TG and TG-MS methods for studies of the reaction between metal oxide and brominated flame retardant in various atmospheres

Sylwia Oleszek [a,b,*], Mariusz Grabda [a,b], Etsuro Shibata [a], Takashi Nakamura [a]

[a] *Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 1,1 Katahira, 2-Chome, Aoba-ku, Sendai 980-8577, Japan*
[b] *Institute of Environmental Engineering of the Polish Academy of Sciences, M. Sklodowska-Curie 34, 41-819 Zabrze, Poland*

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ABSTRACT

TG and TG-MS measurements were used to investigate the reactivity of ZnO with HBr originating from thermal degradation of TBBPA and with $SbBr_3$ under various atmospheres. It was found, that the HBr is an excellent brominating agent for ZnO and separates zinc as a volatile bromide (50 and 70% in He and He + 5 vol% O_2, respectively) from the solid residue. In inert atmosphere the formed char plays an important role as reduction agent for remaining ZnO into metallic Zn, which vaporizes completely from the residue above 890 °C. In presence of oxygen, the char is oxidized into CO and CO_2 and un-reacted ZnO remains. Bromination efficiency from thermal treatment of $SbBr_3$ + ZnO in He is about 14% only. Such low efficiency may results from highly volatile $SbBr_3$ sublimating from the mixture above 100 °C and its high ability to form thermally stable oxybromide compound ($Sb_8O_{11}Br_2$). Simultaneous TG-MS measurements indicate that the presence of ZnO strongly influences the TBBPA degradation pathway and causes enhancement of char formation. Catalyzing effect of ZnO on evaporation of $SbBr_3$ was also observed.

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1. Introduction

Due to the complex composition and nature of Waste Electrical and Electronic Equipment (WEEE or e-waste) its recycling is a technological challenge.

The main component of WEEE is plastics, which often include flame retardants to raise the fire safety of electric and electronic (E&E) appliances [1,2]. Brominated flame retardants (BFRs) are preferred because the highest level of fire safety can be obtained with the lowest amount of flame retardant. Additionally, bromine minimizes the impact of flame retardant additives on the polymer's performance [2]. Tetrabromobisphenol A (TBBPA) is the most widely applied brominated flame retardant (BFR) and is used as reactive BFR for unsaturated polyester and as additive BFR for polybutylene and polyethylene terephthalates. The major applications of TBBPA are in printed circuit board laminates, electric and electronic equipment housing and transportation applications such as car parts [3,4]. Together with BFRs, e-wastes contain a significant number of various metals [2,3,5]. Cui et al. [5] gathered data on the metal composition of different electronic scrap (e.g. mobile phones, PC mainboards, PC boards, calculators, printed circuit boards, TV boards and DVD player scraps). They found that precious metals (e.g. silver, gold, Platinum Group Metals), copper and zinc contribute most to value, while aluminum, lead and iron are important only in volume.

Starting from a variable WEEE composition, the selection of an appropriate recycling method is important and two aspects merit special consideration: (1) economic factors, requiring high recovery of valuable metals; and (2) environmental factors, concerning eco-efficient recycling of the plastic fraction and avoiding dumping of obnoxious compounds into the environment.

In practice, pyrometallurgical processes (e.g. incineration, smelting in a plasma arc or a blast furnace, drossing, sintering, melting, and gas phase conversion at high temperature) are the most effective in recovery of non-ferrous as well as precious metals from e-wastes. A comprehensive review of the techniques is given in Ref. [5]. These methods are also suitable for utilization of the energy content of organic fractions of the WEEE.

Recently, due to environmental, economical and technical (e.g. corrosion of facilities) reasons, a major concern in thermal treatment of E-wastes is the recovery of bromine [2,3]. Many studies [6–11] show that bromine is released mainly as HBr during thermal treatment of BFRs. Tohka and Zevenhoven [4] found the highest levels of HBr in the gas phase; however, the bromine can also be distributed over bottom ash and fly ash. If antimony oxide (Sb_2O_3), often added as a synergistic additive to the BFR [8], is present in

* Corresponding author. Tel.: +48 81 22 217 5214; fax: +48 81 22 217 5214.
E-mail address: sylwia_oleszek@yahoo.com (S. Oleszek).

BFR plastics, then antimony bromide ($SbBr_3$) can be formed as well [12].

Trials performed on the recovery of bromine (TAMARA pilot plant in Germany) during co-combustion of electronic scrap with municipal solid waste (MSW) [2] indicate that the released bromine can react with heavy metals present in MSW and form metal bromides. These bromides are volatile and concentrate in the fly ash, from where bromine can be recovered with an appropriate wet scrubbing system [13,14]. Although the TAMARA test work focused on bromine recovery, the reported results also indicate the advantage of bromine for recovery of metals or metal oxides by their selective bromination and evaporation. Evaluation of bromine partitioning and its influence on metal volatilization in those tests is discussed in details in Ref. [15].

Recent literature [16–23] indicates that such recovery of heavy metals has been proposed by simultaneous treatment of electric arc furnace (EAF) dust with polyvinyl chloride (PVC) waste. In that case, however, chlorine originating from PVC degradation is utilized for selective chlorination and then volatilization of the formed chloride metals.

Our initial studies on selective bromination–evaporation of metal oxides involved thermodynamic computations [24] using the Gibbs energy changes of selected bromination reactions. The results indicated that brominated gases such as HBr and $SbBr_3$, formed during BFRs thermal degradation, could act as bromination agents for metallic oxides (e.g. ZnO, PbO, CuO, and Fe_2O_3). Moreover, these particular metal oxides have a thermodynamic tendency to brominate more easily than Sb_2O_3. Due to their high volatilities, especially for zinc bromide ($ZnBr_2$), the possible separation of the volatile compounds by bromination in thermal treatment of solid wastes with BFR plastics can be considered. Results of our previous experimental investigations [25] on bromination–vaporization of Zn during thermal treatment of the mixture (TBBPA + ZnO) by using differential scanning calorimeter and small laboratory furnace (dynamic heating conditions, inert atmosphere) indicated that the bromination reaction depends mainly on availability of bromine around ZnO particles (it was conformed by additional studies on isothermal treatment of mixture TBBPA + ZnO [26]) while the vaporization of the formed $ZnBr_2$ can be restrained by char which is formed as result of flame retardant degradation. In fact, there is still lack of information concerning the carbothermic reduction of ZnO into Zn in presence of the char and vaporization of the formed Zn. There is still insufficient information on the decomposition pathway of TBBPA in presence of ZnO, which is a clue to understand the bromination reaction mechanism.

