RADIOLYSIS OF POLYCHLORODIBENZODIOXINS IN HEXANE

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In the radiolysis of 2,3,7,8-tetrachlorodibenzodioxin in n-hexane (dose 6.5 Mrad), the degree of its decomposition according to data of chromatography-mass spectrometry is not less than 99.99995 rel. % (detection limit $2 \cdot 10^{-10}$ mass %). In this case, the less-chlorinated dibenzodioxins formed at lower irradiation doses are not detected.

One of the most dangerous environmental pollutants is 2,3,7,8-tetrachlorodibenzodioxin (TCDD); other polychlorodibenzodioxins (PCDD) are also highly toxic. Therefore, the problem of determination of subtrace concentrations of these substances has arisen [1, 2].

Sources of environmental pollution by dioxins are organochlorine pesticides, herebicides, and polychlorobiphenyls, used as transformer oils, and a number of substances obtained from chlorinated phenols containing PCDD impurities. The PCDD are also formed in paper manufacture (by chlorine bleaching), during incineration of refuse and disposal of chemical-industry wastes, in exhaust gases, and in used motor oil when organochlorine additives have been added to the fuel [3].

Therefore, in addition to monitoring of the content of PCDD, the problem of disposal of PCDD-containing wastes must be solved.

Thermal decomposition of PCDD begins at 700°C and occurs most completely at 1100°C [4]. However, despite process optimization, it is precisely during incineration that the formation of PCDD and not the less toxic polychlorinated dibenzofurans (PCDF) occurs [3].

During UV irradiation (313 nm) of solutions in acetonitrile and in a water—acetonitrile mixture for 80 h, the concentration of 1,2,3,4,7,8-hexachlorodibenzodioxin decreased sevenfold, and the quantum yield was $1 \cdot 10^{-4}$ [5, 6]. In [1], Fokin and Kolomiets describe the possibility of chemical decomposition of PCDD, e.g., in the presence of sodium naphthalene.

A significant drawback of the cited papers is detection of the decomposition according to the disappearance of PCDD in the solution, most often without analysis of the composition of the resulting products, which may include highly toxic compounds. In addition, the degree of conversion of the PCDD was studied only at relatively high concentrations (10^{-2}-10^{-5} mass %), whereas their necessary range was 10^{-7}-10^{-8} mass % and even lower.

TABLE 1. Compounds Identified in Products of Radiolysis of 2,3,7,8-TCDD (besides PCDD)

Compound	Irradiation dose, Mrad			Compound	Irradiation dose, Mrad		
	1.0	3.8	6.5		1.0	3.8	6.5
Propylbenzene			+	Heptylbenzene		+	
3-Ethyltoluene			+	4-Benzyltoluene	+		
3-Propyltoluene			+	2,2'-Dimethylbiphenyl	+	+	
2,4-Dimethylpentylbenzene		+		4-Chloroheptylbenzene	+		
				2,3'-Dimethylbiphenyl	+		

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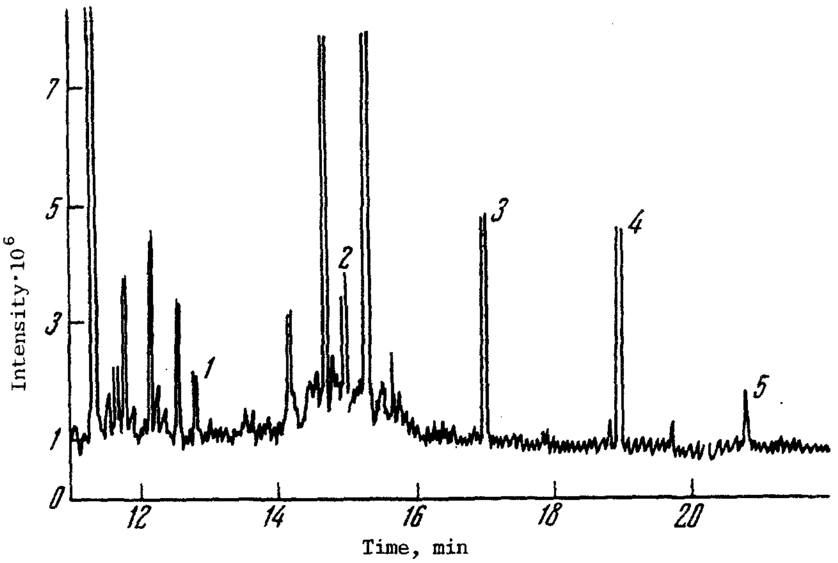

Fig. 1. Part of chromatogram, recorded with respect to total ionic current, of hexane solution of 2,3,7,8-TCDD irradiated with 1 Mrad: 1) dibenzodioxin; 2) monochlorodibenzodioxin; 3) dichlorodibenzodioxin; 4) trichlorodibenzodioxin; 5) 2,3,7,8-tetrachlorodibenzodioxin.

