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An experimental investigation of tetrabromobisphenol A decomposition pathways

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Abstract

The primary thermal decomposition pathways of tetrabromobisphenol A (TBBA), a widely used brominated flame retardant, were investigated. TBBA decomposition was carried out in a laboratory-scale fixed bed reactor in both constant heating rate (10 °C/min, 30–600 °C) and isothermal (210–270 °C) modes. Quantitative data were obtained on the products formed in the thermal degradation process. TBBA decomposition resulted in a competitive process with evaporation, at least in the open system conditions used. Hydrogen bromide, brominated bisphenol A species, brominated phenols and char were the main products generated in the decomposition process. On the basis of the products formed, the decomposition pathways were analysed. Radical debromination reactions and scission reactions to phenols resulted the most important thermal degradation mechanisms of TBBA.
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1. Introduction

In the last decades, brominated flame retardants (BFR) have been widely used in industrial practice to improve the flame resistance of polymeric materials. Among the advantages of BFR are their efficiency, the high compatibility with many polymeric substrates and the limited influence on mechanical properties. The BFR that finds the wider industrial applications is tetrabromobisphenol A (TBBA). This compound is employed both as a reactive flame retardant in the manufacturing of epoxy, phenolic and polycarbonate resins, and as an additive flame retardant, e.g. in acrylonitrile/butadiene/styrene systems. The main application of TBBA is in the production of brominated epoxy resins. These materials, that may contain up to 20–25 wt.% bromine, are commonly employed for printed circuit boards manufacture. The growing production of printed circuit boards is resulting in an increase in TBBA

production (about 120,000 metric tons in 1999, representing itself half of BFR production [1]) and in a wide diffusion of BFR-containing materials.

In parallel with the growth in TBBA use and production, concerns were raised on safety and disposal issues due to the possible formation of polybrominated dibenzo-*p*-dioxins (PBDD) and dibenzofurans (PBDF) in the case of thermal stress of TBBA and of TBBA flame retarded materials. A wide number of studies were dedicated to these aspects [2–10], as well as to environmental and toxicity issues connected to the production and domestic use of products containing TBBA [11–18]. Both fundamental and pilot scale investigations devoted to PBDD and PBDF formation in pyrolysis and combustion of TBBA showed that limited amounts of these compounds are likely to be formed in a wide range of experimental conditions [2–10].

However, several industrial accidents have been reported involving batch reactors during the production of brominated epoxy resins. These events pointed out that the hazards caused by TBBA may as well arise from dangerous substances as hydrogen bromide and brominated phenols, that are formed in large amounts during the uncontrolled

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thermal degradation of this substance. Few studies were devoted to the investigation of TBBA thermal decomposition products, either pure [19–21], or in polymer matrices [22–26]. Factor [19] performed TBBA pyrolysis experiments both in open tube and in evacuated sealed tubes in the low–medium temperature range (200–315 °C). The main decomposition products were identified and a degradation pathway was proposed. However, the quantitative distribution of the products identified was not investigated. The thermal behaviour of TBBA under closed vessel conditions in the medium–high temperature range (350–600 °C) was explored by Borojovich and Aizenshtat [20] and Hornung et al. [21], that reported only qualitative or semiquantitative data on decomposition products.

The present study was dedicated to the experimental investigation of the products formed in the thermal degradation of TBBA. TBBA decomposition was carried out in a laboratory-scale fixed bed reactor using both constant heating rate and isothermal operating modes. Open system conditions were used in order to minimize the effects of secondary reactions. The main effort of the present study was in the achievement of quantitative data on decomposition products formed in the different experimental conditions explored. Data obtained on decomposition products were used for the assessment of TBBA thermal decomposition pathways.

2. Experimental

2.1. Materials

4,4′-Isopropylidenebis(2,6-dibromophenol), commonly referred to as tetrabromobisphenol A, was supplied by Aldrich (Milan, Italy). Phenol, 4-bromophenol, 2,4-dibromophenol, 2,4,6-tribromophenol, 2,6-dibromo-4-methylphenol, 4-isopropylphenol and bisphenol A were purchased from Aldrich (Milan, Italy). Solvents (HPLC grade) and analytical reagents were obtained from Carlo Erba (Milan, Italy).

2.2. Techniques and procedures

A laboratory-scale fixed bed tubular batch reactor (BR) was used to carry out TBBA thermal decomposition runs. Both constant heating rate and isothermal runs were performed. Heating rates of 10 °C/min from ambient temperature to 600 °C were used. Isothermal runs (60 min) were performed at temperatures between 180 and 270 °C. Typical sample weights in experimental runs were of 180–250 mg. All experiments were run at least in duplicate. Experimental runs were performed using a pure nitrogen purge gas flow (80 ml/min) to control reaction environment and to limit the extension of secondary gas-phase reactions. Volatile products evolved during degradation were transferred by the nitrogen flow to a train of cold traps, maintained at −20 °C by

a sodium chloride brine/ice bath, to allow the recovery of condensables. At the end of each experimental run, the collected products were dissolved in acetone and analysed by chromatographic techniques. The traps were followed by a gas sampling cell for FTIR gas analysis. FTIR analysis was carried out using a Bruker Equinox 55 spectrometer. The gas flowed then in two absorbers containing a sodium hydroxide solution for the absorption of gas-phase acidic compounds. At the end of each experimental run, absorbed acidic compounds were quantitatively determined by titration of the alkaline solution with a hydrochloric acid standard solution, using phenolphthalein and methyl orange as indicators. In order to detect the possible presence of molecular bromine, during experimental runs a fluorescein test was carried out on the gas outflow from the reactor [27]. Moreover, the solution collected in alkaline scrubbers at the end of experimental runs was checked by iodometric titration [28]. Further details and a scheme of the experimental apparatus are reported in a previous publication [29].

A Fisons MD 800 quadrupole mass spectrometer interfaced to a Fisons GC 8060 gas chromatograph was used for gas chromatography/mass spectrometry (GC/MS) analysis. A Mega SE30 fused silica capillary column (25 m length, 0.32 mm internal diameter, crossbonded, 0.25 μm film thickness) was employed for the chromatographic separation, with helium as carrier gas. The column temperature programme was the following: 5 min isothermal at 40 °C, heating to 250 °C (6 °C/min), then 20 min isothermal. Splitless injection with the injector at 250 °C was used. Mass spectrometric detection was performed in full scan conditions (scan range, m/z 10–819) in electron impact ionization mode. The estimated detection limit resulted of about 8 ppm (8 mol/10^6 mol of TBBA) in the experimental conditions used for the present study.

