KINETICS OF TETRABROMOBISPHENOL. A PYROLYSIS COMPARISON BETWEEN CORRELATION AND MECHANISTIC MODELS.

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Abstract

Brominated flame retardants are well recognized as being highly effective flame retardants. 4-4'-isopropylidenebis(2,6-dibromophenol), commonly known as tetrabromobisphenol A, is the brominated flame retardant with the largest production volume and is used to improve fire safety, mainly of laminates in electrical and electronic equipment. A kinetic study of the pyrolysis of TBBA has been carried out to obtain decomposition parameters under different operating conditions and taking into account that TBBA is a compound with a high boiling point and that vaporization occurs simultaneously to decomposition. Dynamic runs and dynamic + isothermal run at different heating rates and using different masses of sample were correlated simultaneously. All TG runs were fitted with a unique set of kinetic parameters that is able to explain all the experiments. Moreover, a simplified detailed kinetic model has been developed and the kinetic parameters obtained satisfactorily reproduce the thermal decomposition of TBBA.

Keywords: vaporization, TG, kinetic model, brominated flame retardant.

1. Introduction

Brominated compounds are widely used as flame retardants in industrial operations. Due to their high efficiency, compatibility and small influence on mechanical properties, brominated flame retardants (BFRs) have a broad application area, mainly in the field of polymeric materials. Tetrabromobisphenol A (TBBA) is the

most important BFR, representing around 60 % of BFR total production. The estimated global consumption of TBBA was around 170,000 metric tons for 2004 [1].

TBBA contributes to the fire safety of electrical and electronic equipment and installations where printed wire boards are used, such as consumer electronics (TVs, vacuum cleaners, washing machines...), office and communication equipment (copiers, computers, printers, fax machines, radios, etc.) and automotive, aviation and entertainment equipment. TBBA is also used as an additive flame retardant in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins or high impact polystyrene (HIPS) [2].

Kinetic data are essential for designing any kind of device in which a thermal decomposition takes place. Moreover, kinetics is the starting point to postulate mechanisms for the thermal decomposition [3]. Thermal degradation of pure TBBA is a complex process that takes place in the condensed phase. Factor [4] carried out the thermogravimetric analysis of a TBBA sample in both air and nitrogen and concluded that oxygen is unimportant in this thermal decomposition. Nevertheless, it must be emphasized that the presence of oxygen can promote the formation of brominated dibenzo-p-dioxins and dibenzofurans.

Luda et al. [5] employed differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to study the thermal decomposition of TBBA at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and found two stages of weight loss at 200-290 $^{\circ}\text{C}$ and 290-500 $^{\circ}\text{C}$. These researchers found that TBBA melts at 183 $^{\circ}\text{C}$ and degrades over a broad range of temperatures (200-330 $^{\circ}\text{C}$), corresponding to the first stage of weight loss in the TGA. Marsanich et al. [6] performed several pyrolysis isothermal runs at temperatures between 180 and 270 $^{\circ}\text{C}$ using 15 mg of sample and a nitrogen purge flow of 200 ml min^{-1} . They estimated the values of the pre-exponential factor and the activation energy ($3.76 \cdot 10^{13}\text{ s}^{-1}$ and 179.1 kJ mol^{-1} , respectively) using the results obtained in different isothermal runs carried out in a laboratory-scale fixed bed tubular batch reactor and assuming a zero-order kinetics.

TBBA is a typical example of a compound with a high boiling point and presents vaporization simultaneous to decomposition. In order to correctly understand the process leading to TBBA weight loss at temperatures higher than 180 $^{\circ}\text{C}$, the contribution of evaporation should be assessed. Marsanich et al. [6] developed a method 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.

Barontini et al. [7] proposed pathways for the decomposition of TBBA and concluded that radical debromination reactions and scission reactions to yield phenols resulted in the most important thermal degradation mechanisms of TBBA.

Marongiu et al. [8] presented a semi-detailed kinetic scheme, constituted by more than 900 chemical reactions. It involves about 60 components, pseudo species and their corresponding radicals. The validation of the kinetic scheme relied on several sets of experimental data (under isothermal and dynamic conditions with different heating rates) directly obtained from scientific literature. The contribution of these researchers is very interesting, but has the inconvenience that the kinetic model cannot be used by other researchers.

Chemical engineers use simplified decomposition models, normally obtained from the correlation of experimental results. Among the possible models, potential models are extensively used for modeling and designing the corresponding reactors.

The objective of this paper has been the development of a simplified model that can be easily used. TBBA belongs to the group of backbone flame retardants, because it is linked to polymers, so the effect of the chemical bonds TBBA-polymer can be discussed in terms of kinetic parameters, considering the TBBA decomposition and/or the evolution of HBr and other brominated compounds. A second model, simplification of the Marongiu et al. [8] model, has also been developed. The use of simplified models can be convenient when the material studied is mixed with other compounds, so the decomposition of this material in the mixture can be compared with that observed in the decomposition of pure material.

Experimental

The sample employed in this study was 4,4'-isopropylidenebis(2,6-dibromophenol), a commercial brominated flame retardant commonly referred to as 3,3',5,5'-tetrabromobisphenol-A (TBBA), supplied by Alfa Aesar.

