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FORMATION OF POLYCHLORINATED DIBENZOFURANS (PCDFs)

FROM THE PYROLYSIS OF PCBs

Hans Rudolf Buser and Hans-Paul Bosshardt

Swiss Federal Research Station

CH - 8820 Wädenswil, Switzerland

and

Christoffer Rapps

Department of Organic Chemistry, University of Umeå

S - 901 87 Umeå, Sweden

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Introduction

Polychlorinated biphenyls (PCBs) are industrial chemicals of wide use and now known to be widely distributed in the environment. The commercial products are complex mixtures of at least 60 different substances. Due to their extreme stability in ecological systems, the use of PCBs is now restricted to sealed systems like capacitors and transformers. However, prior to 1972, PCBs due to their good thermal and chemical stability were used in a variety of other applications; in particular the use as heat transfer fluids and casting waxes was associated with the thermal stability.

Very closely related to the PCBs are the polybrominated biphenyls (PBBs), some of which have been used as flame retardants. Of special interest is Fire Master EP-8 or Fire Master BB-1, which were shown to consist mainly of 2,4,5,2',4',5'-hexabromobiphenyl.¹ Intoxication with this PBB has been directly associated with a wide-spread agricultural calamity in Michigan (USA) in 1973-74.²

Microanalysis

Quartz mini-ampoules were made from quartz tubing using a gas-oxygen burner; the lengths of these ampoules were 25-30 mm, the internal diameters 3.4 mm and the volumes 0.3 ml. Using a micro-syringe, 10 µl of a standard solution (corresponding to 10 or 100 µg of compound) was placed into the tip of an ampoule. After complete evaporation of the solvent with the aid of a slight vacuum, the ampoules were closed using a very small flame; care was taken not to heat the tips containing the compounds. The volume of 0.3 ml air in an ampoule was kept approximately constant. The molar ratios of PCB to oxygen in an ampoule were about 1:75 and 1:7.5 for amounts of 10 and 100 µg of PCB, respectively.

The quartz mini-ampoules were placed in an electrical oven (max. temp. 1000°C) preheated to temperatures ranging from 550 to 850°C. The temperature was controlled with a thermocouple in an ampoule placed next to the samples. Heating periods (time between placing a sample ampoule into the oven and removing it) were kept constant at 60 sec. The time required to heat the mini-ampoules up to a temperature within 20°C of the preset value was around 55 sec, the time of a sample at actual pyrolysis temperature thus around 5 sec.

After removing and immediate cooling to room temperature, the tips of the ampoules were broken and 200 µl of benzene added. A 2-µl aliquot was used directly for analysis. Further dilution was required for samples with low decomposition of PCBs to overcome overloading effects of the GC-MS system. Some samples were cleaned-up on an alumina-microcolumn, using 2% and 50% methylenechloride in n-hexane to separately elute PCBs and PCDFs.¹²

GC-MS Analysis

Analyses were carried out on a Finnigan 4000 quadrupole GC-MS instrument equipped with electron-impact ion-source and a Finnigan 6111 data-system. OV-17 glass capillary columns of 25 and 50 m length (0.36 mm ID) were coupled via a platinum interface leading directly into the ion-source. The column conditions were as follows: 100°C, 2 min isothermal, 15°C/min to 145°C, 5°C/min to 230°C for the 25 m OV-17 column; 100°C, 2 min isothermal, 20°C/min to 160°C, 2°C/min to 230°C for the 50 m OV-17 column; helium carrier gas at 0.30 and 1.40 at, respectively. Samples were splitlessly introduced with the vaporizer at 250°C.

Table 2 Pyrolysis of 2,4,6,2',4',6'-hexachlorobiphenyl (100 μ g) in quartz mini-ampoules

Temperature ($^{\circ}$ C)	Decomposition (%)	PCBs formed* (%)	
		tetra-CDF	penta-CDF
550	22	0.5	0.1
600	90	0.5	0.3
650	94	0.35	0.35
700	> 99.99	< 0.01	< 0.01
850	> 99.99	< 0.01	< 0.01

* 1 tetra- and 1 penta-CDF isomer formed

The formation of penta- and hexachlorobenzene was observed with both PCB isomers at temperatures of 650 $^{\circ}$ C (0.05%) and 700 $^{\circ}$ C (0.5-1%). The lower chlorinated benzenes would have escaped detection (elution from capillary column prior to starting of MS scanning). Both, penta- and hexachlorobenzene were decomposed at 850 $^{\circ}$ C.

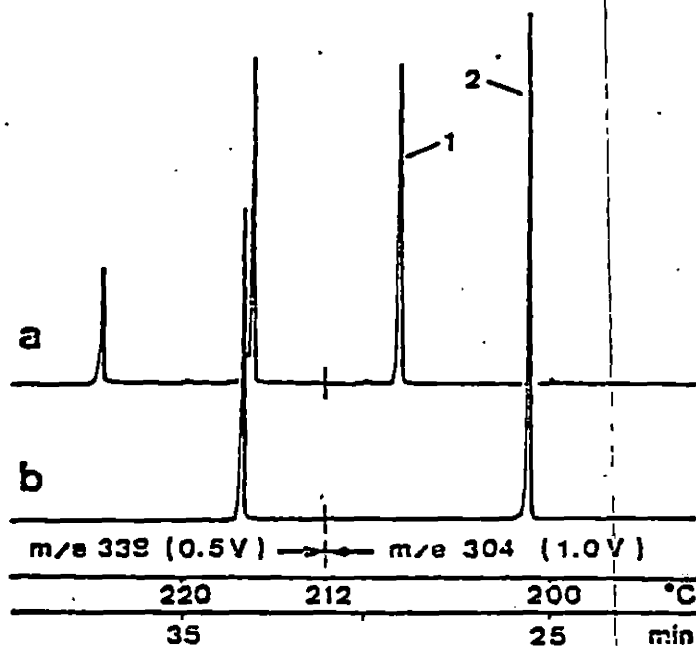


Figure 1 Partial mass fragmentograms (50 m OV-17, m/e 304 and 339) showing elution of tetra- and penta-CDFs in a) pyrolyzed 2,4,5,2',4',5- and b) pyrolyzed 2,4,6,2',4',6'-hexachlorobiphenyl. 1 = 2,3,7,8-tetra-, 2 = presumably 1,3,7,8-tetra-CDF.