Quantitative GC analysis was carried out using a ThermoQuest Trace GC 2000 gas chromatograph equipped with a flame ionization detector (FID). The capillary column and the experimental conditions were identical to those used for GC/MS analysis, detector temperature was fixed at 280 °C. GC response factors with respect to phenol were obtained from calibration runs performed on mixtures of the available GC standards and phenol. Standard samples were available for all the major products formed in thermal decomposition runs, except for bromo-, dibromo- and tribromobisphenol A. However, calibration runs performed with bisphenol A and TBBA revealed almost the same response factor (±0.2%) for the two compounds. Therefore, bisphenol A response factor could be assumed for the brominated bisphenol A species. As expected, response factors resulted mainly dependent on the number of carbon atoms in the molecule. Whenever a standard sample was not available, or a fully structural assignment was not possible, a response factor was assumed on the basis of the number of carbon atoms. The repeatability of GC measurements was verified by the comparison of results obtained in multiple runs. Typical values of the standard deviation were of about 4%.

3. Results and discussion

3.1. Identification of TBBA thermal decomposition products

Following the procedure described in Section 2, constant heating rate TBBA thermal decomposition runs were performed. The experiments were aimed at the recovery and characterization of the different fractions of decomposition products.

The FTIR analysis of the gas outflow from the reactor evidenced the presence of hydrogen bromide among the gaseous decomposition products, along with limited quantities of carbon monoxide and carbon dioxide. Molecular bromine was not detected in the gaseous products, neither by the fluorescein test or by the iodometric titration of the solution collected in the scrubbers at the end of the experimental runs (see Section 2).

No organic compound was detected in the gas flowing through the FTIR cell. This may well suggest that only low volatility organic compounds are formed in TBBA decomposition, which are condensed in the cold traps before entering the gas cell. The GC/MS and GC analyses performed on the condensable product fraction recovered from the traps allowed for the achievement of detailed data on the nature and relative distribution of the products formed. Fig. 1 shows a typical chromatogram obtained by GC/MS analysis of the condensate recovered at the end of a constant heating rate decomposition run. The thermal degradation gives rise to a mixture of products. Mass spectrometric detection enabled the identification of chromatographic peaks, while quantification was carried out by GC/FID analysis. The mass spectra obtained for each product were analysed in order to obtain information about the molecular weight, the number of bromine atoms present and the molecular structure. The structural identification was achieved by the analysis of fragmentation patterns, by the comparison with the best fits found in the NIST spectral library, by the comparison with

published MS data [19,20,26], and by the use of standards. For a limited number of minor peaks, a complete structural assignment was not possible. However, the molecular ion could be clearly identified for all the chromatographic peaks. The quite high intensity of the molecular ion peaks may be related to the aromatic structure of the compounds analyzed. Furthermore, the number of bromine atoms present in the molecule were usually readily apparent because of the characteristic bromine isotope contribution. The isotopic clusters of the molecular and fragment ions are highly diagnostic from this point of view. Thus, when a molecular structure could not be postulated, the molecular weight and the number of bromine atoms were assigned. The results obtained are summarized in Table 1. The table also reports the identification method used for each of the identified compounds. In the case of brominated bisphenol A species representing major peaks in the chromatogram, neither a NIST spectrum nor a standard was available. The analysis of mass spectra, reported in Fig. 2, and their comparison with TBBA spectrum, allowed for structure assignment, which was confirmed by the MS data reported by Factor [19] and Blazsó et al. [26]. Analogously, the compound having retention time 18.52 min (mass spectrum reported in Fig. 3) could be identified as 2-bromo-4-(1-methylethenyl)phenol.

The results reported in Table 1 also evidence the presence of unconverted TBBA among the recovered products. This suggests that TBBA decomposition is a competitive process with evaporation, at least in the experimental conditions used.

Table 1 also includes a comparison with previous studies performed on TBBA. As shown in the table, a sufficient correspondence was found with previous data on TBBA decomposition products [19–21], even if in the present study a wider number of compounds were detected. No brominated dibenzo-*p*-dioxins or dibenzofurans were detected: if present, quantities below the detection limit were formed. Previous studies on PBDD/PBDF formation from TBBA and
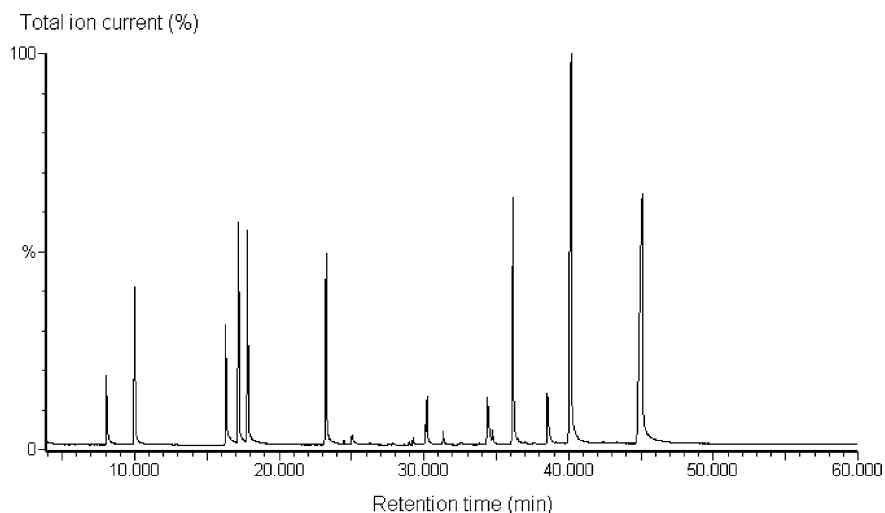

Fig. 1. GC/MS chromatogram of the condensable product fraction recovered at the end of constant heating rate pyrolysis runs (10 °C/min, ambient to 600 °C, 80 ml/min 100% N_2 flow).

Table 1
Results of GC/MS analysis performed on the condensable fraction recovered at the end of constant heating rate pyrolysis runs (10 °C/min, ambient to 600 °C, 80 ml/min 100% N_2 flow)

