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The Thermal Degradation Process of Tetrabromobisphenol A

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This study focused on the investigation of the thermal degradation process of tetrabromobisphenol A (TBBA). The use of combined experimental techniques allowed the quantitative characterization of TBBA decomposition products and the analysis of the thermal degradation rates. The distribution of bromine among the different decomposition product fractions was investigated. In the open configuration used for the experiments, hydrogen bromide, brominated bisphenol A species, and brominated phenols resulted in the main decomposition products. Bromine was mainly evolved as hydrogen bromide, although a relevant quantity resulted present in the primary high molecular weight condensable product fraction, in agreement with the decomposition pathways proposed. The results evidenced that accidents involving TBBA thermal degradation, such as fire or process runaways, may pose relevant safety problems because of the possible release of considerable quantities of hazardous decomposition products.

Introduction

In many fields of application, synthetic polymers have to fulfill special requirements concerning their flammability, which can often be met by the use of flame-retarding chemicals. Among these, brominated flame retardants (BFRs) hold an important market share. Because of their efficiency, compatibility, and small influence on mechanical properties, BFRs have a broad application area. Tetrabromobisphenol A (TBBA) is the largest volume BFR in production today, representing by itself half of BFR production. Around 120 000 metric tons of TBBA were produced in 1999.¹ TBBA is used as an additive flame retardant (mainly in acrylonitrile–butadiene–styrene systems) and as a reactive flame retardant in the manufacturing of epoxy, phenolic, and polycarbonate resins. Its primary use is in the production of epoxy resins with 20–25 wt % bromine, commonly employed for the production of printed circuit boards. It has been estimated that TBBA is contained in 96% of printed wiring boards.

Among other applications, the use of BFRs in the production of epoxy resins for printed circuit boards is the one that is causing a spreadsheet diffusion of materials containing BFRs, because of the growing production of electronic appliances such as personal computers and other high-tech large-diffusion products in which a high degree of flame retardancy is required by regulations. As a matter of fact, electrical and electronic equipment accounts for 56% of the BFR market.¹

The wide diffusion of BFRs in household products caused a concern on safety and disposal problems of products containing BFRs. Several studies were dedi-

cated to environmental and toxicity issues connected to the production and domestic use of products containing TBBA.^{2–10} In recent years, at least five accidents have been reported involving batch reactors (BRs) during the production of brominated epoxy resins, pointing out the potential hazards connected to these processes.¹¹ Moreover, the rapid obsolescence of electronic material posed relevant problems for the safe disposal and recycling of “electronic scrap”, a relevant quantity being composed of electronic components containing BFRs. The presence of BFRs may lead to the emission of high-molecular-weight dangerous compounds in incineration processes for the conventional disposal of municipal solid wastes as well as in specific processes for metal recovery from electronic scrap.

The possible formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) from BFRs in combustion and pyrolysis processes was studied by several authors,^{12–21} although previous work in the field was mainly focused on polybrominated diphenyl ethers. Fundamental studies on PBDD and PBDF formation from TBBA showed that the pyrolysis of pure TBBA mainly yields mono- through tribrominated PBDDs and PBDFs in the ppm range, while a very limited, if any, formation of 2,3,7,8-substituted components was experienced.¹⁸ These results were confirmed also by studies on the laboratory- and pilot-scale pyrolysis and/or incineration of TBBA flame-retarded polymers and polymer wastes.^{16,21–27}

However, the above studies were mainly aimed at the selective analysis of possible PBDD/F formation. Less attention was dedicated to the overall examination of the TBBA thermal degradation process, even if this is known to be responsible for the formation of hazardous products generated in accidents during the manufacture of TBBA flame-retarded products.¹¹ Only a few studies were concerned with the investigation of TBBA thermal decomposition products.^{28–30} Further complementary data are available on brominated epoxy resins^{31–33} and TBBA flame-retarded printed circuit boards.^{34,35} Hy-

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drogen bromide, brominated phenols, brominated bisphenol A species, and char were found to be the main decomposition products of TBBA in all of these studies. However, the yields of hazardous products formed and the quantitative distribution of bromine between the different product fractions were never thoroughly investigated.

This study focused on the characterization of the products formed in the thermal degradation of TBBA. The main aims were the achievement of quantitative data on the primary products formed in the thermal decomposition process and the understanding of the thermal decomposition pathways. The experimental work was addressed mainly to investigate the possible consequences of temperature runaway in industrial processes involving TBBA. TBBA decomposition was carried out at a moderate heating rate (10 °C/min) using thermogravimetric (TG) analyzers and a laboratory-scale fixed-bed reactor. The identification and quantification of decomposition products was based on Fourier transform infrared (FTIR) spectrometry, gas chromatography (GC), and GC/mass spectrometry (MS) techniques. The distribution of bromine among gaseous and condensable decomposition products was also investigated.

Experimental Section

Materials. 4,4'-Isopropylidenebis(2,6-dibromophenol), commonly referred to as TBBA, 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).

Techniques and Procedures. Simultaneous TG and differential scanning calorimetry (DSC) data were obtained using a Netzsch STA 409/C thermoanalyzer. A constant heating rate of 10 °C/min was used in experimental runs. Typical sample weights of 10–15 mg were employed. Runs were carried out using a pure nitrogen purge gas flow of 60 mL/min, unless otherwise stated.

Isothermal runs at temperatures between 180 and 300 °C were performed using a Mettler TG-50 thermobalance. A pure nitrogen purge flow of 200 mL/min and sample weights of 5–10 mg were used in experimental runs. The samples were positioned on the pan of the TG balance and were inserted in the TG furnace preheated at the programmed temperature. Temperature transients due to sample heating were calculated by accounting for convective and conductive heat transfer inside the cylindrical furnace³⁶ and resulted in less than 30 s at temperatures between 200 and 400 °C.

FTIR measurements were carried out using a Bruker Equinox 55 spectrometer equipped with deuterated triglycine sulfate and mercury–cadmium–telluride (MCT) detectors. TG/FTIR simultaneous measurements for the online analysis of volatile compounds formed during TG runs were carried out by coupling the FTIR spectrometer to the Netzsch TG using a 4-mm-i.d. Teflon tube. The 800-mm-long transfer line and the head of the TG balance were heated at a constant temperature of 200 °C to limit the condensation of volatile decomposition products. FTIR measurements were carried out with a MCT detector in a specifically developed low-volume gas cell (8.7 mL) with a 123-mm path length, heated at a constant temperature of 250 °C. The gas

flow from the TG outlet to the IR gas cell was of 60 mL/min, and a residence time of 30 s in the transfer line could be evaluated for the evolved gases. This value was assumed as the time delay correction to be used for the comparison of TG and IR results. During TG/FTIR runs, spectra were collected at 4 cm⁻¹ resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5 s, more than sufficient to follow the gas evolution rates characteristic of TG runs at heating rates of 10 °C/min. Qualitative gas evolution profiles and quantities of gaseous decomposition products formed in TG/FTIR runs were obtained from the experimental data following the procedures described in previous publications.^{37,38}

A laboratory-scale fixed-bed tubular BR was used to carry out TBBA thermal decomposition runs. The experiments were mainly aimed at the recovery and characterization of the different fractions of decomposition products. 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 300 °C. Typical sample weights in experimental runs were of 180–250 mg. Experimental runs were performed using a pure nitrogen purge gas flow (80 mL/min) to control the reaction environment and to limit the extension of secondary gas-phase reactions. Volatile products evolved during degradation were transferred by the nitrogen flow in a series of cold traps, maintained at -20 °C by a sodium chloride brine/ice bath, to allow the recovery of condensables. The traps were followed by a gas sampling cell for FTIR gas analysis. 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. Further details and a scheme of the experimental apparatus are reported in a previous publication.³⁷

At the end of each experimental run, the total amount of condensable products formed was estimated from the weight of the traps before and after the experiment. The collected products were successively dissolved in acetone and their acetone solutions analyzed by chromatographic techniques. The solid residue remaining on the sample holder at the end of the run was weighed and its bromine content determined by elemental analysis (argentometric titration by the Volhard method after combustion).

