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RADIOLYSIS OF CHLORORGANIC PESTICIDES SOLUTIONS IN HEXANE

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Abstract: The kinetics of radiolysis processes of 9 chlorous-organic pesticides (hexachlorbenzene, α-HCH, β-HCH, lindan, 4,4′-DDE, 4,4′-DDD, 4,4′-DDT, aldrin and heptachlor) solutions (10 – 1000 ug/l) in hexane at 13,8; 27,7; 67,4 and 105,4 kGy doses was studied and the radiation-chemical yields of conversion processes were calculated in the work. It was identifed that the conversion of pesitides of 105,4 kGy dose is 65-95%, radiation-chemical yields are (0,009 – 1,247) · 10^{-3} molecules/100 eV. Increasing of initial concentration leads to the radiation-chemical yields raising.

Keywords: radiolysis, pesticide, radiation-chemical yields

1. Introduction

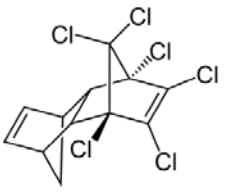
Pesticides are substances included in the Stockholm Convention on Persistent Organic Pollutants. Their production and extensive use in agriculture in Azerbaijan has caused serious pollution of the environment. At present, some methods are used to clean the soil from pesticides. Locating pesticide residues in special polygons is one of the most common method. However, the use of chemical methods to purify soil and water from pesticides is also considered. Among them, radiation-chemical methods play a special role. The advantages of radiation methods are that the processes are one-stage and carried out at low temperatures, mainly without additional chemical reagents. The processes of radiation-chemical conversion of pesticides in various liquid mediums have been studied. Among these research works, works carried out in water dominate [1-3]. In some cases, the processes of pesticides conversion by radiation in various organic solvents have been studied. In [4] the radiation-chemical conversion processes of heptachlor in methanol, and in [5] radiation-chemical conversion processes of α-HCH, γ-HCH, 4,4'-DDT and 4,4'-DDE in hexane and isopropyl alcohol have been studied. In [5] studied the dependence of radiolithic degradation rate of pesticides under γ-rays in the range of 0 to 55.45 kGy on dependence their initial concentration (0.01-1 ug/ml), solvent polarity (hexane and isopropyl alcohol), dissolved oxygen involvement, and dose rate (0.0083 - 2.33 Gy/sec) were studied, and radiation-chemical yields of conversion processes were calculated. It has been identified that the concentration of pesticides decreases with absorbed dose increasing. The degradation rate is higher in isopropyl alcohol than in hexane. Also, as the concentration of pesticides in the primary solution increases, the degradation rate generally decreases. For example, in the 0.1 ug/ml DDE consentration solution degradation rate in hexane and isopropyl alcohol at 1 kGy is ~ 7%, ~ 7% in, respectively ~ 30% and ~ 58% in 10 kGy absorbed dose. But in 1 ug/ml consentration solution the degradation rate in hexane and isopropyl alcohol at 1 kGy absorbed dose is ~ 3%, ~ 7%, and in 10 kGy absorbed dose is ~ 22% and ~ 32% respectively. The dependence of the fractional conversion on dose rate is complex. For example, the degradation rate of the DDE is initially increased in the range of 0.0083 – 2,33 Gy/sec dose rate at the absorbed dose of 10 kGy. Reducing the concentration of soluble oxygen causes 1.5 to 2 times increase of the pesticide conversion rate. The radiation-chemical yeilds of pesticides are

mainly composed of 10^{-3} molecules / 100 eV in the studied systems.

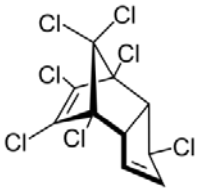
In presented work, the kinetics of radiolysis processes of 9 chlorous-organic pesticides (hexachlorbenzene, α-HCH, β-HCH, lindan, 4,4′-DDE, 4,4′-DDD, 4,4′-DDT, aldrin and heptachlor) solutions in hexane was studied in 0 - 105 kGy doses range, and the radiation-chemical yield of conversion processes were calculated.