In this study, thermogravimetric combined with differential thermal analysis (TG-DTA) were conducted to investigate the reactivity of ZnO with both HBr, originating from the thermal decomposition of TBBPA, and solid $SbBr_3$, which is supposed to form during thermal degradation of BFR plastics containing Sb_2O_3 synergist. The investigations have been performed in inert and oxidative atmosphere, and both, the bromination and vaporization processes are discussed precisely. Additionally, gaseous products that evolved during thermal treatment of the mixtures (TBBPA + ZnO and $SbBr_3$ + ZnO) were qualified by direct combination of thermogravimetry with mass spectrometry (TG-MS). The role of ZnO on degradation pathway of TBBPA was also investigated.

2. Experimental

2.1. Materials

Antimony bromide ($SbBr_3$), zinc bromide ($ZnBr_2$), antimony oxide (Sb_2O_3), and zinc oxide (ZnO), with purities of 99.9% were purchased from Wako Pure Chemical Industries Ltd. Tetrabromo-bisphenol A (TBBPA, 97.0%) was obtained from Sigma Aldrich.

Powder mixtures of TBBPA + ZnO (3.34:1, w/w, assuming that all bromine present in TBBPA releases and reacts with to form $ZnBr_2$) and $SbBr_3$ + ZnO (3:1, w/w) were stirred manually. The sample weights used for thermal analysis were about 5–8 mg.

2.2. Methods

Thermogravimetric (TG) analysis: Thermal analysis of mixtures (TBBPA + ZnO and $SbBr_3$ + ZnO) and pure compounds ($SbBr_3$, ZnO, Sb_2O_3, $ZnBr_2$, and TBBPA) were carried out on a Rigaku Thermo Plus TG 8120 thermobalance. A sample was placed in an open alumina pan and heated up to the desired temperature at a constant heating rate of 10 °C/min. Analysis was carried out in a flow of Helium (He) or a mixture of He + 5 vol% O_2 with a constant rate of 150 mL/min (the applied concentration of oxygen corresponds to that occurring in industrial rotary kiln treatment of WEEE). TG analysis of the mixture was performed at least in triplicate to assure repeatability of the obtained results.

For mixtures of TBBPA + ZnO and $SbBr_3$ + ZnO, the inorganic products were characterized in solid residues collected at 320 °C and 250 °C, respectively, using EPMA (Jeol, JXA-8920) and XRD (Rigaku, Rint 220, Cu-Kα).

For the mixture of TBBPA + ZnO and pure TBBPA the degradation products remaining in solid residue were collected between 250 and 340 °C (every 10 °C) and extracted with acetone (0.5 mL) using an ultrasonic bath. The organic compounds were analyzed by combined gas chromatography (GC, Rigaku 6890N)/mass spectrometry (MS, JEOL, Automass Sun); the chromatogram peaks were identified by comparison of the fragmentation patterns to those of the NIST spectral library.

Simultaneous thermogravimetry-mass spectrometry (TG-MS) *analysis*: Analysis of pure TBBPA and of a mixture of TBBPA + ZnO were carried out with TG (TG-TDA 6200, Seiko Instrument, Extar 6000) combined with a mass selective detector (MSD 5973, Hewlett Packard) connected by a 5 m steel capillary transfer line (Frontier Labo, UADTP-5 M, I.D. 0.25 mm).

Analysis of pure $SbBr_3$ and of a mixture of $SbBr_3$ + ZnO were carried out with TG (Rigaku Thermo Plus TG 8120) combined with a mass spectrometer (JEOL, Automass Sun) connected by capillary transfer line equipped with an Ultra Alloy-DTM column (0.53 mm I.D., 0.75 O.D.).

The TGA sample was placed into the alumina pan and heated (10 °C/min) under a He flow of 150 mL/min. The evolved gases were transferred through the capillary transfer line into the mass detector. The capillary was heated up to 350 °C in order to avoid condensation of degradation products. Note: The MS measurements could not be conducted over 400 °C due to clogging the capillary caused by condensation of the vaporized $ZnBr_2$.

3. Results and discussion

3.1. Thermal treatment of TBBPA + ZnO

Thermograms obtained in inert (He) and oxidizing (He + 5 vol% O_2) atmospheres for the three pure compounds (TBBPA, $ZnBr_2$, and ZnO) and for the mixture of TBBPA + ZnO (3.34:1, w/w) are shown in Fig. 1A and B.

In the inert atmosphere, the decomposition and vaporization of pure TBBPA and also the vaporization of $ZnBr_2$ proceeds in one step with a 100% loss of mass, while ZnO remains unchanged over the entire temperature range (up to 1300 °C) (Fig. 1A). During thermal treatment of the mixture (TBBPA + ZnO) mass losses occur in three distinct stages, at consecutive temperature ranges:

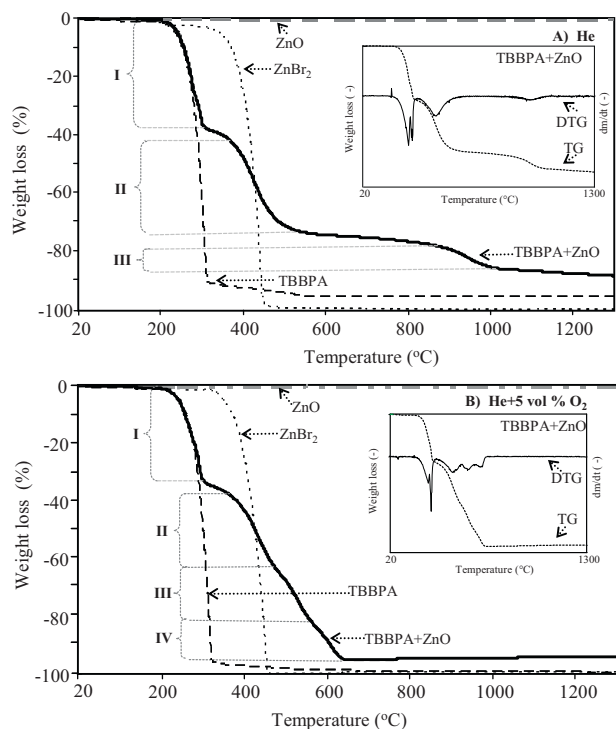**Fig. 1.** TG curves of TBBPA + ZnO (3.34:1, w/w) and pure compounds in an inert He (A) and in an oxidizing He + 5 vol%O_2 (B) gas flow.