Retention time (min)	Compound	Molecular weight	Identified by means of:	Identified also by:
8.24	Phenol	94	NIST library and use of standard	Factor [19], Borojovich and Aizenshtat [20], Hornung et al. [21]
9.93	2-Bromophenol	173	NIST library	Factor [19], Borojovich and Aizenshtat [20], Hornung et al. [21]
12.29	Monobromo compound (n.i.)	185		
16.27	4-Bromophenol	173	NIST library and use of standard	Factor [19], Borojovich and Aizenshtat [20], Hornung et al. [21]
16.35	Bromotrimethylbenzene	199	NIST library	
17.00	2,4-Dibromophenol	252	NIST library and use of standard	Factor [19], Borojovich and Aizenshtat [20], Hornung et al. [21]
17.62	2,6-Dibromophenol	252	NIST library	Factor [19], Borojovich and Aizenshtat [20], Hornung et al. [21]
17.92	Biphenyl	154	NIST library	
18.52	2-Bromo-4-(1-methylethenyl)phenol	213	Analysis of mass spectrum and comparison with MS data reported by Blazsó et al. [26]	
20.52	2,6-Dibromo-4-methylphenol	266	NIST library and use of standard	Borojovich and Aizenshtat [20]
21.29	Dibenzofuran	168	NIST library	
21.74	α,α′-Dimethylbibenzyl	210	NIST library	
22.44	Biphenylmethanol	184	NIST library	
22.44	Dibromo compound (n.i.)	280		
22.46	α,α′-Dimethylbibenzyl	210	NIST library	
22.74	Dibromo compound (n.i.)	278		
23.06	2,4,6-Tribromophenol	331	NIST library and use of standard	Factor [19], Borojovich and Aizenshtat [20], Hornung et al. [21]
23.71	1,3-Diphenylpropane	196	NIST library	
23.84	Dibromo compound (n.i.)	292		
24.37	Dibromo compound (n.i.)	292		
24.52	Non-brominated compound (n.i.)	212		
24.92	Non-brominated compound (n.i.)	198		
25.02	Dibromo compound (n.i.)	292		
25.24	α-Methylstilbene	194	NIST library	
26.54	Ethylphenoxybenzene	198	NIST library	
27.24	α,α′-Dimethylbibenzyl	210	NIST library	
27.41	4-(1-Methyl-1-phenylethyl)phenol	212	NIST library	
27.71	Tribromo compound (n.i.)	371		
27.94	Monobromo compound (n.i.)	277		
28.52	Monobromo compound (n.i.)	277		
28.89	Tribromo compound (n.i.)	371		
29.26	Tribromo compound (n.i.)	371		
29.26	Non-brominated compound (n.i.)	204		
29.57	Tribromo compound (n.i.)	373		
30.08	Tribromo compound (n.i.)	371		
31.12	α,α′-Dimethylbibenzyl	210	NIST library	
31.31	Benzylnaphthalene	218	NIST library	
31.99	Monobromo compound (n.i.)	305		
32.26	Monobromo compound (n.i.)	307		
32.52	Tetrabromo compound (n.i.)	450		
32.59	Bisphenol A	228	NIST library and use of standard	
33.84	Tetrabromo compound (n.i.)	450		
33.88	Monobromo compound (n.i.)	317		
34.22	Bromobisphenol A	307	Analysis of mass spectrum and comparison with MS data reported by Factor [19] and Blazsó et al. [26]	Factor [19]

Table 1 (*Continued*)

Retention time (min)	Compound	Molecular weight	Identified by means of:	Identified also by:
34.62	Tetrabromo compound (n.i.)	450		
35.31	Dibromo compound (n.i.)	386		
35.62	Non-brominated compound (n.i.)	302		
35.76	Tribromo compound (n.i.)	423		
35.99	Dibromobisphenol A	386	Analysis of mass spectrum and comparison with MS data reported by Factor [19] and Blazsó et al. [26]	Factor [19]
36.76	Non-brominated compound (n.i.)	302		
36.84	Dibromo compound (n.i.)	386		
37.14	Non-brominated compound (n.i.)	316		
37.21	Tribromo compound (n.i.)	449		
37.38	Non-brominated compound (n.i.)	312		
37.54	Non-brominated compound (n.i.)	312		
37.71	Non-brominated compound (n.i.)	314		
37.81	Tribromo compound (n.i.)	449		
37.89	Non-brominated compound (n.i.)	312		
38.38	Dibromobisphenol A	386	Analysis of mass spectrum and comparison with MS data reported by Factor [19] and Blazsó et al. [26]	Factor [19]
38.66	Dibromo compound (n.i.)	420		
38.81	Dibromo compound (n.i.)	424		
38.99	Tribromo compound (n.i.)	465		
39.02	Dibromo compound (n.i.)	424		
39.19	Tribromo compound (n.i.)	465		
39.41	Triphenylbenzene or quaterphenyl	306	NIST library	
39.72	Non-brominated compound (n.i.)	312		
39.99	Tribromobisphenol A	465	Analysis of mass spectrum and comparison with MS data reported by Factor [19] and Blazsó et al. [26]	Factor [19]
40.08	Tribromo compound (n.i.)	505		
40.16	Dibromo compound (n.i.)	424		
40.43	Dibromo compound (n.i.)	424		
40.89	Tetrabromo compound (n.i.)	528		
42.86	Triphenylbenzene or quaterphenyl	306	NIST library	
44.64	TBBA	544	NIST library and use of standard	

n.i.: not identified.

TBBA flame retarded polymers pointed out that even in more severe pyrolysis conditions as well as in oxidizing environments, TBBA mainly yields mono- through tribrominated PBDD and PBDF in the ppm range [2–10], while formation of the highly toxic 2,3,7,8-tetrasubstituted congeners was revealed at a ppb level [3] or not detected [2,4]. Nevertheless, direct precursors of PBDD/PBDF are generated during TBBA primary decomposition process, as dibromophenols and tribromophenol [30,31].

Finally, it must be remarked that, as also reported by Factor [19], besides the formation of volatile decomposition products, TBBA thermal degradation also yields a solid residue. This will be indicated as "char" in the following.

3.2. Product distribution in constant heating rate runs

The analysis of the results obtained from constant heating rate runs allowed the estimation of data on the quantitative distribution of products formed. Even if it must be recalled that the quantitative data obtained are strictly related to the experimental pyrolysis conditions (low heating rates and open system conditions), the data are useful to investigate the TBBA decomposition pathways.

Hydrogen bromide was the main gaseous product evolved in the decomposition process. The global amount of hydrogen bromide formed was about 31% with respect to TBBA initial weight, corresponding to 52% of the bromine initially present in the sample. FTIR results indicated that negligible quantities of carbon monoxide and carbon dioxide were formed in the process.