2. Materials and methods

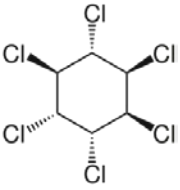
Each pesticide's individual standard has been used for the preparation of model solutions. The formula of the studied pesticides are as follows:



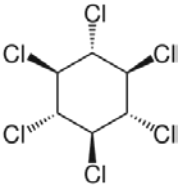
Aldrin ($C_{12}H_8Cl_6$)



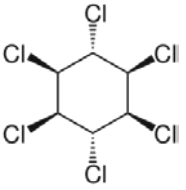
Heptachlor ($C_{10}H_5Cl_7$)



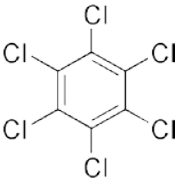
α-HCH



β-HCH

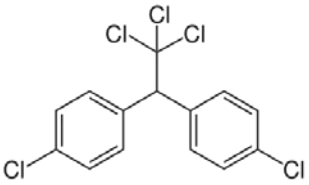


γ-HCH (lindan)

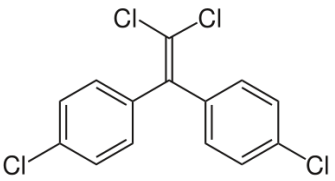


Hexachlorbenzene (C_6Cl_6)

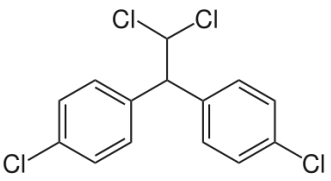
1,2,3,4,5,6- Hexachlorocyclohexane ($C_6H_6Cl_6$)



DDT



DDE



DDD

The initial consentration of pesticides in these solution are given in Table 1.

