



Formation of brominated pollutants during the pyrolysis and combustion of tetrabromobisphenol A at different temperatures



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ABSTRACT

Tetrabromobisphenol A (TBBPA) is the most widely used brominated flame retardant worldwide. A detailed examination of the degradation products emitted during thermal decomposition of TBBPA is presented in the study. Runs were performed in a laboratory furnace at different temperatures (650 and 800 °C) and in different atmospheres (nitrogen and air). More than one hundred semivolatile compounds have been identified by GC/MS, with special interest in brominated ones. Presence of HBr and brominated light hydrocarbons increased with temperature and in the presence of oxygen. Maximum formation of PAHs is observed at pyrolytic condition at the higher temperature. High levels of 2,4-, 2,6- and 2,4,6- bromophenols were found. The levels of polybrominated dibenzo-p-dioxins and furans have been detected in the ppm range. The most abundant isomers are 2,4,6,8-TeBDF in pyrolysis and 1,2,3,7,8-PeBDF in combustion. These results should be considered in the assessment of thermal treatment of materials containing brominated flame retardants.

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1. Introduction

Flame retardants are incorporated in different materials to reduce the risk of fire either by providing increased resistance to ignition or acting to slow down combustion and thereby delay the spread of flames. Tetrabromobisphenol A (TBBPA) is the most widely used brominated flame retardant (BFR) with world market production over 170,000 tonnes in 2004, representing around 60% of BFR total production. It is likely these numbers have continued to increase in recent years as TBBPA has been considered a substitute for certain polybrominated diphenyl ethers (PBDEs) like the commercial octabromodiphenyl ether (OctaBDE) product.

TBBPA is primarily used as a reactive flame retardant, covalently bound to epoxy and polycarbonate resins. It is also used as an intermediate in the production of other brominated flame retardant systems, derivatives and brominated epoxy oligomers where it is integrated into the resin as well. Finally, it is used as an additive flame retardant in the manufacture of acrylonitrile butadiene styrene (ABS) resins, high impact polystyrene (HIPS) and phenolic resins (BSEF, 2013).

Previous studies (Wäger et al., 2011) detected TBBPA in most samples of mixed plastics from Waste Electrical and Electronic

Equipment with average concentration levels typically ranging from 1 to 10 g/kg. The highest concentrations were found in mixed plastics from cathode ray tube (CRT) monitors with an average concentration of 37 g/kg and a maximum level of 63 g/kg.

The increasing presence of this flame retardant in many kinds of wastes poses a potential source of hazardous brominated compounds that must be taken into account.

Some studies have focused on the formation of hazardous products during thermal degradation processes of materials containing TBBPA (Barontini and Cozzani, 2006; Duan et al., 2011, 2012; Grause et al., 2008; Oleszek et al., 2013), as well as on the analysis of the TBBPA degradation process (Barontini et al., 2004a), but there is still a lack of quantitative data on TBBPA decomposition products in the scientific literature.

The similar chemical properties of chlorine and bromine suggest that the two elements behave comparably during thermal processes; in fact, brominated dioxin-like compounds (PBDD/Fs) have formation mechanisms similar to those of chlorinated dioxin-like compounds (PCDD/Fs) due to the similar chemical properties of chlorine and bromine (Weber and Kuch, 2003).

Previous studies (Weber and Kuch, 2003) incise in the fact that in waste incineration processes, chlorine is introduced mainly as inorganic chloride (e.g. NaCl in the organic waste fraction) and from polyvinylchloride (PVC), minimizing the possible formation of PCDD/Fs by the precursor pathway. In contrast, bromine is primarily present in specific plastics in the form of BFRs specifically

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brominated aromatic compounds which can act as precursors for PBDD/Fs formation (e.g. brominated diphenylethers (PBDEs) or brominated phenols (PBP)). Hence, the precursor pathway is of higher relevance for the formation of PBDD/Fs during thermal processes compared to their chlorinated analogues (Weber and Kuch, 2003).

