

## Decomposition of Tetrabromobisphenol A in the presence of UV-light and Hydroxyl radicals.

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### Introduction

Tetrabromobisphenol A (TBBPA) is one of the more commonly used brominated flame retardants (1). Most of it (90%) is used as a reactive flame retardant, i.e. it is covalently bound in to epoxy and polycarbonate polymers used for instance in electric circuit boards. TBBPA is also used as an additive flame retardant and is then mixed as a powder with various polymers. It is produced by bromination of bisphenol A generally in a halocarbon solvent or in 50 % hydrobromic acid. TBBPA has a very low water solubility and vapour pressure, and is therefore mainly expected to be adsorbed to solid particles and organic matters in the environment. The n-octanol/water partition coefficient ( $\log K_{ow}$ ) is 4.5. TBBPA have been detected in sediments, fish (1) and human blood (2). The dimethoxy derivative of TBBPA have been detected in mussels and sediment (1).

The present study was performed within a larger project with the aim (i) to develop experimental conditions for the study of the relative reactivity of potential environmental pollutants, and (ii) to identify major decomposition products from photochemical reactions, mainly in the presence of hydroxyl radicals.

### Materials and Methods

*Chemicals:* 4-isopropylphenol (purum) and 2,4,6-tribromophenol (purum) were obtained from Fluka. Dichloromethane (p.a.), acetone (p.a.), hydrogen peroxide 30% (p.a.), bromine (p.a.), sodium sulphate (p.a.) and acetic acid (p.a.) were from Merck. Tetrachloromethane (p.a.) was from Prolabo. 2,2',3,4',5,6,6'-Heptachlorobiphenyl was used as internal standard for gas chromatographic + massspectrometric (GC + MS) analysis.

*Instruments:* GC-MS was performed on a Finnigan ITS 40 attached to a Varian 3400 gas chromatograph. Electron ionisation (EI) was used as the ionisation method. The gaschromatograph oven temperature was programmed as follows: 80 °C for 2 min, 80 – 300 °C

10 °/min, 300°C was held for 20 min. The UV-light source HB 171/A was obtained from Philips

**Photochemical reactions:** The photochemical reactions have been studied in two types of experiments. *i:* The following procedure is used to determine the rate of decomposition. The compound is dissolved in dichloromethane and thereafter TBBPA (100 µg dissolved in dichloromethane) is placed on one of the surfaces in the quartz cuvette. After the solvent is evaporated, an aluminium cylinder containing hydrogen peroxide (0.5 ml) is placed in the cuvette. Finally, a glass plate is placed on the top of the cuvette and thereafter the cuvette is placed 15 cm from the light source. Eight cuvettes are illuminated for 0, 5, 21, 34, 49, 58, 72 and 100 h, respectively. After the illumination is stopped the aluminium cylinder is removed from the cuvette and the cuvettes and glass plates are each placed in a dichloromethane solution (4 ml) containing 2,2',3,4',5,6,6'-heptachlorobifenyl (60 µg, internal standard). The solution is collected and is then analysed by GC-MS.

*ii:* To trap products from photo chemical reactions, the apparatus in figure 1 and the following procedure is used.

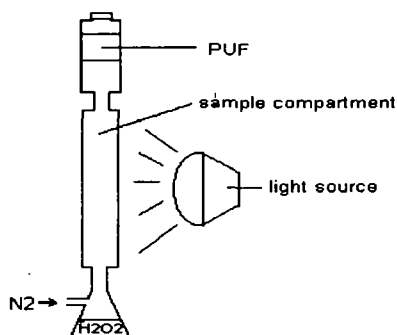


Figure 1. Apparatus used to trap reaction products

The compound (10 mg) is dissolved in dichloromethane (10 ml) and is thereafter placed on the walls in the sample compartment by rotating the vessel until the solvent is evaporated. Nitrogen is introduced over the hydrogen peroxide surface and hydroxyl radicals are formed by illumination of the hydrogen peroxide vapour. The hydroxyl radicals react with the compound in the sample compartment and volatile reaction products are trapped in a polyuretan foam (PUF) on top of the apparatus (see figure 1). After illumination both the PUF plug and the sample compartment were extracted with acetone and the solutions were then analysed by GC-MS.