Table 1. Consentration of pesticides in radiolyzed solutions

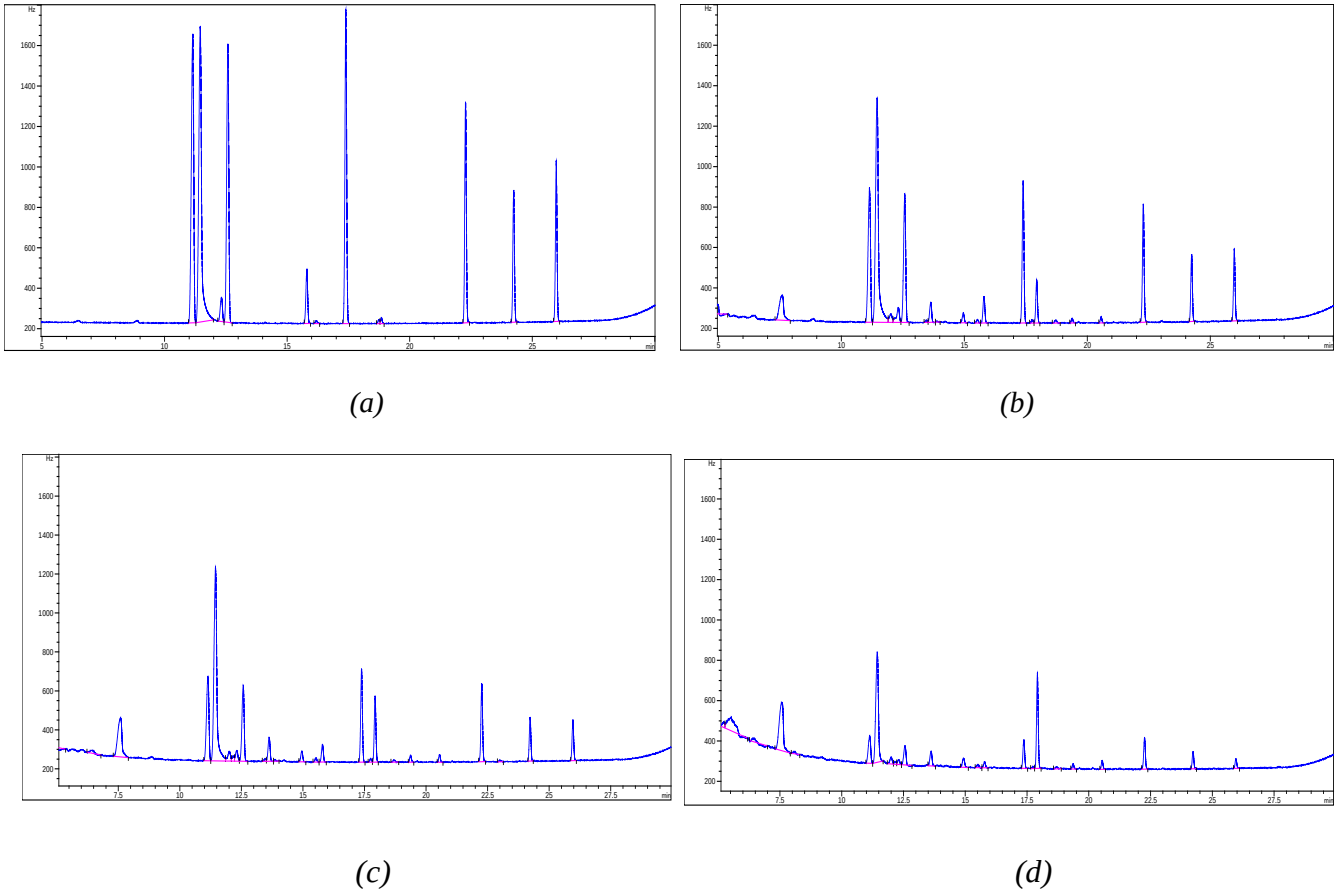
Pesticides	İnitial concentration, mol/*l*			
	I	II	III	IV
Hexachlorbenzene	$1{,}75 \cdot 10^{-7}$	$3{,}51 \cdot 10^{-7}$	$1{,}75 \cdot 10^{-6}$	$3{,}51 \cdot 10^{-6}$
α-HCH	$1{,}72 \cdot 10^{-7}$	$3{,}43 \cdot 10^{-7}$	$1{,}72 \cdot 10^{-6}$	$3{,}43 \cdot 10^{-6}$
β-HCH	$1{,}72 \cdot 10^{-7}$	$3{,}43 \cdot 10^{-7}$	$1{,}72 \cdot 10^{-6}$	$3{,}43 \cdot 10^{-6}$
Lindan	$1{,}72 \cdot 10^{-7}$	$3{,}43 \cdot 10^{-7}$	$1{,}72 \cdot 10^{-6}$	$3{,}43 \cdot 10^{-6}$
4,4′-DDE	$1{,}57 \cdot 10^{-7}$	$3{,}14 \cdot 10^{-7}$	$1{,}57 \cdot 10^{-6}$	$3{,}14 \cdot 10^{-6}$
4,4′-DDD	$1{,}56 \cdot 10^{-7}$	$3{,}12 \cdot 10^{-7}$	$1{,}56 \cdot 10^{-6}$	$3{,}12 \cdot 10^{-6}$
4,4′-DDT	$1{,}41 \cdot 10^{-7}$	$2{,}82 \cdot 10^{-7}$	$1{,}41 \cdot 10^{-6}$	$2{,}82 \cdot 10^{-6}$
Aldrin	$1{,}40 \cdot 10^{-7}$	$2{,}74 \cdot 10^{-7}$	$1{,}40 \cdot 10^{-6}$	$2{,}74 \cdot 10^{-6}$
Heptachlor	$0{,}27 \cdot 10^{-7}$	$0{,}54 \cdot 10^{-7}$	$0{,}27 \cdot 10^{-6}$	$0{,}54 \cdot 10^{-6}$

