

HIGH TEMPERATURE THERMAL DECOMPOSITION OF
POLYBROMINATED FLAME RETARDANT MATERIALS

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Abstract

This laboratory study examined gas phase oxidative and pyrolytic thermal decomposition of three brominated flame retardant materials in a high temperature flow reactor. Products formed included HBr, Br-benzene, Br-phenols, PBDFs and PBDDs (up to approximately 5% yields). No organic products could be detected under the conditions of these experiments after a 800°C exposure at 2.0 seconds residence time.

Introduction

The thermal reaction products of condensed (liquid or solid) brominated flame retardant materials have been examined. Buser (1) reported the formation of polybrominated dibenzofurans (PBDFs) and polybrominated dibenzodioxins (PBDDs) from the thermolysis of three technical grade mixtures of polybrominated diphenylethers (PBDPEs) with total yields of up to 10%. Other studies (2,3) also conducted with condensed phase materials, indicated that some brominated flame retardants, heated to 700-900°C in quartz tubes, formed PBDD and PBDF in yields of 89.6%. Because these materials may ultimately be disposed of by high temperature incineration, the objective of this study was to determine the identity and yields of brominated products from the gas phase pyrolysis and oxidation of brominated flame retardants under conditions appropriate for gas phase incineration.

Experimental

The following flame retardant materials were examined:

- 1) 2,4,6-tribromophenol
- 2) 1,2-bis-(tribromophenoxy) ethane (BTBPE)
- 3) 1:1 weight percent mixture of two commercial polybrominated diphenylether (PBDPE) products (tri- through deca-bromination)

Each sample was subjected to gas phase thermal degradation under pyrolytic and oxidative conditions using a well controlled high temperature flow reactor system known as the System for Thermal Diagnostic Studies (STDS) which has been previously described (4). A 0.3 ul sample of each flame retardant mixture (in toluene at 0.3 to 1.0 weight percent levels) was introduced into the STDS by syringe injection onto quartz wool. The insertion region was raised in temperature and appropriate gas sweeping and pneumatics were used to selectively evaporate the solvent to vent. The solute of interest was then vaporized by temperature programming the insertion region of the STDS from 75-300°C. The gas phase material was quantitatively transported through uncoated fused silica tubing to a quartz thermal reactor where the material was subjected to a series of precisely controlled time-at-temperature exposures (300 to 800°C for 2.0 seconds) in either an air or nitrogen atmosphere. The reaction atmospheres were chosen to envelop the range of reactive conditions that may be present in an incinerator.

After the high temperature thermal exposure, the thermal reaction products and any unreacted parent materials were then swept into a gas chromatograph (HP 5890A) for cryogenic trapping, solute focusing and subsequent GC-MS (HP 5970B) detection. A 12 meter, 0.22 mm ID, 0.1 um film thickness BP-5 (SGE) capillary column was used for all GC analyses. The column was temperature programmed from -60 to 300°C at 12°C per minute with MS scans from 50 to 800 amu. Thermal decomposition products were identified and their various responses (relative to the response of the parent material) were plotted to produce a thermal decomposition profile. Selected ion monitoring (SIM) was performed at intermediate and high temperatures, specifically looking for molecular ion clusters under these highly reactive conditions.

Results and Discussion

Figure 1 displays the results for the 2,4,6-tribromophenol (TBP) for both oxidative and pyrolytic experiments. The trends of the curves indicate that this compound is not particularly stable. Note that even under pyrolytic conditions, the TBP is thermally decomposed to less than the detectable limit at 700°C. Detectability limits were not determined absolutely but were estimated from peak response. Dashed lines in the figures denote that experiments performed at higher temperatures showed no detectable quantities of the solute of interest.

Products of incomplete combustion (PICs) revealed a single isomer of dibromophenol being formed from TBP in a nitrogen atmosphere with a maximum yield of 1.5%. Hydrogen bromide, a thermodynamically stable end product was detected in large yields in nitrogen. Data obtained in air indicated formation of dibromomethylphenol, which would seem unlikely from the parent TBP. Perhaps trace toluene solvent participated in the formation of this product. Note that no HBr was observed in air. Although not shown in this figure, tetrabromodibenzodioxin (TBD) was detected as a PIC at 500°C in an air atmosphere using selected ion monitoring.

