

Spectroscopic behavior of saytex 8010 under UV-visible light and comparative thermal study with some flame bromine retardant



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ABSTRACT

Decabromodiphenyl ethane (DBDPE; saytex 8010) is a replacement for the flame retardant chemical decabromodiphenyl ether (DBDPO; saytex 102E), and has been reported in the environment. The photolytic degradation of DBDPE was investigated in tetrahydrofuran solvent (THF) as well as in solid state phase under artificial ultraviolet–visible light using UV–visible spectroscopy and thermal analysis via differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and derivative thermogravimetry (DTG) monitoring. The degradation kinetic of DBDPE in THF seems to be a very fast reaction. High photolytic efficiency i.e. 63.18% has been achieved within the first 180 s of irradiation time. The experimental data were well described by the pseudo first order kinetic model with high regression coefficient ($R^2 = 0.9373$). The thermal behavior of the irradiated powder of DBDPE for 2 h 30 min differs substantially compared with that of no irradiated DBDPE. The maximum degradation rate of no irradiated powder of DBDPE occurs at $T_d = 423.82^\circ\text{C}$ with 99.80% loss of weight and nearly of 0% of char residue was achieved at $T = 600^\circ\text{C}$. However, the melting temperature of the irradiated powder of DBDPE for 2 h 30 min reduces by about 46.91°C , the weight loss ratio of DBDPE is about 11% and the maximum degradation rate at the maximum weight loss ratio decreases by about 54.30°C . The onset and the maximum degradation rate were also assessed at 5% for different Albemarle flame retardants for comparison reason. Under inert atmosphere, the degradation of DBDPE and DBDPO follow one stage and the melting temperature of DBDPE and DBDPO are located at $T = 351.22^\circ\text{C}$ and $T = 304.01^\circ\text{C}$, respectively. The degradation of each ones is achieved with any residue. However, the thermal degradation of saytex HP800A begins at much lower temperature, whereas saytex BT93 shows slightly enhanced thermal stability and their thermal degradation occurred through two steps. When the temperature reached $T = 680^\circ\text{C}$, almost decomposed and 18.00% and 19.67% char residue were obtained for saytex BT93 and saytex HP800A, respectively. The degradation involves the formation of subsequently less bromine substituted congeners of DBDPE within the irradiation time. Further research is required to understand the photolytic degradation pattern of DBDPE and to facilitate the design of remediation processes as well as help to predict their fate in the environment.

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1. Introduction

Brominated flame retardants (BFRs) are a broad and diverse group of chemicals used at relatively high concentrations in many application including, the manufacture of electronic equipment, textiles, plastic polymers coating and in the car industry [1]. The use of BFRs is primarily to protect materials against

ignition and to prevent fire-related damage. The term BFRs covers a large number of organic substances with bromine in their molecular structure. Halogen containing flame retardants act primarily by a chemical interfering with the radical chain mechanism taking place in the gas phase during combustion. Some highly brominated BFRs have been shown to be of environmental concern owing to their limited biodegradability, potential bioaccumulation and persistence in sediments of their degradation/biotransformation by-products. These include polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). Based on structural and physical–chemical similarities of decabromodiphenyl ethane (DBDPE; saytex 1080) to decabromodiphenylether (DBDPO;

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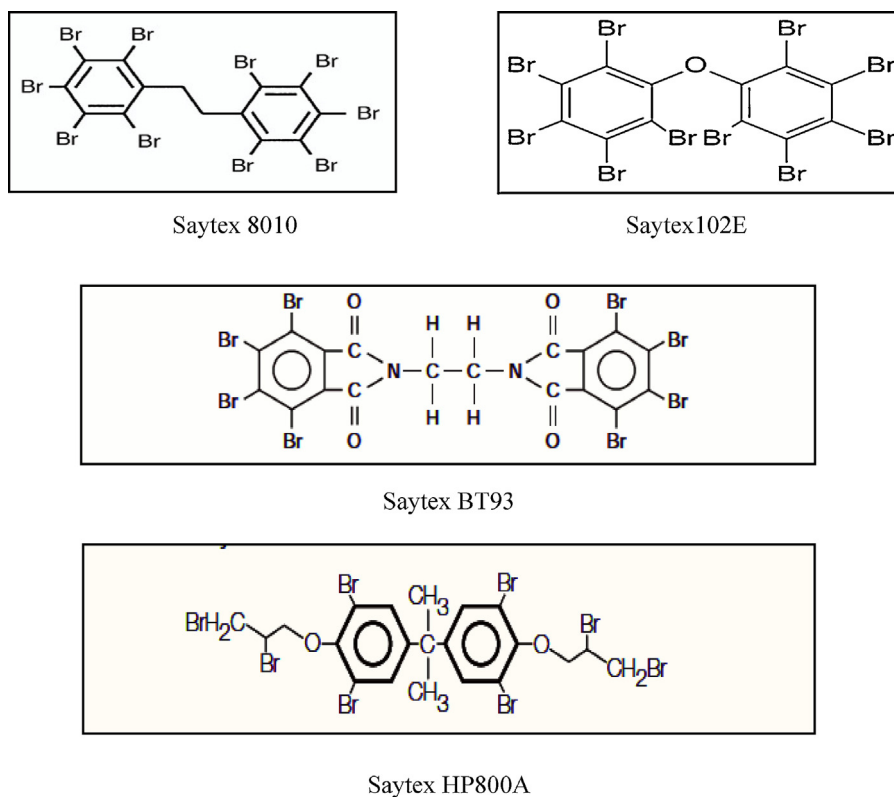