Runs for pyrolysis and combustion analysis were carried out on a Mettler Toledo thermobalance model TGA/SDTA851e/LF/1600. This equipment has a horizontal furnace and a parallel-guided balance. In this way, the position of the sample has no influence in the measurement, and flow gas perturbation and thermal buoyancy are

minimized. The sample temperature was measured with a sensor directly attached to the sample holder (4.9 cm diameter, 4.5 cm height).

For the pyrolysis runs of this research, the atmosphere used was nitrogen with a flow rate of 100 ml min⁻¹.

Dynamic experiments were carried out at heating rates of 5, 10 and 20 K min⁻¹, from room temperature up to 1173 K, including in this way the entire range of TBBA decomposition. Isothermal experiments started with a constant heating rate until the desired temperature was reached, the final temperature was kept constant throughout the pyrolysis process and the experiment was considered to be finished when no weight loss was observed. Different sample masses were used, between 5 and 15 mg.

An experiment with a heating rate of 5 K min⁻¹ using Avicel PH-105 microcrystalline cellulose was done. The kinetic values obtained showed good agreement with the results presented by Grønli et al. [9] in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry. This experiment was used to check the good performance of the thermobalance.

Furthermore, pyrolysis runs were carried out in a laboratory reactor in order to study the emission rate of hydrogen bromide at three different temperatures in the range of TBBA decomposition.

These experiments were carried out in a tubular quartz reactor located inside a horizontal laboratory furnace. The sample is placed in a holder and a small engine introduces it inside the reactor. A detailed description of the system can be found elsewhere [10]. The furnace conditions in the pyrolysis of the samples were 522, 570 and 600 K, respectively. For each experiment, after the furnace had reached the nominal temperature, approximately 50 mg of sample were introduced into the reactor at constant speed (1 mm s⁻¹). The carrier gas (nitrogen) was introduced parallel to the sample, at a constant flow of 300 mL min⁻¹.

The evolved gas was passed through two consecutive impingers containing a sodium carbonate / sodium bicarbonate solution in order to retain the liberated HBr. The amount of bromide ion in the solution was analysed by ion chromatography (IC) in a Dionex DX500.

Another run was carried out at 873 K to determine the gases evolved. The non-condensable gases were collected using Tedlar bags at the outlet of the reactor for a time long enough to collect all the compounds. This sample was analysed by gas chromatography using FID, TCD and MS detectors. Another run at 873 K was carried

out to determine the yields of semivolatile compounds and PAHs, which were collected by adsorption over XAD-2 resin (Supelco, Bellefonte, USA) placed at the outlet of the furnace throughout the experiment. For PAHs and semivolatile compounds analysis, the resin was extracted with a mixture of dichloromethane/acetone (1:1 vol) using Accelerated Solvent Extraction in a DIONEX ASE[®] 100, in accordance with the U.S. EPA 3545A Method.

2. Experimental results

Figure 1a shows the experimental results corresponding to the dynamic runs carried out with approximately 5 mg and at three different heating rates. The Differential Thermal Analysis (DTA) for two runs (5 and 20 K min⁻¹) is also plotted. An endothermic peak can be observed at the DTA runs at 455 K, corresponding to TBBA melting point. It can also be observed that the residue yield at the end of the runs is different, indicating the presence of competitive reactions.

Figure 1

Figures 1b to 1d show the experimental results (TG and DTG at three different heating rates: 5, 10 and 20 K min⁻¹) carried out with approximately 5 mg of TBBA (in this paper, when experimental and calculated papers are plotted in the same graph, experimental data are plotted with thick line). It can be observed that there are at least three fractions. DTG curves show two overlapped peaks around 550 K where the second one is bigger than the first and a third smaller peak is observed at higher temperatures (around 730 K). By increasing the heating rate, the two overlapped peaks are less defined, and only one peak is observed. Considering the fact that there is evaporation, one can deduce that the evaporation is small and/or coincides with another exothermic process, because any other big endothermic peak is observed in the decomposition range in Figure 1a.

Figures 2 and 3 shows the experimental results corresponding to pyrolysis runs carried out with 10 mg and 15 mg of sample, respectively. It can be observed that the lines corresponding to the runs in Figures 2a and 3a cross among themselves, indicating that there is a random factor that causes this fact. Usually, in the process in which evaporation takes place, the runs are not exactly reproducible due to the fact that the diffusion of the volatilized compounds is irregular, with small convection streams inside the holder and different evaporation surfaces of the liquid [11].

Figures 2 and 3

The results of three isothermal runs can be observed in Figure 4a. These runs were carried out at a constant heating rate until reaching the corresponding temperature.

Figure 4

3. Kinetic models

3.1 Correlation model

Initially, a potential model with competitive, parallel and consecutive processes was considered to correlate the experimental results. After analyzing different schemes and correlations, the following scheme was selected for TBBA pyrolysis:

Reaction 1 refers to the vaporization of the TBBA, which has previously melted. Reactions 2 and 3 are consecutive, and reaction 4 was introduced to explain the presence of a small peak at high temperatures (around 730 K) that is easily visible in the runs carried out with 5 mg. Reaction 5 is competitive with reaction 3.