**Synthesis of 2,6-dibromo-4-(2-bromoisopropyl)phenol:** Bromine (2 ml) was added to a solution of 4-isopropylphenol (0.5 g) and conc. acetic acid (300 ml). The solution was stirred for 30 min and then the excess of bromine was evaporated by nitrogen (g). Water (500 ml) was added and the dibromoisopropylphenol was extracted with tetrachloromethane (2 x 100 ml). Thereafter

the solution was illuminated with UV-light and bromine (approximately 1 ml) was added drop wise during 15 min. Thereafter water (2 x 250 ml) was added. The organic phase was collected, dried over sodium sulphate and analysed by GC-MS:  $m/z$  (rel ab., %): 290 (49,  $M^+$ ), 292 (100), 294 (51), 275 [17,  $(M-CH_3)^+$ ], 250 (6), 211 [7,  $(M-Br)^+$ ], 196 [20,  $(M-CH_3-Br)^+$ ], 132 (80), 103 (28) and  $^1H$  NMR (270MHz,  $CDCl_3$ ):  $\delta$  7.7, 5.9, 2.2.

### Results and Discussion

The decomposition of TBBPA has been studied at UV-illumination (>290 nm) and in the presence of hydroxyl radicals. 2,4,6-Tribromophenol (TBP) was identified as one of the major decomposition products of TBBPA. The TBBPA residue was determined at each time-point studied as well as the 2,4,6-tribromophenol formed during the experiment (Figure 2).

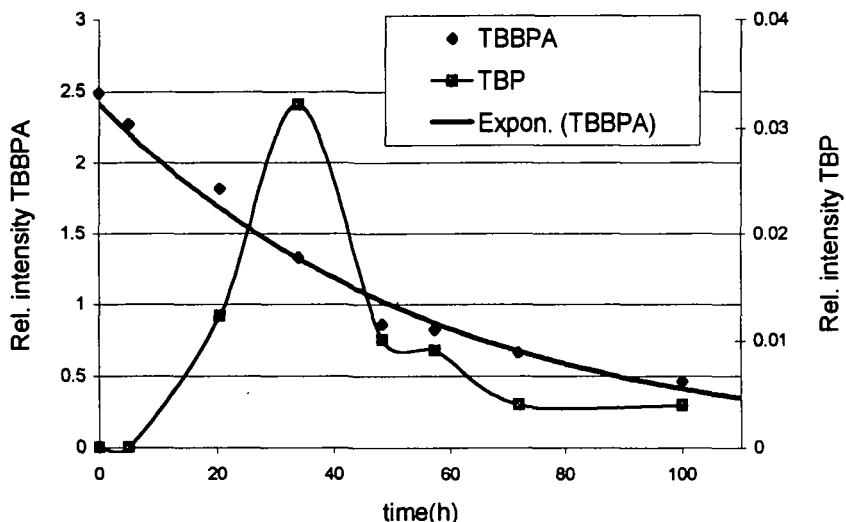


Figure 2. Decomposition of TBBPA and formation of TBP.

All TBBPA seems to decompose in approximately 5-6 days. We have however so far neither measured the vapour pressure of hydrogen peroxide nor the concentration of the hydroxyl radicals, factors that influences the rate of decomposition. The vapour pressure of hydrogen peroxide was calculated to be in the order of 50 pa.

In addition to 2,4,6-tribromophenol at least twenty decomposition products containing bromine were indicated. Some of these were tentatively identified as di- and tri-bromobisphenol A, dibromophenol, 2,6-dibromo-4-(bromoisopropylene)phenol, 2,6-dibromo-4-(dibromoisopropylene)phenol and 2,6-dibromo-1,4-hydroxybenzene. 2,6-Dibromo-4-isopropylphenol (b) has been identified as a decomposition product of TBBPA, cf. Figure

3. The compound was synthesized by bromination of 4-isopropylphenol. An intermediate in the synthetic pathway was however found to have identical mass spectrum and GC retention time as (b) and it is therefore uncertain if (a) and/or (b) are formed in the reaction.

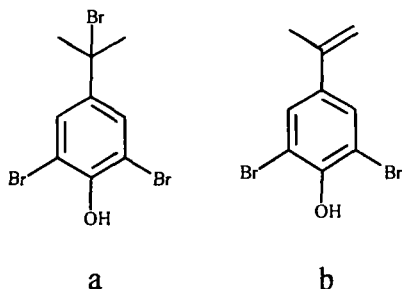


Figure 3. (a) Synthesised compound and (b) structure of one of the decomposition compounds according to GC/MS analysis.

#### References

1. Environmental Health Criteria 172, *Tetrabromobisphenol A and its derivatives*, World Health Organization, Geneva 1995.
2. Klasson Wehler E., Hovander L. and Bergman Å; *Organohalogen Compounds 1997*, 33, 420. 17<sup>th</sup> International Meeting; Dioxin '97, Indianapolis, USA.