A Fisons MD 800 quadrupole MS interfaced to a Fisons 8060 GC was used for GC/MS analysis. A Mega SE30 fused-silica capillary column (25-m length, 0.32-mm i.d., crossbonded, 0.25-μm film thickness) was employed for the chromatographic separation, with helium as the carrier gas. The column temperature program was the following: 5 min isothermal at 40 °C, heating to 250 °C (6 °C/min), and then 20 min isothermal. Splitless injection with the injector at 250 °C was used. MS detection was performed in full scan conditions (scan range, *m/z* 10–819) in electron impact ionization mode.

Quantitative GC analysis was carried out using a ThermoQuest Trace 2000 GC equipped with a flame ionization detector (FID). The capillary column and the experimental conditions were identical with those used

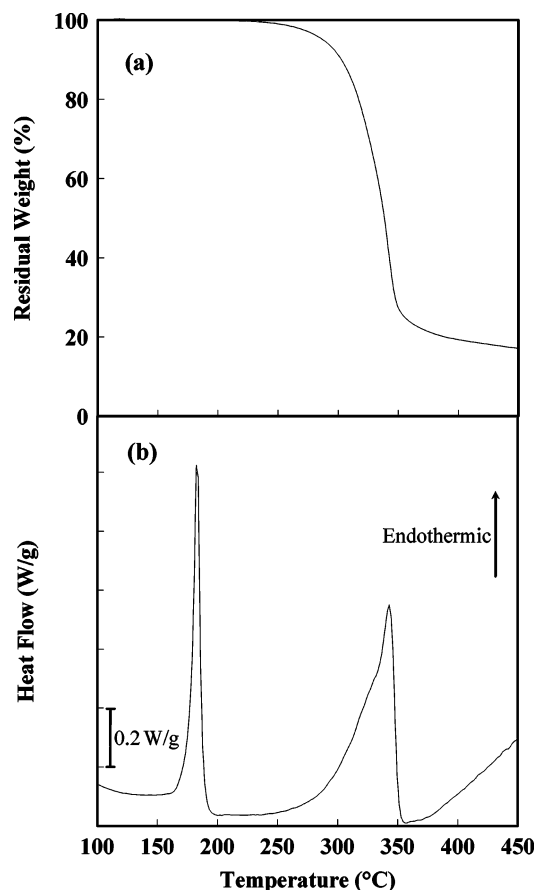


Figure 1. Results of simultaneous TG/DSC runs carried out on TBBA at a heating rate of 10 °C/min in 100% nitrogen: (a) TG data; (b) DSC data.

for GC/MS analysis; the detector temperature was fixed at 280 °C. Response factors with respect to phenol were obtained from calibration runs performed on mixtures of the available GC standards and phenol. The repeatability of the measurements was verified. Typical values of the standard deviation were of about 4%.

Results and Discussion

Thermal Stability. The thermal stability of TBBA and the thermal effects related to TBBA decomposition were investigated. Typical results of constant heating rate runs performed in the simultaneous TG/DSC analyzer are shown in Figure 1. Unless otherwise stated, the data reported in the present study were

calculated as the mean of at least five experimental runs. The TG curve reported in Figure 1a shows that under a nitrogen atmosphere the thermal degradation of TBBA takes place mainly between 240 and 350 °C if a heating rate of 10 °C/min is used. At the end of the run, TBBA yields a black solid residue (named char in the following), which corresponds to about 20% of the initial sample weight at 450 °C. The results shown in Figure 1 agree well with those reported in the literature.^{28,29}

To investigate the influence of oxidizing conditions on TBBA thermal stability, constant heating rate TG/DSC runs were performed using air as the purge gas. As previously reported,^{28,29} no relevant differences were detected in the weight loss in the range of temperatures and heating rates explored. Also the thermal effects of the decomposition are almost unaffected by the presence of air at temperatures below 450 °C.

Identification of Thermal Decomposition Products. TG/FTIR simultaneous measurements allowed for the characterization of volatile products generated during TBBA degradation in the constant heating rate (10 °C/min) TG/DSC runs. Figure 2 shows the typical results of FTIR online analysis of the volatiles evolved in a TG run performed in pure nitrogen. The IR spectra recorded by the system are reported as a function of the sample temperature in the TG furnace. As discussed above, the decomposition process occurs mainly between 240 and 350 °C at a heating rate of 10 °C/min. The FTIR spectra obtained in this temperature interval show the presence of a complex mixture of products containing hydrogen bromide (2780–2400 cm^{-1}), carbon dioxide (2400–2240 cm^{-1}), carbon monoxide (2235–2030 cm^{-1}), and phenolic compounds (3700–3500, 3150–2850, and 1630–700 cm^{-1}), as is evident in Figure 2. The simultaneous evolution of several volatile organic compounds did not allow the identification of the single phenolic species by FTIR spectra analysis. Detailed information about the organic compounds formed during TBBA pyrolysis was thus obtained from GC and GC/MS analysis of the condensable fraction of degradation products recovered at the end of BR runs, as discussed in the following.

Using FTIR data such as those reported in Figure 2, qualitative emission profiles as a function of temperature were obtained for the gaseous compounds evolved, following the procedures described in previous publications.^{37,38} Figure 3a shows a comparison between the qualitative concentration profile of hydrogen bromide and the differential TG (dTG) data. The HBr concentra-

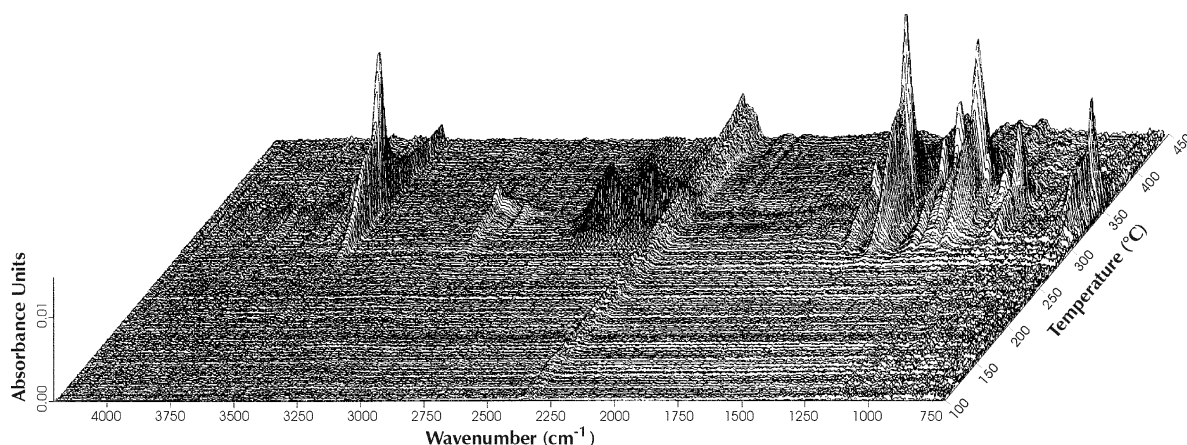


Figure 2. IR spectra collected during a TG/FTIR run carried out on TBBA (10 °C/min, 100% nitrogen).