hexachlorobiphenyls. No 2,4,6,2',4',6'-hexachlorobiphenyl was detected (<1% relative to the 2,4,5,2',4',5'-isomer).

Table 3 Pyrolysis of Arcelor 1254 in quartz mini-ampoules

Temp. (°C)	Amt. (µg)	Decomp. (%)	PCDFs formed* (%)				
			mono-	di-	tri-	tetra-	penta-
550	100	12	0.25	0.65	0.90	0.75	0.20
"	10	80	0.02	0.40	0.70	0.70	0.15
600	100	45	0.10	0.40	0.70	0.60	0.12
"	10	90	< 0.01	0.10	0.25	0.35	0.05
650	100	90	< 0.01	0.02	0.18	0.25	0.12
"	10	98	0.01	0.12	0.25	0.12	< 0.02
700	100	> 99.9	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02
"	10	> 99.9	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02
950	100	> 99.9	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02

* combined values of all isomers of a PCDF

In Table 3 the results of the pyrolysis of Arcelor 1254 in the temperature range of 550-850°C and levels of 10 and 100 µg are reported. At 550-650°C, the decomposition at the 100 µg-level ranged from 12% to 90%, at the 10 µg level from 80 to 98%. Arcelor 1254 was completely destroyed at temperatures of 700°C and above. These decomposition values are based on the hexachlorobiphenyls present. The decomposition of the lower chlorinated biphenyls was somewhat higher than the stated values. No penta- or hexachlorobenzene was detected at any temperature. Again, lower chlorinated benzenes would have escaped detection.

Mono- to penta-CDFs were found at 550-650°C at levels ranging from 0.1-0.9%. The maximum amounts found were at 550°C. Taking into consideration the amount of PCB recovered after pyrolysis, the total yield of PCDFs ranged from 3-23%. In addition to PCDFs, polychlorinated biphenyls as possible precursors were identified at levels of approximately one fifth of the amount of PCDFs present.

In Figure 2 mass fragmentograms of pyrolyzed Arcelor 1254 (100 µg at 650°C, cleaned-up sample) on a 50 m OV-17 glass capillary column are shown. The elution of up to 30 major and more than 25 minor PCDFs can be observed. They range from the mono- (all 4 theoretically possible isomers) to the penta-CDFs. Since 2,4,5,2',4',5'-hexachlorobiphenyl is one of the

main hexachlorobiphenyls in Arcolor 1254, it is of interest to confirm the presence of 2,3,7,8-tetra-PCDF and of the two penta-PCDFs in this complex mixture. The 2,3,7,8-tetra-PCDF is not completely separated on this column from another tetra-PCDF isomer. The tetra-PCDF formed from 2,4,6,2',4',6'-hexachlorobiphenyl was not found to be present.

In case of the major isomers, the discrete PCDFs could be identified by running complete EI mass spectra. All mass spectra showed intense molecular ions with the expected ion clustering due to the chlorine isotopes and the characteristic fragmentation for PCDFs with formation of M^+-COCl and $M^+-COCl-Cl_2$.

Pyrolysis of additional compounds

Additionally we have studied the pyrolysis of 2,6,2',6'-tetrachlorobiphenyl and of Firemaster BP-6 (mainly 2,4,5,2',4',5'-hexabromobiphenyl). Tetrachlorobiphenyl formed at 550°C one di- and one tri-PCDF isomer at levels of 1.6 and 2.5%, respectively. The tri-PCDF must be formed in a rearrangement. At 700°C, the tetrachlorobiphenyl was completely destroyed and no PCDFs were found. Firemaster BP-6 was also completely destroyed at 700°C, but at 600°C new compounds were formed, one of which could be a tetrabromodibenzofuran ($M^+=480$, Br_4 ; major fragment M^+-Br_2 ; other fragments M^+-Br and M^+-COBr). In analogy with the corresponding PCB isomer, it seems most likely that it is the 2,3,7,8-tetra-BDF. The amount formed is about equal to the amount of tetra-PCDF formed from the corresponding PCB.

Conclusions

The results reported in this paper suggest that uncontrolled burning of PCBs can be an important environmental source of the hazardous PCDFs. Although PCDFs have not yet been found in the environment, they have been identified in fly ash from municipal incinerators and industrial heating facilities.^{13,14} Moreover, Nagayama et al.¹⁵ have found highly increased levels of PCDFs in the PCB associated with the Yusho accident in Japan in 1968, and one of the main components was also the 2,3,7,8-tetra-PCDF.¹⁶

In spite of being partly banned, large volumes of PCBs are still in use, especially in transformers and capacitors. In Sweden the amount now in use in capacitors is about 2500 tons; a similar amount applies for Switzerland according to a survey by the Swiss Federal Office of Public Health. It is evident that all disposal of PCBs should be carefully

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