The char yield resulted about 20% of TBBA sample initial weight, and its bromine content, evaluated by elemental analysis (argentometric determination after combustion [28]) was 3% by weight. The GC/FID analyses performed on the condensable products recovered allowed
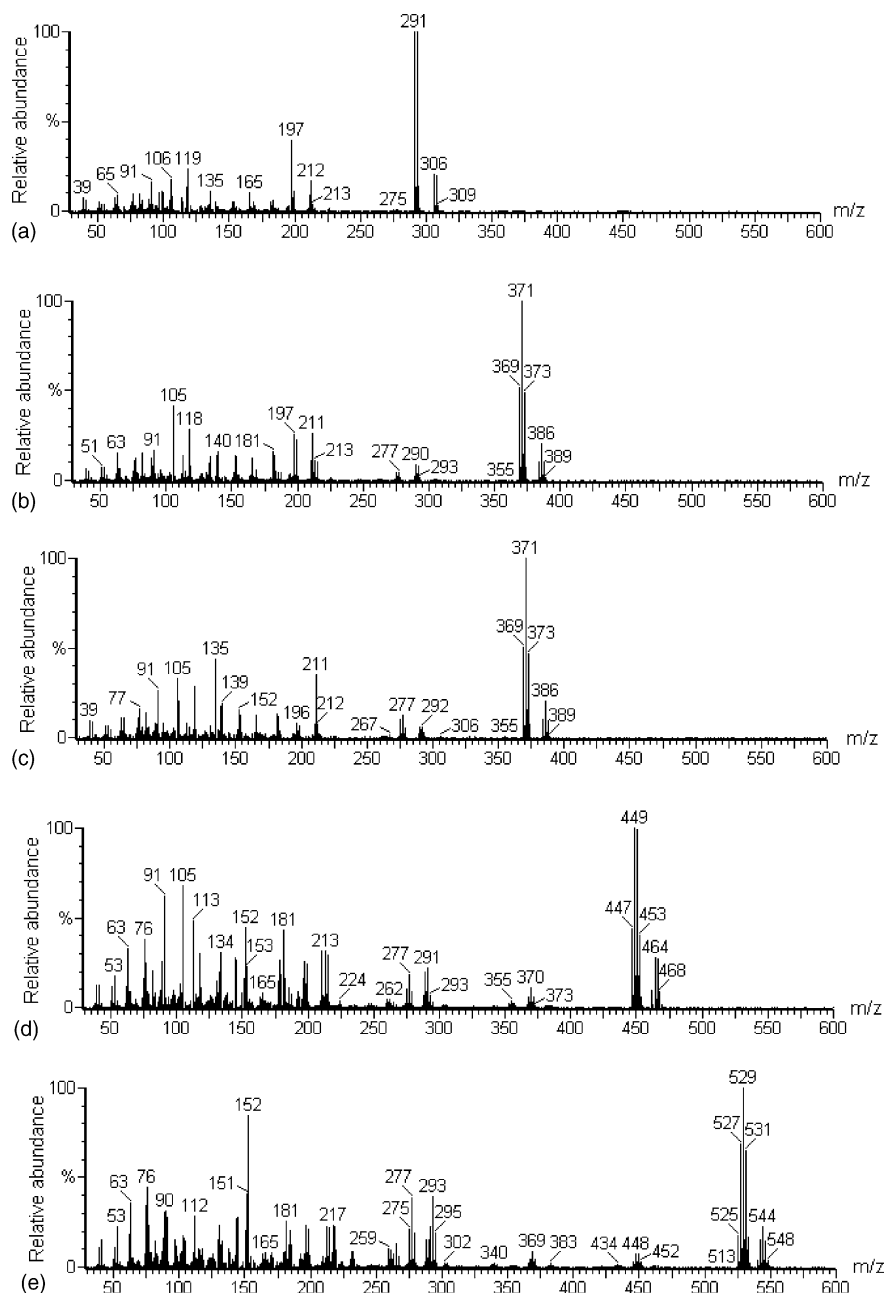
Fig. 2. Mass spectra of brominated bisphenol A species. (a) Bromobisphenol A (retention time 34.22 min); (b) dibromobisphenol A (isomer 1) (retention time 35.99 min); (c) dibromobisphenol A (isomer 2) (retention time 38.38 min); (d) tribromobisphenol A (retention time 39.99 min) and (e) TBBA.

for the quantification of TBBA evaporated and of the condensable decomposition products. The results obtained indicated that about 11.7% of TBBA initially present evaporates in the constant heating rate runs. The relative amounts of decomposition products are summarized in Fig. 4. The figure only reports the products formed in quantities higher than 1% (by mol) of initial TBBA. Besides hydrogen bromide, the figure shows that the main volatile products generated in the thermal degradation process were brominated phenols and brominated bisphenol A species.

3.3. Product distribution in isothermal runs

In order to better investigate the influence of temperature on the formation of degradation products and on the relative contributions of the evaporative and degradative phenomena, isothermal runs were also carried out. Experimental runs lasting 1 h were performed at temperatures between 180 (corresponding to the melting point of TBBA) and 270 °C. This temperature range was chosen to minimize the effect of secondary reactions on the decomposition products.
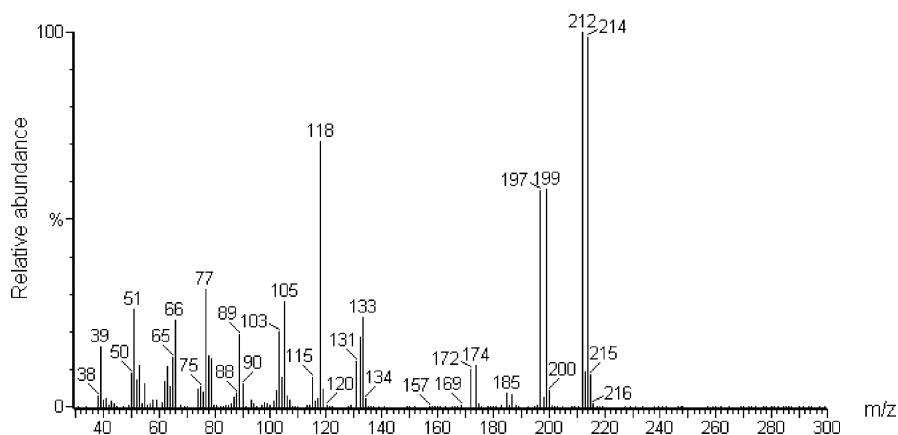
Fig. 3. Mass spectrum of 2-bromo-4-(1-methylethenyl)phenol (retention time 18.52 min).

In the experimental conditions used (low temperatures, 1 h run time duration), the sample conversion was not complete at the end of pyrolysis runs. However, the experiments performed are useful to obtain indicative values of the relative amounts and the relative distribution of primary products formed in the thermal degradation process. From the analysis of experimental data, the contributions of TBBA evaporation and decomposition could be estimated at the different temperatures explored. Fig. 5a shows the relative quantities of TBBA evaporated and decomposed, while the absolute weight losses due to the evaporative and degradative components are reported in Fig. 5b. The results of Fig. 5 clearly show that both the amount of TBBA evaporated and the amount of TBBA decomposed increase with increased temperatures, as expected. However, the evaporative component decreases with respect to the degradative one as the temperature increases. Degradation phenomena become relevant at temperatures equal or higher than 250 °C. Even if the trends in Fig. 5 have a general validity, it must be remarked that from a quantitative point of view the relative importance of the evaporative component, shown in Fig. 5, is strongly affected also by other experimental conditions, such as the sample surface available for evaporation.

The absolute and relative quantities of each decomposition product formed were evaluated as a function of the different pyrolysis temperatures. The results obtained for the main decomposition products are reported in Figs. 6–11. Figs. 6–10 show the moles of each product generated with respect to the overall moles of decomposition products, and the absolute moles formed with respect to those of TBBA