Model solutions were radiated with γ-rays (^{60}Co) with the dose rate of 0.16 Gy/sec in static condition and at room temperature. The identification of pesticides was conducted using a Gas Chromatography (Agilent Technologies 7820A). N_2 was used as the gas carrier in the

chromatography (obtained from the nitrogen generator and is purified by filter (99.95%)). The gas flow rate was 1.4 ml/min. The Agilent J&W Capillary GC column (HP-5MS, 30 m x 0,250 mm x 0,25 um) was used for analysis, the temperatures of the injector, thermostat and detector (ECD) were 210°C, 290°C and 300 °C accordingly.

3. Results and discussion

Figure 1 shows chromatograms for the III solution.



(a) *(b)*

(c) *(d)*

Fig. 1. Chromatograms for hexane solutions of pesticides (III solution):
a - primary; b - 13,8 kGy; c - 27.7 kGy; d - 67.4 kGy (1 - α - HCH; 2 - hexachlorobenzene; 3 - β-HCH; 4 - lindan; 5-heptachlor; 6-aldrin; 7.4.4'-DDE; 8 - 4,4'-DDD; 9 - 4. 4'-DDT).

As seen from the comparison of chromatograms in Figure 1, the area of peaks corresponding to primary pesticides decreases during the radiolysis. The reason for this is the conversion (transformation) of pesticides as a result of radiolysis. Also, number of peaks in the chromatograms (b, c, and d) of the radiolyzed samples exceeds the number of peaks in chromatograms (a) corresponding to the primary solution. This is due to the formation of other organic compounds as a result of transformation of pesticides within the primary solution.

Figure 2 shows the dependency graphs of the pesticide concentration (C) on the absorbed dose (D) during the radiolysis of the IV solution.

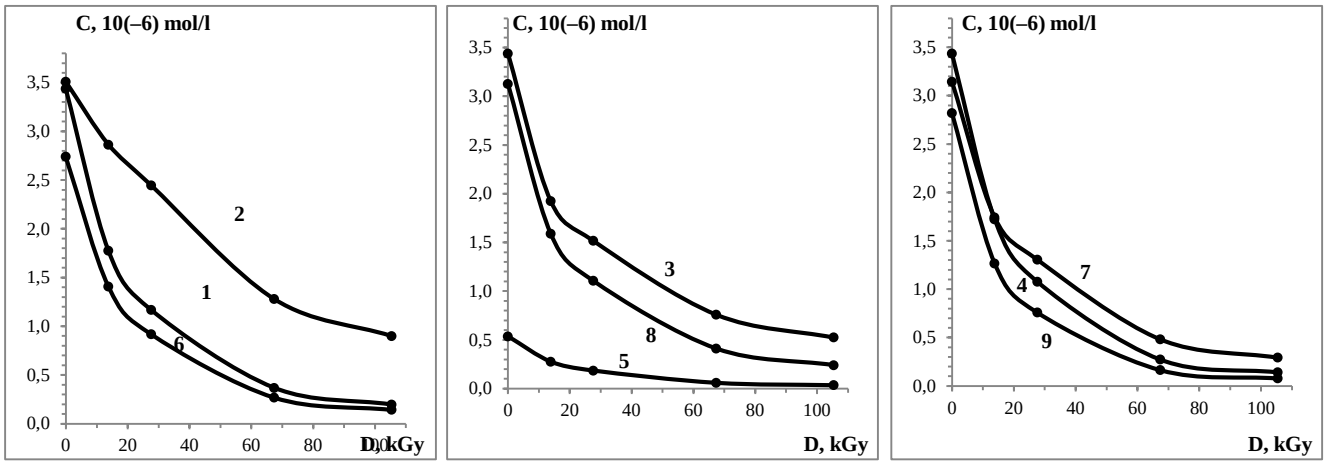


Fig. 2. The conversion kinetics during the radiolysis of pesticides solutions in hexane (1 - α - HCH, 2 - hexachlorobenzene, 3 - β - HCH, 4 - lindan, 5 - heptachlor, 6 - aldrin, 7 - 4,4' - DDE; 4,4'-DDD; 9-4,4'-DDT).

