

Evaporation and thermal degradation of tetrabromobisphenol A above the melting point

Katia Marsanich^a, Severino Zanelli^a, Federica Barontini^b, Valerio Cozzani^{c,*}

^a *Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università degli Studi di Pisa, via Diotisalvi n.2, 56126 Pisa, Italy*

^b *Gruppo Nazionale per la Difesa dai Rischi Chimico-Industriali ed Ecologici, Consiglio Nazionale delle Ricerche, via Diotisalvi n.2, 56126 Pisa, Italy*

^c *Dipartimento di Ingegneria Chimica, Mineraria e delle Tecnologie Ambientali, Università degli Studi di Bologna, viale Risorgimento n.2, 40136 Bologna, Italy*

Received 29 January 2004; received in revised form 24 March 2004; accepted 27 March 2004

Available online 20 May 2004

Abstract

The volatility and the thermal degradation process of tetrabromobisphenol A (TBBA) were investigated. The quantitative assessment of the thermal degradation process and of the evaporation rate of TBBA required the use of an integrated approach, based on different calorimetric and analytical techniques. TBBA decomposition was carried out at temperatures between 180 and 270 °C, using thermogravimetric (TG) devices and a laboratory-scale batch reactor. The identification and quantification of decomposition products was based on GC and GC/MS techniques. The apparent kinetic parameters for TBBA decomposition were obtained, and a simplified method was used for a rough estimate of the vapor pressure from TG data. Thermal degradation of TBBA, although present even at temperatures as low as 185 °C, becomes relevant only above 230 °C. A preliminary evaluation of the Antoine correlation parameters for TBBA showed that the vapor pressure of this compound is comprised between 0.1 and 5 Pa at temperatures between 180 and 270 °C. The results obtained confirmed that TBBA processing at temperatures above the melting point (180 °C) may cause the release of TBBA in the environment due to evaporation phenomena.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Tetrabromobisphenol A; Thermal stability; Thermal degradation; Volatile emission; Evaporation

1. Introduction

Tetrabromobisphenol A (TBBA) is the most important brominated flame retardant (BFR), representing about 50% of BFR total production. About 120 000 metric tons of TBBA were produced in 1999 [1]. The main use of TBBA is for the production of brominated epoxy resins for printed circuit boards, containing up to 20–25 wt.% bromine. However, TBBA is also used as an additive flame retardant, mainly in the production of acrylonitrile–butadiene–styrene copolymers.

In recent years, a growing concern was raised on environmental and toxicity issues related to the use of TBBA in electronic products that have a widespread diffusion. Several studies examined TBBA exposure in computer workers [2–5], and TBBA toxicity was the object of many

investigations [6–8]. The current state of knowledge about environmental sources, behavior and toxicity of BFR was recently reviewed [9,10]. The present regulatory tendency to improve the recycling of polymer material waste from electrical and electronic equipment in which BFR and in particular TBBA are largely present, requires new data on thermal stability and reactions of these flame retardants. The possible formation of hazardous products during thermal degradation processes of materials containing TBBA was examined by several authors [11–27]. However, while a number of studies were focused on the selective analysis of polybrominated dibenzo-*p*-dioxins and dibenzofurans formed in TBBA thermal degradation, limited data are present on TBBA thermal stability and thermal decomposition products. Only few investigations were concerned with the analysis of TBBA thermal degradation process [20–22]. Further complementary data are available for brominated epoxy resins and printed circuit boards [23–27]. Although the presence of evaporation phenomena was observed by

* Corresponding author. Tel.: +39-0512093141; fax: +39-051581200.
E-mail address: valerio.cozzani@mail.ing.unibo.it (V. Cozzani).

Nomenclature

A	Antoine parameter
A_c	surface available for mass transfer (m^2)
A_d	pre-exponential factor (s^{-1})
B	Antoine parameter (K)
C	Antoine parameter (K)
D	diffusivity ($m^2 s^{-1}$)
E_a	activation energy ($J mol^{-1}$)
f_c	char fraction
k_0	arbitrary constant ($m^2 s^{-1} K^{-1.5}$)
K	kinetic constant (s^{-1})
L	crucible height (m)
L_I	crucible internal depth (m)
N_b	overall molar bulk flow ($mol s^{-1}$)
N_{deg}	degradative molar flow ($mol s^{-1}$)
N_{ev}	evaporative molar flow ($mol s^{-1}$)
P	total pressure (Pa)
P_{sat}	vapor pressure (Pa)
R	universal gas constant ($J mol^{-1} K^{-1}$)
s	sample height (m)
t	time (s)
T	temperature (K)
w	weight of unconverted TBBA (g)
w_{ev}	weight of TBBA evaporated (g)
w_0	initial sample weight (g)
y	molar fraction
y_s	molar fraction in the gas phase at sample surface
z	position on z -axis in Fig. 5 (m)

Greek letters

ξ	conversion
χ_{ev}	fraction of TBBA evaporated

Subscripts

i	i th experimental run
-----	-------------------------

some authors [24,25], scarce attention was devoted to the influence of TBBA volatility on its thermal stability and environmental release during processing.

The presence of evaporation phenomena may become relevant both during TBBA processing and in the study of the thermal degradation process. Evaporation may take place and, as well as thermal degradation, may cause emission problems during process operations involving TBBA, resulting both in environmental pollution and in safety concerns for the workers exposed. On the other hand, evaporation phenomena may heavily influence the TBBA decomposition pathways, enhancing the importance of gas-phase reactions with respect to reactions taking place in the melt, thus influencing the products formed in the decomposition process.