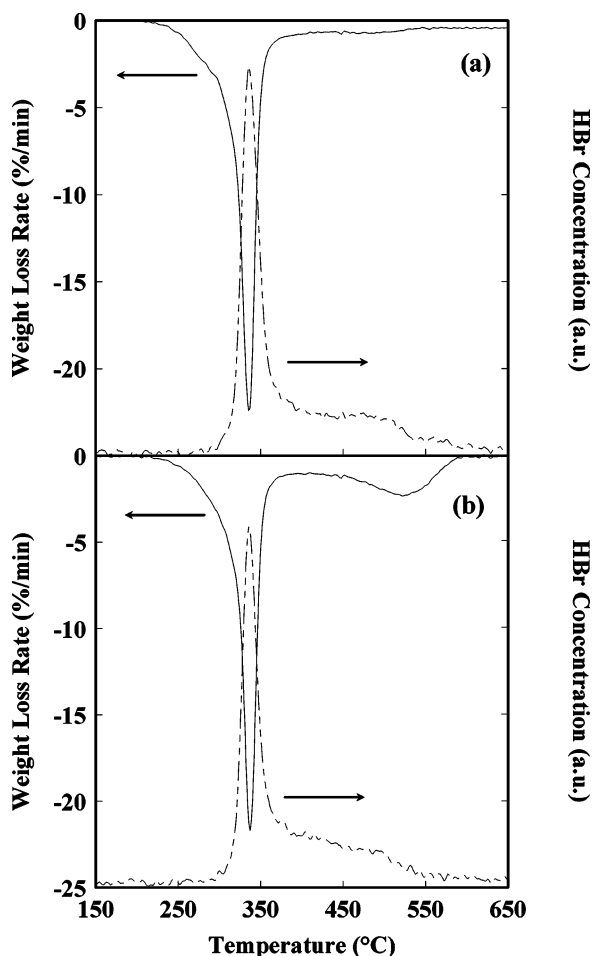


Figure 3. Qualitative profile of hydrogen bromide emission during TBBA decomposition in TG/FTIR runs (10 °C/min) compared to dTG data: (a) 100% nitrogen; (b) air.

tion in the gas outflow from the TG analyzer shows a single peak, corresponding to the maximum of the sample weight loss rate. A shoulder in HBr emission appears at about 370 °C up to 550 °C. A corresponding behavior is shown by the weight loss rate.

To be sure that no interference was due to condensation and decomposition in the transfer line, further experimental runs were performed. Sample heating was stopped at a temperature of 370 °C, and the residue was cooled to ambient temperature. The sample was removed from the TG/FTIR system, which was heated to 800 °C using a 160 mL/min nitrogen flow to purge the transfer line. A further constant heating rate run was then performed on the 370 °C residue, under the standard conditions of TG/FTIR runs. The results, reported in Figure 4, showed that only at temperatures higher than 370 °C a further weight loss took place. Only HBr, CO, and CO₂ were detected in the evolved products during the weight loss of the 370 °C residue. No phenolic compounds were detected, thus suggesting that the shoulder in Figure 3 is reasonably caused by further dehydrobromination and aromatization reactions taking place in the solid residue formed during the main thermal degradation process.

TG/FTIR data confirmed that the presence of oxygen hardly influences the primary thermal decomposition process, at least at the heating rates used in the present work. Figure 3b reports the evolution profile of HBr along with the weight loss rate curve obtained in experimental runs carried out using air as the purge

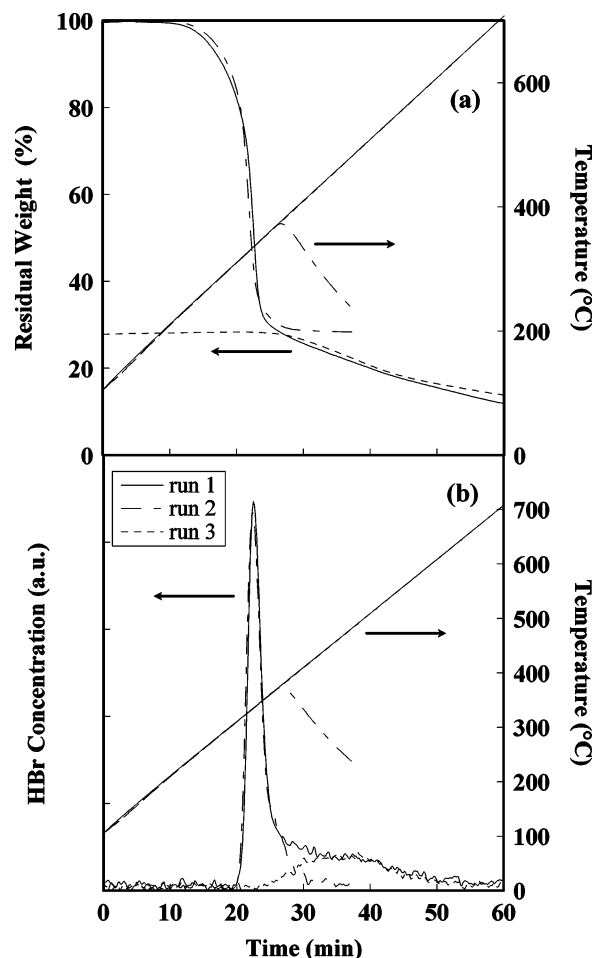


Figure 4. Results of TBBA thermal degradation in TG/FTIR carried out in 100% nitrogen: (a) weight loss data; (b) hydrogen bromide emission. Run 1: TBBA, ambient to 800 °C, 10 °C/min. Run 2: TBBA, ambient to 370 °C, 10 °C/min, cooling to ambient at a nominal rate of 10 °C/min. Run 3: residue of run 2, ambient to 800 °C, 10 °C/min.

gas. Negligible differences are present with respect to the data reported in Figure 3a for TG/FTIR runs in pure nitrogen.

The pyrolysis experiments performed in the laboratory-scale fixed-bed tubular BR allowed for the characterization of the different fractions of TBBA decomposition products (gases, condensables, and char). Experimental runs were carried out in 100% nitrogen at a heating rate of 10 °C/min from ambient temperature to 600 °C. The recovery and analysis of pyrolysis products were performed following the procedure described in the Experimental Section. The experiments were mainly aimed at the estimation of the bromine distribution among thermal decomposition product fractions, as well as at the characterization of the condensable product fraction, which could not be achieved by TG/FTIR analysis.