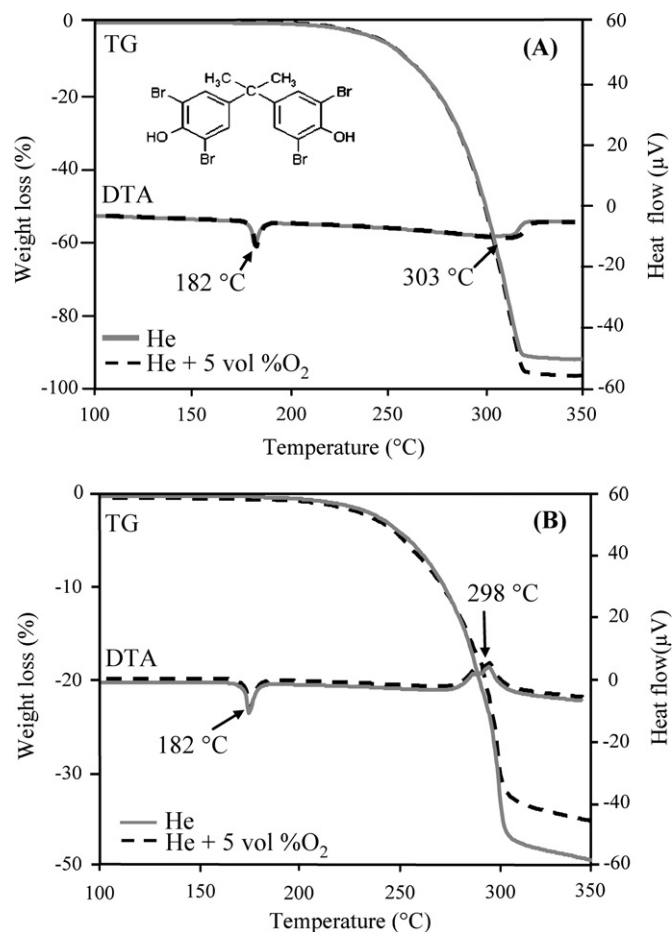**Fig. 2.** Comparison between TG-DTA curves for TBBPA (A) and TBBPA + ZnO (B) in an inert He (A) and in an oxidizing He + 5 vol%O_2 (B) gas flow.

220–320 °C (stage I), 360–540 °C (stage II) and 890–1020 °C (stage III).

In stage I (220–320 °C), the TG profile of the mixture (TBBPA + ZnO) coincides with that of pure TBBPA, suggesting that only degradation and evaporation of TBBPA occurs. Simultaneous TG-DTA analysis of pure TBBPA (Fig. 2A) and the mixture (Fig. 2B) performed over narrow temperature ranges are very helpful in understanding the phenomena occurring in stage I (see Fig. 1A). The DTA of pure TBBPA (Fig. 2A) exhibits two endothermic peaks. The sharp with maximum at 182 °C indicates the melting of TBBPA, while the other broad peak at 220–320 °C (with maximum at 303 °C) corresponds to TBBPA degradation and evaporation. These data are comparable to our previous investigation on TBBPA decomposition by differential scanning calorimeter [25]. In contrast to pure TBBPA, the DTA of the mixture (TBBPA + ZnO) (Fig. 2B) shows an exothermic peak (maximum at 298 °C), which may indicate reaction between ZnO and products of TBBPA degradation. Comprehensive data on the decomposition pathways of TBBPA [6–10] indicate that HBr is the main gaseous product formed during thermal treatment of TBBPA. Released HBr thus can react with ZnO according to Eq. (1):

$$2HBr(g) + ZnO(s) \rightarrow ZnBr_2(s) + H_2O(g) \tag{1}$$
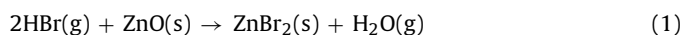
The X-ray pattern (Fig. 3A) of the solid residue collected at 320 °C under He flow confirmed the presence of the formed $ZnBr_2$ and of un-reacted ZnO.

Within the temperature range of 320–360 °C (Fig. 1A), the change in mass is insignificant, associated mainly with further degradation products evolving from the organic remains. The bromination of ZnO may also still proceed in this step.

In stage II (360–540 °C), the TG profile of the mixture is coincident with that of pure $ZnBr_2$, indicating evaporation of the $ZnBr_2$ formed (Eq. (2)):

$$ZnBr_2(s, l) \rightarrow ZnBr_2(g) \tag{2}$$

Negligible mass change is observed between 540 and 890 °C. In this step, carbothermic reduction of remaining ZnO to metallic Zn is taking place, with evolution of CO according to Eq. (3):

$$ZnO(s) + C(s) \rightarrow Zn(s) + CO(g) \tag{3}$$
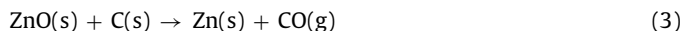
The mass loss at stage III (890–1020 °C, Fig. 1A) is associated with evaporation of the formed metallic Zn (Zn boiling point is 907 °C [27]). Thermal treatment of ZnO + C (1:1, w/w) by TG, using the same experimental conditions as for the TBBPA + ZnO mixture, confirmed the occurrence of carbothermic reduction of ZnO. From the TG profile (data not shown) a one-step mass loss was observed over the temperature range from 900 to 1100 °C. At the end of the
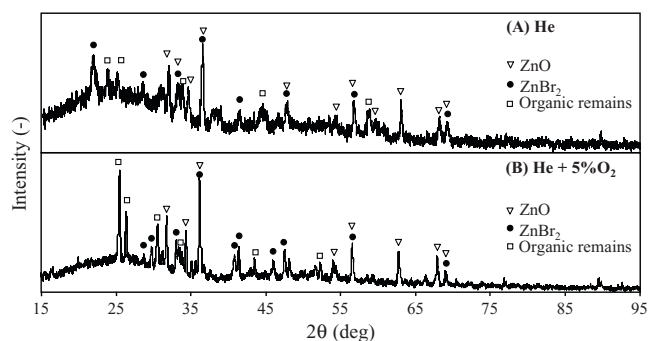

Fig. 3. X-ray diffraction patterns of reaction products in solid residues collected at 320 °C after thermal treatment of TBBPA + ZnO in an inert He (A) and in an oxidizing He + 5 vol%O_2 (B) gas flow.

experimental run (1300 °C) only un-reacted carbon remained in the pan.

Thermal treatment of TBBPA + ZnO at temperatures above 1020 °C under He flow, leads to a stable black residue.