In the previous reactions, TBBA_1 and TBBA_2 refer to different parts of the original material, “Volatiles_i” are the gases + volatiles evolved in the corresponding reactions ($i = 1$ to 5) and “Residue_i” is the residue formed in the decomposition of each reaction ($i = 1$ to 5). On the other hand, the small letters represent the yield coefficients representative of each reaction and, consequently, it is considered that they change neither with time nor with the extension of the reaction.

Moreover, each fraction has a yield coefficient that represents the maximum mass fractions obtainable by each reaction. In this way, $v_{i\infty}$ is the yield coefficient for the Volatiles_i and V is the mass fraction of volatiles.

It is very useful to introduce the concept of the conversion degree for each reaction, which is defined as the ratio between the mass fraction of volatiles obtained at any time during which the reaction is taking place (v_i) and the corresponding yield coefficient or mass fraction of volatiles at infinite time ($v_{i\infty}$), so:

$$\alpha_i = \frac{V_i}{V_{i\infty}} \quad i = 1 \text{ to } 5 \quad (1)$$

The kinetic equations, considering conversion/process degrees are the following:

$$\frac{d\alpha_1}{dt} = k_1(1 - \alpha_1 - \alpha_2)^{n_1} \quad (2)$$

$$\frac{d\alpha_2}{dt} = k_2(1 - \alpha_1 - \alpha_2)^{n_2} \quad (3)$$

$$\frac{d\alpha_3}{dt} = k_3(\alpha_2 - \alpha_3 - \alpha_5)^{n_3} \quad (4)$$

$$\frac{d\alpha_4}{dt} = k_4(\alpha_3 - \alpha_4)^{n_4} \quad (5)$$

$$\frac{d\alpha_5}{dt} = k_5(\alpha_2 - \alpha_3 - \alpha_5)^{n_5} \quad (6)$$

The kinetic constants can be expressed by the Arrhenius law as:

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right) \quad i = 1 \text{ to } 5 \quad (7)$$

By numerical integration of these equations, it is possible to calculate α_1 to α_5 at each time if the temperature program is known; the relationship between α_i values and the weight fraction (w) measured in the thermobalance is related with the volatiles (V) obtained by:

$$w = 1 - V = 1 - (v_{1\infty}\alpha_1 + v_{2\infty}\alpha_2 + v_{3\infty}\alpha_3 + v_{4\infty}\alpha_4 + v_{5\infty}\alpha_5) \quad (8)$$

The parameters obtained minimize the differences between experimental and calculated weight loss, as can be seen in Figures 1 to 3.

The objective function (OF) to minimize was the sum of the square differences between experimental and calculated weight loss values:

$$OF = \sum_{m=1}^M \sum_{j=1}^N (w_{mn}^{\text{exp}} - w_{mn}^{\text{calc}})^2 \quad m \text{ runs, } j \text{ points} \quad (9)$$

The model validity has been tested calculating the variation coefficient (VC):

$$VC(\%) = \frac{\sqrt{OF/(N-P)}}{\overline{w_{\text{exp}}}} \cdot 100 \quad (10)$$

where N and P are the number of data and parameters fitted, respectively, and $\overline{w_{\text{exp}}}$ is the average of the experimental weights. According to the procedure suggested by Martín-Gullón et al. [12], the optimization was performed in terms of a 'comparable

kinetic constant' K_i^* instead of optimizing k_{0i} . This constant is calculated at a temperature around the maximum decomposition rate ($T_{\max}$). A value of 0.64 was obtained from the optimization program for decreasing the great interrelation between the pre-exponential factor, the apparent activation energy and the reaction order. Since K_i^* , E_i and n_i are optimized, the pre-exponential factor k_{0i} is calculated using the following expression:

$$K_i^* = k_i (0.64)^{n_i} = k_{0i} \exp\left(\frac{-E_i}{RT_{\max}}\right) (0.64)^{n_i} \quad (11)$$

Consequently, the parameters optimized to minimize the objective function and the variation coefficient are the five values of K_i^* , apparent activation energy E_i and reaction orders n_i and four values of $v_{i\infty}$ for the reactions 2 to 5, because for the first reaction $v_{1\infty}$ is considered to be 1 due to the fact that it is an evaporation process.

All the runs shown previously have been correlated to the same set of parameters. The results are presented in Table 1.

Table 1

In view of Table 1, the analysis of the initial assumption and parameters can be more easily comprehensible.

For process 1, which represents the vaporization, the order obtained was very close to zero and the maximum weight fraction was assumed to be equal to 1. The pre-exponential factor and the apparent activation energy were calculated from the correlation of the data. Note that the apparent activation energy (around 63 kJ mol⁻¹) is close to the vaporization enthalpy of some organic compounds. In accordance with the analysis carried out elsewhere [13], the pre-exponential factor for the vaporization process 1, is related to the crucible dimension and operating condition, so:

$$\frac{d\alpha_1}{dt} = k_{o,1} \exp\left(-\frac{E_1}{RT}\right) = \frac{M}{m_o} \frac{FA_c D_o}{LR y_{air,ml}} (1/T_o)^{1.5} T^{0.5} P_v^o \quad (12)$$

where M is the molecular weight (544 kg kmol⁻¹), m_o is the initial amount (5, 10 and 15 mg), factor F can be considered equal to the unity, A_c is the cross area of the crucible (1.885·10⁻⁵ m²), L is height (4.5·10⁻³ m), R is the gas constant, $y_{air,ml}$ is the logarithmic mean value between the molar fraction of nitrogen on the liquid surface and at the top of the crucible (close to 1), T_o is a temperature inside the vaporization range (around 600 K), T is the real temperature and P_v^o is the vapor pressure. The value of the apparent activation energy should correspond to the slope for the variation of logarithm of