The results of BR runs confirmed the presence of hydrogen bromide, carbon monoxide, and carbon dioxide among the gaseous decomposition products. No organic compound was detected in the FTIR analysis of pyrolysis products during BR runs. This may well suggest that only low volatility organic compounds are formed in TBBA decomposition, which are condensed before entering the gas cell. It must be recalled that in BR runs the gas flows through surface condensers at -20 °C before entering the gas sampling cell, while in TG/FTIR

Table 1. Products Identified by GC/MS Analysis of the Condensable Fraction Recovered from BR Pyrolysis Runs Carried out on TBBA

compound	mol wt	also identified by
Nonbrominated		
phenol	94	Factor, ²⁸ Borojovich and Aizenshtat, ²⁹ Hornung et al. ³⁰
biphenyl	154	
dibenzofuran	168	
α-methylstilbene	194	
1,3-diphenylpropane	196	
ethylphenoxybenzene	198	
α,α'-dimethylbibenzyl	210	
4-(1-methyl-1-phenylethyl)phenol	212	
bisphenol A	228	
Monobrominated		
2-bromophenol	173	Factor, ²⁸ Borojovich and Aizenshtat, ²⁹ Hornung et al. ³⁰
4-bromophenol	173	Factor, ²⁸ Borojovich and Aizenshtat, ²⁹ Hornung et al. ³⁰
bromotrimethylbenzene	199	Factor ²⁸
2-bromo-4-(1-methylethenyl)phenol	213	
bromobisphenol A	307	
Dibrominated		
2,4-dibromophenol	252	Factor, ²⁸ Borojovich and Aizenshtat, ²⁹ Hornung et al. ³⁰
2,6-dibromophenol	252	Factor, ²⁸ Borojovich and Aizenshtat, ²⁹ Hornung et al. ³⁰
2,6-dibromo-4-methylphenol	266	Borojovich and Aizenshtat ²⁹
dibromobisphenol A (two isomers)	386	Factor ²⁸
Tribrominated		
2,4,6-tribromophenol	331	Factor, ²⁸ Borojovich and Aizenshtat, ²⁹ Hornung et al. ³⁰
tribromobisphenol A	465	Factor ²⁸
Tetrabrominated		
TBBA	544	

runs the TG furnace is connected to the FTIR analyzer by a transfer line heated at 200 °C. From the results obtained in TG/FTIR and BR runs, it may thus be inferred that the gaseous fraction of TBBA thermal degradation products is mainly constituted of hydrogen bromide, along with carbon monoxide and carbon dioxide.

The condensable fraction of pyrolysis products resulted in about 49% of the initial sample weight. The GC/MS and GC analyses performed allowed us to obtain detailed data on the nature and relative distribution of the products formed. The thermal degradation gives rise to a mixture of products. MS detection enabled the identification of chromatographic peaks, while quantification was carried out by GC/FID analysis.

The structural identification of compounds from the MS data was achieved by analysis of fragmentation patterns, by comparison with the best fits found in the NIST spectral library, as well as by comparison with published MS data^{28,29,35} or by the use of standards. For some minor peaks, a complete structural assignment was not possible, and only the molecular weight and number of bromine atoms present could be clearly identified.

Table 1 reports the products identified in the condensable fraction recovered from pyrolysis runs. It is worthwhile to point out the presence of TBBA among the products identified. This suggests that TBBA decomposition results in a competitive process with evaporation, at least under the experimental conditions used in the present work. This point will be further discussed in the following.

As shown in Table 1, a sufficient correspondence was found with previous data on TBBA decomposition products,^{28–30} even if in the present study a wider number of compounds were detected.

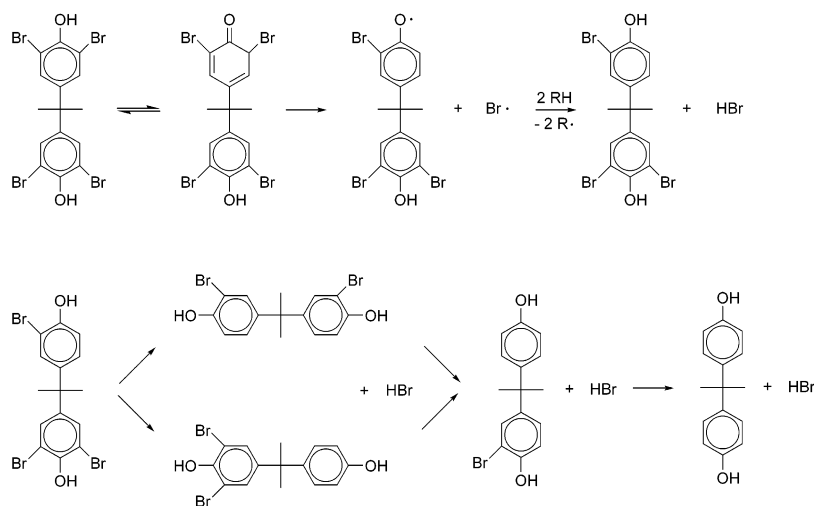
No brominated dibenzo-*p*-dioxins or dibenzofurans were detected in the present study. This confirms the results of previous investigations^{16,18,21–27} that showed

that TBBA and its flame-retarded polymers yielded PBDD/PBDF only at a ppm level under several pyrolysis and combustion conditions. Nevertheless, direct precursors of PBDD/PBDF are generated during the TBBA primary decomposition process, such as dibromophenols and tribromophenol (see Table 1). It is well-known that halogen-containing phenols, under pyrolytic or oxidative conditions, may give halogenated dibenzo-*p*-dioxins, through gas-phase reaction pathways.^{39–41} The formation of PBDD in the pyrolytic decomposition of 2,4,6-tribromophenol and of 2,6-dibromophenol has been reported in several works.^{14,30,42} In particular, the high-temperature thermal oxidation of 2,4,6-tribromophenol resulted in the formation of high yields of 1,3,6,8- and 1,3,7,9-tetrabrominated dibenzo-*p*-dioxins by a homogeneous gas-phase mechanism.⁴⁰

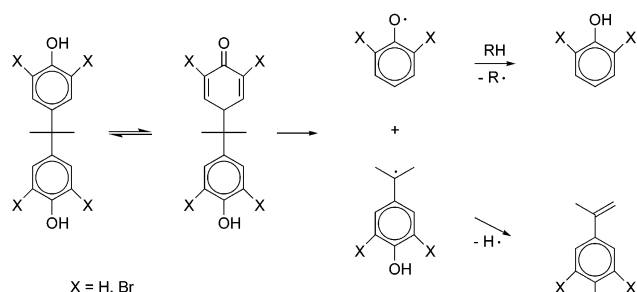
Decomposition Pathways of TBBA. The compounds identified allowed the investigation of the TBBA primary decomposition process. The pathways suggested (Schemes 1–3), derived from those proposed originally by Factor,²⁸ involve mainly radical reactions. As a matter of fact, Factor revealed the formation of free radicals during TBBA decomposition. A likely path for the generation of radicals from TBBA is the formation of an unstable halocyclohexadienone via a keto–enol tautomerization. The cleavage of a carbon–bromine bond, with the release of a bromine radical, can lead, after hydrogen abstraction, to hydrogen bromide and tribromobisphenol A (Scheme 1). By a similar mechanism, tribromobisphenol A can yield dibromobisphenol A (two isomers, as found by GC/MS analysis). This, in turn, may yield bromobisphenol A and finally bisphenol A (Scheme 1). The mechanism proposed may thus well explain the formation of hydrogen bromide and of the different brominated bisphenol A species.

