

FORMATION OF BROMINATED DIBENZODIOXINS AND -FURANS BY THERMOLYSIS OF
POLYBUTYLENE-TEREPHTHALATE CONTAINING DECABROMODIPHENYLETHER - INFLUENCE OF
TEMPERATURE, ANTIMONY TRIOXIDE AND WATER

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ABSTRACT

PBrDDs and PBrDFs including 2,3,7,8-tetrabromoisomers are formed by thermolysis of decabromodiphenylether with polybutylene-terephthalate at temperatures between 400 °C and 700 °C in ppm concentrations. In this temperature range, the presence of Sb_2O_3 facilitates the formation of these compounds. Experiments with H_2O and D_2O show that moisture plays an important role in the formation of these compounds.

INTRODUCTION

At present, investigations on the formation of polybrominated dibenzodioxins (PBrDDs) and polybrominated dibenzofurans (PBrDFs) by combustion processes are conducted because many plastics contain brominated aromatic compounds as flame retardants.¹⁻⁵

A technically important flame retardant is decabromodiphenylether (DBrDPE), which is employed together with Sb_2O_3 as synergist in manufacturing polyesters and acrylonitrile-butadiene-styrene (ABS) - plastics.⁶

In the following, the results of the thermolysis of Crastin^R, a polybutylene-terephthalate (PBTP) containing 10% DBrDPE and 6% Sb_2O_3 are presented. The influence of chamber temperature, Sb_2O_3 and water on the formation of PBrDDs and PBrDFs is studied.

EXPERIMENTAL PART

The combustion experiments were carried out in a simulation chamber (BIS-apparatus) by defined temperatures and constant gas flow (0.5 l/min). In a typical experiment, the polymer Crastin^R (100 mg) was thermolysed in the presence of air at 400 °C - 1000 °C.

The thermolysis gases were absorbed in n-hexane:dichloromethane (1:1). The solution was pre-cleaned on a 1 N NaOH/silicagel (1:2, 3g) - Na_2SO_4 /seasand (1:1, 6g) - Florisil (12g) - column and concentrated to 4 ml. The extract was fractionated on Na_2SO_4 (3g)/Alumina B-Super I (15g) (ICN Bio-

medicals) with 100 ml benzene, 50 ml n-hexane:dichloromethane (9:1), 150 ml n-hexane:dichloromethane (1:1) and 50ml dichloromethane. PBrDDs/PBrDFs were eluted with the third fraction and after concentration (1 ml) analysed by GC/MS-SIM.

For identification of PBrDDs and PBrDFs three ions of the typical M^{+} -cluster and the $(M-COBr)^{+}$ -fragment were monitored in SIM-mode (figure 1). Excluding interferences of polybromodiphenylethers with two more bromineatoms in the PBrDF-analysis the most intense molecular ion of the ether was detected. Identification of the 2,3,7,8-tetrabromoisomers and check of recovery was done by using ^{13}C -standards, quantification by external standardisation.

The efficiency of clean up was determined with the 12 PBrDD and 3 PBrDF standards. The recoveries were 79 to 120 %.

The detection limit which varies with degree of bromination was 1 to 100 ng/g (ppb).

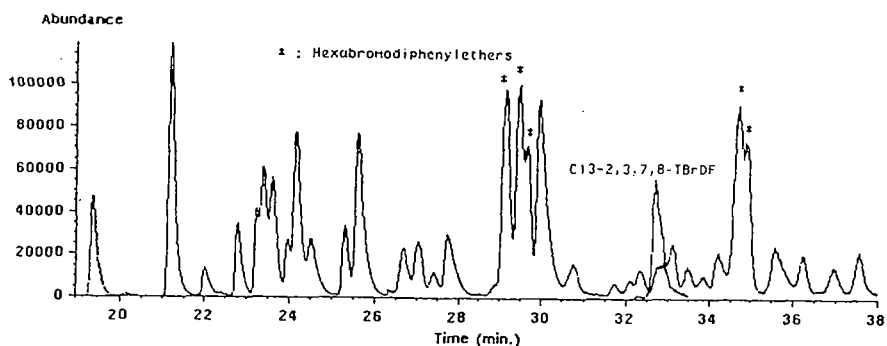


Figure 1 SIM-Chromatogram of tetrabromodibenzofurans (TBrDFs) produced by thermolysis of PBTP with 10% DBrDPE and 6% Sb_2O_3 at 400 °C. GC-conditions: quartz capillary column, 20 m x 0.25 mm i.d. SP2330, 0.25 μm ; 1 min at 150 °C, 12 /min to 200 °C, 1 min at 200 °C, 1 /min to 247 °C, carrier gas: helium.

RESULTS AND DISCUSSION

1. Influence of chamber temperature on the formation of PBrDDs/PBrDFs

The results of the thermolysis of PBTP containing 10 % DBrDPE and 6% Sb_2O_3 at temperatures between 400 °C and 1000 °C showed that PBrDFs, including 2,3,7,8-TBrDF were formed in ppm concentrations. The maximum of formation for the tetrabromodibenzofurans is at 400 °C. PBrDDs are formed in lower concentrations. The maximum formation of tetrabromodibenzodioxins (TBrDDs) is at 500 °C (4.8 ppm). The most toxic 2,3,7,8-TBrDD isomer is also detected at a concentration of 0.1 ppm (Table 1). The concentrations of TBrDFs and TBrDDs decrease with higher temperatures. At 700 °C no higher brominated dibenzodioxins and at 1000 °C no higher brominated dibenzofurans could be detected.