Under oxidizing atmosphere (He + 5 vol% O_2) the TG profiles of the pure compounds are comparable to those obtained under inert atmosphere (Fig. 1B). That of the mixture, however, differs significantly especially above 360 °C. Similar to the results obtained under He, mass loss in stage I (220–320 °C) can be associated with degradation and vaporization of TBBPA. Detailed TG-DTA analysis of pure TBBPA (Fig. 2A) and the mixture (Fig. 2B) performed in the flow of He + 5 vol% O_2 also produces very similar results to those in inert atmosphere. The X-ray pattern (Fig. 3B) of solid residue collected at 320 °C is also comparable to that obtained under He. These similarities indicate that both the TBBPA decomposition and the bromination reaction are hardly affected by the presence of oxygen, at least at the experimental conditions applied in this study. Slow mass loss up to 360 °C (Fig. 1B) may be associated with continuous vaporization of degradation products of TBBPA. In these step the bromination may still proceed.

At temperatures above 360 °C rapid mass loss occurs in three successive stages ending at 650 °C. The stages II (360–480 °C), III (480–570 °C), and IV (570–650 °C), can be distinguished only on a plot of derivative thermogravimetry (DTG) (Fig. 1B inset). The mass loss in the second (II) stage, like in He flow, can be mostly associated with the vaporization of the formed $ZnBr_2$ (see Eq. (2)). The quick mass losses at stages III and IV (Fig. 1B) which were not observed under inert conditions are mostly associated with oxidation of organic residue to carbon mono- and dioxide, according to reactions (4) and (5):

$$C(s) + O_2(g) \rightarrow CO_2(g) \tag{4}$$

$$C(s) + 1/2 O_2(g) \rightarrow CO(g) \tag{5}$$
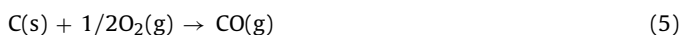
At these stages progressive char depletion may result in liberation and evaporation of $ZnBr_2$ trapped within the char. It should be noted, that the different processes of stages II–IV may occur simultaneously or overlap each other, and this renders determination of thermal boundaries for each stage difficult. No further change in mass of sample is observed while heating the mixture up to 1300 °C (Fig. 1B). In fact, only white solid residue identified as ZnO (XRD data not shown here) remains at the end of the experimental run in the pan.

3.1.1. Quantification of $ZnBr_2$ formed in inert and oxidizing atmospheres

As each distinct stage identified in the TG profiles refers to a specific process during the thermal treatment of mixture of TBBPA + ZnO, the sample mass loss at each stage can be used to estimate the efficiency of the related process.

Inert atmosphere: Assuming that stage (I) corresponds to degradation and evaporation of TBBPA, the mass loss at this step (ΔW_{II}^{He}) can be expressed as:

$$\Delta W_I^{He} = \Delta W_{TBBPA} \tag{6}$$

Mass loss in stage II (ΔW_{II}^{He}) corresponds to evaporation of formed $ZnBr_2$ and can be expressed as:

$$\Delta W_{II}^{He} = \Delta W_{ZnBr_2} \tag{7}$$

while the mass loss in stage III (ΔW_{III}^{He}) corresponding to evolution of metallic Zn vapors, can be described as:

$$\Delta W_{III}^{He} = \Delta W_{Zn} \tag{8}$$

Based on the above assumptions, the following efficiencies were estimated for each of the processes:

- 53 ± 3% of the initial amount of TBBPA vaporizes in stage I,
- 50 ± 4% of the initial amount of Zn vaporizes as $ZnBr_2$ in stage II,
- 52 ± 12% of the initial amount of Zn vaporizes as metallic zinc in stage III.

Taking into account the amount of zinc vaporized in stage II (360–540 °C) as $ZnBr_2$, we may conclude that during thermal treatment of a TBBPA + ZnO mixture in an inert atmosphere at least 50% of Zn is brominated. However, the bromination yield may be higher, as some $ZnBr_2$ can be trapped within the char, and is very likely to vaporize during further heating. This result is in good agreement with our previous investigations [25] where the bromination effectiveness of ZnO was found to be 41% (DSC) and 64% (small laboratory furnace). The un-reacted ZnO can be reduced completely to metallic Zn, and in this form, vaporize from the solid residue at the higher temperatures (890–1020 °C).

Oxidizing atmosphere: During stage (I) the mass loss in He + 5 vol% O_2 corresponds to the degradation and evaporation of TBBPA, exactly as in an inert He atmosphere:

$$\Delta W_I^{He+5\%O_2} = \Delta W_{TBBPA} \tag{9}$$

As discussed earlier, mass loss in stage (II) is mostly associated with vaporization of $ZnBr_2$; however, initial evolution of CO and CO_2 cannot be excluded. Therefore, the mass change in II stage can be expressed as follows:

$$\Delta W_{II}^{He+5\%O_2} = \Delta W_{ZnBr_2} + \Delta W_{CO/CO_2} \approx \Delta W_{ZnBr_2} \tag{10}$$

The mass losses in stages III and IV are mainly associated with CO and CO_2 evolution and the contribution of gradually liberated volatile form of zinc (zinc bromide/zinc oxybromide) is less important:

$$\Delta W_{III+IV}^{He+5\%O_2} = \Delta W_{CO/CO_2} + \Delta W_{ZnBr_2/ZnOBr} \tag{11}$$

The overlap of the simultaneous processes reveals that precise determination of the amount of vaporized $ZnBr_2$ on the basis of the TG profile is not feasible. However, in this case the amount of reacted zinc ($Zn_{(ZnBr_2)}$) can be calculated from differences between the initial amount of Zn (Zn^o) in the mixture and the remaining (Zn^r) in the sample pan at the end of experiment. The remaining amount of Zn was quantified by ICP in three independent experimental runs after dissolution of the ZnO in 0.1 M HCl. This allowed calculation of the amount of reacted zinc according to:

$$Zn_{(ZnBr_2)} = Zn^o - Zn^r \tag{12}$$

From chemical analysis, it was found that about 30 ± 0.02% of initial mass of zinc remains at the end of experiment. This estimation reveals that as much as 70 ± 2% of initial amount of ZnO is brominated under oxidizing conditions.

The obtained value indicates that the bromination yield in presence of oxygen is higher, of about 20%, than that obtained in inert atmosphere. Taking into account thermodynamics and fact that an increase in partial pressure of oxygen tends to stabilization of the oxides and restricts their bromination, formation of other volatile forms of zinc should be considered. Matsuura and Tsukihashi [28] who studied chlorination of ZnO in flow of Ar–Cl_2–O_2 gas, observed increase in chlorination yield of zinc oxide with increase in partial pressure of oxygen. He revealed that together with zinc chloride, zinc oxychloride (ZnOCl) was formed, however due to its instability and sampling difficulties, presence of the ZnOCl was not confirmed. As the thermal behavior of chlorine is similar to that of bromine, formation of the zinc oxybromide (ZnOBr), additionally to $ZnBr_2$, should be involved into our estimations (Eq. (11)).