$T^{0.5}P_v^o/y_{\text{air,ml}}$ vs. $1/T$. With other crucibles, the apparent pre-exponential factor could be different in accordance with equation (12). In accordance with literature [13], it was explained that the parameters estimated from the TG data can be useful for other reaction/vaporization systems with convective transport. In the vaporization processes, the pre-exponential factor is proportional to the inverse of the initial mass, so the values for the other two initial masses are obtained taking into account this variation.

The remaining parameters were also obtained from the correlation of the data, except for reaction 4, whose order was assumed to be 2 and the value E_4/R to be 40000 K, to obtain a small peak in the DTG around 730 K. Therefore, the apparent activation energy of the reaction 4 (332 kJ mol^{-1}) is very high, as a consequence of the correlation of the data for considering this small fraction corresponding to 0.058 mass fraction of volatiles.

For reactions 2 and 3, the apparent activation energy values are around 150 kJ mol^{-1} , and are similar to other values considering thermal decompositions. The values of the reaction orders are a consequence of the correlation of the data, considering a complex system.

For reaction 5, the apparent activation energy is small (around 80.9 kJ mol^{-1}) probably indicating that there are many reactions involved with different temperature reaction ranges.

The simulated results are presented in Figures 1 to 4, together with the experimental ones. Note that in some cases the thick line corresponding to the experimental data and the thin line corresponding to the calculated data cannot be distinguished very well, indicating that they are close and the correlation was acceptable. Figures 4b to 4c and Figure 5 also show the volatile mass fraction evolved corresponding to each process: line 1 corresponds to the vaporization and lines 2 to 5 correspond to the reactions.

The overall variation coefficient is 7.0 %, which is an acceptable value considering that all dynamic and isothermal runs have been correlated with the same set of parameters.

Figure 5

3.2 Simplified mechanistic model

Considering the interesting paper of Marongiu et al. [8], a simplified kinetic model has been developed. The reactions considered are shown in Table 2.

Table 2

These reactions correspond to the initiation and first recombination reactions, taking into account the most important chemical species, compounds and radicals (indicated with an asterisk). The pre-exponential factor and the activation energy are the same as those presented in the paper by Marongiu et al. [8]. One of the simplifications assumed is that after the formation of molecules with 30 carbon atoms, the reaction follows to form a mixture of volatiles ($C_3H_2O_2Br_2$) and a residue. For these reactions of formation of $C_3H_2O_2Br_2$ 1 to 5, the pre-exponential factor and the activation energy are deduced from the correlation of the experimental data.

In addition to the chemical reactions, the evaporation process has been taken into account for tetrabromobisphenol A (TBBA) and tribromobisphenol A (TriBBA), in accordance with the equations:

$$N_{TBBA}^{evap} = F_{TBBA} \frac{A_c k^0}{LR} T^{1/2} \frac{1}{y_{TBBA}} \exp\left(A - \frac{B}{T - C}\right) \quad (13)$$

$$N_{TriBBA}^{evap} = F_{TriBBA} \frac{A_c k^0}{LR} T^{1/2} \frac{1}{y_{TriBBA}} \exp\left(A - \frac{B}{T - C}\right) \quad (14)$$

where N_i^{evap} is the molar flow of the compound of interest due to evaporation, A_c the cross area of the crucible ($1.88 \cdot 10^{-5} \text{ m}^2$), L the height from the level of the liquid to the top of the crucible (the height of the crucible is $4.5 \cdot 10^{-3} \text{ m}$), T the absolute temperature, y_{TBBA} and y_{TriBBA} are the molar fractions of TBBA and TriBBA, respectively, k^0 is the Chapman-Enskog constant, and A , B , C the Antoine constants which were estimated experimentally by Marsanich et al. [6] ($k^0 = 4.75 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1.5}$, $A = -8.43$; $B = 255$ and $C = -409$). For TBBA, a factor F_{TBBA} close to the unit must be considered, whereas for TriBBA, the corresponding factor F_{TriBBA} must be higher than the unit, because the same values of k^0 , A , B and C have been considered for both species. These two correcting factors have been optimized, but considering the yields of both compounds reported in literature. For dibromobisphenol (DBBA), it was assumed that the vaporization was immediate.

The kinetic equations considered for each component N_j are the following:

$$\frac{d \frac{m_i}{M_i}}{dt} = \sum \alpha_{ij} R_j M_i - N_i^{evap} M_i \quad (15)$$

where m_i is the mass of component i , M_i the corresponding molecular weight, V the volume of the liquid, R_j the reaction rate in accordance with the corresponding elemental reaction and α_{ij} is the stoichiometric coefficient of component i in reaction j .