In this framework, the present study was carried out to shed some light on the relevance of TBBA volatility in the

thermal degradation process. The quantitative assessment of the thermal degradation process and of the evaporation rate of TBBA required the use of an integrated approach, based on different calorimetric and analytical techniques. TBBA decomposition was carried out at temperatures between 180 and 270 °C, using thermogravimetric (TG) devices and a laboratory-scale batch reactor. The identification and quantification of decomposition products was based on gas-chromatography (GC) and gas-chromatography coupled to mass spectrometry (GC/MS) techniques. Conventional methods for the estimation of vapor pressure proved difficult to apply, since TBBA is a solid at temperatures lower than 180 °C, while thermal degradation phenomena become relevant above 230 °C. Thus, a specific experimental strategy was applied to estimate the TBBA volatility from TG data.

2. Experimental**2.1. Materials**

4,4'-Isopropylidenebis(2,6-dibromophenol), commonly referred to as tetrabromobisphenol A (TBBA), was supplied by Aldrich (Milan, Italy). The following standards for GC calibration were purchased from Aldrich: phenol, 4-bromophenol, 2,4-dibromophenol, 2,4,6-tribromophenol, 2,6-dibromo-4-methylphenol, 4-isopropylphenol and bisphenol A. Solvents (HPLC grade) and analytical reagents were obtained from Carlo Erba (Milan, Italy).

2.2. Techniques

A Mettler TG-50 thermobalance was used to perform isothermal runs at temperatures between 180 and 270 °C. Typical sample weight was of 15 mg and run duration was of 60 min. A pure nitrogen purge flow of 200 ml/min was used in experimental runs, in order to reduce the residence time in the hot zones of the furnace and to minimize secondary gas-phase reactions. The sample was positioned on the pan of the TG balance and was inserted in the TG furnace pre-heated at the programmed temperature. Temperature transients due to sample heating were calculated accounting for convective and conductive heat transfer inside the cylindrical furnace, and resulted of less than 30 s in the temperature range of interest [28]. Tests were performed using different types of cylindrical crucibles. Table 1 lists the relevant characteristics of the crucibles used.

Table 1
Geometrical characteristics of crucibles used in isothermal TG runs

Type	Material	Internal height, L_I (mm)	Open surface, A_c (mm^2)
A	Al ₂ O ₃	4.2	33.2
B	Al	4.1	19.6
C	Al ₂ O ₃	4.2	15.9
D	Al ₂ O ₃	4.2	0.8
E	Al	4.1	0.2

A laboratory-scale fixed bed tubular batch reactor (BR) was used to carry out isothermal runs on larger TBBA samples (typically 250 mg). The experiments were mainly aimed at the recovery and characterization of the volatiles formed in the experimental runs. Isothermal runs (60 min) were performed at temperatures between 180 and 270 °C. BR runs were also performed in a constant heating rate mode (10 °C/min) from ambient temperature to 600 °C. The sample was positioned on the sample holder and inserted in the temperature-controlled furnace at the beginning of the run. Experimental runs were performed using a pure nitrogen purge gas flow (80 ml/min). Volatile products evolved during degradation were quenched and transferred by the nitrogen flow in a series of cold traps, maintained at –20 °C by a sodium chloride brine/ice bath, which allowed the recovery of condensables. The collected products were dissolved in acetone and analyzed by GC and GC/MS techniques. The traps were followed by a gas sampling cell for gas analysis by FTIR. Finally, the gas flowed in two absorbers containing a sodium hydroxide solution for the absorption of gas-phase acidic compounds. At the end of each experimental run, absorbed acidic compounds were quantitatively determined by titration of the alkaline solution with a hydrochloric acid standard solution, using phenolphthalein and methyl orange as indicators. In order to detect the possible presence of molecular bromine, during experimental runs a fluorescein test was carried out on the gas outflow from the reactor [29]. Moreover, the solution collected in alkaline scrubbers at the end of experimental runs was checked by iodometric titration [30]. The solid residue remaining on the sample holder at the end of the run was weighed. Further details and a scheme of the experimental apparatus are reported in a previous publication [31].

FTIR measurements were carried out using a Bruker Equinox 55 spectrometer. A Fisons MD 800 quadrupole mass spectrometer interfaced to a Fisons GC-8060 gas chromatograph was used for GC/MS analysis. The GC was equipped with a Mega SE30 fused silica capillary column (25 m × 0.32 mm, cross-linked, 0.25 μm film thickness). The column temperature program was the following: 5 min isothermal at 40 °C, heating to 250 °C (6 °C/min), then 20 min isothermal. Splitless injection with the injector at 250 °C was used. Mass spectrometric detection was performed in full scan conditions (scan range, m/z 10–819) in electron impact ionization mode.

Quantitative GC analysis was carried out using a ThermoQuest Trace GC 2000 gas chromatograph equipped with a flame ionization detector. The capillary column and the experimental conditions were identical to those used for GC/MS analysis, 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%.

3. Results and discussion

3.1. Evaporation and thermal degradation of TBBA

TBBA is known to undergo a thermal degradation process at temperatures higher than 200 °C [20,21]. Fig. 1 reports the results of isothermal TG runs performed at temperatures between 210 and 270 °C. The data reported in this and in the following figures were calculated as the mean of at least three experimental runs. Relative differences in weight loss with respect to time in different runs were always lower than 2%. TBBA thermal degradation process results in a consistent weight loss (about 80% of initial sample weight) and in the formation of a black solid residue, usually referred to as char. As shown in Fig. 1, the weight loss rate at a given temperature may be considered constant in the temperature range explored.