Fig. 1. Molecular structures of some Albemarle bromine-based flame retardant BFRs.

saytex 102E), DBDPE is now a commercially important alternative to DBDPO [2]. The inclusion of Ethane Bridge between the aromatics rings makes it slightly more hydrophobic which gives the molecule conformational flexibility as compared to DBDPO. DBDPE attracted growing interest in recent years as a result of its worldwide occurrence as contaminant in sewage sludge [3,4], in water [5,6], in soil and sediment [7,8] indoor and outdoor air and house dust samples [9,10]. There is increasing evidence that some BFRs, like DBDPE and DBDPO, bioaccumulate in the food chain, as increasing concentrations of these BFRs are found in species higher in the food chain, such as zooplankton, invertebrates, fish and sea mammals [11–16].

The implementation of strict bans on the use of some widely used BFRs and their voluntary withdrawal from the market [17] has paved the way for the use of “novel” BFRs as alternatives for the banned formulations. DBDPE, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO) and tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-BDPE) belong to the group of “novel” BFRs.

DBDPE was positively identified by means of the high-resolution mass spectrometry and quantified by low-resolution mass spectrometry with electron capture negative ionization. It was found in 25 of the 50 Swedish sewage treatment plants investigated, with estimated levels up to about 100 ng/g dry weight. The DBDPE concentration in sediment from Western Scheldt in the Netherlands was 24 ng/g dry weight, and in an air sample from a Swedish electronics dismantling facility it was 0.6 ng/m³ [18]. Oral administration of DBDPE through a single dose and long term (90 days) in rats resulted in high LD₅₀ values (>5000 mg/kg body wt) and LD_{Lo} (90 g/kg/90days). In the other hand, the highest doses gave changes in liver weight and slight histomorphological effects [19]. From

the flammability and thermal stability properties of flame retarded polymers, it was evident in 1999 that both DBDPE and DBDPO flame retarded polymers have the same flame retarding mechanism [20]. Zuo et al. [21] studied the fire retardant property of DBDPE in the presence of antimony trioxide (Sb₂O₃) by cone calorimeter and thermogravimetry analysis (TGA) in the acrylonitrile butadiene styrene (ABS) matrix. They suggest that the DBDPE/Sb₂O₃ system has the analog flame retardant behavior (flammability parameters and thermal composition) to DBDPO/Sb₂O₃. Under natural sunlight conditions, DBDPO in pulverized HIPS (high-impact polystyrene) matrix was completely degraded within a half-life of 51 days. However, no obvious loss of DBDPE was observed throughout the conducting tests period of 224 days, as a result of the lack of the biphenyl ether based BFR that has been reported not to produce furan derivatives under pyrolysis environment [22]. To the best of our knowledge, for the first time in 2012, photolytic degradation of DBDPE, as an alternative BFR to DBDPO, was investigated in various media including, n-hexane, tetrahydrofuran, methanol/water, humic acid/water, and silica gel matrixes under artificial ultraviolet light, and in n-hexane under natural light. The photolytic decomposition of DBDPE obviously occurs in the all investigated matrixes within an irradiation time less than 320 min [23].

The aim of the present study is to preliminarily investigate the photolytic degradation of DBDPE, as an alternative flame retardant to DBDPO, in tetrahydrofuran solvent as well as in solid state phase under artificial ultraviolet-visible light using UV-visible spectroscopy and thermal analysis using differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and derivative thermogravimetry (DTG) monitoring. The onset temperature for each one was detected under our conditions. The thermal stability of others BFRs were investigated for comparison reason, without any matrix, the curves are presented and discussed.

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