching maximum amount, CB products start to degrade at additional applied doses. The highest degradation of CBs observed in hexane solutions. It can be explained with the possible reactions between complicated radiolysis byproducts of hexane [25] with CB products in the solutions.

3.1.4. Benzene product
Benzene molecules were identified in TCB + methanol, ethanol, and hexane systems. As shown in Fig. 5, in methanol, sharp increase of benzene curve is observed at 0–3 kGy dose and between 3 and 456.9 kGy no strict change in the amount of benzene has been
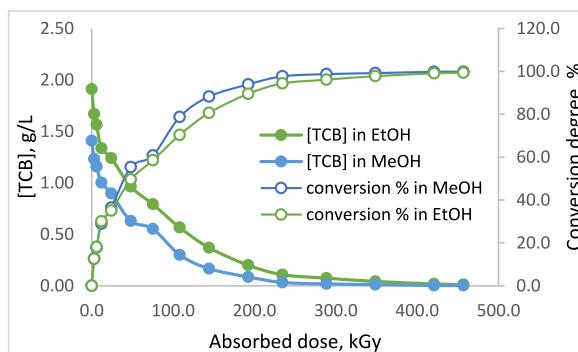

Fig. 2. Concentration and conversion degree of TCB as a function of absorbed doses.
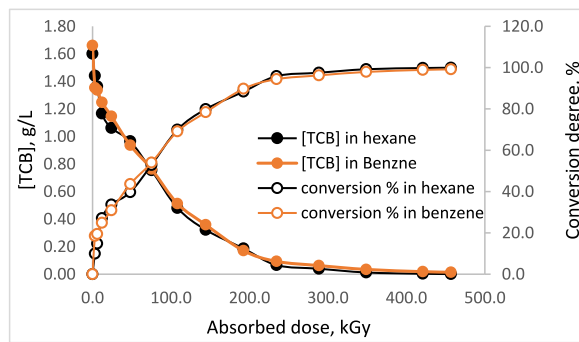
Fig. 3. Concentration and conversion degree of TCB as a function of absorbed doses.

Fig. 4. The changes of the concentration of MCB (A), 1,2-DCB (B), 1,3-DCB (C) and 1,4-DCB (D) in irradiated TCB + solvent systems: blue, orange, black, green curves indicate methanol, ethanol, hexane, and benzene solutions, respectively.

Fig. 5. The concentration of benzene as a function of absorbed dose: blue, orange, black are in methanol, ethanol, and hexane solutions, respectively.