2. Influence of antimony trioxide on formation of tetrabromodibenzofurans

The results given in Table 2 show that the formation of TBrDFs is facilitated by the presence of Sb_2O_3 at temperatures 500 °C - 600 °C. In contrast to this, by 800 °C in the absence of Sb_2O_3 , higher amounts of TBrDF's were detected.

Table 1 Formation of PBrDDs and PBrDFs by combustion of PBTP containing 10 % DBrDPE and 6 % Sb₂O₃ at temperatures between 400 °C and 1000 °C. The total amounts and some selected isomers are listed (ppm)

Temperature (°C)	400	500	600	700	800	1000
ΣBromodibenzofurans						
Mono-	31	175	440	105	20	1.0
Di-	228	757	428	28	0.4	≤0.003
Tri-	312	344	121	3.6	0.03	≤0.001
Tetra-	5680	3535	911	24	0.2	≤0.01
Penta-	7481	4379	885	17	0.3	≤0.05
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2,3,7,8-TBrDF	52	32	5.7	0.3	≤0.01	≤0.01
1,2,3,7,8-PBrDF	63	22	3.2	≤0.05	≤0.05	≤0.05
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ΣBromodibenzodioxins						
Mono-	≤0.003	0.2	0.2	0.03	≤0.003	≤0.003
Di-	≤0.003	0.9	0.1	≤0.003	≤0.003	≤0.003
Tri-	0.04	0.4	0.03	≤0.001	≤0.001	≤0.001
Tetra-	0.5	4.8	0.1	≤0.01	≤0.01	≤0.01
Penta-	1.5	13	1.5	≤0.05	≤0.05	≤0.05
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2,7/2,8-DBrDD	≤0.003	0.4	0.03	≤0.003	≤0.003	≤0.003
2,3,7-TBrDD	0.004	0.06	0.006	≤0.001	≤0.001	≤0.001
2,3,7,8-TBrDD	0.02	0.1	≤0.01	≤0.01	≤0.01	≤0.01
1,3,6,8-TBrDD	0.2	0.4	0.05	≤0.01	≤0.01	≤0.01
1,3,7,9-TBrDD	≤0.01	0.4	0.05	≤0.01	≤0.01	≤0.01
1,3,7,8-TBrDD	0.02	0.4	≤0.01	≤0.01	≤0.01	≤0.01
1,2,3,7,8-PBrDD	≤0.05	0.6	≤0.05	≤0.05	≤0.05	≤0.05

* The ppm-values are based on material used

Table 2 Formation of tetrabromodibenzofurans by the thermolysis of PBTP containing 10 % DBrDPE with and without Sb₂O₃, in µg/g (ppm)

Temperature (°C)	500		600		800	
	A	B	A	B	A	B
ΣTBrDF	3535	105	911	148	0.2	5.2
2,3,7,8-TBrDF	32	2.5	5.7	4.2	≤0.01	0.08

* The ppm-values are based on material used

A = PBTP with 10 % DBrDPE and 6 % Sb₂O₃

B = PBTP with 10 % DBrDPE, without Sb₂O₃

3. Influence of water on formation of tetrabromodibenzofurans

The role of water in this reactions was examined by thermolysis under dry and wet nitrogen atmosphere at 600 °C (Table 3). It is evident from these experiments that the presence of H₂O or O₂/H₂O plays an important role in the formation of TBrDFs; H₂O enhances the formation of 2,3,7,8-TBrDF by a factor of ten.

Table 3 Formation of tetrabromodibenzofurans by thermolysis of PBTP containing 10 % DBrDPE and 6 % Sb₂O₃ in different reaction atmospheres at 600 °C, in µg/g (ppm)

	dry nitrogen	wet nitrogen	atm. air
ΣTBrDF	152	650	911
2,3,7,8-TBrDF	0.5	4.7	5.7

* The ppm-values are based on material used

By thermolysis of DBrDPE at 600 °C in N₂/D₂O atmosphere a number of polybrominated deuterio-dibenzofurans including monobromo-heptadeutero-dibenzofuran were identified in the exhaust gas (Figure 2). These results denote that water does take part in the reaction processes that lead to the formation of PBrDFs and PBrDDs.

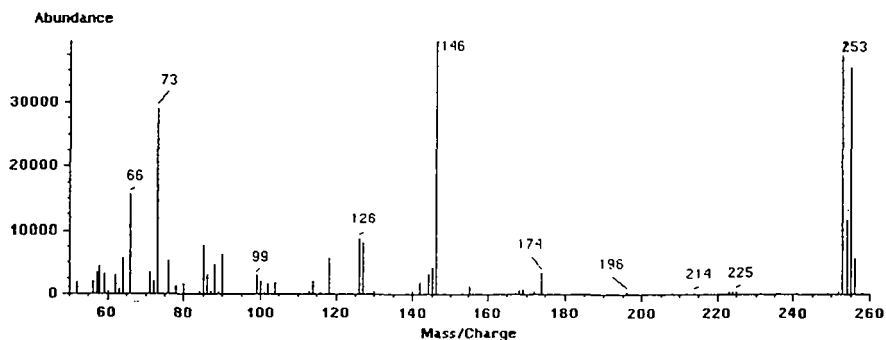


Figure 2 Mass spectrum (GC/MS-EI, m/z 50 - 800) of a monobromo-heptadeutero-dibenzofuran by thermolysis (600 °C) of DBrDPE in N₂/D₂O atmosphere

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