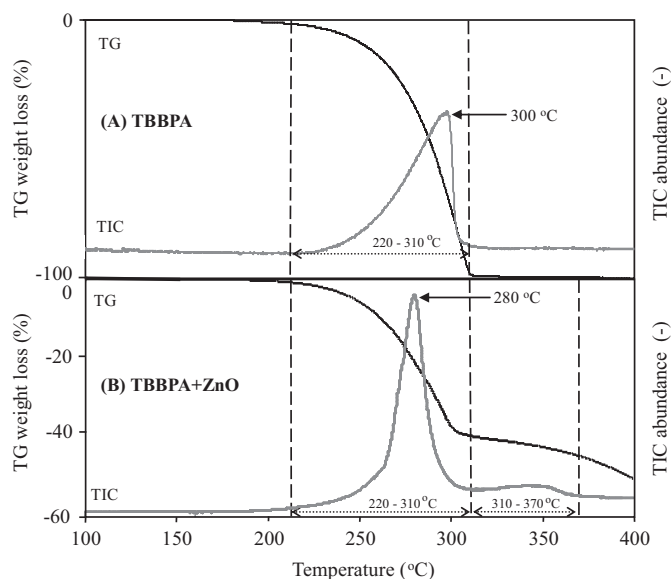Based on the above assumptions the following efficiencies were obtained:

Fig. 4. Simultaneous TG-MS (TIC) measurement for TBBPA (A) and TBBPA + ZnO (B) in He.

- 42 ± 2% of the initial amount of TBBPA vaporizes in stage I,
- 43 ± 2% of the initial amount of Zn vaporizes as $ZnBr_2$ in stage II,
- 27% of the initial amount of Zn vaporizes in forms of $ZnBr_2$ and possibly ZnOBr in stages III and IV,
- 30 ± 0.02% of initial mass of zinc remains in pan at 1300 °C.

3.1.2. Effect of ZnO on thermal degradation of TBBPA

Simultaneous TG-MS analyses were applied to study the thermal degradation behavior of pure TBBPA and in mixture with ZnO within 100–400 °C in a He atmosphere.

TG plot and total ion chromatogram (TIC) obtained during thermal treatment of pure TBBPA are shown in Fig. 4A. The TIC showed one broad peak between 220 and 310 °C corresponding to the one step degradation with maximum at about 300 °C. The mass spectrum taken at the peak maximum (Fig. 5A) were characterized by various m/z ions. Some of these ions were identified as: HBr ($m/z = 82$), biphenyl ($m/z = 154$); monobromophenols ($m/z = 173$), dibromophenols ($m/z = 252$), and tribromobisphenol A ($m/z = 465$). TBBPA ($m/z = 544$) was also identified among the products indicating that degradation and evaporation are simultaneous processes during thermal treatment of TBBPA. This observation was in good agreement with literature data [6–10]. TIC curves of the selected

Fig. 5. Comparison between the mass spectra of pure TBBPA and those of a mixture of TBBPA + ZnO, taken at the maximum of peaks shown in Fig. 4.

molecular ions (Fig. 6A) were observed within the same temperature range. Only evolution of HBr was released below 200 °C. This observation suggested that TBBPA degradation mechanism is initiated by formation of hydrogen bromide (Scheme 1): The TBBPA may tautomerize to the keto structures, which generate radicals through cleavage of carbon–bromine bond. The bromine radical, after hydrogen abstraction, yields HBr and tribromobisphehol A. By the same mechanisms, the tribromobisphenol A can be successively debrominated forming bisphenol A [7,9]. It must be pointed out however, that progressive degradation of TBBPA involves a number of competitive reactions, which are described in details in Refs. [6–10].

Fig. 7A illustrates the composition of solid residue collected from thermal treatment of TBBPA at various temperatures. Each sample of solid residue was dissolved in acetone and analyzed by GC–MS. TBBPA was the only compound identified in the residue. The other degradation products characterized by high volatility were immediately transformed into the gas phase.

TG-TIC curves from thermal treatment of TBBPA with ZnO are shown in Fig. 4B. In contrast to pure TBBPA, two degradation peaks were observed within 220–310 °C and 310–370 °C. Mass spectrum (Fig. 5B) taken at the maximum of the first peak (280 °C) was dominated by brominated phenols (especially dibromophenols with $m/z = 252$). That taken at top of the second peak (345 °C) revealed variety of TBBPA degradation products. TIC of the selected molecular ions (Fig. 6B) showed that the 1st degradation step was initiated by releasing of traces of water at 220 °C. Strong peaks of main degradation products (HBr, phenol and its derivatives, bisphenol) were observed within 250–310 °C, together with very small peak of tetrabromobispehnol. In this temperature range, water evolution intensified as well, indicating on progressive bromination reaction (Eq. (1)).

According to Barontini et al. [7,9], domination of phenol and its derivative peaks may indicate that the cleavage of the carbon–carbon bond in bromobisphenols structures is a prevailing mechanism in TBBPA degradation (Scheme 1). However, parallel formation of HBr peak at the same temperature range (Fig. 6B) indicates that debromination of TBBPA through generation of free radicals (cleavage of carbon–bromine bond) proceeds simultaneously in this degradation step.

In the 2nd degradation step, above 310 °C traces of bisphenol and HBr were released (traces of various other compounds were also detected). Their presence might indicate progressive degradation of the brominated compounds during subsequent heating. Evolution of these species lasted up to 370 °C.

GC–MS analysis (Fig. 7B) revealed presence of tetrabromobisphenol A and tribromobisphenol in residue collected at 250 °C and 280 °C confirming initial decomposition of TBBPA by its debromination. At 290 °C, a variety of the organic compounds (e.g. phenol, monobromophenol, dibromophenols) were detected in the residue suggesting advanced decomposition of TBBPA at this stage. In samples collected from 310–340 °C the phenol only was identified. The fact that high volatile compounds (phenol and its brominated derivatives) remained in solid residue in contrast to the sample of pure TBBPA (Fig. 7A) might indicate that the presence of ZnO char formation is enhanced and restricts their vaporization.

Enhancing effect of some metal oxides and their halides on formation of char were reported by many researchers [29–31].

