# Radiochemical Decomposition of Polychlorodibenzodioxins in Alkaline Isopropanol Solution in the Absence of Air.

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**Abstract.** The mixture of 16 most toxic PCDDs with chlorine atoms in 2,3,7,8 positions in alkali ispropanol (concentrations $10^{-5}$ - 10-6 % mass ) was irradiated by γ-source in the absence of air. No congeners of initial mixture was observed after dose 20 kGy with detection limit $1 \times 10^{-12}$ - $5 \times 10^{-12}$ % mass.

**Introduction**. Radiochemical method of cleaning of water and air from different contaminants and especially from chlorinated compounds is a very perspective one and was developed very quickly last time[1)] . The method has some advantages: 1) efficiency; 2)complex character (a series of substances can be destroyed simultaneously; 3) opportunity of activities in closed volumes; 4) high speed of the process due to utilization of a major impact power, especially if the electron beam accelerators are used.

Meanwhile, there are only a few articles in scientific literature dedicated to the problem of radiolytical decomposition of PCDDs. The results of investigation of the radiolytical decomposition of 2,3,7,8-TCDD [2-5)] are quiet contradictory. Buser [2)] described the successful dechlorination of pure 2,3,7,8-TCDD in n-hexane, isopropanol, laboratory waste and soil under the action of γ-irradiation with the yield of decomposition of 99, 95, 99.4 and 95.3 % respectively, and an exposition time of 280 h. In contrast, Buser[3)] described the treatment of chemical waste and oils with high doses of irradiation (up to 1000 kGy) as ineffective. In alkaline isopropanol about 65 % of TCDD was dechlorinated. The authors considered this to be unacceptable for practical application.

Some interesting results were published recently [6,7)] . Their authors had reached a relatively high level of decomposition of 2,3,7,8-TCDD in contaminated soil - more than 90% in the presence of surfactant RA-40™. Nevertheless, the contamination of soil by surfactant does not look promising for cleaning of soil from dioxins. The proposed mechanism of direct radiation effect of decomposition contradicts the common point of view[9)] and does not look convincing.

Many more article are devoted to the radiochemical decomposition of PCBs[8-10)]. The authors usually tried to intensify the process. It was found that the presence of KOH in solution increases the process of destruction. Alkaline isopropanol solutions of commercial available mixtures Delor -103 and Delor-106[9)] were subjected to γ-irradiation. After dose of 1800 kGy, 93% of Delor -103 and 96% of Delor -106 were decomposed. The products of decomposition in above mentioned works both for PCDDs and for PCBs were not studied.

We do not know any works devoted to radiolysis of water solutions of PCDDs and related compounds. The investigation of the possibility to decompose PCDDs in water is a very important problem, as due to the importance of cleaning PCDDs from water and due to nowadays existence of suitable devices ( the γ-sources and the electron beam accelerator) which allow to carry on the cleaning of water with high efficiency in the case of converting PCDDs to nontoxic compounds.

Pikaev describes[1] the application of different radiochemical methods of cleaning the wastes and drinking water both for γ-sources and for accelerators beam in different condition.

In the part of the book concerning the decomposition of chlorinated compounds , the decomposition of volatile chloroorganic compounds, such as trichloromethane, was described. The composition of formed in the process of irradiation compounds was not analyzed.

Most attention now paid to thermal methods of destruction of PCDDs [11] . However, these methods are sometimes extremely dangerous because they lead to formation of PCDF in the process of combustion of PCDDs [12,13].

It is necessary to mention that radiochemical method can be very promising compared to the thermal process in the cleaning of chemical production, such as tetrachloromethane and methylene chloride from PCDDs and PCDFs. In this case the thermal method is completely unacceptable.

To solve the problem of decomposition of these substances, to safety level it was necessary to develop the method of their determination in small volumes ( less than 1 ml) which were irradiated at the level of $10^{-10}$ -$10^{-12}$ % mass.

The necessity to increase sensitivity erose on the one hand, by the limited capability to concentrate the samples of the small volumes, and on the other, by the the requirement to simplify the sample preparation in order to minimize the possibility of changing the analyzed mixture in time and necessity to shorten the time of analysis.

The authors had done some works in that direction [14-18]. The best efficiency of decomposition of PCDDs the authors have achieved was in hexane solution in the absence of air[14] and some others [2,9] before had achieved their best results in the alkaline isopropanol. Air in their experiments was not evacuated.