Fig. 2 reports weight loss data obtained in isothermal TG runs at 210 and 230 °C using different crucibles (see Table 1). Qualitatively similar results were obtained in all the temperature range explored (180–270 °C). Fig. 2 points out that, even if the same initial weight of TBBA was used (about 15 mg), different weight loss rates were experienced. The main difference in the experimental conditions employed is the different free surface available for evaporation and volatile loss, ranging from 0.2 to 33.2 mm², as shown in Table 1. Thus, the presence of different evaporation rates due to differences in surface available for mass transfer is the most reasonable explanation of the results in Fig. 2. This, in turn, points out that the weight loss process shown in Fig. 1 is caused by the concurrent evaporation and thermal degradation of TBBA. However, TG data only yield the total weight loss of the sample, not allowing the identification of the phenomena responsible of the weight loss process.

In order to perform a quantitative assessment of the different phenomena leading to TBBA weight loss at temperatures

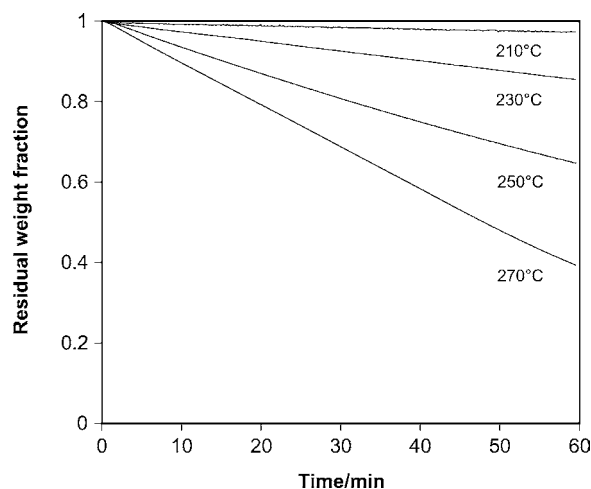


Fig. 1. Results of isothermal TG runs carried out on TBBA samples at temperatures between 210 and 270 °C (200 ml/min pure nitrogen flow, type B crucible).

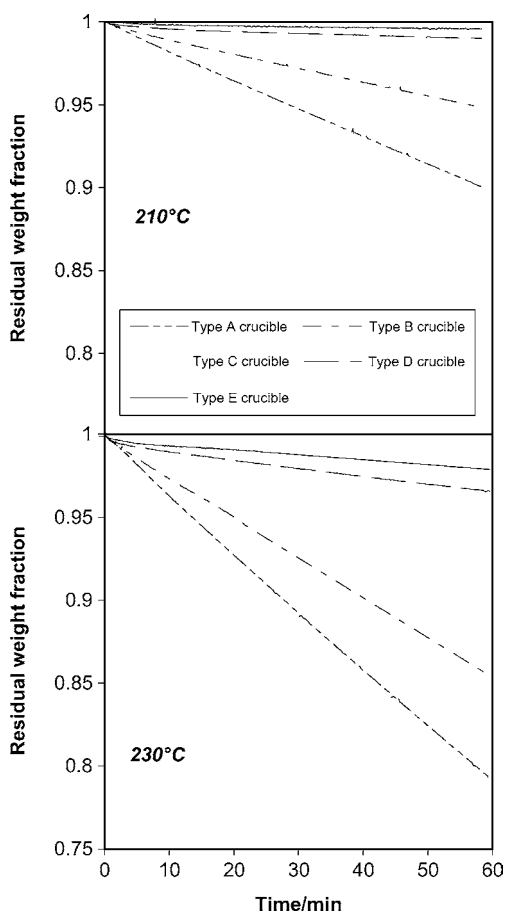


Fig. 2. Results of isothermal TG runs carried out on TBBA samples in 100% nitrogen at 210 and 230 °C using different crucible types (see Table 1).

higher than 180 °C, TG data were compared to the results of experimental runs performed using the batch reactor described in Section 2. Constant heating rate experiments were performed in the BR from ambient temperature to 600 °C at 10 °C/min. BR runs allowed the characterization and the

quantification of the different fractions of TBBA decomposition products. FTIR analysis showed that only hydrogen bromide and negligible quantities of carbon monoxide and carbon dioxide were present in the gaseous fraction. The fluorescein test and the iodometric titration of the solution collected in the scrubbers at the end of the experimental runs (see Section 2) did not evidence the presence of molecular bromine. This indicated that negligible quantities of Br₂, if any, were formed in the TBBA thermal degradation. On the other hand, the titration of the alkaline solution allowed the calculation of the amount of hydrogen bromide generated. GC and GC/MS analysis of the condensable fraction recovered in the cold traps allowed the identification and the quantification of the higher molecular weight products formed. Table 2 reports the composition of the volatile degradation product fraction recovered at the end of BR runs. The data in the table were obtained as the mean of at least three experimental runs. The category “others” in Table 2 includes all the compounds present in quantities lower than 0.5% (mol).