Fig. 4. Decomposition product yields in the thermal degradation of TBBA (constant heating rate runs, 10 °C/min, ambient to 600 °C).
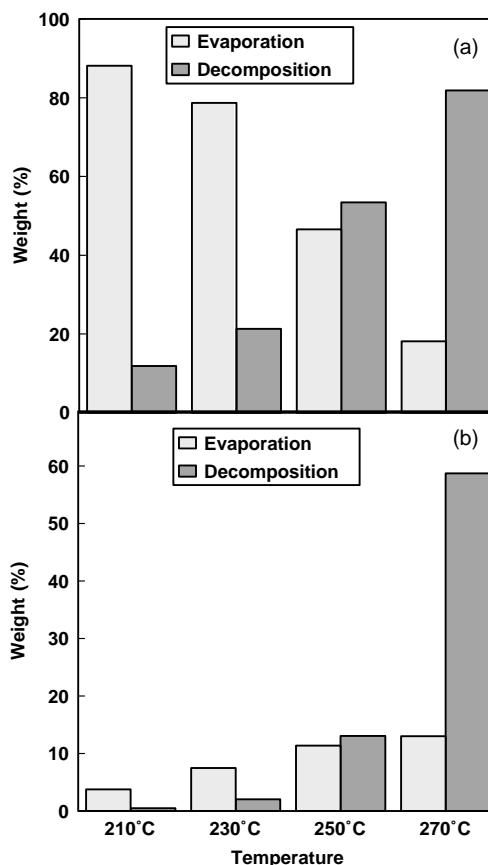
Fig. 5. Evaporation and thermal degradation of TBBA in 1 h isothermal runs. (a) Relative contribution (wt.%) to total weight loss of evaporation and decomposition. (b) Weight loss due to evaporation and to thermal degradation with respect to initial sample weight.
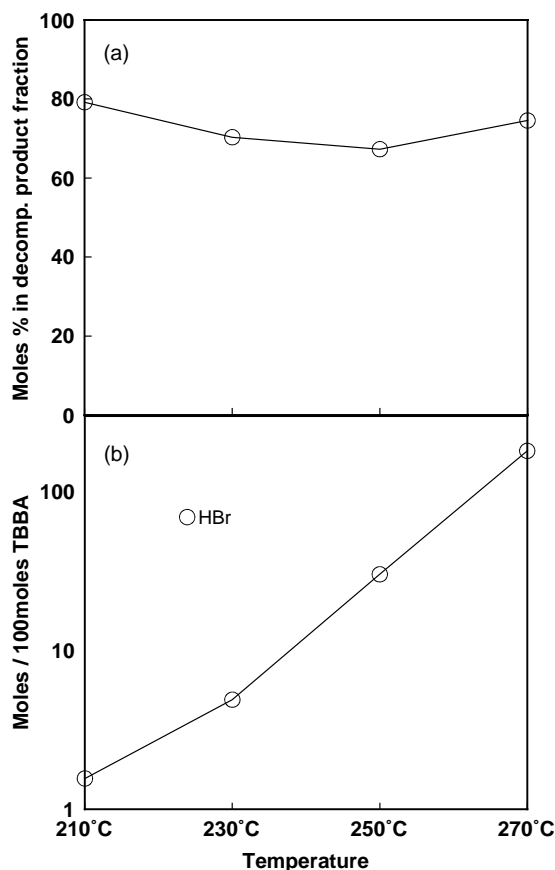
Fig. 6. Hydrogen bromide yield at the end of 1 h isothermal runs as a function of BR temperature: (a) mol% in decomposition products; (b) mol% with respect to initial moles of TBBA.
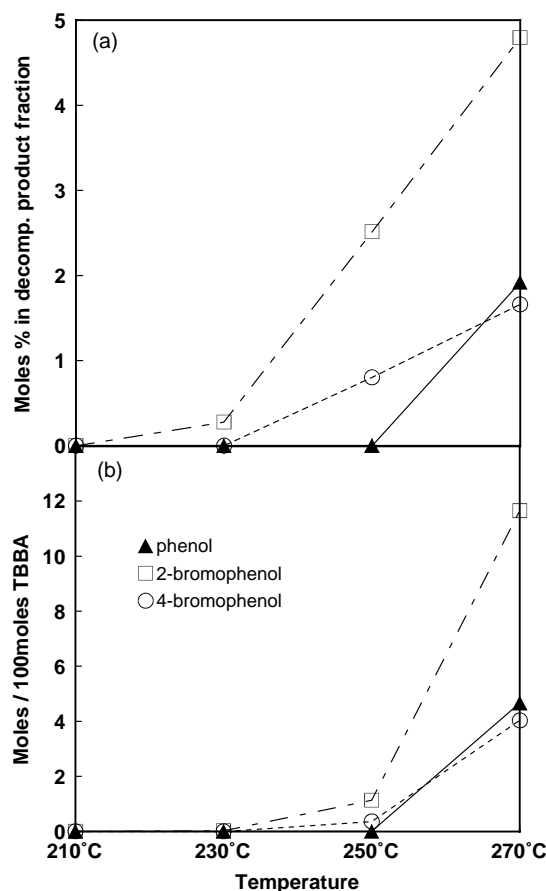

Fig. 7. Phenol, 2-bromophenol and 4-bromophenol yields at the end of 1 h isothermal runs as a function of BR temperature: (a) mol% in decomposition products and (b) mol% with respect to initial moles of TBBA.

initially present in the sample. Fig. 11 summarizes the quantities (by weight) of degradation products formed with respect to TBBA initial weight.

The results obtained clearly indicate that the absolute amount of each decomposition product increases with the increase of the pyrolysis temperature. An almost exponential increase was experienced for some species, as evidenced in Figs. 6 and 10. However, important differences were observed in the trends of the relative distribution of degradation products.

Hydrogen bromide was detected even at the lowest temperature and its relative amount in the decomposition product fraction resulted fairly constant with temperature, as shown in Fig. 6.

The relative amount in the decomposition products of several higher molecular weight species showed a constant increase with temperature. This is the case of bromophenols and of dibromobisphenol A isomers, as shown in Figs. 7 and 9 respectively. On the other hand, dibromophenols and tribromophenol showed a maximum in the molar fraction. Fig. 8 evidences that the relative amount of 2,6-dibromophenol in the decomposition product fraction was found to have a maximum at 230 °C. 2,4-Dibromophenol and 2,4,6-tribromophenol presented a

maximum at 250 °C, and their relative amount decreases at higher temperatures. Tribromobisphenol A molar fraction in decomposition products showed a constant decrease with temperature starting from 230 °C, as evidenced in Fig. 10. Finally, Figs. 7 and 9 point out that phenol and bromobisphenol A were only detected in the decomposition products at 270 °C, that is the highest temperature used in experimental runs.