A study of the thermal degradation of TBBPA has been carried out in the present work to assess the emission of pollutants under different operating conditions of atmosphere and temperature. The analysis, identification and quantification of gases, semivolatiles (bromophenols, polycyclic aromatic hydrocarbons and others) and PBDD/Fs have been performed. A special effort has been made to identify brominated compounds in the combustion gases.

2. Experimental

2.1. Materials

4,4'-isopropylidenebis(2,6-dibromophenol), commonly known as TBBPA, was supplied by Alfa Aesar GmbH & Co. Fig. 1 shows the chemical structure of TBBPA, together with a scheme of the possible scission of the molecule. Characterization of TBBPA was performed. Elemental analysis was carried out in a Carlo Erba Instrument, model CHNS O EA110 and the results are 33.9% C, 2.2% H, 0.31% N <0.01% S. The amount of ash is lower than 0.01%. Determination of inorganic anions by ion chromatography using EPA method 9056A is performed giving the following results: 55.3% bromine, 0.03% chlorine, <0.01% fluorine. The low calorific value of the sample (determined in a LECO-calorific bomb AC-350) is 12,858 kJ/kg.

All solvents for organic trace analysis were purchased from Merck (Germany) and are pesticide grade; the standards for the bromophenols analysis were supplied by Wellington Laboratories (Ontario, Canada); the standards for the PAHs analysis were supplied by Dr. Ehrenstorfer-Schäfers (Augsburg, Germany); and the standards of PBDD/F were obtained from Cambridge Isotope Laboratories (Andover, USA).

2.2. Experimental setup

Pyrolysis and combustion runs were carried out in a laboratory reactor in order to study TBBPA decomposition products under different operating conditions. The experiments were carried out in a tubular quartz reactor located inside a horizontal laboratory furnace. This equipment has been previously described in detail (Conesa et al., 2005; Fullana et al., 2000). The sample is placed in a holder and a small engine introduces it inside the reactor. During each run, after the furnace had reached the nominal temperature, approximately 50 mg of sample were introduced into the reactor at constant speed (1 mm s⁻¹). The carrier gas (nitrogen or synthetic air, for pyrolysis and combustion runs, respectively) was introduced into the furnace flowing parallel to the sample movement, at a constant flow of 300 mL min⁻¹. Both pyrolysis and combustion experiments ('P' and 'C' runs) were conducted at two different temperatures (600 and 850 °C). These temperatures were chosen because EU legislation sets a minimum of two seconds at 850 °C for the post-combustion zone of an incinerator; the lower temperature (600 °C) is enough to decompose TBBPA and represents low temperature zones in the chamber. The compounds leaving the laboratory reactor were sampled for subsequent analysis but PBDD/Fs analysis was performed only at the higher temperature, that is the actual temperature of many post-combustion chambers.

The bulk air ratio (λ) parameter was defined (Fullana et al., 2000) as the ratio between the actual air flow and the stoichiometric air flow necessary for complete combustion, assuming that the combustion of the solid occurs at the same rate as that being introduced. Bulk air ratio is an indicator of the quantity of oxygen present in the process ($\lambda = 0$ in the pyrolysis processes, $\lambda = 1$ when the oxygen present is the stoichiometric necessary one for a complete combustion, and $\lambda > 1$ for the run with excess of oxygen).

2.3. Analytical procedure

For each experimental condition, four runs were carried out. In a first run, evolved gas was passed through two consecutive impingers containing a sodium

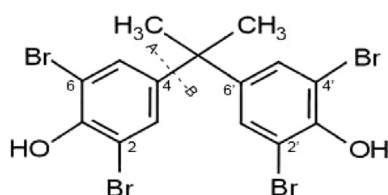


Fig. 1. Chemical structure of TBBPA.

carbonate/sodium bicarbonate solution in order to retain the released HBr. The amount of bromide ion in the solution was analyzed by ion chromatography in a Dionex DX500. By using this method, Br₂ is displaced to HBr and the total amount of both species is analyzed as HBr.