Relevant quantities of unreacted TBBA were found in the condensable fraction recovered from BR runs. This confirmed that TBBA decomposition results in a competitive process with evaporation, at least at the low heating rates and low temperatures used in the present work. Thus, isothermal BR runs were performed at temperatures between 180 and 270 °C in order to separate the contribution of evaporation from that of thermal degradation. Since the melting point of TBBA is around 180 °C, this had to be assumed as the lowest temperature limit for the experimental runs. The condensate recovered in the traps at the end of the BR runs was analyzed by GC, and the content of TBBA was determined. The fraction χ_{ev} of TBBA evaporated over the weight of converted TBBA was calculated as:

$$\chi_{ev} = \frac{w_{ev}}{w_0 - w} \quad (1)$$

where w_0 is the initial sample weight, w the weight of unconverted TBBA (if present), w_{ev} the weight of TBBA

Table 2
Results of the characterization of volatile degradation products collected at the end of BR runs in 100% nitrogen

	210 °C	230 °C	250 °C	270 °C	10 °C/min
Hydrogen bromide (mol%)	79.2	70.3	67.3	74.6	76.1
Phenol (mol%)	0.0	0.0	0.0	1.9	1.1
2-Bromophenol (mol%)	0.0	0.3	2.5	4.8	1.1
4-Bromophenol (mol%)	0.0	0.0	0.8	1.7	1.9
2,4-Dibromophenol (mol%)	1.1	3.2	4.9	2.5	2.7
2,6-Dibromophenol (mol%)	3.0	7.0	3.3	2.2	3.4
2,4,6-Tribromophenol (mol%)	1.9	6.3	9.2	2.1	2.4
Bromobisphenol A (mol%)	0.0	0.0	0.0	0.2	0.7
Dibromobisphenol A ^a (mol%)	0.2	0.3	1.0	2.0	3.2
Tribromobisphenol A (mol%)	8.6	8.8	5.7	4.5	5.2
Others (mol%)	6.0	3.8	5.3	3.5	2.2
Mean molecular weight (g/mol)	140.6	158.8	158.3	131.5	136.5
χ_{ev} (wt.%)	85.6	74.7	41.1	15.1	12.1

^a All isomers.

evaporated and recovered in the condensable products. χ_{ev} was calculated at the different temperatures used for experimental runs. The results obtained at the end of 1 h experimental runs are reported in Table 2. The value of χ_{ev} resulted reasonably independent from the duration of the run.

3.2. Apparent kinetics of the thermal degradation process

The analysis of the BR data allowed the estimation of the overall apparent kinetics of the thermal degradation process and the separation of the contribution due to evaporation from the total weight loss of TBBA.

At the end of each BR pyrolysis run, TBBA sample conversion caused by the thermal decomposition process was estimated as:

$$\xi = \frac{w_0 - w - w_{ev}}{w_0 - w_{ev}} \quad (2)$$

where w is the weight of unconverted TBBA at the time of interest. Even if the actual TBBA decomposition is a complex process involving an extended reaction network, the apparent overall decomposition rate in the conditions of isothermal runs at temperatures between 180 and 270 °C could be effectively calculated by an Arrhenius single step kinetic model. Since the overall weight loss rate resulted constant (see Fig. 1) and the evaporation rate at constant temperature is obviously time-independent, a zero-order kinetics was assumed:

$$\frac{d\xi}{dt} = K(T) = A_d e^{-E_a/RT} \quad (3)$$

where t is the time, T the temperature, K the kinetic constant, A_d the pre-exponential factor, E_a the activation energy, and R the gas constant. The kinetic constant was calculated from conversion data using the following expression:

$$K(T) = \frac{\xi}{t} \quad (4)$$

The values of the pre-exponential factor and of the activation energy were calculated by a linear least-squares approach, and resulted respectively of $3.76 \times 10^{13} \text{ s}^{-1}$ and of 179.1 kJ/mol. Due to the oversimplification of the kinetic model, the validity of the above parameters is limited to the conditions of experimental runs. Table 3 shows a comparison between the experimental results obtained with the BR and kinetic model predictions. The sufficient agreement shown by data in Table 3 confirms that the apparent kinetic model

may be used to represent the thermal degradation process of TBBA in the temperature interval of interest. In the range of temperatures where the model holds, the weight loss rate due to thermal degradation in BR isothermal runs could thus be calculated as a function of time and temperature:

$$\left. \frac{dw}{dt} \right|_{\text{deg}} = -w_0 [K(T)(1 - f_c)] \quad (5)$$

where f_c is the experimentally determined char fraction at total sample conversion, that resulted almost independent of temperature and equal to 0.2.

3.3. TBBA evaporation rates

In order to correctly understand the process leading to TBBA weight loss at temperatures higher than 180 °C, the contribution of evaporation should be assessed. As discussed above, no data are reported in the literature with respect to the vapor pressure of TBBA. However, experimental evaporation rates of TBBA may be calculated from TG data. Overall evaporation rates are obviously dependent on experimental conditions as temperature, surface area available for evaporation, and purge gas flow. Nevertheless, their evaluation may be a first step towards the estimation of TBBA volatility in the temperature range of interest.

Several TG isothermal runs were carried out using different crucible types (see Table 1) and different surface areas available for evaporation. As shown in Fig. 2, the weight loss rate always decreases as the surface area available for evaporation is decreased. Qualitatively similar results were obtained for all the isothermal TG runs carried out at temperatures between 180 and 270 °C.

The weight loss rates obtained in the TG isothermal runs are always the sum of the degradative and evaporative terms. Nevertheless, the above discussed kinetic model was used to calculate the degradative contribution to the total weight loss rate, as shown in Eq. (5). Thus, the evaporation rate was calculated from the weight loss rate with the following expression:

$$\left. \frac{dw}{dt} \right|_{\text{ev}} = \left. \frac{dw}{dt} \right|_{\text{deg}} - \left. \frac{dw}{dt} \right|_{\text{deg}} \quad (6)$$

Fig. 3 shows some results obtained for isothermal TG runs carried out between 210 and 270 °C. Experimental data are reported for the overall weight loss rate, while values obtained from Eq. (6) are reported for the weight loss rate due to evaporation. From Eq. (6), the molar evaporation rates may also be obtained, if the composition of the volatile flow is known. Data in Table 2 allow the estimation of the mean molecular weight of the volatile degradation products as a function of temperature. The apparent zero order of the kinetic process allows the assumption of a constant composition of the volatiles formed during the isothermal degradation runs. Fig. 4 reports the calculated molar evaporation rates, N_{ev} , and the molar volatile flows due to the degradation process, N_{deg} , correspondent to data in Fig. 3.