As seen from Figure 2, the amount of pesticides decreases during their radiation in the hexane solution. α-HCH exposes to 90.2%, hexachlorobenzene to 65.3%, β-HCH to 78.2%, linden 92.1%, hetaactor 89.0%, aldrin 90.7%, 4.4 ' -DDE 85.7%, 4.4'-DDD 86.7% and 4.4'-DDT 93.8% conversion in 105.4 kGy absorbed dose. Table 2 shows the radiation-chemical yields (G) of pesticide conversion processes.

Table 2. Radiation-chemical yields of pesticides conversion processes during radiolysis of pesticides in hexane solutions.

Pesticide	Radiation-chemical yield (G), 10^{-3} molecule /100 eV			
	I solution	II solution	III solution	IV solution
Alfa-HCH	0,061	0,127	0,666	1,159
Hexachlorobenzene	0,025	0,059	0,376	0,450
Betta-HCH	0,057	0,100	0,543	1,247
Lindan	0,062	0,129	0,679	1,194
Heptachlor	0,009	0,018	0,100	0,181
Aldrin	0,050	0,103	0,544	0,928
4,4-DDE	0,049	0,098	0,534	0,978
4,4-DDD	0,053	0,104	0,587	1,070
4,4-DDT	0,054	0,107	0,597	1,084

As seen in Table 2, the values of radiation-chemical yields of pesticide conversion processes in the given concentrations are $(0.009 - 1{,}247)\cdot 10^{-3}$ molecules/100eV. Figure 3 gives a curve of dependence of the radiation-chemical yields (G) of the conversion processes on the initial concentration (C) during the α-HCH radiolysis.

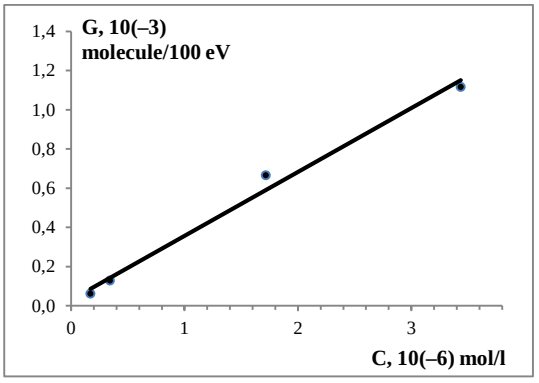


Fig. 3. The dependence of the radiation-chemical yield (G) on the initial concentration (C) of the conversion processes during the α-HCH radiolysis.

As seen from Figure 3, the radiation-chemical yield of α-HCH conversion processes during radiolysis increases depending on its initial concentration raising. The corresponding dependency is similar to other components too. The electron density of hexane is greater than the electron density of pesticides and dissolved oxygen in the studied systems. For example, the total density of pesticides in the IV solution is $2.53 \cdot 10^{21}$ electrons/l, of the dissolved oxygen is $\sim 4.3 \cdot 10^{22}$ electrons/l, and of the hexane is $3{,}29 \cdot 10^{26}$ electrons/l. Therefore, the ionization energy are mainly absorbed by hexane molecules. Hexane molecules are energized by the effects of this energy (1) or the electron separation from its molecule occurs (2).

