The Investigation of the Products of Radiochemical Decomposition of PCBs in Hexane Solution.

Mitroshkov A.V., Podsoblyaev A. P., Revelsky I. A., SPA "Typhoon", Obninsk, 249020, Russia.

Introduction

Polychlorinated biphenyls (PCBs), which were produced for a long period of time, have been the intensive source of environmental contamination. PCBs are present in wastewater of some industrial enterprises and in the products and wastes of chemical plants. The soil is also contaminated by PCBs at the sites of their production and area of active use. In particular, PCBs were widely used and still are used as an additives to the transformer oil. It is well known that in the process of their exploitations PCBs can form PCDDs and PCDFs[1]. Because the level of contamination of environment by the PCBs is relatively high, the problem of remediation for PCBs is very important.

The purpose of this work was to investigate the composition of mixtures obtained in the process of γ-irradiation of hexane solutions of PCBs. Special attention was paid to the control of concentration of PCDDs and PCDFs in solution of PCBs, which could be in the initial solutions and/or be formed in the process of radiochemical decomposition of PCBs. Experiment were carried on in the presence of air. We have shown in the previous works that the presence of air can affect the process of radiolysis of PCDDs and PCDFs[4].

Material and Methods

In the process of experiments two Hewlett-Packard GC/MS systems were used: HP5970/MSD 5970 and HP5970/HP5988. On both systems EI mode of ionization was used and the solutions were analyzed at least two times: in scan mode in the range 50-550 a.m.u. in order to identify all the compounds, which could be formed in the solutions and in SIM mode to determine if there are some PCDDs and PCDFs as a result of irradiation. In order to achieve high sensitivity of determination of PCDDs and PCDFs, the method of chemical ionization was used with the registrations of negative ions (NICI) with the mixture argon/methane (95:5) as a gas reagent. For identification of products of experiments, the Willey library of full mass spectra containing 130.000 compounds was used.

At the system HP5988 was installed quartz capillary column with bonded stationary phase (SE-30, 50 m, 0.20 mm i.d.), at system HP5980 with MSD5970 were used two capillary columns: 1-st HP-1, the 2-nd Ultra-2 (both with length 25m, id. 0.2mm and 0.32 mm., accordingly. Different temperature profiles were programed for each GC. The best separation for PCBs was achieved with the column HP-1, and for PCDDs and PCDFs with the Ultra-2 column. The injection volume was 2 μl. The sample was injected in split/splitless mode. The temperature of injector was 250°C. Temperature programming: 50°C(1min.)-20°C/min.-140°C-8°C/min.-250°C.

The PCBs sample with doses from 10 kGy to 60 kGy was analyzed at the MSD in EI mode. In EI mode sensitivity of method was sufficient to determine concentration of PCBs in the range $10^{-2} - 10^{-5}$ % mass. The samples with lower concentration were analyzed at HP5988 in NICI mode. The detection limit for total PCB was 1pg in injection.

The molecular ions of PCBs, PCDDs and PCDFs were registered in SIM mode. As in EI mode, for most of the congeners they were also the most intensive in the mass spectra obtained in NICI mode

The solution of the mixture of Arochlor 1260 with the initial concentration of 1×10^{-2} % mass was used in the experiments. Aliquots of the solutions were put into the ampoule of volume 0.5 ml and sealed. The air was not evacuated. The volume of solution in each ampoule was 0.2 ml.

The samples were irradiated by the ^{60}Co source. One ampoule from each series was left as a control and was not irradiated. The external standard method was used for the quantitative analysis of irradiated samples.

Results and Discussion

The analysis of the initial PCB solution had indicated that there were present PCDFs as an admixture with the concentration of 4×10^{-9} % mass. These PCDFs were not observed after a dose of irradiation 5 kGy. PCDDs were not found in the samples with the detection limit 2×10^{-10} % mass. The dependence of concentration of total PCB on the dose of irradiation is shown in the Table1. The concentrations of different group of congeners by using method described [2] were determined and are shown at the Picture 1. Obviously, as the result of irradiation and subsequent step-by-step dechlorination the congener composition of the mixture have changed to the favor of less chlorinated congeners. The concentrations of group of congeners in A1242 and A1260 are taken from [3].

Toxic compounds were not detected in the reaction mixture. The compound, which was detected in the highest concentration, was dodecane, which is the result of recombination of hexane radicals. Hexanone, hexanol and few alkanes and alkenes were also found . It is worthwhile to mention that biphenyl or any other aromatic compounds were not found, proving that biphenyl has been quickly destroyed. The PCB mixture became nontoxic more quickly than it is destroyed completely, because less chlorinated PCBs (less than 3 chlorine atoms) are almost nontoxic.