The results of the thermal decomposition of 1,2-bis-(tribromophenoxy) ethane (BTBPE) are depicted in Figure 2. Both oxidative and pyrolytic experiments showed similar parent

material stabilities, with the BTBPE degrading by 475°C in both cases. Detectable product formation was limited to TBP with a yield of approximately 30% at 475°C in nitrogen. Oxidative data indicated large amounts (up to 20%) of tribromophenoxy ethane as well as large amounts of tetra-BDD. At least two isomers of tetra-BDD were observed with a total yield of 5%. These isomers of tetra-BDD themselves decomposed in air at temperatures below 800°C.

Figure 3 presents results of the thermal decomposition of the polybrominated diphenylether (PBDPE) mixture. Since numerous tri- through deca- isomers were present, only the total decomposition profiles for all isomers are shown. Isomers with higher levels of bromination were generally more stable (than lower brominated PBDPEs) under both oxidative and pyrolytic conditions. Because of the number of PICs observed in each set of experiments, the PIC response is summed for all detectable organic products and plotted as shown. Note that HBr is the major product in both experiments. Table 1 gives the approximate yields for product formation from PBDPE. All experiments conducted at 800°C in air or nitrogen showed that all products were decomposed to HBr or non-detectable products. Neither PBDF, PBDD nor any of the parent materials could be detected at 800°C.

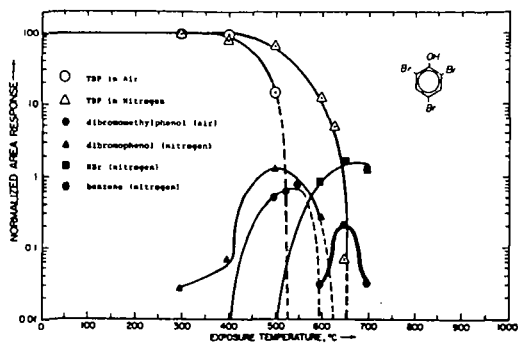
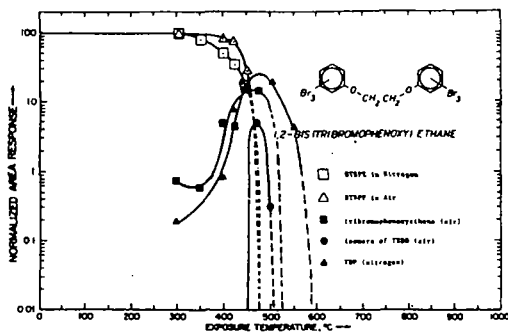


Figure 1. Thermal Decomposition Profile of 2,4,6-tribromophenol (TBP) in air and nitrogen

Figure 2. Thermal Decomposition Profile of 1,2-bis-(tribromophenoxy) ethane (BTBPE) in air and nitrogen



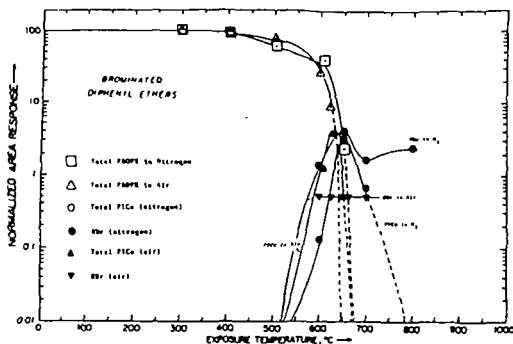


Figure 3. Thermal Decomposition Profile of Poly-brominated Diphenyl-ether (PBDFE) mixture in air and nitrogen

Table I
Products of Thermal Decomposition from the PBDFEs

Product	Maximum Yield (%) ¹	
	Nitrogen (650°C)	Air (625°C)
dibromobenzene	0.35	ND
tribromobenzene	0.64	0.92
tetrabromobenzene	0.43	0.95
Unknown, possibly pentabromobenzene	0.04	0.24
brominated alkanes, alkenes and all other PICs	1.40	0.77
di-BDFs	0.03	ND
tri-BDFs	0.03	0.03
tetra-BDFs	0.03	0.03
di-BDOs	ND	0.04
tri-BDOs	ND	0.04
tetra-BDOs	ND	0.01

¹ Given as percent of percent based on area counts at temperature of maximum yield
ND = not detected

The results of this study indicate that none of these materials were unusually stable under the conditions investigated. However, brominated products were formed at intermediate temperatures which may be of environmental concern. Although these compounds were destroyed in laboratory experiments at 800°C, one must recognize the possibility of poorly controlled incinerators having low temperature pathways which can result in the formation and emission of potentially toxic materials. However, under the conditions of these experiments using a high temperature flow reactor, PBDD and PBDF yields were somewhat lower than some existing condensed phase data.

References

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