Table 3
TBBA conversion (see Eq. (2)) at the end of 1 h isothermal BR runs (100% nitrogen)

Temperature (°C)	ξ (experimental)	ξ (kinetic model)
210	0.007	0.006
230	0.028	0.034
250	0.185	0.176
270	0.844	0.804

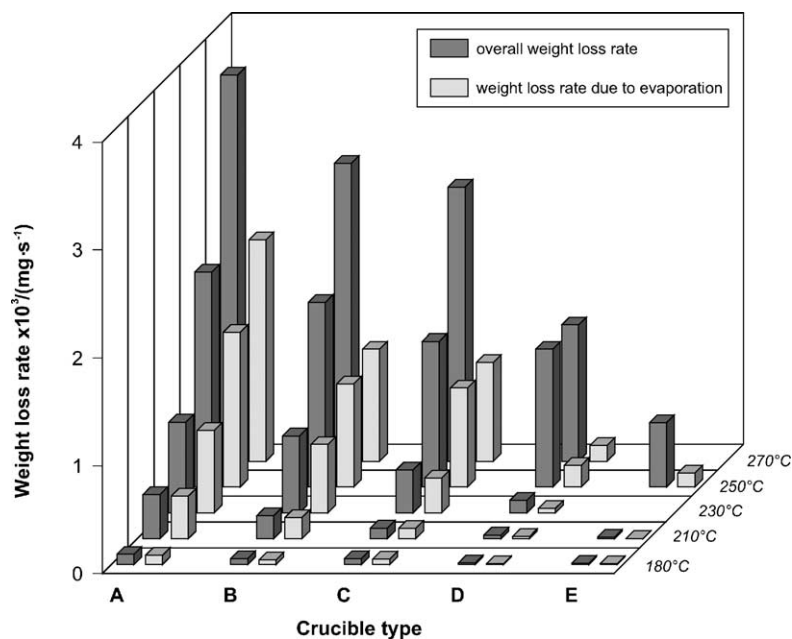


Fig. 3. Experimental overall weight loss rate and calculated weight loss rate due to evaporation in isothermal TG runs carried out using different crucibles (see Table 1).

3.4. Estimation of TBBA volatility from evaporation rate data

It is well known that evaporation rates of low-volatility compounds in TG devices are controlled by diffusive phenomena [32]. Fig. 5 shows a schematization of the mass transfer process that takes place during the simultaneous evaporation and thermal degradation of TBBA. If perturbations due to the nitrogen purge flow around the crucible are limited, a monodimensional analysis may be applied to the problem. Thus, assuming steady-state conditions,

the following differential molar balance on z -axis (see Fig. 5) may be derived from the application of Fick's law [33]:

$$N_{ev} = -A_c \frac{DP}{RT} \frac{dy}{dz} + yN_b \quad (7)$$

where N_{ev} is the molar flow of the compound of interest due to evaporation, A_c the surface available for mass transfer, D the diffusivity of the compound in the gas mixture, P the total pressure, y the molar fraction of the compound of interest and N_b the overall molar bulk flow. In the absence of

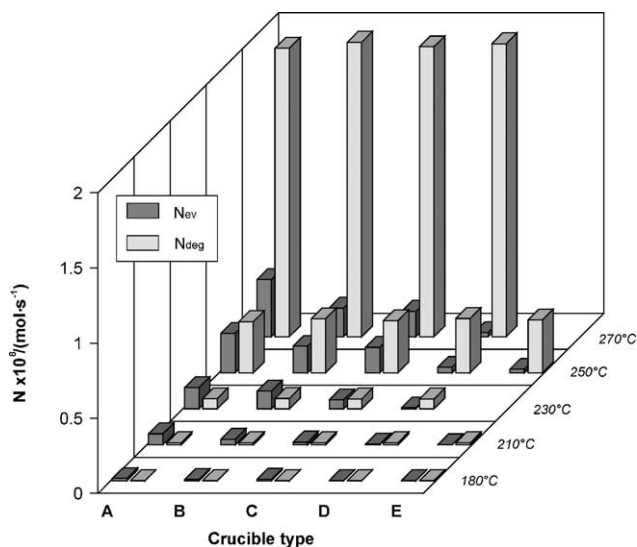


Fig. 4. Molar evaporation rates and molar flow due to thermal degradation calculated for the conditions of isothermal TG runs.

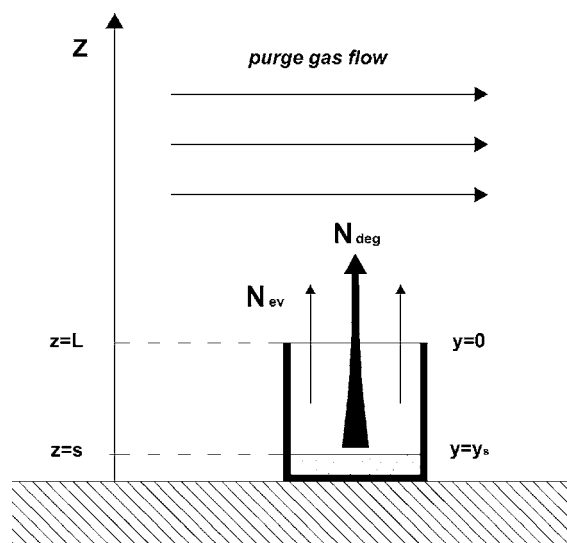


Fig. 5. Schematization of the mass transfer process during the simultaneous evaporation and thermal degradation of TBBA.