defined. In ethanol the start of the formation of benzene is like TCB + methanol system. The second sharp increase is obs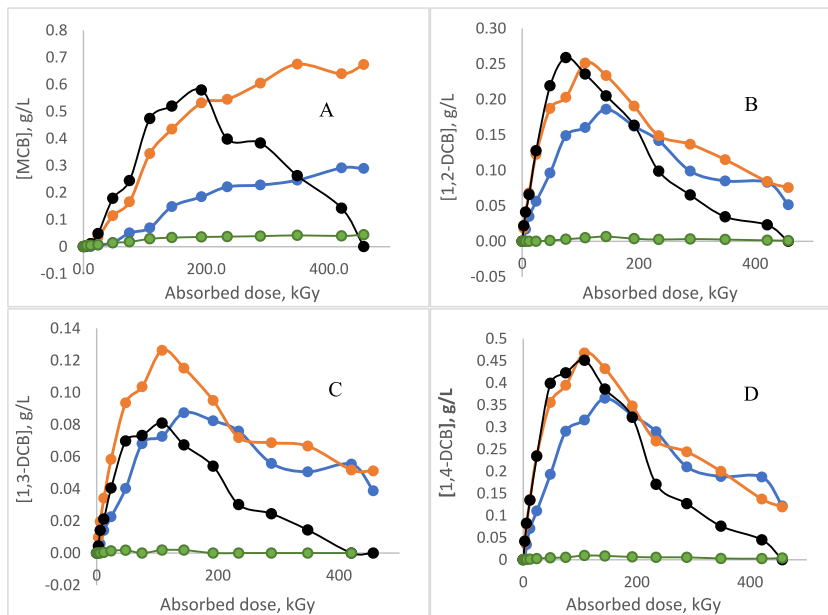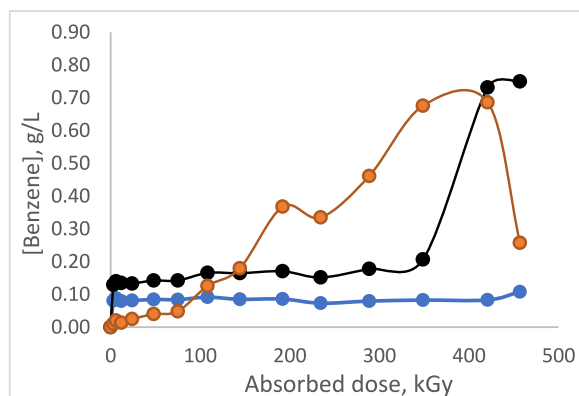erved at 348.7–420.8 kGy doses. In hexane solution the curve increases slightly at 0–420.8 kGy. This increase may be related due to the dehydrogenation of cyclic hydrocarbon products of gamma radiolysis of hexane [25]. Between 420.8 and 456.9 kGy, benzene degrades or converts into both ethanol and hexane solutions. Benzene has not been studied in TCB + benzene systems because the solvent is considered non-changed in concentration. Additionally, various polychlorinated biphenyl molecules have been identified in the irradiated systems of TCB + benzene.

3.1.5. The kinetics of TCB dechlorination by gamma radiolysis

The mole ratio of TCB to solvent in the selected systems exhibit a significant difference. Degradation in this type of medium is considered a pseudo first-order process [26,27]. Ln [TCB has been plotted against irradiation time in Fig. 6. The obtained numerical results, including the experimental radiation chemical yield (the G value) of TCB consumption at 12 kGy, have been calculated and are presented in Table 1.

3.1.6. Solvent radiolysis and possible reactions

When solvents are exposed to gamma rays, active particles such as radicals and free ions are formed. The kinetics of solvent radiolysis has been investigated in various research projects. Table 2 presents some of the main primary active products with their corresponding G values in selected solvents.

The gamma radiolysis of the selected systems was conducted in the presence of air, allowing available molecules, including solvated oxygen in the selected systems to interact with primary products during gamma radiolysis. Rate constants for possible reactions of active particles ·H and $e_{sol.}^-$ are shown in Table 3. Notably, the rate constants for TCB + ·H and $e_{sol.}^-$ were not found in scientific sources. Instead, the rate constants for benzene + ·H and $e_{sol.}^-$ were used, assuming that the dechlorination occurs in the aromatic ring of TCB.

Table 3 indicates that ·H and $e_{sol.}^-$ are scavenged by solvent, oxygen and TCB molecules to varying degrees. To clarify the relative scavenging of both active particles the following formulas were used: [4]: – The average rate of reactions [31]; – The relative G values [13]; – The percentage of active particles undergoing chemical interaction.

$$\alpha = \frac{k_n[R_1][R_2]}{k_n[R_1][R_2] + k_m[R_1][R_3] + k_p[R_1][R_4]} \qquad\qquad 1$$

$$Relative\ G = \alpha * G(ref.) \qquad\qquad 2$$

$$\%\ of\ particle = \frac{Relative\ G}{G(ref.)} * 100\% \qquad\qquad 3$$

k values were appropriately selected from Table 3, where R_1 represents ·H and $e_{sol.}^-$, R_2, R_3, R_4 represent solvent, oxygen and TCB reactants. All the calculated values are given in Table 4.