PCDDs and PCDfs were not found in the products of radiochemical decomposition of PCBs. As one can see in the Table 1, after dose of 60 kGy, 90.4% of PCBs were destroyed. After the dose was increased up to 300 kGy, the degree of decomposition was already 99,99999985 % and products of decomposition were nontoxic.

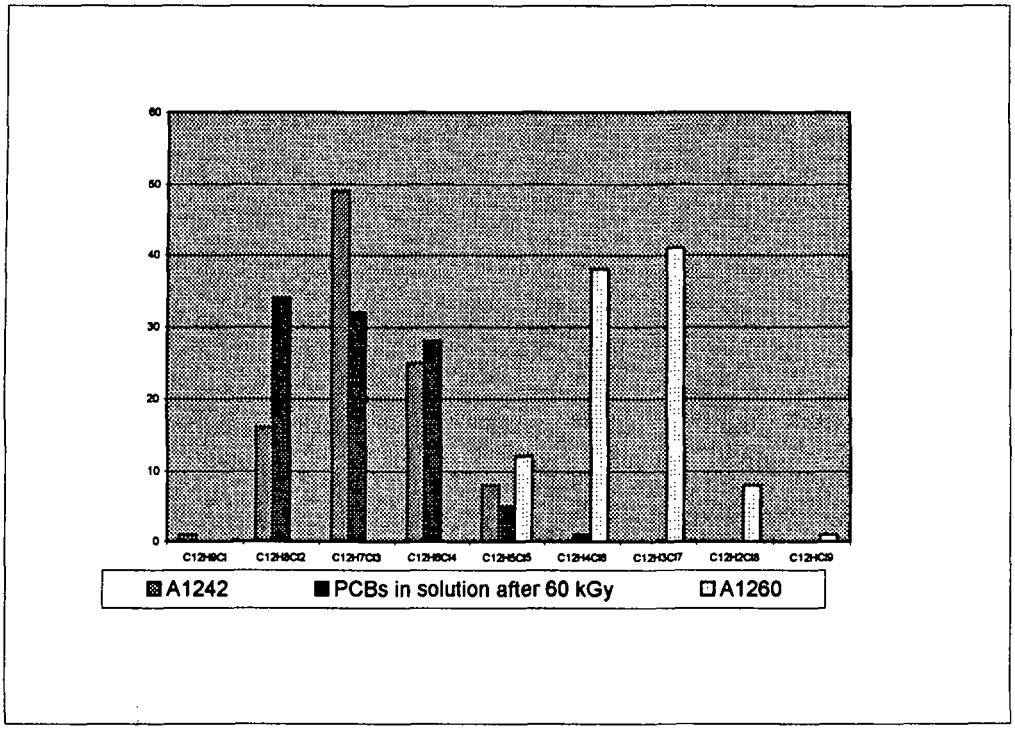
Similar to the decomposition of PCDDs and PCDFs, radiochemical decomposition of PCBs is a step-by-step process of dechlorination of more chlorinated congeners and formation of less chlorinated PCBs and their subsequent dechlorination in their turn.

Table 1. Concentration of PCBs in the mixture vs. dose of irradiation.

Dose, kGy	Concentration of PCBs in solution, % mass
0	1×10^{-2}
2	9.3×10^{-3}
5	7.4×10^{-3}
10	6.9×10^{-3}
40	1.9×10^{-3}
60	9.6×10^{-4}
200	4.5×10^{-8}
300	1.5×10^{-11}

References

1. Ch. Rappe. Swedish view of the dioxin issue. *Vatten*, **1988**, vol. 44, pp. 137 - 144.
2. Mitroshkov, A.V; Kiryuhin V.P; Rahmanova, T.V. *Proceeding of Institute of Experimental Meteorology*, **1990**, *17(145), 118-124 (in Russian).*
3. Pal D.,Weber J.B.and Overcash M.R. *Residue Reviews*,**1980**, vol. 74,p. 45.
4. Mitroshkov A.V; Revelsky I.A; Podsoblyaev A.P; Rachmanova, T.V.;Galahov, I.V.; Kurochkin V.K. *Proceeding of International Symposium "DIOXIN-93", Vienna, Austria,* **1993**, *vol.12, p. 69.*



Picture 1. Distribution of group of congeners in A 1242, A 1260 and in the experimental solution of PCBs after dose 60 kGy.