$$C_6H_{14} = C_6H_{14}^* \quad (1)$$

$$C_6H_{14} = C_6H_{14}^+ + e^- \quad (2)$$

And the conversion of pesticides occurs by the transfer of energy from hexane molecules to the pesticide molecules (3) or by the anion load change with the pesticide molecule (4). For example, this process can be shown for α-HCH as follows:

$$C_6H_{14}^* + C_6H_6Cl_6 = C_6H_{14} + C_6H_6Cl_6^* \quad (3)$$

$$C_6H_{14}^+ + C_6H_6Cl_6 = C_6H_{14} + C_6H_6Cl_6^+ \quad (4)$$

The reason of (4) reaction occurence can be seen from the comparison of ionization potentials (E) of hexane and pesticide molecules. ΔE = E(hexane) – E(α-HCH) = 11,114 – 9,589 = 1,525 eV, since E(hexane) = 11,114 eV and E(α-HCH) = 9,589 eV. That is, this process takes place with the yield of 1,525 eV energy. The ionization potential of other pesticides is smaller than the hexane ionization potential too. For DDE and DDT this value is 9,084 and 9,429 eV respectively. The radiation-chemical yield of solvated electrons during hexane radiolysis is ~ 0.12 ion/100 eV, and their reactions with pesticidal molecules do not play an important role in the radiolysis process, especially in the presence of adsorbed oxygen.

Different radiation-chemical yields observed for various pesticide conversion processes may be due to the variations in their reaction rate with hydrogen atoms and radicals. The difference observed in various isomers (α-HCH, β-HCH and γ-HCH) may be due to the energy of spherical isomeric structures with C – Cl bonds in their molecules.

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РАДИОЛИЗ РАСТВОРОВ ХЛОРОРГАНИЧЕСКИХ ПЕСТИЦИДОВ В ГЕКСАНЕ

М.А. Курбанов, Э.Т. Абдуллаев, С.А. Керимов, У.А. Кулиева

Резюме: Изучена кинетика процессов радиолиза 9 хлорорганических пестицидов (гексахлорбензол, α-HCH, β-HCH, линдан, 4,4′-ДДЕ, 4,4′-ДДД, 4,4′-ДДТ, алдрин и гептахлор) в гексане в интервале концентраций 10 – 1000 мкг/*л* и дозах 13,8; 27,7; 67,4 и 105,4 кГр. Рассчитаны радиационно-химические выходы процессов превращения пестицидов. Установлено, что степень превращения пестицидов составляет 65 – 95% при 104,5 кГр, а радиационно-химические выходы находятся в пределах $(0{,}009–1{,}247)\cdot10^{-3}$ молек/100 эВ. Радиационно-химические выходы растут с повышением начальных концентраций пестицидов в гексане.

Ключевые слова: радиолиз, пестицид, радиационно-химические выходы

XLORLU ÜZVİ PESTİSİDLƏRİN HEKSANDA MƏHLULLARININ RADİOLİZİ

M.Ə. Qurbanov, E.T. Abdullayev, S.Ə. Kərimov, Ü.A. Quliyeva

Xülasə: Tədqiqat işində 9 xlorlu üzvi pestisidin (heksaxlorbenzol, α-HCH, β-HCH, lindan, 4,4′-DDE, 4,4′-DDD, 4,4′-DDT, aldrin və heptaxlor) heksanda 10 – 1000 mkq/*l* qatılıq intervalında 13,8; 27,7; 67,4 və 105,4 kGy dozalarda məhlullarının radioliz proseslərinin kinetikası öyrənilmiş, çevrilmə proseslərinin radiasiya-kimyəvi çıxışları hesablanmışdır. Müəyyən edilmişdir ki, pestisidlərin 105,4 kGy dozada çevrilmə dərəcəsi 65 – 95%, radiasiya-kimyəvi çıxışları $(0{,}009 – 1{,}247)\cdot10^{-3}$ molekul/100 eV olur. İlkin qatılıq artdıqca radiasiya-kimyəvi çıxış da artır.

Açar sözlər: radioliz, pestisid, radiasiya-kimyəvi çıxış.