For each reaction R_j the corresponding kinetic equation can be expressed as:

$$R_j = A_j T^m \exp\left(-\frac{E_j}{RT}\right) \prod \frac{m_i}{M_i} \quad (16)$$

where A_j is the pre-exponential factor, m an exponent depending on the reaction and the last term corresponds to the product of the molar concentrations of the components involved in the reaction.

The kinetic parameters for the formation of the compounds $C_7H_5O_2Br$ (A , n and E) and the molecular weights have also been optimized for all the dynamic runs, whereas for the isothermal ones, a molecular weight was determined for each run. Note that the reaction corresponding to the formation of these compounds is an overall reaction, considering the formation of the compounds not previously considered: bromobisphenol A, bisphenol, bromophenols and more HBr . The results are shown in Table 3.

Table 3

Figures 6 to 8 show the variation of the weight fraction and DTG (experimental and calculated values) of the runs carried out at different heating rates and using 5, 10 and 15 mg of sample, respectively. Figure 9 shows the variations corresponding to the isothermal runs. The variation coefficient is 8.2 %, indicating an acceptable correlation.

Figures 6 to 9

It can be observed that the apparent activation energy of the overall reaction is low, considering that this reaction involves several reactions with different kinetics.

The molecular weight of the volatiles evolved in the dynamic runs, in accordance with the formula $C_7H_5O_2Br$ is 126, corresponding to a mixture of bromobisphenol A, bisphenol, bromophenols and HBr . A similar molecular weight is deduced for the isothermal run carried out at 600 K. Nevertheless, the molecular weight for the volatiles evolved at 522 K is nil, indicating that there are no reactions for the formation of these volatiles, and evaporation is the main process. At 570 K, the molecular weight is 67, which is lower than the molecular weight of HBr (80), indicating that only some reactions take place and mainly leading to the formation of HBr .

The simplified model is an alternative between the potential model and the mechanistic one. It is more adaptable and reproduces the second process of decomposition, after the first peak, which is not reproduced by the mechanistic model. This second process has been also observed in a recent paper [13], when studying the thermal degradation of TBBA in the presence of metal oxide. Nevertheless, it must be clarified that the simplified mechanistic model only gives information on the weight loss of the sample, the vaporization process and the average molecular weight of the volatiles evolved. The distribution of products should be obtained experimentally.

The simulated results, considering the vaporization of TBBA, TriBBA and DBBA and the evolution of HBr are coherent with those shown by Marongiu et al. [8].

The results predicted by the model are also consistent with those obtained in the experiments carried out in the laboratory for measuring the emission rate of HBr (Figure 9). These results of IC-determination of HBr are given in Table 4. Nevertheless, it must be emphasized that the data obtained with the laboratory reactor are the results of a primary decomposition (similar to that of TGA) and to the secondary reactions inside the reactor.

On the other hand, the results corresponding to the evolution of TBBA, triBBA, DBBA and the sum HBr+other volatiles are consistent with the data presented by Marongiu et al. [8]. An exact comparison cannot be done due to the diffusion effect that depends on the geometry of the crucible used.

For the experiment carried out at 873 K, different compounds were detected in significant concentrations: bromomethane, benzene, dibromomethane, tribromomethane, phenol, 1,3 diethyl-5-methylbenzene, benzoic acid, 2-bromo-4-methyl-phenol, naphthalene, bromophisphenol A, DBBA, TriBBA, TBBA and many other brominated and non-brominated compounds as a consequence of the complexity of the primary and secondary reactions involved. The presence of DBBA, TriBBA and TBBA are consistent with the experimental models of decomposition.

The development of simple decomposition models can be used for the design of reactors, and the composition of the product stream, with a complex network of reactions, can be deduced experimentally.

With the simplified mechanistic model, the primary decomposition can be obtained for operating conditions in the range of those considered in this paper, integrating the differential equations corresponding to the reaction involved. This simplified model only gives information about the yields of TBBA, TriBBA, DBBA

and HBr+volatiles. The determination of products and the corresponding yields in reactors, including brominated dioxins, will be the subject of another work.

If only an approximation of the evaporation/decomposition of TBBA is sufficient, the potential model could be used, but taking into account that the vaporizations depends on the TBBA diffusion.

Table 4

4. Conclusions

The volatilization process of the complex TBBA pyrolysis can be reproduced by two correlation models, without ignoring the vaporization process that takes place during the decomposition. By the potential model, the experimental values are correlated satisfactorily considering five processes: the TBBA volatilization and four processes, considering chemical reactions and vaporizations. A simplified model of a mechanistic one has been also useful to correlate the volatilization process.