In a second run, the non-condensable gases were collected using Tedlar[®] bags at the outlet of the reactor for a time long enough to collect all the compounds (approx. 5 min) (Conesa et al., 2009). The analysis of CO₂, CO, oxygen and nitrogen was carried out in a Shimadzu GC-14A gas chromatograph equipped with a concentric packed Alltech CTR I column (6 ft × 1/8 in. and 6 ft × 1/4 in. for inner and outer columns, respectively) and a thermal conductivity detector. Light hydrocarbons (ranged from methane to xylenes) were detected in a Shimadzu GC-17A gas chromatograph with a Supelco capillary Alumina-KCl Plot column (30 m × 0.32 mm) with a flame ionization detector. For the identification and quantification, an external standard calibration of each compound was carried out.

Moreover, the non-condensable gases were analyzed by GC-MS using an Agilent 5973N mass spectrometer in SCAN mode coupled to an Agilent 6890N gas chromatograph with a J&W Scientific Products capillary DB-624 column (30 m × 0.25 mm × 1.4 μm). Brominated compounds were specifically searched throughout the peaks of the chromatography.

Finally, semivolatiles compounds and PBDD/Fs were collected in four different runs with sorbent (polyaromatic Amberlite[®] XAD-2, Supelco, Bellefonte, USA) placed at the outlet of the furnace during the entire run. Before the decomposition runs, a blank run was conducted, using the laboratory-scale reactor and reproducing the same experimental conditions.

For the analysis of PAHs, brominated phenols and other semivolatiles compounds, the resin was extracted with a mixture of dichloromethane/acetone (1:1 vol.), using Accelerated Solvent Extraction in a DIONEX ASE[®] 100. The samples were analyzed by HRGC-MS in an Agilent 5973N spectrometer coupled to a gas chromatograph Agilent 6890N with a chromatographic column Agilent HP5-MS (30 m × 0.25 mm i.d. × 0.25 μm).

The XAD-2 resin where PBDD/Fs were collected was extracted with dichloromethane and purified using an automated clean-up system (Power Prep, FMS Inc., Boston, MA) with two different columns: silica and alumina. The method is based on that for chlorinated analogues (US EPA, 1994), with some modifications pointed out in scientific literature. The purified extract was analyzed for tetra- through hexabrominated dioxins and furans by HRGC-HRMS, on an Autospec Ultima-NT high resolution mass spectrometer (Micromass, UK) with a positive electron impact (EI+) source and interfaced with a Hewlett-Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph equipped with a split/splitless injector. An Agilent DB5-MS

Table 1
Evolution of gases and volatile compounds during thermal decomposition of TBBPA.

Experiment	P600	C600	P850	C850
Compound	mg compound/kg sample (ppm)			
Analysis by ionic chromatograph				
Hydrogen bromide	283,100	417,500	459,000	549,200
Analysis by GC-TCED				
Carbon monoxide	–	267,680	104,250	460,660
Carbon dioxide	3780	303,400	8320	482,330
$R_{CO} = CO/(CO + CO_2)$	0	0.47	0.93	0.49
Analysis by GC-FID				
Methane	14,430	15,170	19,410	1870
Ethane	30	–	–	–
Ethylene	120	70	1160	–
Propylene	30	–	40	–
n-Butane	30	600	350	–
1,3-Butadiene	–	–	120	–
1-Butyne	–	–	–	830
n-Hexane	–	–	240	–
n-Heptane	–	90	–	–
Benzene	290	90	7860	–
1-Heptene	3470	–	–	–
Isooctane	770	–	–	–
Toluene	–	300	1800	–
Xylenes (p-,m-,o-)	–	–	840	820
Analysis by GC-MS				
Bromomethane	200	1930	–	3900
Benzene	500	140	–	–
Dibromomethane	–	540	–	1870
Tribromomethane	–	–	–	150
Bromobenzene	100	160	–	160
Phenol	2140	530	–	–
2-Bromo-4-methyl-phenol	300	50	–	–
1-Bromononane	–	270	–	–
3,5-Dibromo-4-methylphenol	200	–	–	–

(–): not detected.

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