3.4. Bromine balance and distribution in product fractions

A further result that was obtained from the quantitative analysis of the data on decomposition products was the trend of bromine distribution between the different fractions of pyrolysis products as a function of temperature. Fig. 12 shows the distribution of bromine among the different product fractions, as estimated from experimental data. The figure evidences that most of the bromine present in converted TBBA is found as hydrogen bromide and in the high molecular weight volatile organic product fraction, at least in the conditions used in the present study. Constant heating rate runs
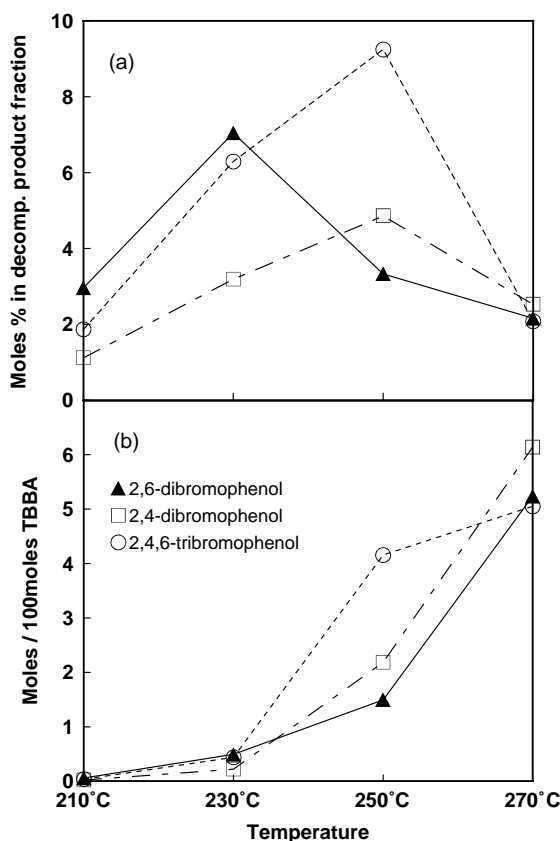
Fig. 8. 2,6-Dibromophenol, 2,4-dibromophenol and 2,4,6-tribromophenol yields at the end of 1 h isothermal runs as a function of BR temperature: (a) mol% in decomposition products and (b) mol% with respect to initial moles of TBBA.
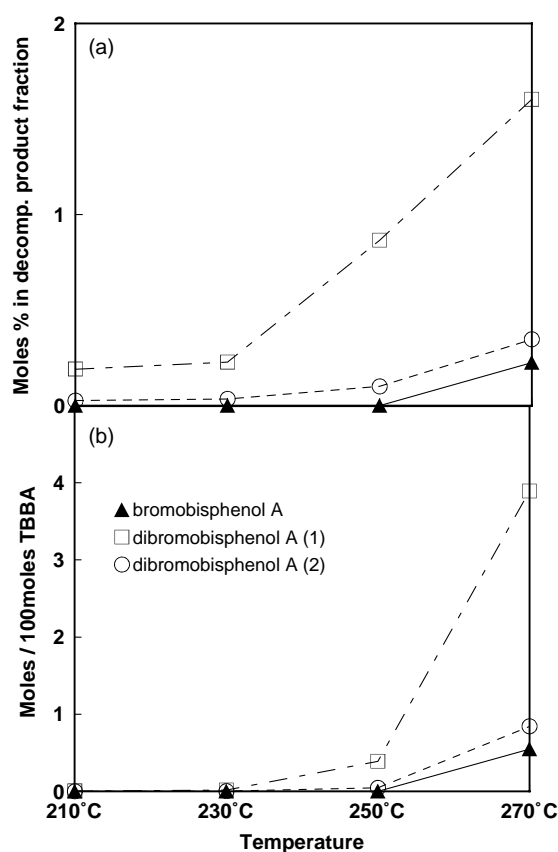

Fig. 9. Bromobisphenol A, dibromobisphenol A (1) and dibromobisphenol A (2) yields at the end of 1 h isothermal runs as a function of BR temperature: (a) mol% in decomposition products and (b) mol% with respect to initial moles of TBBA.

allowed the complete conversion of the TBBA sample. In these experiments, hydrogen bromide emissions account for 52% of bromine initially present in the sample, while 45 and 1% of bromine initially present are recovered in condensables and char, respectively. The results are in sufficient agreement with the trend shown in isothermal runs.

3.5. Analysis and assessment of TBBA thermal degradation pathways

On the basis of the identified products, the primary decomposition pathways of TBBA were investigated. The reaction network assumed for the primary thermal decomposition of TBBA is summarized in Schemes 1–8. The schemes were in part based on those proposed originally by Factor [19], and involve mainly free-radical reactions.

As reported in Scheme 1, the TBBA molecule may tautomerize to the keto forms. The equilibria lie well on the side of the phenolic form, however the keto structures may generate radicals. The cleavage of a carbon–bromine bond may lead to a phenoxy and a bromine radical which yield, after hydrogen abstraction, tribromobisphenol A and hydrogen bromide. On the other hand, the cleavage of a carbon–carbon bond may generate a phenoxy

and a carbon radical. The former may abstract hydrogen and yield 2,6-dibromophenol. The latter may lead to a brominated 4-(1-methylethenyl)phenol, after β-scission with hydrogen loss. The carbon radical and the generated 4-(1-methylethenyl)phenol may also be involved in the formation of higher molecular weight and crosslinked compounds. The bromine and phenoxy radicals generated according to Scheme 1 may abstract hydrogen directly from the TBBA molecule to yield hydrogen bromide, phenols and a TBBA-derived phenoxy radical (Scheme 2). The mechanism outlined in Scheme 1 may well constitute the initiating step of TBBA decomposition. The pathway proposed suggests the formation of resonance-stabilized phenoxy radicals in the process. The phenoxy and bromine radicals formed according to Schemes 1 and 2 may be involved in the formation of 2,4,6-tribromophenol. Likely pathways are reported in Schemes 3 and 4.

The tribromobisphenol A formed in the pyrolysis process may undergo a debromination reaction sequence, by a mechanism similar to that reported for TBBA. Tribromobisphenol A may yield dibromobisphenol A (two isomers), and this, in turn, bromobisphenol A and finally, bisphenol A, besides hydrogen bromide (Scheme 5). By analogy with TBBA, any of the bisphenol A species reported in Scheme 5
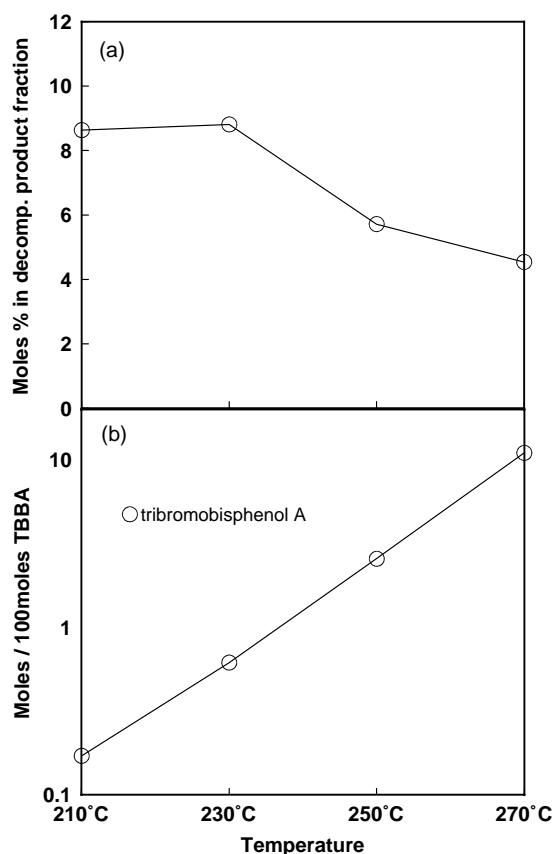
Fig. 10. Tribromobisphenol A yield at the end of 1 h isothermal runs as a function of BR temperature: (a) mol% in decomposition products and (b) mol% with respect to initial moles of TBBA.
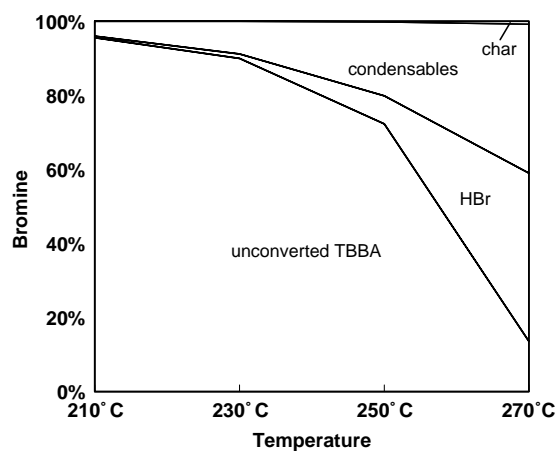