On the contrary, the cleavage of a carbon–carbon bond may generate two radicals that can yield phenols and 4-(1-methylethenyl)phenols, as outlined in Scheme 2. This sequence may involve any of the bisphenol A

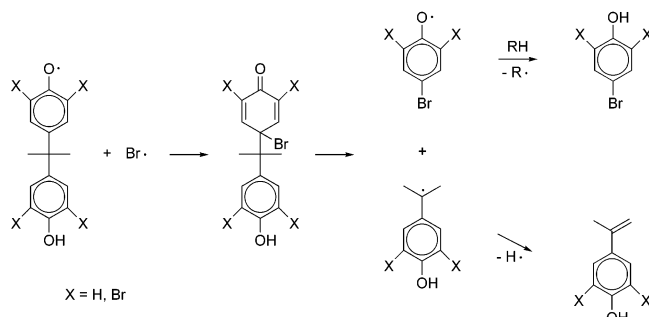
Scheme 1



Scheme 2



Scheme 3



species formed in the pyrolysis process (X: hydrogen or bromine in Scheme 2). The formation of phenol, 2-bromophenol, 2,6-dibromophenol, and 2-bromo-4-(1-methylethenyl)phenol, all detected among decomposition products (see Table 1), may therefore be explained. The presence, among the decomposition products, of *p*-bromo-substituted phenols, namely, 4-bromophenol, 2,4-dibromophenol, and 2,4,6-tribromophenol, might involve the interaction of a bromine radical generated in the process with the phenoxy radical. A likely pathway for the formation of these products is shown in Scheme 3.

The formation of char during the pyrolysis process is evidenced by the TG results in Figure 1. A likely pathway for the formation of higher molecular weight and cross-linked compounds might involve the 4-(1-methylethenyl)phenols formed according to the mechanisms reported in Schemes 2 and 3.

It must be remarked that the present investigation was limited to the decomposition pathways and pyrolysis products of pure TBBA. If a polymeric material

containing TBBA as an additive or as a reactive BFR undergoes a thermal degradation process, it should be expected that the bromine radicals generated from the TBBA unit may interact with the primary pyrolysis products and lead to the formation of further hazardous brominated products.^{31,35}

Quantitative Data on Decomposition Products.

The analysis of the quantitative distribution of decomposition products was undertaken on the basis of both TG/FTIR and BR data. TG/FTIR results were used to obtain information on the quantities of gaseous compounds formed in TBBA decomposition. The use of specific calibrations, performed following the methodologies extensively described elsewhere,^{37,38} allowed for the estimation of the quantities of hydrogen bromide, carbon monoxide, and carbon dioxide formed in TG/FTIR runs. Quite low quantities of CO and CO₂ were generated, about 0.032 and 0.025 g/100 g of TBBA initial sample weight, respectively. On the other hand, hydrogen bromide was the main gaseous product evolved in the decomposition process. The global quantity of HBr formed resulted in 30.6 g/100 g of TBBA initial sample weight, which corresponds to 51.5% of bromine initially present in the sample. This value was obtained as the mean of six experimental runs, with errors being less than 4% with respect to the HBr weight. The analysis of the results reported in Figure 4 allowed one to verify that 38% HBr is formed during the main weight loss peak, at temperatures between 300 and 370 °C using a heating rate of 10 °C/min. The further 13.5% is formed at higher temperatures (370–600 °C), possibly from dehydrobromination reactions of the solid residue. The formation of hydrogen bromide, carbon monoxide, and carbon dioxide (11.4% of initial sample weight between 370 and 600 °C from the analysis of run 3 in Figure 4) may well justify the further sample weight loss in this temperature interval (11.6% with respect to initial sample weight, as shown in Figure 4a).

The analysis of the TG/FTIR data obtained from runs carried out using air as the purge gas showed that no relevant differences could be observed in the formation of hydrogen bromide when oxygen is present. The amount of bromine released as HBr resulted in about 50.5% of bromine initially present in the sample. The presence of air did not affect the yields of CO and CO₂ during the main thermal decomposition process. Limited quantities of CO and CO₂ were formed (about 0.1 g of

Table 2. Results of Quantitative GC/FID Analysis Performed on the Condensable Product Fraction Recovered from TBBA Pyrolysis Runs

compound	mol % in condensable fraction	wt % in condensable fraction	wt % with respect to sample initial mass	mol % with respect to sample initial moles
phenol	3.7	1.0	0.5	2.9
2-bromophenol	4.0	2.0	1.0	3.0
4-bromophenol	6.6	3.3	1.6	5.0
2,4-dibromophenol	9.5	6.9	3.4	7.2
2,6-dibromophenol	12.0	8.7	4.2	9.2
2,4,6-tribromophenol	8.6	8.1	4.0	6.5
bromobisphenol A	2.6	2.3	1.1	2.0
dibromobisphenol A (1)	9.5	10.5	5.2	7.3
dibromobisphenol A (2)	1.9	2.1	1.0	1.5
tribromobisphenol A	18.5	24.7	12.1	14.2
others	7.8	6.6	3.2	5.9
TBBA	15.3	23.8	11.7	11.7

CO and 0.06 g of CO₂ per 100 g of TBBA). Nevertheless, in the presence of air, the char formed in the primary pyrolysis stage undergoes oxidation reactions at temperatures higher than 450 °C, which result in the formation of relevant quantities of CO and CO₂.

The titration of the alkaline solution present in absorbers at the end of BR experiments allowed for estimation of the total amount of HBr formed during TBBA pyrolysis in nitrogen. The results indicated the formation of 32% of HBr with respect to the TBBA initial weight. This result is in good agreement with the data obtained from the TG/FTIR runs.

Quantitative GC/FID analysis of condensable products formed in BR runs was performed, following the procedure described in the Experimental Section. Standard samples were available for all of the major peaks detected, except for bromo-, dibromo-, and tribromobisphenol A. However, calibration runs performed with bisphenol A and TBBA revealed almost the same response factor ($\pm 0.2\%$) for the two compounds. Therefore, the bisphenol A response factor could be assumed for the brominated bisphenol A species. As expected, response factors were 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, leading to sufficiently low errors in the analysis.

Table 2 shows the results of the quantitative GC/FID analysis performed. Only the products higher than 1 mol % are reported in the table. Based on the weight of condensable pyrolysis products with respect to the sample initial weight, the amount of each product formed per 100 g of TBBA could be included in Table 2. Even if the quantitative data obtained are strictly related to the experimental pyrolysis conditions, namely, low heating rates and open system conditions in the present study, Table 2 allows important considerations to be drawn on the TBBA decomposition pathways.

The significant amounts of bromophenols, dibromophenols, and tribromophenol formed in the process suggest that reactions such as those reported in Schemes 2 and 3 represent important pathways of TBBA decomposition. As discussed previously, the different brominated phenols may be formed from TBBA or from any of the bisphenol A species generated from TBBA according to the mechanism shown in Scheme 1. In conjunction with the considerable quantities of tribromo- and dibromobisphenol A found in the volatile decomposition product fraction, this in turn supports the belief that the debromination reactions reported in Scheme 1

Table 3. Bromine Distribution in the Product Fractions Obtained from TBBA Thermal Degradation (100% Nitrogen)

	gas	condensable	residue
fraction of sample initial mass (wt %)	31	49	20
fraction of bromine initially present (wt %)	52	45	1
bromine content (wt %)	99	54	3

are key steps in the TBBA decomposition process. The relevance of debromination steps is confirmed as well by the large amount of hydrogen bromide formed (more than 50% of bromine initially present in the sample is released as HBr).

On the other hand, the limited quantities of 4-(1-methylethenyl)phenols detected may suggest that these are intermediate products, thus confirming the possible role of these unsaturated species in char formation, as suggested also by Hornung et al.³⁰

Distribution of Bromine among the Different Product Fractions. The quantitative data obtained in the present work allowed an estimation of bromine distribution between the different fractions of TBBA decomposition products. The amount of hydrogen bromide formed in the decomposition was obtained by both TG/FTIR and BR data. The quantitative data obtained from GC analysis of the condensable allowed the estimation of the bromine content in this product fraction, which resulted in about 54 wt %. The weight of char at the end of BR runs was about 20% of the TBBA initial sample weight, in agreement with the value obtained in TG runs. Its bromine content resulted of 3 wt %.