It was found, that the increased charring of some organic materials (even such that do not naturally produce char or produce only small amount of char) in the presence of some metal oxides and halides, results from strong Lewis acidity of the metal-containing compounds. Lewis acids are able to accept an electron pair and create a coordinate bond, what may change the polymer degradation mechanism. Usually dehydrogenation of the polymer occurs at unsaturated site leading to its crosslinking and eventual
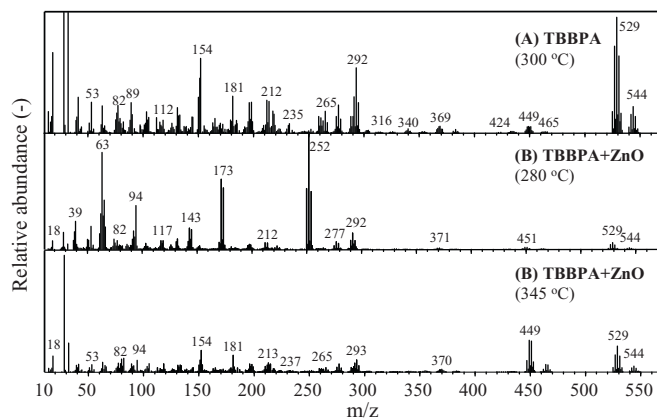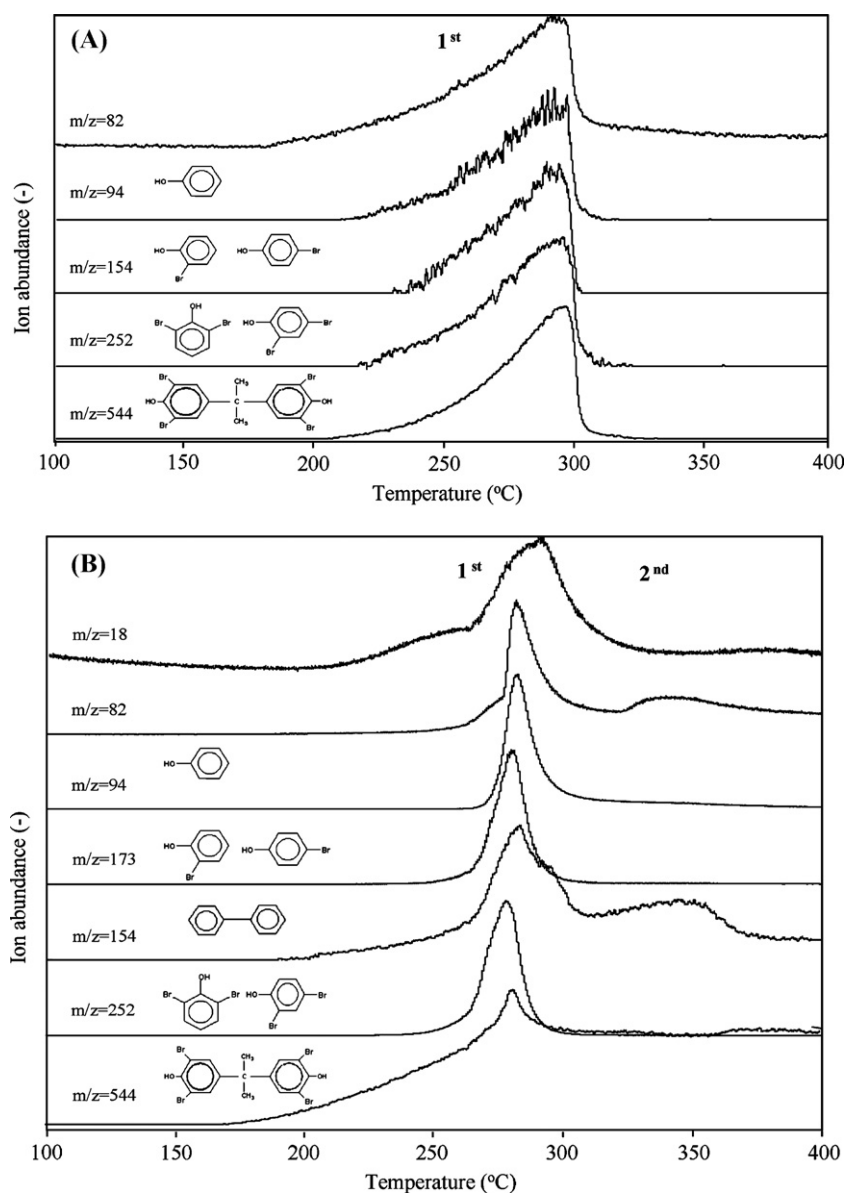
Fig. 6. Ion currents of selected masses of pure TBBPA (A) and mixture of TBBPA + ZnO (B): H_2O (m/z = 18), HBr (m/z = 82), phenol (m/z = 94), mono-bromophenols (m/z = 173), bisphenol (m/z = 154), di-bromophenols (m/z = 252), tribromobisphenol A (m/z = 465), and tetrabromobispehnol A (m/z = 544).

graphitization. In fact the ZnO and formed $ZnBr_2$ are both strong Lewis acids and thus effective crosslinking catalysts.

3.2. Thermal treatment of ZnO in mixture with $SbBr_3$

Sb_2O_3 is often used as a synergistic additive for TBBPA to enhance flame retardation of BFR plastics. In the presence of solid Sb_2O_3 gaseous $SbBr_3$ forms during thermal treatment of TBBPA [12]. This $SbBr_3$ can be considered as an additional brominating agent for ZnO.

Fig. 8 shows TG profiles for the four pure compounds (Sb_2O_3, $SbBr_3$, ZnO, and $ZnBr_2$) and for a mixture of $SbBr_3$ + ZnO (3:1, w/w) under He flow. Mass loss occurs in one single step for pure Sb_2O_3, $SbBr_3$, and $ZnBr_2$, while ZnO does not exhibit any mass change up to 650 °C. The TG curve of the mixture of $SbBr_3$ + ZnO exhibits four stages of mass loss, with a thermally stable residue left at 525–650 °C. Stage I, from 85–150 °C, can be associated with vaporization of $SbBr_3$ by comparison with the curves of pure compounds. Slow mass loss of the sample from 150 to 285 °C suggests that

reaction between $SbBr_3$ and ZnO occurs (Eq. (13)).