thermal degradation, the neat overall bulk flow N_b equals the evaporative flow N_{ev} , and Eq. (7) may be easily integrated to yield the classical expression for diffusion through a stagnant gas [33,34]:

$$N_{ev} = -A_c \frac{DP}{RT(L-s)} y_s \quad (8)$$

where L is the height of the crucible, s the sample height, and y_s the value of TBBA molar fraction in the gas phase at the surface of the molten sample (see Fig. 5). The presence of the purge gas allows the assumption of $y = 0$ at the crucible surface. If the sample is a pure liquid, y_s equals the ratio between the vapor pressure of the liquid and the total pressure of the system at the temperature of the TG device. This approach was followed to estimate the vapor pressure of low-volatility compounds from TG data, provided that the vapor pressure of the substance is sufficiently low to verify a quasi-steady-state assumption [32,35,36].

If, as in the case, a limited bulk flow of volatiles formed in the thermal degradation process is present, the overall bulk flow has the following expression:

$$N_b = N_{ev} + N_{deg} \quad (9)$$

where N_{deg} is the molar flow of volatiles formed in the thermal degradation process. The above analysis may be applied if the value of N_{deg} is known or may be calculated. In isothermal runs at temperatures between 210 and 270 °C, the limited rates of evaporation and thermal degradation allow a quasi-steady-state assumption for the integration of Eq. (7). Moreover, since an apparent zero-order kinetics well represents the thermal degradation

process, N_{deg} may be assumed reasonably constant with respect to conversion and thus to time. If a sufficient purge flow is supplied, TBBA molar fraction at the crucible top may be reasonably approximated to zero [33]. The following expression thus results for the evaporative molar flow:

$$N_{ev} = -A_c \frac{DP}{RTL_I} \frac{1}{(1 + (N_{deg}/N_{ev}))} \times \ln \left[1 - \left(1 + \frac{N_{deg}}{N_{ev}} \right) y_s \right] \quad (10)$$

The weight loss of the sample was low and the sample height in the crucibles was usually less than 0.3 mm (small sample quantities were used). Thus, the distance between crucible top and sample surface ($L - s$) was assumed to be constant in data analysis, and was approximated with the internal depth of the crucible, L_I , reported in Table 1. It must be remarked that, for small values of y_s and if $N_{ev} \gg N_{deg}$ (e.g. at temperatures between 180 and 210 °C), the N_{deg}/N_{ev} ratio approaches zero and Eq. (10) may be approximated by Eq. (8). In Eq. (10), the Chapman–Enskog relation for diffusivity, as reported by Bird et al. [33], allows the following approximation:

$$D = k_0 T^{3/2} \quad (11)$$

where k_0 is a constant that comprehends the Chapman–Enskog parameters for TBBA diffusivity. Eq. (10) may be used for a rough estimate of TBBA vapor pressure from experimental TG and BR data. Neglecting the influence of decomposition products in the liquid phase, the molar fraction of TBBA at sample surface, y_s , may be approximated as the

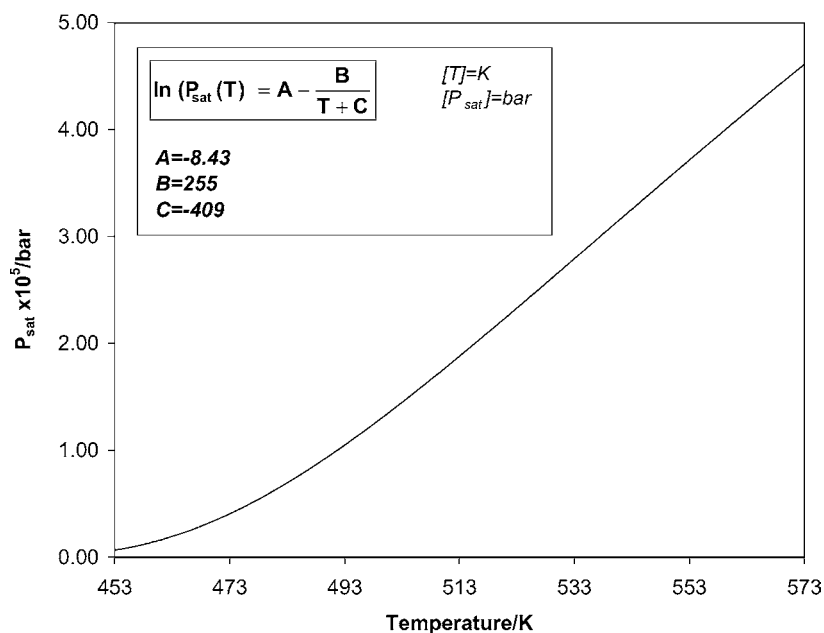


Fig. 6. TBBA vapor pressure as a function of temperature calculated with the approach developed in the present study.

ratio of vapor pressure over total pressure. Thus, Eq. (10) may be written as follows:

$$N_{ev} = -A_c k_0 \frac{PT^{1/2}}{RL_I} \frac{1}{(1 + (N_{deg}/N_{ev}))} \times \ln \left[1 - \frac{1}{P} \left(1 + \frac{N_{deg}}{N_{ev}} \right) \exp^{(A - (B/(T+C)))} \right] \quad (12)$$

where A , B , and C are the parameters of the widely used Antoine relation for vapor pressure. It is clear that the substitution of the diffusivity with the approximated expression given in Eq. (11) leads to the inclusion in the constant k_0 of any deviation of the overall mass transfer coefficient from the ideal laminar flow to which Fick's law applies.