Table 3 shows the calculated bromine distribution among the different product fractions. Bromine mass balance was possible with a reasonable approximation from experimental data obtained for each product fraction. The results obtained show that most of the bromine initially present in TBBA is found as hydrogen bromide and in the high-molecular-weight aromatic decomposition products at the end of the primary pyrolysis process carried out under the conditions used in the present study.

Because of the lack of quantitative data on TBBA decomposition products in the literature, only a limited comparison with published data was possible. Borojovich and Aizenshtat²⁹ estimated the overall bromine content of the solid and condensable fractions recovered from TBBA pyrolysis performed in a closed vessel for 1 h at 600 °C. Their results (35.0 wt % Br) agree well with the present findings. As a matter of fact, if the overall

bromine content of the char and condensable fractions is calculated starting from the data in Table 3, this results in 39.2 wt %. Borojovich and Aizenshtat²⁹ also reported data on hydrogen bromide formation. Lower amounts of hydrogen bromide (about 13% of the TBBA initial weight) were formed in their experiments with respect to the quantities found in the present work. However, the higher temperatures and closed-vessel conditions used by these authors for TBBA decomposition, allowing pressure buildup and secondary reactions, may well justify lower yields of primary gaseous pyrolysis products as hydrogen bromide. Factor²⁸ also reports data on the formation of HBr in isothermal runs at 220 °C. The results obtained by Factor (HBr formed: 2% of TBBA initial weight) may be compared to the results obtained from isothermal BR runs performed in the present study. When the results obtained after 1 h are extrapolated to complete sample conversion, an HBr yield of 4.8% TBBA initial weight was estimated at 220 °C. The different evaporation conditions in the experimental devices may well justify the differences in the results.

Thermal Effects of TBBA Decomposition. So far, no data were reported on the thermal effects of TBBA decomposition. The DSC curve shown in Figure 1b evidences the presence of two endothermic peaks. The first one, around 182 °C, corresponds to the melting of TBBA. The second peak is caused by the overall thermal effects derived from the evaporation and decomposition processes, as evidenced by the comparison with the weight loss curve in Figure 1a. From baseline subtraction and integration of the heat flow curve, an overall endothermic heat of 119 J/g ($\pm 2\%$) could be estimated from experimental data. Data in Table 2 show that about 12% of TBBA initially present in the sample is recovered in the condensable fraction. On the basis of the typical values reported for the latent heat of evaporation of organic compounds, a conservative value of 280 J/g can be assumed for the latent heat of evaporation of TBBA. Thus, a rough estimate can be made of the endothermic effects associated with the TBBA thermal decomposition process, which result in at least 90 J/g. Obviously, this should be taken only as an indicative value of the overall decomposition heat under the experimental conditions used in the present study, because of the oversimplifying assumptions made in the analysis. However, since radical formation is an endothermic process, the presence of endothermic effects during TBBA decomposition is in agreement with the proposed decomposition pathway.

Apparent Kinetics of TBBA Decomposition. As discussed above, TBBA thermal degradation and evaporation processes take place simultaneously during experimental runs carried out under the operating conditions of the present study. However, the quantitative analysis of condensable products made possible the separation of the evaporative contribution from the overall process, thus allowing kinetic data for the main step of the thermal decomposition process to be obtained from BR experimental runs.

The low-temperature primary decomposition process was studied by isothermal BR runs performed at temperatures between 180 and 270 °C. This temperature range was chosen to minimize the effect of secondary reactions on the decomposition products. TBBA conversion values were estimated at the end of the BR runs, lasting 60 min. The weight loss of the sample, as well

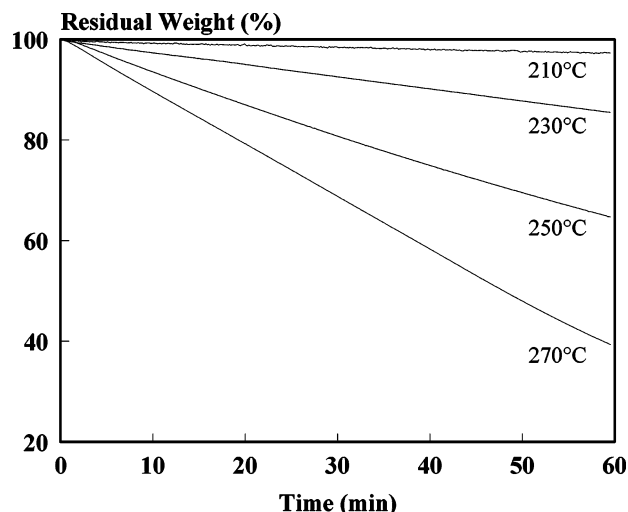


Figure 5. Results of isothermal TG runs carried out on TBBA (100% nitrogen).

as the TBBA present in the condensable products recovered, was determined. This allowed us to estimate TBBA conversion:

$$\xi = \frac{m_0 - m_f - m_{ev}}{m_0 - m_{ev}} \quad (1)$$

where m_0 is the initial sample weight, m_f the weight of unconverted TBBA at the end of the run, and m_{ev} the weight of TBBA recovered in the condensable products. To estimate m_f , the final conversion to nonvolatile char was experimentally determined.

As shown above, the overall decomposition process of TBBA is rather complex. However, the primary decomposition reactions that trigger the thermal degradation process are mainly characterized by bromine radical formation.²⁸ This is confirmed by the prevalence of endothermic reaction thermal effects throughout the sample during the decomposition process (see Figure 1b). Thus, an Arrhenius n th-order single-step kinetic model may be adequate to represent the apparent kinetics of the rate-controlling step in the TBBA decomposition:

$$d\xi/dt = Ae^{-E_a/RT}(1 - \xi)^n \quad (2)$$

where t is the time, T is the temperature, A is the preexponential factor, E_a is the activation energy, and R is the gas constant. The reaction order was assumed on the basis of the results of isothermal TG runs performed in the same temperature range of BR experiments. As shown in Figure 5, all of the samples show a constant weight loss rate at temperatures between 210 and 270 °C. Clearly, the weight loss rate is determined by the sum of evaporation and decomposition processes. However, because isothermal evaporation obviously results in a constant weight loss rate, an overall linear weight loss rate may result only if n equals zero in eq 2, which means an apparent zero order with respect to TBBA conversion in the decomposition reaction. The presence of an apparent zero-order process governing the weight loss rate is also suggested by the shape of the constant heating rate and reaction heat flow curves shown in Figure 1, which evidence an abrupt termination of the weight loss and thermal effects of the main decomposition process at temperatures around 360 °C.

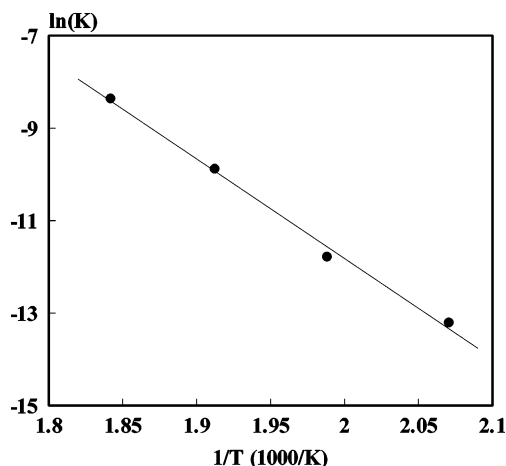


Figure 6. Arrhenius plot for TBBA decomposition.