$$10SbBr_3(s) + 14ZnO(s) \rightarrow 14ZnBr_2(s) + Sb_8O_{11}Br_2(s) + Sb_2O_3(s) \tag{13}$$
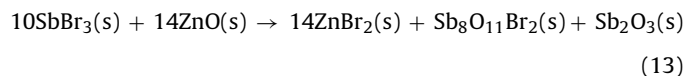
All these products were identified in the solid residue obtained at 250 °C (from a separate TG run) and analyzed by XRD (Fig. 9) and EPMA (data not shown here).
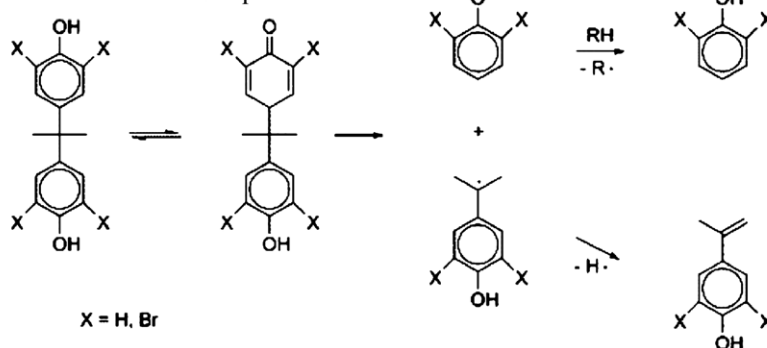
The products of stages III and IV were identified by comparison with TG profiles of the pure compounds. Thus, in stage III (335–400 °C), the mass loss can be related with the sublimation of the formed $ZnBr_2$ (Eq. (14)) while the mass loss in stage IV (480–525 °C) corresponds to the sublimation of pure Sb_2O_3 (Eq. (15)):

$$ZnBr_2(s) \rightarrow ZnBr_2(g) \tag{14}$$

$$Sb_2O_3(s) \rightarrow Sb_2O_3(g) \tag{15}$$

Initial reaction: Formation of bromine radicals
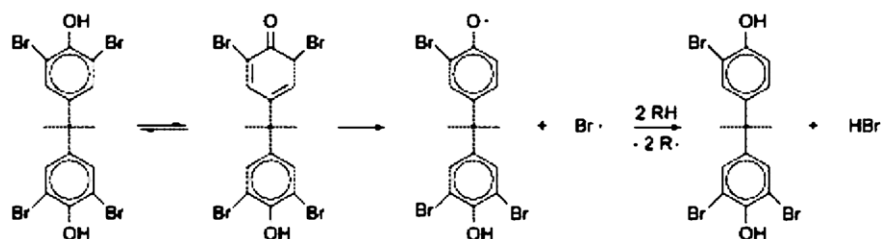
Formation of brominated phenols

X = H, Br

Scheme 1. Important pathways of TBBPA degradation: examples selected from Refs. [8,9].
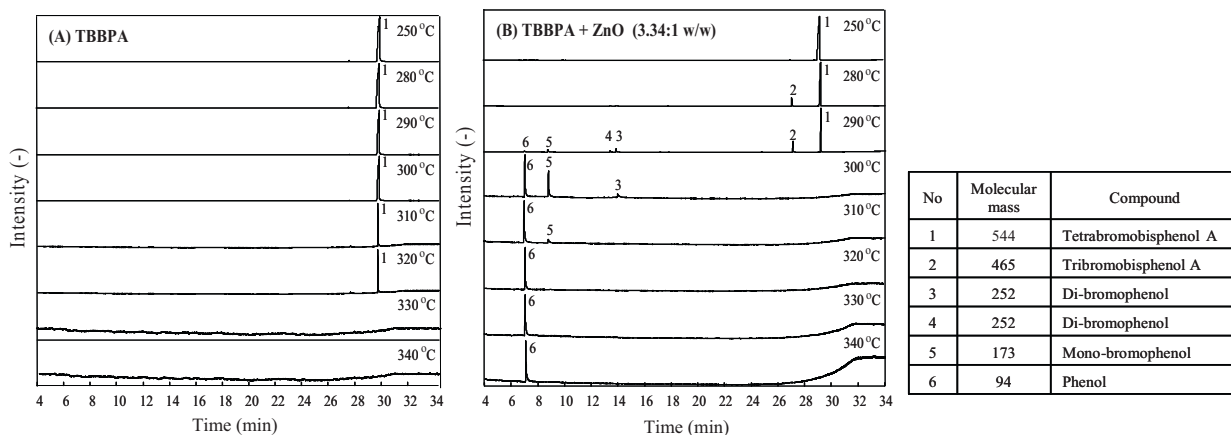

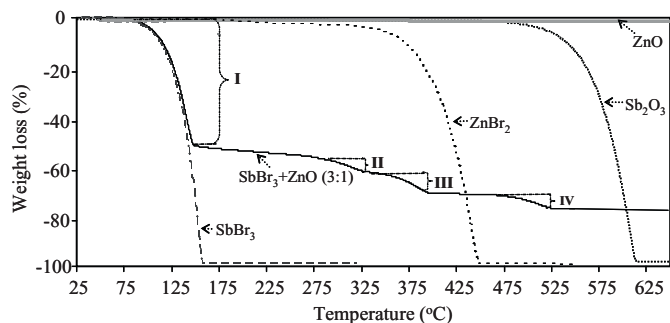| No	Molecular mass	Compound
1	544	Tetrabromobisphenol A
2	465	Tribromobisphenol A
3	252	Di-bromophenol
4	252	Di-bromophenol
5	173	Mono-bromophenol
6	94	Phenol

Fig. 7. Gas chromatograms of products in solid residue collected from thermal treatment of TBBPA (A) and mixture of TBBPA + ZnO (B) at various temperatures in He.

From the obtained TG profiles, it was not possible to identify the product of stage II. To obtain more information on stage II, simultaneous TG-MS analyses were conducted.

Fig. 8. TG curves of SbBr$_3$ + ZnO (3.34:1, w/w) and pure compounds from thermal treatment in He.

3.2.1. TG-MS analysis

During the thermal treatment of SbBr$_3$ + ZnO under He flow, two peaks appeared in the MS (Fig. 10B): the first, a large peak (corresponding to stage I in Fig. 8) at 138 °C, the second, small peak (corresponding to stage II in Fig. 8) at 320 °C. The mass spectrum (Fig. 11B) taken at the maximum of the first peak confirmed the
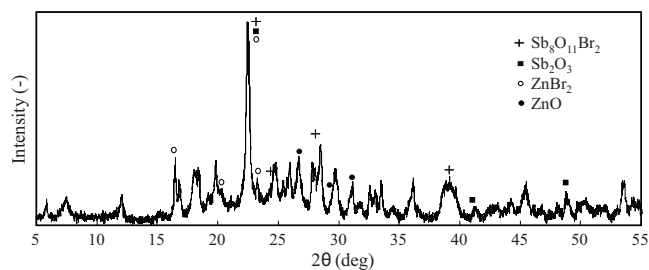
Fig. 9. X-ray diffraction patterns of products in solid residue collected at 250 °C after thermal treatment of the TBBPA + SbBr$_3$ in He.
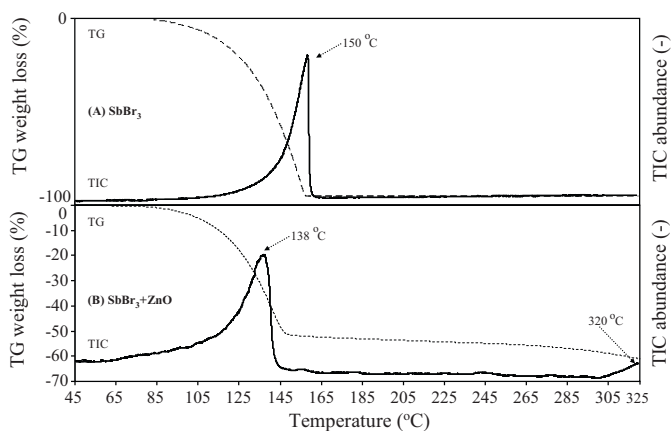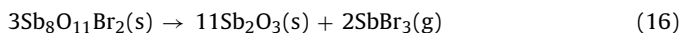
Fig. 10. Simultaneous TG-MS (TIC) measurement for SbBr$_3$ (A) and SbBr$_3$ + ZnO (B) in He.