Fig. 12. Bromine distribution in the different product fractions as a function of temperature in isothermal BR runs.

are expected to be involved in the decomposition pathways leading to phenols and *para*-bromo-substituted phenols (Schemes 6–8).

However, Schemes 1–8 suggest a number of competitive reactions. In order to shed some light on the relative importance of the alternative pathways for TBBA decomposition, quantitative data on decomposition products from isothermal runs were analysed.

A general trend of the results reported in Figs. 6–10 is that relevant amounts of higher brominated species as tribromobisphenol A and tri- and dibrominated phenols are present in the decompositions products at low temperatures.
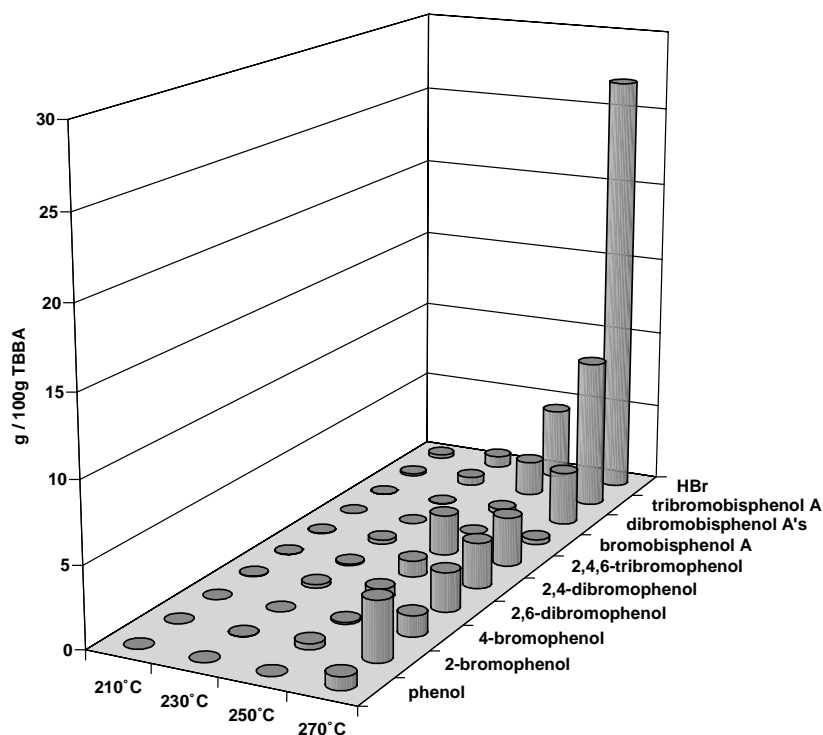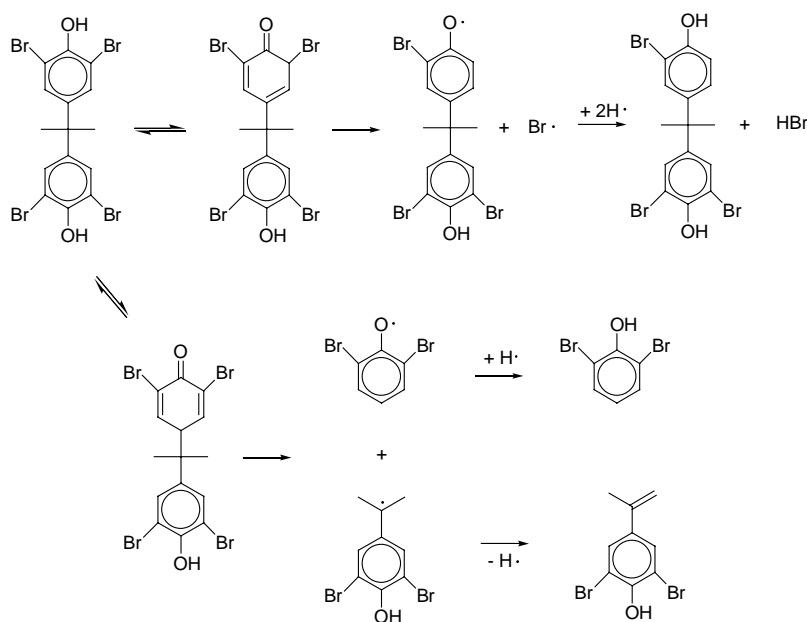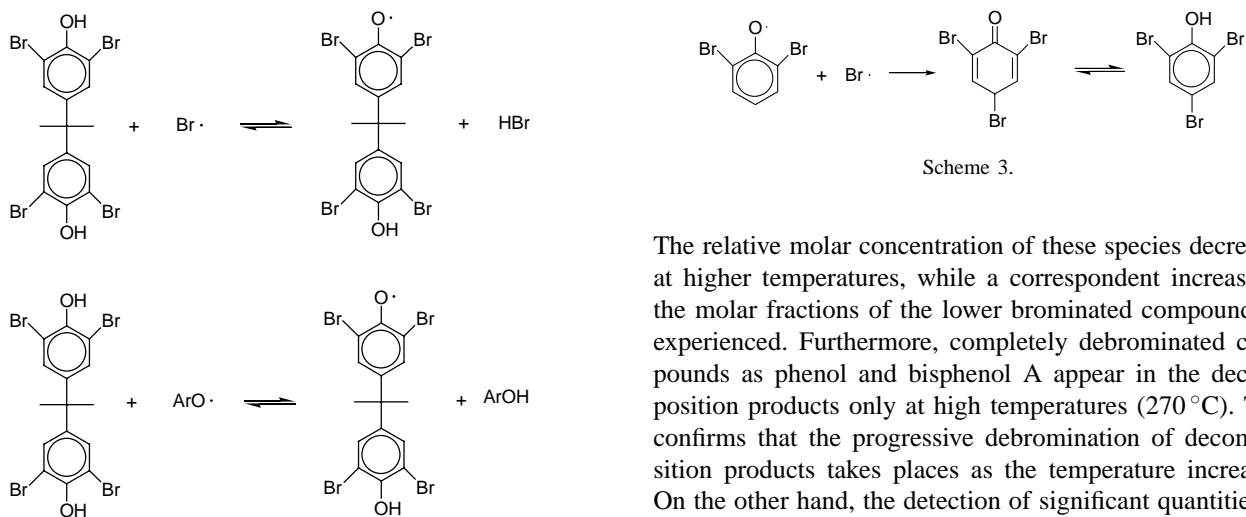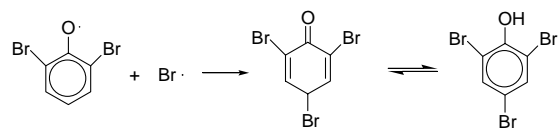

