Radiolytic Decomposition of Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans in Hexane

Mitroshkov A.V.[a], Revelsky I.A.[b], Podsoblyaev A.P.[c], Rachmanova T.V.[a], Galahov I.V.[b], Kurochkin V.K.[b]
[a] NPO "Typhoon", 249020, Obninsk, Russia
[b] Institute of Physical Chemistry, 117915, Moscow, Russia
[c] Institute of Physical Chemistry, 249020, Obninsk, Russia

Besides the necessity to detect and analyse for polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the environment, various materials and products there is the strong need to destruct PCDD and PCDF that have been formed. There are many publications dedicated to this theme but none of these methods described is totally satisfactory.

Different methods such as incineration, thermocatalysis, photochemical decomposition etc. are described in a comprehensive review [1].

There are some articles devoted to the problem of radiolytic decomposition of PCDD [2,3] but we do not know any paper devoted to radiolytic decomposition of PCDF.

The results given in Refs. [2,3] are contradictory. In Ref. [2] for pure 2,3,7,8-TCDD in n-hexane, isopropanol, laboratory waste and soil the dechlorination occurred successively under the action of γ-irradiation.

In contrast, in [3] the treatment of chemical waste and oils with rather high doses (up to 100 Mrad) was ineffective. In alkaline isopropanol about 65% of 2,3,7,8-TCDD was decomposed. The authors considered it unacceptable for practical application.

Earlier [4] we investigated the radiolytic decomposition of 2,3,7,8-TCDD in hexane and found that the process of decomposition of 2,3,7,8-TCDD proceeds more slowly in the presence of air than in the absence of air. The work presented here we give the results of our stduies of these processes for mixtures of PCDD and PCDF.

Experimental

A gas chromatograph HP 5890, used in this work, was coupled with either a quadrupole Hewlett-Packard mass-spectrometer HP 5988 or a mass-selective detector HP 5970 A. The separation of different PCDD and PCDF was realized by two capillary silica columns: Ultra 2 (25 m, ID 0.32 mm, temperature programmed 50-270°C, 25°C/min) and HP-1 (12 m, ID 0.2 mm, temperature programmed 50-250°C, 20°C/min). For MSD analysis electron impact mode of ionization was used.

The samples being exposed to doses of 0.1-6 Mrad were analysed by GC/MSD. The samples exposed to doses of radiation from 15 to 30 Mrad were analysed on GC/MS HP 5988 by using negative ions chemical ionization mode. The detection limit was 10 fg for 2,3,7,8-TCDD and 1 fg for any another PCDD and PCDF. The method was described previously [5]. A column HP-1 was used (50 m, ID 0.32 mm, temperature programmed 50-270°C, 10°C/min).

The ion source temperature was 325°C; the ion source pressure was 0.65 torr. The mixture argon/methane (90:10) was used as reagent gas. At both instruments the injector temperature was 270°C. The samples were injected in a split/splitless mode. The detection limit of the method in electron impact mode is about 2 pg of any PCDD and PCDF.

The mixture of PCDD and PCDF extracted from commercial sodium pentachlorophenate was used. After qualitative analysis the sample was dissolved in hexane and separated into two series in 5 aliquots of 200 μl in volumes.

The first series was frozen in liquid nitrogen, the air was evacuated and the ampoules were sealed off. The ampoules of another series were sealed off with the air.

The samples were irradiated with γ-rays from a ^{60}Co source.

The authors have investigated the process of radiolytic decomposition of PCDD and PCDF mixture in the 0-6 Mrad dose range in the presence of air and in the 0-30 Mrad dose range in the absence of air.

As an example, the results of PCDF decomposition at the dose rate 0-6 Mrad are shown in Tables 1 and 2.

The main conclusions of this work are the following:

1. The increase of radiation results in a decrease of PCDD and PCDF in the system without air (see Table 1).

2. A significant difference in decomposition of congeners of each substance group (PCDD and PCDF) is not observed. A gradual dechlorination with formation of less chlorinated PCDD and PCDF takes place.

3. There are no peculiarities in the 2,3,7,8-TCDD behaviour relative to other congeners.

4. Though it is rather difficult to estimate the effects of the radiation on the mixture, one can conclude that PCDF are not more stable to radiation as compared to PCDD.

5. After the dose of 30 Mrad no PCDF and PCDD could be detected in the absence of air at the detection level 2×10^{-10} % mass, though the initial concentrations were as much as 2.4×10^{-3} % mass for Octa-CDD and 2.6×10^{-4} % mass for Octa-CDF.

References:

1 Martinetz D., Chemische Technik **39**, 466-470 (1987).

2 Buser H.R., Lehnder H., J. Experientia **41**, 1082-1084 (1985).

3 Buser H.R., Lehnder H., J. Stuttgarter Ber. Abfallwirtschaft **22**, 121 (1986).

4 Mitroshkov A.V., Revelsky I.A., Podsoblyaev A.P., The Radio-Chemical 2,3,7,8-TCDD Decomposition in Water and Different Organic Solvents. Presented at DIOXIN'92, Tampere/Finland, 1992.

5 Mitroshkov A.V., Revelsky I.A., Sarkisyan A.M., Kolomiets L.N., Femtogramm High Selective 2,3,7,8-TCDD Determination Using Chemical Ionization with Low Resolution Mass-Spectrometer. Organohalogen Compounds **8**, 113 (1992).

Table 1: The dependence of decomposition and formation of various PCDF on the γ-irradiation dose in the absence of air.

Substance	Concentration of isomer group (mass %) depending on a dose (Mrad)							
	0	0.5	1	4	6	15	23	30
Tri-CDF (from 4 to 6 isomers)	4.0×10^{-5}	3.4×10^{-5}	2.9×10^{-5}	2.9×10^{-5}	1.4×10^{-5}		$< 2\times10^{-10}$	
Tetra-CDF (from 6 to 10 isomers)	4.5×10^{-5}	3.5×10^{-5}	2.5×10^{-5}	2.2×10^{-5}	7.0×10^{-6}	8.9×10^{-10}	$< 2\times10^{-10}$	
Penta-CDF (from 6 to 10 isomers)	7.9×10^{-5}	5.4×10^{-5}	5.2×10^{-5}	6.6×10^{-5}	2.3×10^{-5}	4.7×10^{-9}	$< 2\times10^{-10}$	
Hexa-CDF (6 isomers)	1.2×10^{-4}	9.9×10^{-5}	9.2×10^{-5}	7.8×10^{-5}	1.4×10^{-5}	1.4×10^{-8}	5.8×10^{-10}	$< 2\times10^{-10}$
Hepta-CDF (4 isomers)	2.5×10^{-4}	4.7×10^{-4}	4.9×10^{-4}	2.6×10^{-4}	4.2×10^{-5}	2.5×10^{-8}	9.3×10^{-10}	$< 2\times10^{-10}$
Octa-CDF	2.6×10^{-4}	1.3×10^{-4}	5.4×10^{-5}	1.0×10^{-6}	4.3×10^{-7}	1.2×10^{-8}	2×10^{-9}	$< 2\times10^{-10}$