The data on N_{ev} and N_{deg} reported in Fig. 4, obtained at different temperatures and using different crucible types, may be used to calculate the Antoine parameters and the k_0 value for TBBA. A non-linear least-squares algorithm was applied to minimize the following objective function:

$$F = \sum_{i=1}^n [N_{ev,i}^{exp} - N_{ev,i}^{mod}]^2 = \sum_{i=1}^n \left[N_{ev,i} + A_{c,i} k_0 \frac{PT_i^{1/2}}{RL_{I,i}} \frac{1}{(1 + (N_{deg,i}/N_{ev,i}))} \times \ln \left[1 - \frac{1}{P} \left(1 + \frac{N_{deg,i}}{N_{ev,i}} \right) \exp^{(A - B/(T_i + C))} \right] \right]^2 \quad (13)$$

where the subscript i ($i = 1, 2, \dots, n$) identifies the values of N_{ev} , N_{deg} , T , A_c and L_I in the i th experimental run. A value of $4.75 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1.5}$ was obtained for k_0 . The values obtained for the Antoine parameters are reported in Fig. 6, that shows the estimated values of TBBA vapor pressure in the temperature range of interest. As evident in Fig. 6, the vapor pressures of TBBA between 180 and 270 °C range between 0.1 and 5 Pa. Even if these values are not very

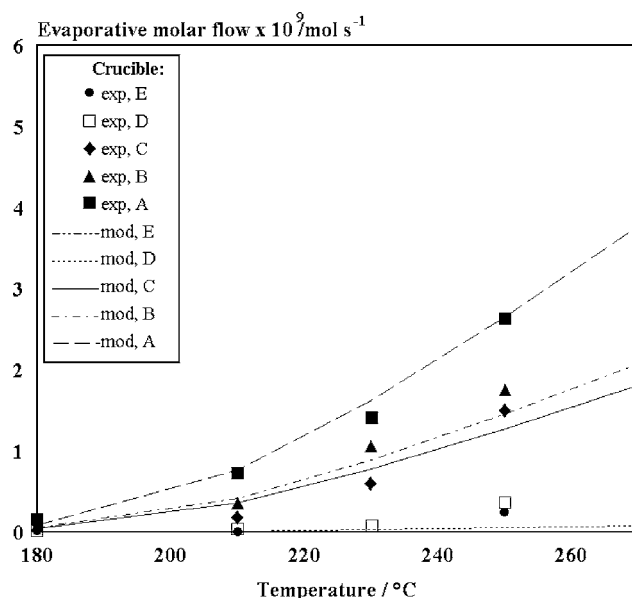


Fig. 7. Comparison of evaporation rates estimated from experimental TG data (dots) and from the model developed in the present study (lines).

high, it must be considered that the high molecular weight of TBBA may cause a non-negligible weight loss associated to evaporation.

Fig. 7 shows a comparison between experimental data and the evaporation rates calculated by means of Eq. (10). As shown in the figure, the evaporation rates are reasonably approximated by the simplified model introduced. Fig. 8 shows a comparison between the experimentally determined quantity of TBBA evaporated at the end of BR runs and the values calculated with Eq. (12). The model data reported in Fig. 8 were calculated taking into account the different flow pattern present in the BR with respect to that of the TG analyzer. The results obtained point out that the simplified model developed in the present study predicted with

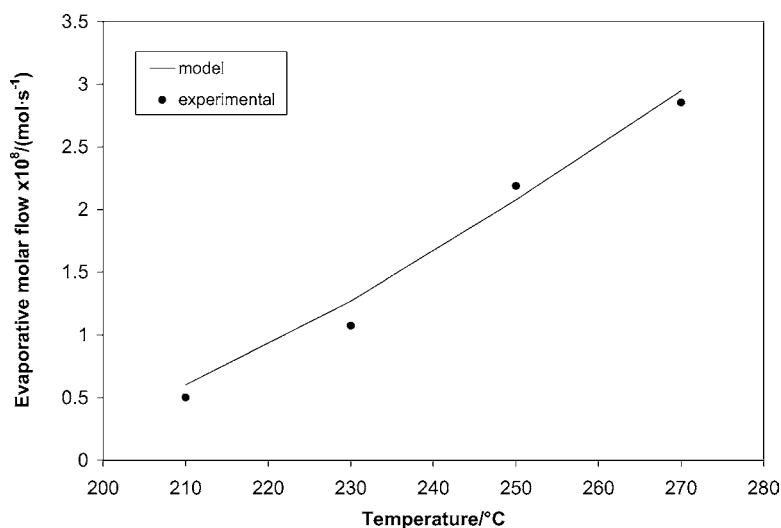


Fig. 8. Comparison of evaporation rates estimated from experimental BR data (dots) and from the model developed in the present study (lines).

sufficient accuracy the contribution of evaporation to the total mass loss also in BR runs. Obviously, the vapor pressure data in Fig. 6 only represent an approximation of the actual values of the vapor pressure, since several simplifications were introduced in the calculations. However, the values obtained allow at least a rough estimate of TBBA volatility, and the preliminary assessment of TBBA evaporation rates during processing at high temperatures.

4. Conclusions

The analysis of data obtained from a fixed bed reactor and a TG analyzer allowed the separation of thermal degradation and evaporation contributions to the weight loss of TBBA samples at temperatures between 180 and 270 °C. The apparent kinetic parameters for TBBA thermal degradation were estimated, showing that thermal degradation phenomena, although present even at temperatures as low as 185 °C, become relevant only above 230 °C.