As shown in Table 4, because the calculated relative G values are too small than experimental values in all the systems, TCB is not considered to be consumed in primary reactions with active particles but reacts in molecular reactions. However, the calculated 22.86 %, 14.57 %, 6.01 %, 0.78 % of ·H show the reduction reaction between TCB to convert it into less chlorinated molecules respectively in methanol, ethanol, hexane, and benzene solutions. The small values of 0.78 % ·H involving in the reaction with TCB, and CB products' concentrations identified in irradiated TCB + benzene solutions show that, the decrease of TCB is taken place due to the formation of polychlorinated biphenyl congeners (Table 5.).
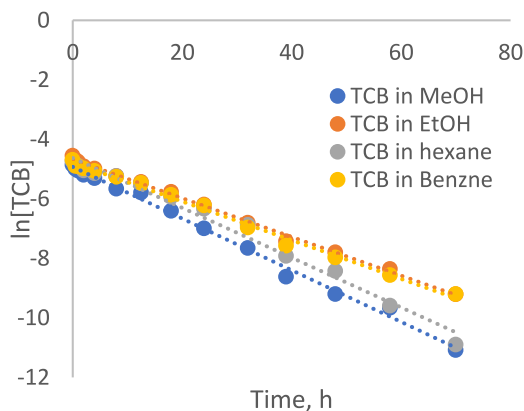

Fig. 6. Ln [TCB] versus time in irradiated TCB + solvent systems.

Table 1

The experimental kinetic properties of TCB + solvent systems.

	Mole ratio: solvent: TCB	The effective rate constant, h-	Linear correlation coefficient	Experimental G, 100eV-
TCB + methanol	3180:1	8.7×10^{-2}	0.994	1.83
TCB + ethanol	1631:1	8.4×10^{-2}	0.985	2.56
TCB + hexane	869:1	6.5×10^{-2}	0.995	1.93
TCB + benzene	1219:1	6.5×10^{-2}	0.996	1.84

Table 2

The main primary active products of the solvents' radiolysis and relevant radiation-chemical yields.

Solvent	Products (G values, 100eV$^-$)
Methanol	$e_{sol.}^-$ (3.1 [28]); ·H (2.02[[29,30]]); CH$_2$O· (1.44[[29]]); ·CH$_2$OH (2.7[[31]]); ·CH$_3$(1 [[31]]); and heavy ions
Ethanol	$e_{sol.}^-$ (1.7[[32]]); ·H (2.6[[31]]); CH$_3$CHO (1.7[[33,32]]); ·CH$_3$(0.4 [[32]]); and heavy ions
Hexane	·H (3.16 [[34]]); ·CH$_3$(0.92 [[34]]); C$_2$H$_5$(0.92 [[34]]); C$_3$H$_7$(0.92[[34]]); and heavy ions
Benzene	·H (0.72 [[35]]); ·C$_6$H$_5$(0.72[[35]]); and heavy ions

Table 3

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)	Ref.	rate constant, L/(mol x s)	Ref.
CH3OH	1.7×10^6	[[36]]	10^4	[[37]]
C2H5OH	1.7×10^7	[[37]]	1.7×10^5	[[32]]
C6H14	1.4×10^8	[[37]]	–	
C6H6	9.1×10^8	[[37]]	9×10^6	[[37]]
O2	2.1×10^{10}	[[37,36]]	1.9×10^{10}	[[36]]
TCB	9.1×10^8	[[37]]	9.1×10^6	[[37]]

Table 4

The calculated relative G values and % of the active particles in primary reactions with solvent, oxygen, TCB, and experimental G values (Exp.) of TCB obtained from selected systems' gamma irradiation.