Thus, the purpose of this article was to investigate the process of radiochemical decomposition of PCDDs in alkaline isopropanol in the absence of air.

**Experimental method.** The investigation was carried out by using the Hewlett-Packard GC/MS System HP 5988 and Gas chromatograph HP 5890 Ser.II with a quartz capillary column ( bonded stationary phase SE-30, 50 m, 0.20 mm i.d.,)

The sample, 2 ul in volume, was injected into the chromatograph in a split/splitless mode. The injector temperature was 270° C. The initial temperature of a column (during 1 min ) was 50° C. The temperature has been increased by 10°/min. up to 140°C and 5°C/min. up to 280° C. Helium was used as a carrier gas.

Electron impact (EI) mode of ionization was used in this investigation. The temperature of ion source was 250°C.

The determination of PCDDs concentration was done in the selected ion monitoring mode (SIM). The Phrasor Attachment device was used in order to increase the sensitivity of method and the detection limit was about $1 \times 10^{-12}$ - $5 \times 10^{-12}$ g in injection for different congeners.

The mixture of the most toxic congeners of PCDDs, containing the chlorine atoms mainly in the position 2,3,7,8 ( see 1st column of Table 1) was used as the model mixture.

The solution of PCDDs in alkaline isopropanol was prepared according to procedure developed by author[9]. The samples were dissolved in alkaline isopropanol and divided in aliquots of 100 µl each, placed in the ampoule (200 µl volume) and were frozen in liquid nitrogen. The air was evacuated and the ampoules were sealed off.

The ampoules were irradiated by $^{60}Co$ as the γ-ray source. The intensity of irradiation was 100 rad/sec ( 1Gy/sec). One ampoule was used as a control sample. The control sample was analyzed immediately after analyzing the irradiated samples. A quantitative analysis was performed by the external standard method.

**Results and Discussion**

Table 1. The results of radiolytical decomposition of PCDD in alkaline isopropanol in the absence of air.

| Substances | Concentration, 10-6 % mass | | | |
|---|---|---|---|---|
| | Dose, Mrad (kGy) | | | |
| | 0 | 1(10) | 2(20) | 3(30) |
| | | | | |
| Mono-CDD | nd | 3 | 14.7 | 9.1 |
| Di-CDD | nd | 4.6 | 8.5 | 3.9 |
| 1,2-DiCDD | 4.5 | nd | | |
| 1,2,3-TriCDD | 5.5 | 0.11 | nd | |
| 1,3,6,8-TCDD | 2 | nd | | |
| 1,3,7,8-TCDD | 3.7 | nd | | |
| 1,2,3,4-TCDD | 6.2 | 0.11 | nd | |
| 1,2,7,8-TCDD | 3.3 | nd | | |
| 2,3,7,8-TCDD | 5.1 | nd | | |
| 1,4,7,8-TCDD | 3 | nd | | |
| 1,2,6,8-TCDD | 2 | nd | | |
| 1,2,7,9-TCDD | 0.9 | nd | | |
| 1,2,3,7,8-PeCDD | 12.6 | nd | | |
| 1,2,3,6,8-PeCDD | 6.3 | nd | | |
| 1,2,3,6,7,8-HxCDD | 1 | nd | | |
| 1,2,3,4,7,8-HxCDD | 3.8 | nd | | |
| 1,2,3,7,8,9-HxCDD | 4.3 | nd | | |
| 1,2,3,4,7,8,9-HeCDD | 9 | nd | | |

COMMENT: **nd** in the table means that this substances was not detected.

It is important to mention, that the initial concentrations in this experiments were rather low in comparison with the concentrations which were used in [2,10]. Usually, the smaller concentration corresponds to the lower rate of decomposition with equal doses. Meanwhile, in our experiment the process of decomposition was very intensive and after dose of 10 kGy, toxic congeners were not detected. Still observed were 1,2,3,4-TCDD and less chlorinated PCDDs, that practically are not toxic.

In the first line of table 1 the sum of Mono-CDDs is shown and in the 2nd line - the sum of isomers of Di-CDD.

It is also important, that after a dose of 1 Mrad (10 kGy) neither the PCDDs with 5 to 7 chlorine atoms nor TCDDs were not observed which can form from more chlorinated

congeners. At the same time in hexane solutions in the absence of air, the TCDDs were observed until dose of 23 Mrad( 230 kGy)[19].

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