presence of gaseous SbBr$_3$. The mass spectrum taken at the maximum of the second peak also showed the presence of SbBr$_3$ which resulted from successive decomposition of the formed oxybromide (see Eq. (13)) according to:

$$3Sb_8O_{11}Br_2(s) \rightarrow 11Sb_2O_3(s) + 2SbBr_3(g) \qquad (16)$$

For comparison, the TG-MS results and corresponding mass spectra of pure SbBr$_3$ are shown in Figs. 10 and 11A.

3.2.2. Quantification of the formed ZnBr$_2$

Assuming, on the basis of TG-MS results (Fig. 9B), that the mass losses in stages I and II correspond to the vaporization of SbBr$_3$ from the mixture:

$$\Delta W_I^{He} + \Delta W_{II}^{He} = \Delta W_{SbBr_3} \qquad (17)$$

and that the mass losses in stages III and IV (Fig. 8) correspond to the vaporization of ZnBr$_2$ and Sb$_2$O$_3$, respectively:

$$\Delta W_{III}^{He} = \Delta W_{ZnBr_2} \qquad (18)$$

$$\Delta W_{IV}^{He} = \Delta W_{Sb_2O_3} \qquad (19)$$

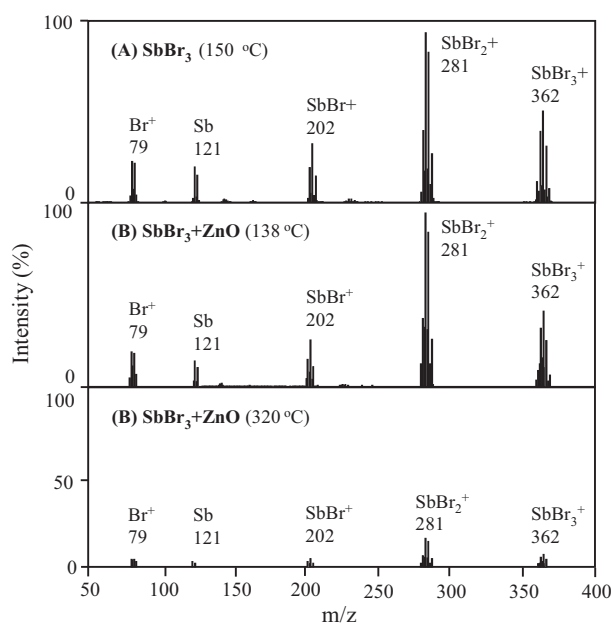**Fig. 11.** Mass spectra of pure SbBr$_3$ and mixture of SbBr$_3$ + ZnO taken at the maximum of peaks shown in Fig. 10.

The following results were obtained (based on three independent experimental runs):

- 78 ± 6% of the initial amount of SbBr$_3$ vaporizes in stages I and II,
- 14 ± 2% of the initial amount of Zn is brominated and evaporated as ZnBr$_2$ in stage III,
- 18 ± 4% of the initial amount of Sb is converted into Sb$_2$O$_3$ and vaporizes in stage IV.

From these estimates it can be concluded that the efficiency of bromination of ZnO in the presence of SbBr$_3$ is almost four times lower than that obtained during thermal treatment of TBBPA + ZnO. Such low efficiency may results from quick sublimation of highly volatile SbBr$_3$ (boiling point is 280 °C [27]) from the mixture and its high ability to form thermally stable oxybromide compound (Sb$_8$O$_{11}$Br$_2$) [32].

4. Conclusions

TG and TG-MS measurements were used to investigate the reactivity of ZnO with HBr originating from thermal degradation of TBBPA and with SbBr$_3$. The obtained results lead to the following conclusions:

(1) Hydrogen bromide originating from TBBPA decomposition is an excellent brominating agent for ZnO and separates zinc as a volatile bromide from the solid residue, formed during decomposition of TBBPA. In He atmosphere, at least 50 ± 4% of Zn can be brominated, as this amount of ZnBr$_2$ vaporizes between 360 and 540 °C. However, the yield of bromination may be even higher, as some ZnBr$_2$ can be trapped and either remained within the char and slowly vaporized during further heating. In an oxidizing atmosphere almost 70 ± 2% of Zn is brominated. Of this, at least 43% is in form of ZnBr$_2$ and vaporizes within 360–480 °C. The other 27% in form of ZnBr$_2$ and possibly ZnOBr vaporizes gradually together with successive degradation of surrounding organic char at the higher temperature.
(2) In inert atmosphere the formed char (rich in carbon) plays an important role as reduction agent for remaining ZnO, thus the un-reacted ZnO undergoes the carbothermic reduction into metallic Zn, which completely vaporizes from the residue above 890 °C. In oxidizing atmosphere, solely un-reacted ZnO remains, as the char is completely oxidized to CO and CO$_2$.
(3) Thermal treatment of SbBr$_3$ + ZnO (3:1, w/w) in flow of He shows that the bromination of ZnO proceeds at temperatures between 150 and 285 °C with a brominating efficiency of 14 ± 2%. Such low efficiency may results from highly volatile SbBr$_3$ sublimating from the mixture above 100 °C and its high ability to form thermally stable oxybromide compound (Sb$_8$O$_{11}$Br$_2$).
(4) Simultaneous TG-MS measurements indicate that the presence of ZnO strongly influences the TBBPA degradation pathway and causes enhancement of char formation. Catalyzing effect of ZnO on evaporation of SbBr$_3$ was also observed.

Acknowledgements

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