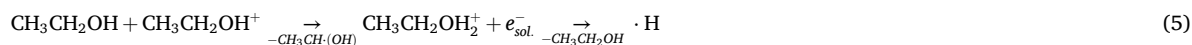| IN METHANOL (CALCULATED)					EXP.	IN HEXANE (CALCULATED)					EXP.
	$e_{sol.}^-$		·H		100eV$^-$		$e_{sol.}^-$		·H		100eV$^-$
	Relative G	%	Relative G	%			Relative G	%	Relative G	%	
METHANOL	4.3×10^{-3}	0.14	2.74×10^{-1}	13.55		Hexane	–	–	2.55	80.59	
OXYGEN	3.1	99.86	1.28	63.58		Oxygen	–	–	4.23×10^{-1}	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

3.1.7. The predicted reaction mechanisms

When the solvent exposed to gamma irradiation, solvated electrons, $e_{sol.}^-$ form in the media [11]. $e_{sol.}^-$ reacts with methanol to form H atoms as shown in the reaction [4]:

$$CH_3OH + e_{sol.}^- \rightarrow CH_3O^- + ·H \tag{4}$$
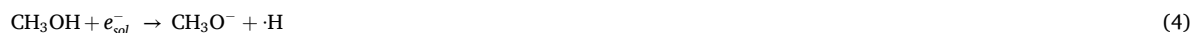
[[37,36]]

The similar reaction occurs between $e_{sol.}^-$ and protonated CH$_3$CH$_2$OH$_2^+$ in ethanol [31]:

$$CH_3CH_2OH + CH_3CH_2OH^+ \underset{-CH_3CH·(OH)}{\rightarrow} CH_3CH_2OH_2^+ + e_{sol.}^- \underset{-CH_3CH_2OH}{\rightarrow} ·H \tag{5}$$

[[37,32]]

Normal hexane and benzene give H atoms in first step reactions of [13,20] respectively during irradiation:

$$C_6H_{14} \xrightarrow{\gamma\ irradiation} ·C_6H_{13} + H \tag{6}$$

[[37]]

$$C_6H_6 \xrightarrow{\gamma\ irradiation} ·C_6H_5 + H \tag{7}$$

Table 5
The area of identified byproducts at appropriate absorbed doses in irradiated TCB + solvent systems.