TABLE 2. Relation of Concentration of 2,3,7,8-TCDD and Other Dibenzodioxins in Hexane to Irradiation Dose*

Irradiation dose, Mrad	Concentration, mass %	
	2,3,7,8-TCDD	PCDD
0	$1{,}1\cdot 10^{-3}$	
1	$1{,}8\cdot 10^{-4}$	$1{,}7\cdot 10^{-4}$ – tri-CDD $2{,}1\cdot 10^{-4}$ – di-CDD $2{,}4\cdot 10^{-4}$ – CDD $0{,}8\cdot 10^{-4}$ – DD
3,8	$\leqslant 2\cdot 10^{-10}$	$3{,}4\cdot 10^{-6}$ – tri-CDD $4{,}5\cdot 10^{-6}$ – di-CDD $2{,}2\cdot 10^{-5}$ – CDD $4{,}0\cdot 10^{-4}$ – DD
6,5	$\leqslant 2\cdot 10^{-10}$	$\leqslant 5\cdot 10^{-10}$ all CDD $2{,}7\cdot 10^{-4}$ – DD

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*Concentrations at a level of 10^{-9}-10^{-10} mass % were determined in the selective ion-detection mode.

For the case of dieldrin, it has been shown that decomposition of organochlorine substances in organic and aqueous solutions is possible by using ^{60}Co γ-radiation at concentrations $5\cdot 10^{-4}$ mass % [7].

However, as in other methods, the degree of decomposition was considered in a narrow concentration range, and in most cases the composition of the conversion products was not determined.

In the present paper, we investigated the possibility of decomposition of PCDD in the presence of γ-radiation in hexane, in which both PCDD and chemical wastes possibly containing them dissolve well.

EXPERIMENTAL

We used a ^{60}Co γ-radiation source, a Hewlett–Packard model HP5890 chromatograph, and a Hewlett–Packard model MSD 5970 mass-selective detector. The mixtures being analyzed were separated on an HP-1 quartz capillary column with an SE-30-type grafted phase (column length 12 m and inside diameter 0.20 mm). A 2-μliter sample was introduced into the vaporizer of the chromatograph in a separationless mode (with flow separation) at 250°C. During sample

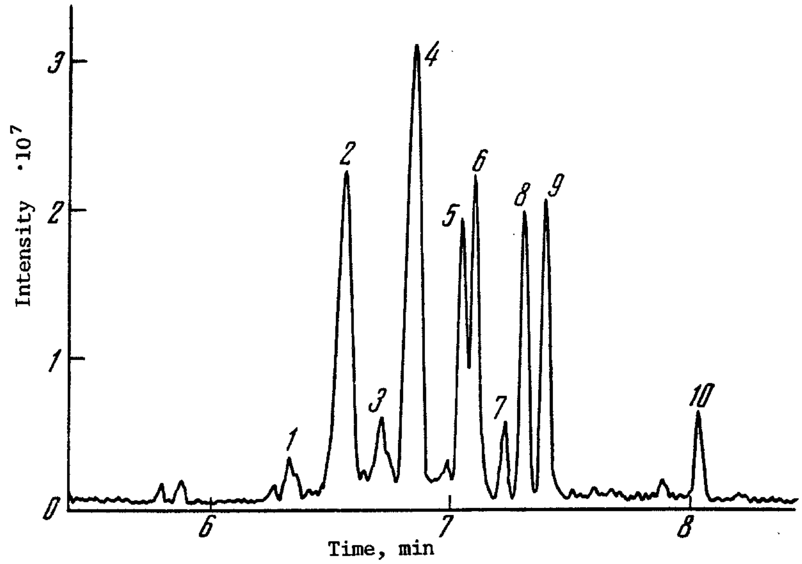

Fig. 2. Part of chromatogram of sample of hexane irradiated at 3.8 Mrad: 1-10) dodecane isomers.