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REFERENCES

- [1] EBFRIIP (European Brominated Flame Retardant Industry Panel), 2006. Update on TBBPA risk assessment (1) : <<http://www.bsef.com/media-room/2006-2>>.
- [2] A. Covaci, S. Voorspoels, M.A.-E. Abdallah, T. Geens, S. Harrad and R.J. Law, Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives, *J. Chromatogr. A* 1216 (2009) 346-363.
- [3] J.A. Caballero, J.A. Conesa, Kinetics in thermal decomposition, *J. Ana. Appl. Pyrolysis* 73,(2005) 85-100.
- [4] A. Factor, Thermal decomposition of 4,4'-isopropylidene bis-2,6-dibromophenol (tetrabromobisphenol-A, *J. Polym. Sci. part. A, Polym. Chem.* 11 (1973) 1691-1701.
- [5] M.P. Luda, A.I. Balabanovich, A. Hornung and G. Camino, Thermal degradation of a brominated bisphenol a derivative, *Polym. Adv. Technol.* 14 (2003) 741-748.
- [6] K. Marsanich, S. Zanelli, F. Barontini and V. Cozzani, Evaporation and thermal degradation of tetrabromobisphenol A above the melting point, *Thermochim. Acta* 421 (2004) 95-103.
- [7] F. Barontini, V. Cozzani, K. Marsanich, V. Raffa, L. Petarca, An experimental investigation of tetrabromobisphenol A decomposition pathways, *J. Anal. Appl. Pyrolysis.* 72 (2004) 41-53.
- [8] A. Marongiu, G. Bozzano, M. Dente, E. Ranzi, T. Faravelli, Detailed kinetic modelling of pyrolysis of tetrabromobisphenol A, *J. Anal. Appl. Pyrolysis* 80 (2007) 325-345.
- [9] M. Grønli, M.J. Antal, G. Varhegyi, A round-robin study of cellulose pyrolysis kinetics by thermogravimetry, *Ind. Eng. Chem. Res.* 38 (1999) 2238-2244.
- [10] J. Moltó, R. Font, A. Gálvez, J.A. Conesa, Pyrolysis and combustion of electronic wastes, *J. Anal. Appl. Pyrolysis*, 84, (2009) 68-78.
- [11] R. Font, M.F. Gómez-Rico, N. Ortuño, Analysis of the vaporization process in TG apparatus and its incidence in pyrolysis, *J. Anal. Appl. Pyrolysis*, 91(2011), 89-96.
- [12] I. Martín-Gullón, M.F. Gómez-Rico, A. Fullana, R. Font, Interrelation between the kinetic constant and the reaction order in pyrolysis, *J. Anal. Appl. Pyrolysis* 68-69 (2003) 645-655.
- [13] O. Terakado, R. Ohhashi and M. Hirasawa, Thermal degradation study of tetrabromobisphenola under the presence metal oxide: compariosn of bromine fixation ability. *J. Anal Appl. Pyrolysis*, 91 (2011) 303-309.

LEGEND OF TABLES

TABLE 1. Kinetic parameters of the correlation model

TABLE 2. Reactions considered in the simplified mechanistic model.

TABLE 3. Optimized parameters for the simplified mechanistic model

TABLE 4. HBr emission (in weight percentage) in the pyrolysis of TBBA at three different temperatures.

LEGEND OF FIGURES

FIGURE 1. Different pyrolysis runs for TBBA carried out with 5 mg of sample. Experimental and correlated potential model data:

- a) Variation of the weight fraction and DTA of the runs carried out with 5 mg.
- b) Variation of the weight fraction and DTG of the run carried out with 5 mg at 5 K min^{-1} .
- c) Variation of the weight fraction and DTG of the run carried out with 5 mg at 10 K min^{-1} .
- d) Variation of the weight fraction and DTG of the run carried out with 5 mg at 20 K min^{-1} .

FIGURE 2. Different pyrolysis runs for TBBA carried out with 10 mg of sample. Experimental and correlated potential model data:

- a) Variation of the weight fraction and DTA of the runs carried out with 10 mg.
- b) Variation of the weight fraction and DTG of the run carried out with 10 mg at 5 K min^{-1} .
- c) Variation of the weight fraction and DTG of the run carried out with 10 mg at 10 K min^{-1} .
- d) Variation of the weight fraction and DTG of the run carried out with 10 mg at 20 K min^{-1} .

FIGURE 3. Different pyrolysis runs for TBBA carried out with 15 mg of sample. Experimental and correlated potential model data:

- a) Variation of the weight fraction and DTA of the runs carried out with 15 mg.
- b) Variation of the weight fraction and DTG of the run carried out with 15 mg at 5 K min^{-1} .
- c) Variation of the weight fraction and DTG of the run carried out with 15 mg at 10 K min^{-1} .
- d) Variation of the weight fraction and DTG of the run carried out with 15 mg at 20 K min^{-1} .

FIGURE 4. Isothermal pyrolysis runs for TBBA carried out with 5 mg of sample. Experimental and correlated potential model data:

- a) Variation of the experimental weight fraction vs. time in isothermal runs (dynamic runs to the nominal temperature).
- b), c) and d) Variation of the simulated weight fraction and volatile mass fraction corresponding to the reactions.

FIGURE 5. a), b) and c) Pyrolysis runs for TBBA carried out with 5, 10 and 15 mg of sample, respectively. Variation of the simulated weight fraction and volatile mass fraction corresponding to the reactions by the potential model.