Assuming $n = 0$, the kinetic constant could be evaluated from conversion data integrating eq 2:

$$K(T) = \xi/t \quad (3)$$

The logarithm of the kinetic constants evaluated from experimental data were reported in an Arrhenius plot, shown in Figure 6. The good linearity of the experimental data versus the reciprocal of temperature confirms that the simplified kinetic model is adequate to represent the main step of the actual decomposition process under the conditions of experimental investigations and in the temperature range of interest (210–370 °C). The values calculated by a linear least-squares approach for the preexponential factor and activation energy resulted respectively of $3.76 \times 10^{13} \text{ s}^{-1}$ and 179.1 kJ/mol.

Figure 7 shows a comparison of the conversion and heat flow obtained by the kinetic model with those calculated respectively from TG and DSC data for the TBBA decomposition process. The heat flow was calculated from the kinetic model assuming constant thermal effects for the reaction and the above-estimated value for the reaction heat. The figure evidences that the kinetic model, obtained from the analysis of BR isothermal data, is able to approximate with sufficient accuracy the main decomposition process of TBBA also in constant heating rate dynamic TG/DSC runs. Obviously, the above model only represents the apparent kinetics of the overall TBBA decomposition process at the low temperatures and low heating rates used in the present study. However, the kinetic data obtained are sufficient to give some useful quantitative indications on the TBBA thermal stability. In particular, no evidence of an autocatalytic decomposition behavior, reported for other BFRs as hexabromocyclododecane (HBCD), was found in the case of TBBA. The TBBA decomposition process also requires a higher activation energy with respect to HBCD, whose decomposition process has an activation energy between 90 and 130 kJ/mol.³⁷

Conclusions

The thermal decomposition process of TBBA was investigated in the low–medium temperature range. The main aim of the study was to obtain information on the primary thermal degradation pathways. The use of combined experimental techniques allowed the quantitative characterization of TBBA decomposition products and the analysis of the thermal degradation rates. The kinetic and calorimetric analysis of the decomposi-

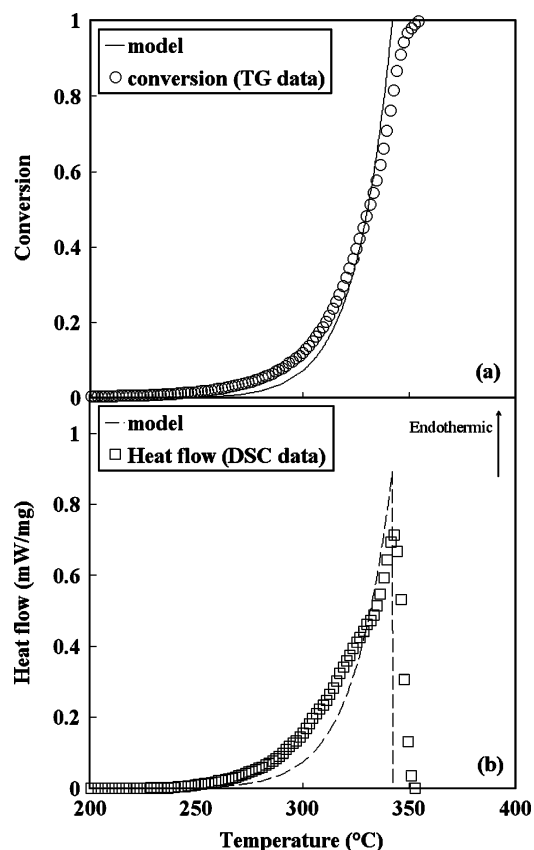


Figure 7. Comparison between experimental data and kinetic model predictions for TBBA decomposition process: (a) conversion; (b) heat flow.

tion process evidenced that the TBBA thermal degradation requires a rather high apparent activation energy and is characterized by endothermic effects. This may suggest that the rate-controlling step of the primary decomposition process is the formation of radicals.

In the open configuration used for the experiments, hydrogen bromide, brominated bisphenol A species, and brominated phenols resulted the main decomposition products. Appreciable quantities of possible precursors of PBDDs, such as 2,4,6-tribromophenol, were detected. Bromine mainly evolved as hydrogen bromide, although a relevant quantity was present in the primary high-molecular-weight condensable product fraction, in agreement with the decomposition pathway proposed on the basis of the analysis of decomposition products. The results obtained evidence that accidents involving TBBA thermal degradation, such as fire or runaways, may pose relevant safety problems because of the possible release of important quantities of hazardous decomposition products. Furthermore, it is worth a reminder that, in the pyrolysis of polymeric materials containing TBBA, the bromine radicals generated from TBBA decomposition may lead to the formation of secondary brominated products by interaction with the primary pyrolysis products.

Acknowledgment

The authors gratefully acknowledge financial support from CNR, Gruppo Nazionale di Ricerca per la Difesa dai Rischi Chimico-Industriali ed Ecologici.

Literature Cited

- (1) Bromine Science and Environmental Forum. *An introduction to Brominated Flame Retardants*; BSEF: Bruxelles (B), Belgium, 2000.

