

FORMATION OF BROMINATED DIBENZOFURANS AND -DIOXINS FROM THE COMBUSTION OF THE FLAME RETARDANT DECABROMODIPHENYL ETHER UNDER DIFFERENT CONDITIONS

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ABSTRACT

Decabromodiphenyl ether was pyrolysed in the DIN-oven and in a sealed quartz ampoule at temperatures between 300°C and 800°C under two conditions of combustion: an industrial polypropylene sample containing 12.5% decabromodiphenyl ether and 7.5% antimony(III) oxide as synergist and pure decabromodiphenyl ether without additive.

The results show that decabromodiphenyl ether burned within a polymer matrix leads to brominated dibenzofurans as main products whereas pure decabromodiphenyl ether forms hexabromobenzene and only small amounts of brominated dibenzofurans.

INTRODUCTION

Decabromodiphenyl ether is used as a flame retardant in various types of polymers at concentrations of 5 to 15%, mostly in combination with antimony(III) oxide, as synergist (1,2). As shown earlier (3,4,5) polymers containing decabromodiphenyl ether form large amounts of polybrominated dibenzofurans on combustion. Pure decabromodiphenyl ethers leads to a small amount of brominated dibenzofurans and -dioxins. The polymer matrix and also antimony(III) oxide increases the amount of brominated dibenzofurans.

EXPERIMENTAL

The following two samples were investigated:

- Pure decabromodiphenyl ether
- Polypropylene/12.5% decabromodiphenyl ether/7.5% antimony(III)oxide (a commercially available sample)

Pyrolysis

The polymer (1.0 g) and the pure decabromodiphenyl ether (50 mg), were burned in the DIN-apparatus (6). In the combustion zone the air-flow was 170 ml/min. The combustion gases were collected on a XAD-2 adsorption tube. In addition, the samples were pyrolysed in sealed quartz ampoules. The products of this thermolysis were extracted with toluene.

Clean-up of the pyrolysis products

The adsorption tube with XAD-2 and the solid combustion residues were soxhlet extracted with toluene for 48 hours. The two extracts were combined, concentrated and transferred to a multilayer column. This column contains silica gel/sulphuric acid and silicagel/sodium hydroxide and was eluted with n-hexane. The eluates were concentrated and analysed via GC/MS.

Quantification of bromine, hydrogenbromide and carbon dioxide

For the determination of bromine, hydrogen bromide and carbon dioxide the combustion gases were passed through impingers with defined solutions of potassium iodide, silver nitrate and barium-hydroxide. The amounts of these compounds have been determined by titration.

GC/MS analysis

PBDF/D, the decabromodiphenyl ether and the bromobenzenes were quantified by GC/MS using external standards. The instrument was a Hewlett Packard GC/MSD in EI-mode with a 12 m Ultra 2 column in the SIM-mode.

Temperature program:

Initial temperature: 100°C; initial time 1 min

Rate I: 20°C/min; final temperature I: 180°C

Rate II: 5°C/min; final temperature II: 320°C; final time 7 min.

RESULTS

Using the DIN-oven the following results were obtained:

(Br₁₀DE = decabromodiphenyl ether, HBBz = hexabromobenzene, PBDF = polybrominated dibenzofurans, PBDD = polybrominated dibenzodioxins)

Table 1: Combustion products of the pure decabromodiphenyl ether (left) and in a polypropylene matrix (right). Yields in %.

Compound	400°C	600°C	800°C	Compound	400°C	600°C	800°C
Br ₁₀ DE	22.3	---	---	Br ₁₀ DE	---	---	---
HBBz	12.3	56.8	0.6	HBBz	---	---	---
PBDF/D	0.1	0.3	0.2	PBDF/D	25.5	12.4	5.5
CO ₂	4.5	9.9	16.3	CO ₂ ^x	3.0	3.5	4.3
HBr	---	---	---	HBr	---	1.0	2.2
Br ₂	---	9.5	10.9	Br ₂	---	---	---

^x) related to the total amount of carbon

Table 2: PBDF and PBDD from combustion of pure decabromodiphenyl ether. Yields in ppm.