FIGURE 6. Different pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 5 mg of sample:

- a) Variation of the weight fraction and DTG of the run carried out with 5 mg at 5 K min⁻¹.
- b) Variation of the weight fraction and DTG of the run carried out with 5 mg at 10 K min⁻¹.
- c) Variation of the weight fraction and DTG of the run carried out with 5 mg at 20 K min⁻¹.
- d) Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

FIGURE 7. Different pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 10 mg of sample:

- a) Variation of the weight fraction and DTG of the run carried out with 10 mg at 5 K min⁻¹.
- b) Variation of the weight fraction and DTG of the run carried out with 10 mg at 10 K min⁻¹.
- c) Variation of the weight fraction and DTG of the run carried out with 10 mg at 20 K min⁻¹.
- d) Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

FIGURE 8. Different pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 15 mg of sample:

- a) Variation of the weight fraction and DTG of the run carried out with 10 mg at 5 K min⁻¹.
- b) Variation of the weight fraction and DTG of the run carried out with 10 mg at 10 K min⁻¹.
- c) Variation of the weight fraction and DTG of the run carried out with 10 mg at 20 K min⁻¹.
- d) Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

FIGURE 9. Isothermal pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 5 mg of sample:

- a) Variation of the experimental and calculated weight fractions vs. time.
- b), c) and d) Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

TABLE 5. Kinetic parameters of the correlation model

PYROLYSIS OF TBBA	
$\text{TBBA}_1 \xrightarrow{1} \text{Volatiles}_1$ $\text{TBBA}_2 \xrightarrow{2} (1 - v_{2\infty}) \text{Residue}_2 + v_{2\infty} \text{Volatiles}_2$ $(1 - v_{2\infty}) \text{Residue}_2 \xrightarrow{3} (1 - v_{2\infty} - v_{3\infty}) \text{Residue}_3 + v_{3\infty} \text{Volatiles}_3$ $(1 - v_{2\infty} - v_{3\infty}) \text{Residue}_3 \xrightarrow{4} (1 - v_{2\infty} - v_{3\infty} - v_{4\infty}) \text{Residue}_4 + v_{4\infty} \text{Volatiles}_4$ $(1 - v_{2\infty}) \text{Residue}_2 \xrightarrow{5} (1 - v_{2\infty} - v_{5\infty}) \text{Residue}_5 + v_{5\infty} \text{Volatiles}_5$	
$k_{10} (\text{s}^{-1})$ (for 10 mg)	$2.650 \cdot 10^2$
(value proportional to the inverse of the initial mass)	
$E_1 (\text{kJ mol}^{-1})$	63.34
n_1	0
$v_{1\infty}$	1
$k_{20} (\text{s}^{-1})$	$7.008 \cdot 10^{10}$
$E_2 (\text{kJ mol}^{-1})$	145.9
n_2	0.0754
$v_{2\infty}$	0.303
$k_{30} (\text{s}^{-1})$	$2.695 \cdot 10^{10}$
$E_3 (\text{kJ mol}^{-1})$	132.7
n_3	5.89
$v_{3\infty}$	0.596
$k_{40} (\text{s}^{-1})$	$4.45 \cdot 10^{22}$
$E_4 (\text{kJ mol}^{-1})$	332.5
n_4	2
$v_{4\infty}$	0.058
$k_{50} (\text{s}^{-1})$	$4.427 \cdot 10^3$
$E_5 (\text{kJ mol}^{-1})$	80.9
n_5	2.66
$v_{5\infty}$	0.238
V.C (%)	7.0

TABLE 6. Reactions considered in the simplified mechanistic model.

Reaction						A (s ⁻¹)	m	E (J mol ⁻¹)
	C ₁₅ H ₁₂ Br ₄ O ₂	→	*C ₁₅ H ₁₂ Br ₃ O ₂	+ *Br		8.00E+13	0	180000
*C ₁₅ H ₁₂ Br ₃ O ₂	+ *C ₁₅ H ₁₂ Br ₃ O ₂	→	C ₃₀ H ₂₄ Br ₆ O ₄			3.1623E+08	1	30000
	C ₃₀ H ₂₄ Br ₆ O ₄	→	C?H?O?Br1	+ residue1		?	0	?
C ₁₅ H ₁₂ Br ₄ O ₂	+ C ₁₅ H ₁₂ Br ₄ O ₂	→	C ₁₅ H ₁₃ Br ₃ O ₂	+ *Br	+ *C ₁₅ H ₁₁ Br ₄ O ₂	1.00E+13	0	172000
*C ₁₅ H ₁₁ Br ₄ O ₂	+ *C ₁₅ H ₁₁ Br ₄ O ₂	→	C ₃₀ H ₂₂ Br ₈ O ₄			3.1623E+08	1	30000
	C ₃₀ H ₂₂ Br ₈ O ₄	→	C?H?O?Br2	+ residue2		?	0	?
C ₁₅ H ₁₃ Br ₃ O ₂	+ C ₁₅ H ₁₃ Br ₃ O ₂	→	C ₁₅ H ₁₄ Br ₂ O ₂	+ *Br	+ *C ₁₅ H ₁₂ Br ₃ O ₂	1.00E+13	0	172000
*C ₁₅ H ₁₂ Br ₃ O ₂	+ *C ₁₅ H ₁₂ Br ₃ O ₂	→	C ₃₀ H ₂₄ Br ₆ O ₄			3.1623E+08	1	30000
	C ₃₀ H ₂₄ Br ₆ O ₄	→	C?H?O?Br3	+ residue3		?	0	?
C ₁₅ H ₁₃ Br ₃ O ₂		→	*C ₁₅ H ₁₃ Br ₂ O ₂	+ *Br		8.00E+13	0	180000
C ₁₅ H ₁₄ Br ₂ O ₂	+ C ₁₅ H ₁₄ Br ₂ O ₂	→	C ₁₅ H ₁₅ BrO ₂	+ *Br	+ *C ₁₅ H ₁₃ Br ₂ O ₂	1.00E+13	0	172000
*C ₁₅ H ₁₃ Br ₂ O ₂	+ *C ₁₅ H ₁₃ Br ₂ O ₂	→	C ₃₀ H ₂₆ Br ₄ O ₄			3.1623E+08	1	30000
	C ₃₀ H ₂₆ Br ₄ O ₄	→	C?H?O?Br4	+ residue4		?	0	?
C ₁₅ H ₁₄ Br ₂ O ₂		→	*C ₁₅ H ₁₄ BrO ₂	+ *Br		8.00E+13	0	180000
*C ₁₅ H ₁₄ BrO ₂	+ *C ₁₅ H ₁₄ BrO ₂	→	C ₃₀ H ₂₈ Br ₂ O ₄			3.1623E+08	1	30000
C ₃₀ H ₂₈ Br ₂ O ₄		→	C?H?O?Br5	+ residue5		?	0	?