Fig. 11. Yields (wt.%) of main TBBA decomposition products in isothermal runs at temperatures between 210 and 270 °C.
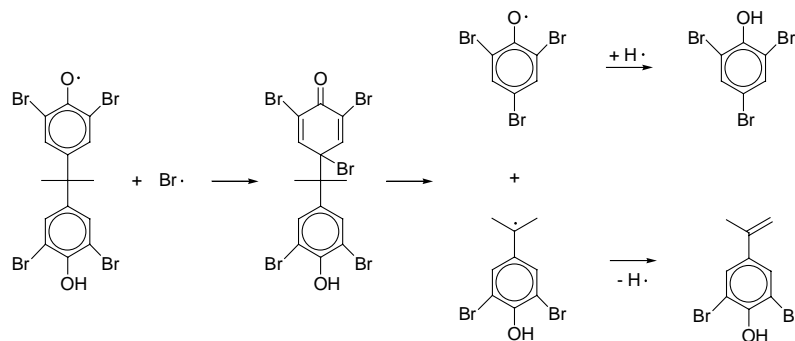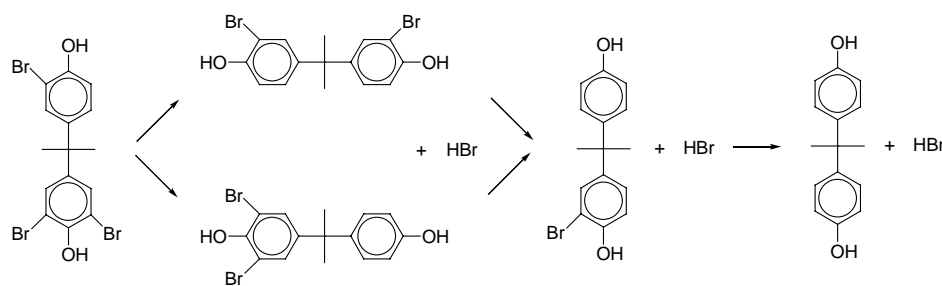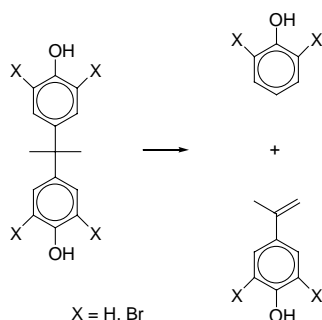
Scheme 1.

Scheme 2.

Scheme 3.

The relative molar concentration of these species decreases at higher temperatures, while a correspondent increase of the molar fractions of the lower brominated compounds is experienced. Furthermore, completely debrominated compounds as phenol and bisphenol A appear in the decomposition products only at high temperatures (270 °C). This confirms that the progressive debromination of decomposition products takes places as the temperature increases. On the other hand, the detection of significant quantities of phenolic species over the entire temperature range suggests that the scission reactions of the bisphenol A species are important decomposition pathways even at low temperatures.
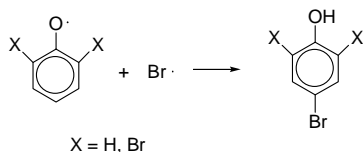

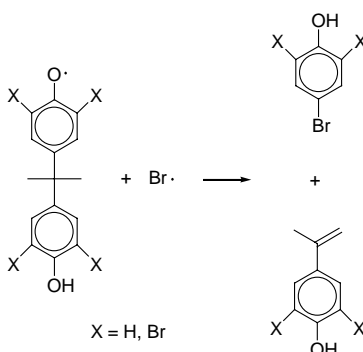Scheme 4.

Scheme 5.

X = H, Br

Scheme 6.

Since the high amounts of phenols detected in decomposition products indicate that the cleavage of the bisphenol A structure is a prevailing mechanism of TBBA decomposition, it is rather surprising that only limited quantities of 4-(1-methylethenyl)phenols were detected in the decomposition products (<0.1 mol%). This may suggest that these unsaturated species are intermediates in char formation, as supposed also by Hornung et al. [21]. As a matter of fact, a black char appears in the residual sample also at low temperatures, and char yield is of about 20 wt.% when the complete conversion of TBBA is achieved.

X = H, Br

Scheme 7.

X = H, Br

Scheme 8.

Coming to the yields of specific products, Fig. 10 shows that the relative amount of tribromobisphenol A in the decomposition product fraction decreases with increasing temperatures. This confirms that tribromobisphenol A is only an intermediate product in the formation of lower brominated bisphenol A species (Scheme 5) and of brominated phenols (Schemes 6–8). The limited amounts of dibromobisphenol A isomers and the high molar fractions of dibrominated and brominated phenols present between 230 and 250 °C seem to suggest that the brominated bisphenol A species produced according to Scheme 5 are key intermediate in the formation of the phenolic compounds, as suggested by the reactions reported in Schemes 6–8. The detection of 2,6-dibromophenol in the 210 °C pyrolyzate indicates that the cleavage of the bisphenol A structure (Scheme 1), is already active at this temperature. The presence of 2,4-dibromophenol and 2,4,6-tribromophenol as well, suggests that the radical bromination reactions depicted in Schemes 3,4,7,8 are significant even at temperatures as low as 210 °C.

The products indicated in the schemes account for more than 96% of the overall moles of volatile decomposition products. It may be concluded that the decomposition pathways proposed in Schemes 1–8 well represent the reaction network involved in the formation of the main decomposition products detected in TBBA thermal degradation process.

4. Conclusions

The present work was concerned with the analysis and assessment of TBBA primary thermal degradation pathways. The open system conditions used allowed for the minimization of secondary reactions. Experimental runs were performed in the low–medium temperature range, in both constant heating rate and isothermal conditions. The quantitative data obtained showed that hydrogen bromide, brominated phenols and brominated bisphenol A species are the main TBBA decomposition products. Several alternative TBBA degradation pathways were identified. The data collected on decomposition products suggested that debromination reactions and scission reactions to yield phenols are the most important decomposition pathways.

Secondary radical bromination reactions were found to be responsible for the formation of *para*-bromo-substituted phenols. Higher temperatures promote a more extended debromination of intermediate products, leading to the formation of non-brominated phenols and bisphenol A species. The scission of the bisphenol A structure is also responsible for the formation of unsaturated 4-(1-methylethenyl)phenol species, that are suspected to have a role in the formation of the solid char fraction. The proposed pathways for the decomposition of TBBA account for the formation of more than 96 mol% of volatile decomposition products formed in the experimental runs.

Acknowledgements

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