Compound	400°C	600°C	800°C	Compound	400°C	600°C	800°C
Br ₁ DF	---	---	---	Br ₁ DD	---	---	---
Br ₂ DF	---	---	---	Br ₂ DD	---	---	---
Br ₃ DF	---	---	11	Br ₃ DD	---	---	8
Br ₄ DF	---	---	28	Br ₄ DD	---	---	17
Br ₅ DF	---	---	35	Br ₅ DD	---	---	35
Br ₆ DF	96	447	81	Br ₆ DD	6	50	74
Br ₇ DF	204	1449	959	Br ₇ DD	45	68	104
Br ₈ DF	107	860	---	Br ₈ DD	313	329	452
ΣPBDF	407	2756	1114	ΣPBDD	364	447	690

Table 3: PBDF from decabromodiphenyl ether in a polypropylene matrix. Yield in ppm, related to Br₁₀DE.

Compound	400°C	600°C	800°C
Br ₁ DF	14432	10676	4192
Br ₂ DF	26462	14845	4850
Br ₃ DF	39997	24036	8354
Br ₄ DF	107517	49677	29147
Br ₅ DF	37419	18458	6867
Br ₆ DF	24432	5465	948
Br ₇ DF	4762	1033	353
Br ₈ DF	---	---	---
ΣPBDF	255021	124190	54711

No PBDF/D were found.

From the pyrolysis in sealed quartz ampoules the following results were obtained:

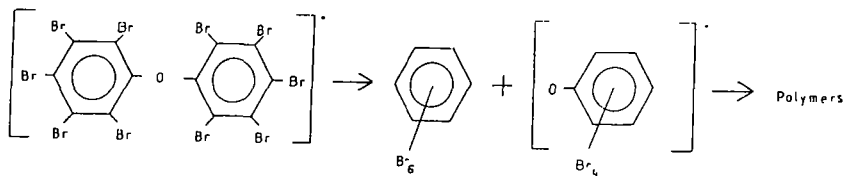
Table 4: PBDF from decabromodiphenyl ether in a polypropylene matrix

Compound	600°C
Br ₁ DF	8860
Br ₂ DF	55990
Br ₃ DF	118910
Br ₄ DF	142940
Br ₅ DF	65770
Br ₆ DF	---
Br ₇ DF	---
Br ₈ DF	---
ΣPBDF	392570

NO PBDD were found

The amount of PBDF and PBDD formed from the thermolysis of pure decabromodiphenyl ether in a sealed quartz ampoule is almost the same as in the DIN-oven.

Black and insoluble residues were always produced in both types of pyrolysis. Pyrolysis under this condition show one main pathway:



The results from different types of pyrolysis show no great difference in the products of pyrolysis. They form the same patterns of PBDF and PBDD. Only the PBDF-amounts from the polymer sample in the sealed quartz ampoule were a little higher.

Surprisingly, there is a great difference in the main products of pyrolysis of pure decabromodiphenyl ether and decabromodiphenyl ether in a polymer matrix. The pure flame retardant produces a lower quantities of highly brominated PBDF and PBDD. The main product was hexabromobenzene. A large quantity of PBDF is formed when the flame retardant is present in a polymer matrix. PBDD have not been detected. All degrees of bromination including a maximum of the tetrabrominated congeners can be detected. PBDF are the main products here, and no hexabromobenzene was found in the combustion products.

DISCUSSION

The results show that the pyrolysis conditions have no significant influence on the reaction products. But the polymer matrix is responsible for a change in the reaction mechanism. Pyrolysis reactions are mostly radical reactions. For the decabromodiphenyl ether the most likely probable radical reactions are the dissociation of the C - Br or the C - O bonds. In case of the pure decabromodiphenyl ether there is a surplus of bromine radicals but no substituents for them like hydrogen. The formation of the very stable hexabromobenzene and also the formation of highly brominated dibenzofurans and -dioxins can thus be explained. However if the decabromodiphenyl ether is included in a polymer matrix like polypropylene, the bromine can be substituted by hydrogen from the hydrogens of the polymers. The decabromodiphenyl ether is very voluminous and maybe constrained in the polymer matrix (like in a cage). Thus can only react with itself by a ring closure to form dibenzofuran. This explains the formation of all bromination degrees and the high yield of brominated dibenzofurans.

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