TABLE 3. Relation of Total Yield of Dodecane Isomers to Dose during Irradiation of Solution of 2,3,7,8-TCDD in Hexane and of Pure Hexane

Irradiation dose, Mrad	Total dodecane concentration, mass %	
	in hexane solution of 2,3,7,8-TCDD	in hexane
1,0	$3{,}8\cdot10^{-2}$	–
2,0	–	$4{,}1\cdot10^{-2}$
3,8	$1{,}2\cdot10^{-1}$	$6{,}0\cdot10^{-2}$
6,5	$2{,}2\cdot10^{-1}$	–

injection, the column temperature was 50°C, the valve of the flow separator was opened 1 min after injection, and the column was heated at a rate of 10°C/min to 250°C and held there for 5 min.

The model compound was 2,3,7,8-TCDD, the most dangerous of the PCDD, 0.5-ml portions of a solution of which in hexane (concentration $1.1\cdot10^{-3}$ mass %) were placed in ~1-ml glass ampuls. The ampuls were frozen with liquid nitrogen, evacuated, sealed, and irradiated in doses of 1.0, 3.8, and 6.5 Mrad. One control ampul was not irradiated, and the 2,3,7,8-TCDD concentration in it was determined before and after each run.

The mixture components were identified using mass-spectrum scanning (in the range 50-500 amu) and selective ion-detection modes (ionization by 70-eV electron impact). The minimum determinable amount of the substance was 10^{-9}-10^{-10} g in the scanning mode and about $2\cdot10^{-12}$ g (ions with m/z 320, 322, and 324 were detected, each during 0.1 sec) in the selective ion-detection mode. Files of the complete mass spectra of 42,200 substances (EPA/NIH) were used in the identification. Quantitative analysis was carried out using the external-standard method. A sample of a standard solution of 2,3,7,8-TCDD was introduced into the chromatograph after the mixture being analyzed. The concentration was calculated according to the areas of the corresponding peaks. During analysis of solutions irradiated at high doses, the samples were concentrated because the concentration of 2,3,7,8-TCDD and other PCDD decreased sharply. In this case, the minimum determinable concentration in the selective ion-detection mode was ~$2\cdot10^{-10}$ mass %.

RESULTS AND DISCUSSION

The analysis of samples of the irradiated solutions indicated that the decomposition of 2,3,7,8-TCDD occurred with the formation of trichlorodibenzodioxin (tri-CDD), dichlorodibenzodioxin (di-CDD), chlorodibenzodioxin (CDD), dibenzodioxin (DD), and other products (Table 1).

On the basis of the corresponding mass chromatograms, it was shown (Fig. 1) that only one isomer corresponds to each of the dioxins that is formed during radiolysis. From Table 2 it is clear that at an irradiation dose of 3.8 Mrad 2,3,7,8-TCDD was not detected at a level of $2 \cdot 10^{-10}$ mass % (degree of conversion not less than 99.99995 mass %), but at a dose of 6.5 Mrad the less-chlorinated dibenzodioxins were also not detected (detection limit $5 \cdot 10^{-10}$ mass %).

In the selective ion-detection mode we did not detect PCDD with more than four chlorine atoms and polychlorodibenzofurans (PCDF), which indicates decomposition of 2,3,7,8-TCDD to nontoxic compounds.

The radiation-chemical yield in the decomposition of 2,3,7,8-TCDD, calculated according to the equation $G = 6 \cdot 10^{25}$ C/D, where G is the radiation-chemical yield, molecules/100 eV, C is the concentration of 2,3,7,8-TCDD, moles/g, and D is the irradiation dose, eV/g (or $6.24 \cdot 10^{19}$ Mrad), was 0.025 molecule/100 eV.

In the analysis of samples of irradiated hexane solutions of 2,3,7,8-TCDD, we observed the formation of a series of dodecane isomers. Therefore, we studied the radiolysis of pure hexane, accompanied, as it was found, by the formation of a series of saturated hydrocarbons, the amount of which increased with increasing irradiation dose. The strongest peaks in the chromatogram (Fig. 2) corresponded to dodecane isomers, which were identified according to the presence of the peak of the molecular ion (m/z 170) and correspondence to file mass spectra. The radiation-chemical yield of dodecanes during radiolysis of hexane was ~1.2 molecules/100 eV, which agrees with the data of [8]. The increase of the total amount of the resulting dodecanes with increasing irradiation dose is shown in Table 3, from which it is evident that in the hexane solution of 2,3,7,8-TCDD the yield was about twice as great as in pure hexane.

Thus, it was shown that it is promising to use γ-radiation for decomposition of PCDD in wastes from chemical and petrochemical industries.

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