Names of the main byproducts	Absorbed doses (kGy)										
In benzene	0	3	6	24	48	108	144	192	235	349	457
The area of the peaks in chromatograms											
1,1′-biphenyl	83,128	191,178	736,286	1,428,187	3,730,047	4,180,785	5,004,368	5,817,256	6,828,482	7,889,551	9,814,584
4,4′-dichlorobiphenyl	745,262	1,686,529	5,107,450	7,707,647	10,202,783	9,101,394	6,223,205	4,782,536	4,050,135	2,934,228	187,401
2,4′-dichlorobiphenyl	32,673	70,844	280,477	448,149	629,809	570,097	129,759	288,850	240,580	166,574	94,424
N-Heptane	93,424	87,359	91,847	90,590	84,936	83,378	82,827	77,802	80,312	86,826	82,375
Ethylcyclopentane	63,920	60,920	62,620	56,692	45,209	45,857	40,487	38,719	35,440	36,574	41,514
Methylcyclohexane	304,697	285,459	281,460	263,259	219,204	218,617	200,863	186,726	183,138	193,062	190,044
P-Terphenyl, 4-chloro-	–	–	92,843	346,932	2,063,893	2,412,571	2,479,951	2,586,490	2,893,354	2,823,501	3,156,859
2-chlorobiphenyl	–	–	–	70,658	1,301,473	1,756,926	2,561,424	2,966,636	3,479,367	3,890,861	4,375,498
3-chlorobiphenyl	–	–	–	117,833	1,301,471	948,806	1,300,932	1,389,631	1,517,640	1,584,161	1,464,210
3,5-dichlorobiphenyl	–	–	–	–	32,222	53,324	59,079	–	–	–	–
Phenol	25,453	49,019	235,712	458,638	606,568	531,694	399,349	468,689	508,773	429,038	492,075
In hexane											
N-Heptane	133,858	179,685	251,824	288,472	320,431	345,167	446,921	448,645	505,470	708,641	652,929
Hexan-3-one	104,445	306,849	1,086,602	1,418,255	1,440,447	1,350,882	1,377,032	1,565,282	1,399,727	1,631,360	1,387,191
Hexan-2-one	96,363	316,145	1,169,491	1,580,521	1,631,850	1,559,099	1,640,354	1,851,948	1,734,010	2,033,887	1,718,947
Hexan-3-ol	90,619	285,995	1,111,755	2,025,636	2,500,427	2,362,391	2,484,920	2,701,586	2,559,217	2,986,194	2,388,977
Toluene	57,905	85,510	141,434	133,605	117,964	17,003	179,832	115,002	134,539	176,242	134,057
Benzene	50,325	143,368	172,677	279,763	886,463	1,264,745	2,587,736	2,356,879	3,246,266	4,758,332	1,811,598
Hexan-2-ol	156,696	309,234	1,083,425	2,295,031	3,005,958	2,925,268	3,072,889	3,270,495	3,296,402	3,875,457	3,104,246
2-chlorohexane	–	–	52,895	1,688,820	3,364,804	4,332,050	6,624,736	6,691,860	8,935,712	12,305,442	9,805,607
4,5-diethyl-octane	–	–	88,104	381,955	1,984,641	2,705,577	3,625,582	4,022,339	9,305,658	24,630,535	25,670,698
N-Dodecane	–	18,125	55,546	125,776	19,497	399,606	595,174	720,768	870,484	1,250,352	1,412,343
In ethanol											
Benzene	335,839	356,301	936,419	1,000,996	1,165,353	1,159,569	1,199,845	1,067,164	1,250,256	1,453,529	1,558,912
1,1-diethoxyethane	648,320	5,240,451	13,940,790	19,658,198	28,507,960	31,538,077	33,741,001	36,063,946	38,763,592	46,097,017	52,290,597
Toluene	59,650	223,923	214,767	274,445	276,754	266,943	170,172	589,728	1,647,621	163,001	–
Butane-2,3-diol	–	–	–	857,953	3,209,404	4,059,708	5,825,140	7,076,476	8,194,303	10,899,169	14,360,611
Alpha.-methyl-2,3-dichlorobenzenemethanol	–	–	63,287	208,892	629,725	739,334	760,219	760,566	740,889	825,869	730,718
In methanol											
Benzene	568,485	623,894	571,263	593,535	643,761	598,515	603,600	513,650	558,910	580,889	759,530
Toluene	205,350	346,625	479,213	2,695,202	245,768	366,383	18,227	953,729	154,655	170,395	264,388
3,4,6-trichloro-o-cresol	–	–	39,227	223,717	174,020	150,040	111,076	68,838	47,266	43,559	–
2,4-dichlorobenzenemethanol	–	–	–	–	349,126	307,983	406,088	370,985	373,903	369,592	275,260
Ethylene glycol	–	–	–	86,459	425,251	632,189	772,840	798,475	860,714	1,800,849	363,617

[[37]]

The further reactions occur between the H atoms and CBs to form less chlorinated products of [2].

$$C_6H_3Cl_3 + H \underset{-Cl\cdot}{\rightarrow} C_6H_4Cl_2 + H \underset{-Cl\cdot}{\rightarrow} C_6H_5Cl + H \underset{-Cl\cdot}{\rightarrow} C_6H_6 \tag{8}$$

The degradation pathway of TCB in organic solvents.

The obtained results are used for formulation of the TCB dechlorination pathway and are shown in Fig. 7.

The obtained reduction pathway agrees with the pathway reported in some TCB dechlorination studies by different methods [38, 39,11,40,41]. This pathway is similar for all 4 TCB + solvent systems with only little difference in benzene. The dechlorination starts with formation of 1,4-DCB in methanol, ethanol and hexane solutions as mentioned above. 1,3-DCB is the main product in benzene solutions. 1,2-DCB is the minor DCB product among all isomers in all irradiated systems. The next dechlorination product is MCB, forms in direct and indirect dechlorination of TCB and DCBs, respectively. Benzene is the final and non-chlorinated aromatic molecule of complete gamma radiolytic dechlorination of TCB in selected organic solvents in liquid phase.