- (2) De Wit, A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583.
- (3) Sjödin, A.; Carlsson, H.; Thuresson, K.; Sjölin, S.; Bergman, A.; Ostman, C. Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environ. Sci. Technol.* **2001**, *35*, 448.
- (4) Jakobsson, K.; Thuresson, K.; Rylander, L.; Sjödin, A.; Hagmar, L.; Bergman, A. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. *Chemosphere* **2002**, *46*, 709.
- (5) Nagayama, J.; Tsuji, H.; Takasuga, T. Comparison between brominated flame retardants and dioxins or organochlorine compounds in blood levels of Japanese adults. *Organohalogen Compd.* **2000**, *48*, 27.
- (6) Thomsen, C.; Lundanes, E.; Becher, G. Brominated flame retardants in plasma samples from different occupational groups in Norway. *J. Environ. Monit.* **2001**, *3*, 366.
- (7) Hagmar, L.; Sjödin, A.; Hoglund, P.; Thuresson, K.; Rylander, L.; Bergman, A. Biological half-lives of polybrominated diphenyl ethers and tetrabromobisphenol A in exposed workers. *Organohalogen Compd.* **2000**, *47*, 198.
- (8) Meerts, I. A. T. M.; Van Zanden, J. J.; Luijckx, E. A. C.; Van Leeuwen-Boi, I.; Marsch, G.; Jakobsson, E.; Begman, A.; Brouwer, A. Potent competitive interactions of some brominated flame retardants and related compounds with human transthyretin in vitro. *Toxicol. Sci.* **2000**, *56*, 95.
- (9) Kitamura, S.; Jinno, N.; Ohta, S.; Kuroki, H.; Fujimoto, N. Thyroid hormonal activity of the flame retardants tetrabromobisphenol A and tetrachlorobisphenol A. *Biochem. Biophys. Res. Commun.* **2002**, *293*, 554.
- (10) Eriksson, P.; Jakobsson, E.; Fredriksson, A. Brominated flame retardants: A novel class of developmental neurotoxicants in our environment? *Environ. Health Perspect.* **2001**, *109*, 903.
- (11) Barontini, F.; Cozzani, V.; Petarca, L.; Zanelli, S. Modeling the Formation and Release of Hazardous Substances in the Loss of control of Chemical Systems containing Brominated Flame Retardants. *Proceedings of the 10th International Symposium on Loss Prevention and Safety Promotion in the Process Industries*; Elsevier: Amsterdam, 2001; p 1251.
- (12) Thoma, H.; Rist, S.; Hauschulz, G.; Hutzinger, O. Polybrominated dibenzodioxins and -furans from the pyrolysis of some flame retardants. *Chemosphere* **1986**, *15*, 649.
- (13) Buser, H. R. Polybrominated Dibenzofurans and Dibenzodioxins: Thermal Reaction Products of Polybrominated Diphenyl Ether Flame Retardants. *Environ. Sci. Technol.* **1986**, *20*, 404.
- (14) Thoma, H.; Hutzinger, O. Pyrolysis and GC/MS-analysis of brominated flame retardants in on-line operation. *Chemosphere* **1987**, *16*, 1353.
- (15) Bienek, D.; Bahadir, M.; Korte, F. Formation of heterocyclic hazardous compounds by thermal degradation of organic compounds. *Heterocycles* **1989**, *28*, 719.
- (16) Dumler, R.; Thoma, H.; Lenoir, D.; Hutzinger, O. PBDF and PBDD from the combustion of bromine containing flame retarded polymers: a survey. *Chemosphere* **1989**, *19*, 2023.
- (17) Dumler, R.; Lenoir, D.; Thoma, H.; Hutzinger, O. Thermal formation of polybrominated dibenzofurans and dioxins from decabromodiphenyl ether flame retardant: influence of antimony-(III) oxide and the polymer matrix. *Chemosphere* **1990**, *20*, 1867.
- (18) Thies, J.; Neupert, M.; Pump, W. Tetrabromobisphenol A (TBBA), its Derivatives and their Flame Retarded (FR) Polymers. Content of Polybrominated Dibenzodioxins (PBDD) and Dibenzofurans (PBDF). PBDD/F Formation under Processing and Smouldering (Worst Case) Conditions. *Chemosphere* **1990**, *20*, 1921.
- (19) Luijk, R.; Wever, H.; Olie, K.; Govers, H. A. J.; Boon, J. J. The influence of the polymer matrix on the formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). *Chemosphere* **1991**, *23*, 1173.
- (20) Striebich, R. C.; Rubey, W. A.; Tirey, D. A.; Dellinger, B. High-temperature degradation of polybrominated flame retardant materials. *Chemosphere* **1991**, *23*, 1197.
- (21) Luijk, R.; Govers, H. A. J. The formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) during pyrolysis of polymer blends containing brominated flame retardants. *Chemosphere* **1992**, *25*, 361.
- (22) Dumler-Gradl, R.; Tartler, D.; Thoma, H.; Vierle, O. Detection of polybrominated diphenyl ethers (PBDE), dibenzofurans (PBDF), and dibenzodioxins (PBDD) in scrap of electronics and recycled products. *Organohalogen Compd.* **1995**, *24*, 101.
- (23) Riess, M.; Ernst, T.; Popp, R.; Müller, B.; Thoma, H.; Vierle, O.; Wolf, M.; van Eldik, R. Analysis of flame retarded polymers and recycling materials. *Chemosphere* **2000**, *40*, 937.
- (24) Sakai, S.; Watanabe, J.; Honda, Y.; Takatsuki, H.; Aoki, I.; Futamatsu, M.; Shiozaki, K. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* **2001**, *42*, 519.
- (25) Söderström, G.; Marklund, S. PXDD and PXDF from combustion of bromoflameretardant containing MSW. *Organohalogen Compd.* **2000**, *47*, 225.
- (26) Söderström, G.; Marklund, S. PBCDD and PBCDF from Incineration of Waste-Containing Brominated Flame Retardants. *Environ. Sci. Technol.* **2002**, *36*, 1959.
- (27) Wichmann, H.; Dettmer, F. T.; Bahadir, M. Thermal formation of PBDD/F from tetrabromobisphenol A—a comparison of polymer linked TBBP A with its additive incorporation in thermoplastics. *Chemosphere* **2002**, *47*, 349.
- (28) Factor, A. Thermal Decomposition of 4,4'-Isopropylidene Bis-2,6-dibromophenol (Tetrabromobisphenol A). *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1691.
- (29) Borojovich, E. J. C.; Aizenshtat, Z. Thermal behavior of brominated and polybrominated compounds I: closed vessel conditions. *J. Anal. Appl. Pyrolysis* **2002**, *63*, 105.
- (30) Hornung, A.; Balabanovich, A. I.; Donner, S.; Seifert, H. Detoxification of brominated pyrolysis oils. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 723.
- (31) Luda, M. P.; Balabanovich, A. I.; Camino, G. Thermal decomposition of fire retardant brominated epoxy resins. *J. Anal. Appl. Pyrolysis* **2002**, *65*, 25.
- (32) Danzer, B.; Riess, M.; Thoma, H.; Vierle, O.; van Eldik, R. Pyrolysis of plastics containing brominated flame retardants. *Organohalogen Compd.* **1997**, *31*, 108.
- (33) Luijk, R.; Pureveen, J. M.; Commandeur, J. M.; Boon, J. J. Characterization of fire retardant polymer blends by temperature resolved in-source pyrolysis mass spectrometry. *Makromol. Chem., Macromol. Symp.* **1993**, *74*, 235.
- (34) Webb, M.; Last, P. M.; Breen, C. Synergic chemical analysis—the coupling of TG with FTIR, MS and GC-MS. 1. The determination of the gases released during the thermal oxidation of a printed circuit board. *Thermochim. Acta* **1999**, *326*, 151.
- (35) Blazsó, M.; Czégény, Zs.; Csoma, Cs. Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis. *J. Anal. Appl. Pyrolysis* **2002**, *64*, 249.
- (36) Cozzani, V.; Petarca, L.; Tognotti, L. Devolatilization and pyrolysis of Refuse Derived Fuel: characterization and kinetic modelling by a thermogravimetric and calorimetric approach. *Fuel* **1995**, *74*, 903.
- (37) Barontini, F.; Cozzani, V.; Petarca, L. Thermal Stability and Decomposition Products of Hexabromocyclododecane. *Ind. Eng. Chem. Res.* **2001**, *40*, 3270.
- (38) Marsanich, K.; Barontini, F.; Cozzani, V.; Petarca, L. Advanced pulse calibration techniques for the quantitative analysis of TG-FTIR data. *Thermochim. Acta* **2002**, *390*, 153.
- (39) Choudhry, G. G.; Hutzinger, O. *Mechanistic Aspects of the Thermal Formation of Halogenated Organic Compounds Including Polychlorinated Dibenzodioxins*; Gordon and Breach Science Publishers: New York, 1983.
- (40) Sidhu, S. S.; Masquid, L.; Dellinger, B.; Mascolo, G. The Homogeneous, Gas-Phase Formation of Chlorinated and Brominated Dibenzodioxin from 2,4,6-Trichloro- and 2,4,6-Tribromophenols. *Combust. Flame* **1995**, *100*, 11.
- (41) Weber, R.; Hagenmaier, H. Mechanism of the Formation of Polychlorinated Dibenzodioxins and Dibenzofurans from Chlorophenols in Gas-Phase Reactions. *Chemosphere* **1999**, *38*, 529.
- (42) Borojovich, E. J. C.; Aizenshtat, Z. Thermal behavior of brominated and polybrominated compounds II: Pyroproducts of brominated phenols as mechanistic tools. *J. Anal. Appl. Pyrolysis* **2002**, *63*, 129.

Received for review July 23, 2003

Revised manuscript received December 23, 2003

Accepted January 20, 2004