A simplified method was used to estimate the apparent values of the vapor pressure from TG data, based on the use of crucibles with different surface areas available for evaporation. The data obtained allowed the evaluation of TBBA vapor pressure at temperatures between 180 and 270 °C. TBBA showed a non-negligible volatility in this temperature range, with vapor pressures ranging between 0.1 and 5 Pa. The results obtained confirmed that TBBA processing at temperatures above the melting point (180 °C) may cause the release of TBBA in the environment due to evaporation phenomena.

Acknowledgements

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

References

- [1] Bromine Science and Environmental Forum, An introduction to brominated flame retardants, BSEF, Bruxelles (B), 2000.
- [2] K. Jakobsson, K. Thuresson, L. Rylander, A. Sjödin, L. Hagmar, A. Bergman, *Chemosphere* 46 (2002) 709.
- [3] A. Sjödin, H. Carlsson, K. Thuresson, S. Sjölin, A. Bergman, C. Ostman, *Environ. Sci. Technol.* 35 (2001) 448.
- [4] C. Thomsen, E. Lundanes, G. Becher, *J. Environ. Monit.* 3 (2001) 366.
- [5] L. Hagmar, A. Sjödin, P. Hoglund, K. Thuresson, L. Rylander, A. Bergman, *Organohalogen Compd.* 47 (2000) 198.
- [6] S. Kitamura, N. Jinno, S. Ohta, H. Kuroki, N. Fujimoto, *Biochem. Biophys. Res. Comm.* 293 (2002) 554.
- [7] P. Eriksson, E. Jakobsson, A. Fredriksson, *Environ. Health Perspect.* 109 (2001) 903.
- [8] I.A.T.M. Meerts, J.J. Van Zanden, E.A.C. Luijckx, I. Van Leeuwen-Boi, G. Marsch, E. Jakobsson, A. Begman, A. Brouwer, *Toxicol. Sci.* 56 (2000) 95.
- [9] A. De Wit, *Chemosphere* 46 (2002) 583.
- [10] I. Watanabe, S. Sakai, *Environ. Int.* 29 (2003) 665.
- [11] R. Dumler, H. Thoma, D. Lenoir, O. Hutzinger, *Chemosphere* 19 (1989) 2023.
- [12] J. Thies, M. Neupert, W. Pump, *Chemosphere* 20 (1990) 1921.
- [13] R. Luijk, H.A.J. Govers, *Chemosphere* 25 (1992) 361.
- [14] R. Dumler-Gradl, D. Tartler, H. Thoma, O. Vierle, *Organohalogen Compd.* 24 (1995) 101.
- [15] M. Riess, T. Ernst, R. Popp, B. Müller, H. Thoma, O. Vierle, M. Wolf, R. van Eldik, *Chemosphere* 40 (2000) 937.
- [16] S. Sakai, J. Watanabe, Y. Honda, H. Takatsuki, I. Aoki, M. Futamatsu, K. Shiozaki, *Chemosphere* 42 (2001) 519.
- [17] G. Söderström, S. Marklund, *Organohalogen Compd.* 47 (2000) 225.
- [18] G. Söderström, S. Marklund, *Environ. Sci. Technol.* 36 (2002) 1959.
- [19] H. Wichmann, F.T. Dettmer, M. Bahadir, *Chemosphere* 47 (2002) 349.
- [20] A. Factor, *J. Polym. Sci., Polym. Chem. Ed.* 11 (1973) 1691.
- [21] E.J.C. Borojovich, Z. Aizenshtat, *J. Anal. Appl. Pyrol.* 63 (2002) 105.
- [22] A. Hornung, A.I. Balabanovich, S. Donner, H. Seifert, *J. Anal. Appl. Pyrol.* 70 (2003) 723.
- [23] M.P. Luda, A.I. Balabanovich, G. Camino, *J. Anal. Appl. Pyrol.* 65 (2002) 25.
- [24] M. Riess, H. Thoma, O. Vierle, R. van Eldik, *J. Anal. Appl. Pyrol.* 53 (2000) 135.
- [25] R. Luijk, J.M. Pureveen, J.M. Commandeur, J.J. Boon, *Makromol. Chem., Macromol. Symp.* 74 (1993) 235.
- [26] M. Webb, P.M. Last, C. Breen, *Thermochim. Acta* 326 (1999) 151.
- [27] M. Blazsó, Zs. Czégény, Cs. Csoma, *J. Anal. Appl. Pyrol.* 64 (2002) 249.
- [28] V. Cozzani, L. Petarca, L. Tognotti, *Fuel* 74 (1995) 903.
- [29] F. Feigl, *Spot Tests*, 4th ed., vol. 1, Elsevier, Amsterdam, 1954, p. 337.
- [30] D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, 6th ed., Saunders College Publishing, Philadelphia, 1992.
- [31] F. Barontini, V. Cozzani, L. Petarca, *Ind. Eng. Chem. Res.* 40 (2001) 3270.
- [32] N. Pieterse, W.W. Focke, *Thermochim. Acta* 406 (2003) 191.
- [33] R.B. Bird, W.E. Stewart, E.N. Lightfoot, *Transport Phenomena*, Wiley, NY, 1960.
- [34] J.M. Coulson, J.F. Richardson, *Chemical Engineering*, Pergamon Press, Oxford, UK, 1991.
- [35] K. Chatterjee, D. Dollimore, K.S. Alexander, *Thermochim. Acta* 392 (2003) 107.
- [36] D.M. Price, M. Hawkins, *Thermochim. Acta* 329 (1998) 73.