3.2. Byproduct variety in different solvents

Our analysis focused on identifying the most suitable solvent based on the byproducts generated during the degradation process. Some main identified byproduct molecules have been given in Table 5. Among the solvents tested, hexane and benzene, both nonpolar solvents, produced the most undesirable byproducts, rendering them less suitable for the remediation of POPs. Ethanol and methanol, on the other hand, exhibited a lower production of undesirable byproducts, indicating their potential for more efficient POPs degradation. Our findings suggest that methanol is the most appropriate solvent for the remediation of POPs using gamma radiolysis. Methanol not only demonstrated a lower production of undesirable byproducts compared to other solvents but also exhibited a high efficiency in degrading POPs, as indicated by the calculated 22.86 % of hydrogen radicals undergone in the chemical reaction.

This finding underscores the potential of gamma radiolysis as a scalable, cost-effective, and environmentally friendly solution for treating POPs contamination in soil and water on an industrial scale.

4. Conclusion

Gamma radiolysis is an effective method for removal of chlorinated organic compounds, in this case TCB, from the environment. Complete dechlorination of aromatic ring in TCB has been achieved in polar solvents of methanol, ethanol more advantageous. The comparable values of calculated relative G and experimental G show the degradation of TCB happens in molecular reactions and some part of hydrogen atoms attack TCB molecules to dehalogenase it into low chlorinated benzenes. The pathway of TCB dechlorination has been obtained from the plot of DCB concentration as a function of absorbed doses, and shown that, the primary dechlorination product of TCB is 1,4-DCB. Although the amount of TCB similarly decreases in benzene solution, this solvent is not useful for degradation of chlorinated aromatic compounds, because of formation of different toxic polychlorinated biphenyl molecules. Further research on chlorinated benzene degradation in organic solvents by gamma radiolysis is suggested, to study kinetic properties of the final – gas products of those systems.

5. Data availability statement

All data, including chromatograms, mass spectra, numerical and other results, generated for this study are freely available without
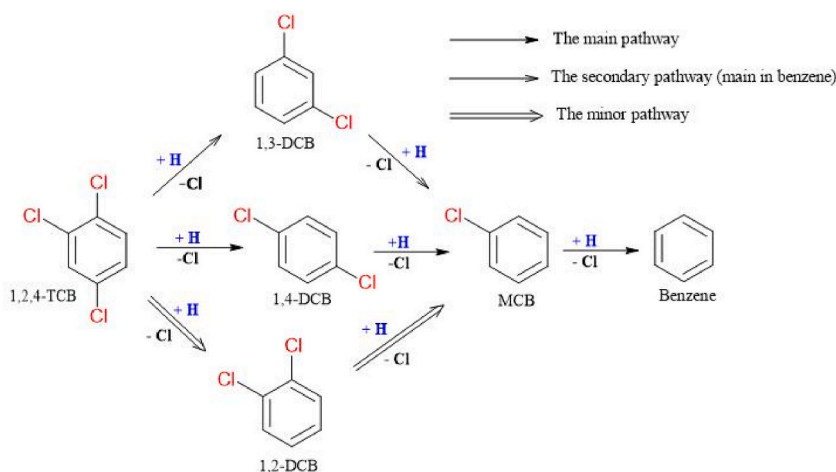

Fig. 7. The complete dechlorination pathway of TCB.

the use of any external dataset repository. Please contact the corresponding author for access to the data.

CRediT authorship contribution statement

Samir Karimov: Writing – original draft, Investigation. **Elshad Abdullayev:** Writing – original draft, Supervision, Investigation. **Maurice Millet:** Writing – review & editing. **Muslum Gurbanov:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Samir Karimov reports equipment, drugs, or supplies was provided by Azerbaijan State Oil and Industry University. Muslum Gurbanov reports equipment, drugs, or supplies and writing assistance were provided by Azerbaijan National Academy of Sciences Institute of Radiation Problems.

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