TABLE 7. Optimized parameters for the simplified mechanistic model

Parameter	Value
F_{TBBA}	1.2
F_{TriBBA}	7.0
$A \text{ (s}^{-1}\text{)}$	$2.60 \cdot 10^{-3}$
$E \text{ (J mol}^{-1}\text{)}$	23181
Molecular weight $\text{C}_7\text{H}_7\text{O}_2\text{Br}$? dynamic runs	126
Molecular weight $\text{C}_7\text{H}_7\text{O}_2\text{Br}$? isothermal run 600 K	120
Molecular weight $\text{C}_7\text{H}_7\text{O}_2\text{Br}$? isothermal run 570 K	67
Molecular weight $\text{C}_7\text{H}_7\text{O}_2\text{Br}$? isothermal run 522 K	0
V.C. (%)	8.2

TABLE 8. HBr emission (in weight percentage) in the pyrolysis of TBBA at three different temperatures.

Temperature (K)	522	570	600
% (g HBr / 100 g TBBA)	2.4	14.3	21.4

FIGURE 1. Different pyrolysis runs for TBBA carried out with 5 mg of sample. Experimental and correlated potential model data:

- Variation of the weight fraction and DTA of the runs carried out with 5 mg.
- Variation of the weight fraction and DTG of the run carried out with 5 mg at 5 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 5 mg at 10 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 5 mg at 20 K min⁻¹.

FIGURE 2. Different pyrolysis runs for TBBA carried out with 10 mg of sample. Experimental and correlated potential model data:

- Variation of the weight fraction and DTA of the runs carried out with 10 mg.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 5 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 10 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 20 K min⁻¹.

FIGURE 3. Different pyrolysis runs for TBBA carried out with 15 mg of sample. Experimental and correlated potential model data:

- Variation of the weight fraction and DTA of the runs carried out with 15 mg.
- Variation of the weight fraction and DTG of the run carried out with 15 mg at 5 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 15 mg at 10 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 15 mg at 20 K min⁻¹.

FIGURE 4. Isothermal pyrolysis runs for TBBA carried out with 5 mg of sample. Experimental and correlated potential model data:

a) Variation of the experimental weight fraction vs. time in isothermal runs (dynamic runs to the nominal temperature).

b), c) and d) Variation of the simulated weight fraction and volatile mass fraction corresponding to the reactions.

FIGURE 5. a), b) and c) Pyrolysis runs for TBBA carried out with 5, 10 and 15 mg of sample, respectively. Variation of the simulated weight fraction and volatile mass fraction corresponding to the reactions by the potential model.

FIGURE 6. Different pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 5 mg of sample:

- a) Variation of the weight fraction and DTG of the run carried out with 5 mg at 5 K min⁻¹.
- b) Variation of the weight fraction and DTG of the run carried out with 5 mg at 10 K min⁻¹.
- c) Variation of the weight fraction and DTG of the run carried out with 5 mg at 20 K min⁻¹.
- d) Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

FIGURE 7. Different pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 10 mg of sample:

- Variation of the weight fraction and DTG of the run carried out with 10 mg at 5 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 10 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 20 K min⁻¹.
- Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

FIGURE 8. Different pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 15 mg of sample:

- Variation of the weight fraction and DTG of the run carried out with 10 mg at 5 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 10 K min⁻¹.
- Variation of the weight fraction and DTG of the run carried out with 10 mg at 20 K min⁻¹.
- Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.

FIGURE 9. Isothermal pyrolysis runs (experimental and calculated values obtained with the simplified mechanistic model) for TBBA carried out with 5 mg of sample:

a) Variation of the experimental and calculated weight fractions vs. time.

b), c) and d) Variation of the simulated weight fraction and weight fractions of vaporized TBBA, TriBBA, DBBA and evolved HBr+volatiles at 20 K min⁻¹.