Heats of Combustion of Brominated Epoxies

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16. Abstract

The widespread use of brominated flame retardants and fire extinguishing agents in aircraft cabins and recent concerns about their combustion toxicity and environmental impact prompted a study to understand the mechanism by which bromine inhibits the flaming combustion of plastics as a first step towards identifying alternative chemicals or compounds. The heats of combustion of bromine-containing epoxies were calculated from the known atomic composition and compared to measured values in flaming and nonflaming combustion. The heat of flaming combustion was measured in a fire/cone calorimeter (CC) and by burning pyrolysis products in a methane laminar diffusion flame (pyrolysis-flaming combustion calorimetry (PFCC)). Heats of nonflaming combustion were measured by pyrolysis-combustion flow calorimetry (PCFC). The results of these tests indicate that the combustion heat released by these materials decreases with increasing amounts of brominated components as a result of incomplete combustion, char formation, and dilution of the materials with noncombustible bromine. Gas-phase combustion efficiency in the various test methods decreased as: PCFC > PFCC > CC.

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LIST OF ACRONYMS

DDA	Diglycidylether of bisphenol A
BDBA	Tetrabromodiglycidylether of bisphenol A
BBA	Tetrabromobisphenol A
CC	Cone calorimeter
PCFC	Pyrolysis-combustion flow calorimetry
PFCC	Pyrolysis-flaming combustion calorimetry
Avg.HRR	Average heat release rate
THR	Total heat released
Avg.MLR	Average mass loss rate
ΔH_c	Heat of complete combustion

EXECUTIVE SUMMARY

The widespread use of brominated flame retardants and fire extinguishing agents in aircraft cabins and recent concerns about their combustion toxicity and environmental impact prompted a study to understand the mechanism by which bromine inhibits the flaming combustion of plastics as a first step towards identifying alternative chemicals or compounds. The heats of combustion of bromine-containing epoxies were calculated from the known atomic composition and compared to measured values in flaming and nonflaming combustion. The heat of flaming combustion was measured in a fire/cone calorimeter (CC) and by burning pyrolysis products in a methane laminar diffusion flame (pyrolysis-flaming combustion calorimetry (PFCC)). Heats of nonflaming combustion were measured by pyrolysis-combustion flow calorimetry (PCFC). The results of these tests indicate that the combustion heat released by these materials decreases with increasing amounts of brominated components as a result of incomplete combustion, char formation, and dilution of the materials with noncombustible bromine. Gas-phase combustion efficiency in the various test methods decreased as: PCFC > PFCC > CC.

BACKGROUND

Halogen-containing flame retardants are the largest single category of chemical additive used to reduce the flammability of plastics used for home furnishings, textiles, electrical equipment, consumer electronics, automobile interiors, and commercial aircraft cabin materials. Halogen (e.g., bromine, chlorine, fluorine, iodine) is the active ingredient in most of the flame retardants used for aircraft cabin materials and all of the fire extinguishing and suppression agents used in aviation, despite the fact that very little is known about its mode of action. The reason that bromine is so efficient at preventing ignition of plastics and suppressing fires is because bromine interferes with (inhibits) the normal chemical combustion processes so that combustion is incomplete and by-products such as unburned hydrocarbons, toxic carbon monoxide, and soot (visible smoke) are produced in large yield. In the early stages of a compartment fire, such as in a room or aircraft cabin, these incomplete combustion products accumulate and become the primary hazard to occupants. In addition to their combustion toxicity, flame-retardant chemicals containing bromine have been found to pose unacceptable environmental risks because they accumulate in animal (e.g., human) tissue and are persistent in the environment (e.g., marine sediments). Two of the most widely used brominated flame retardants for home furnishings have been banned in Europe and California beginning in 2005 and many others are under scrutiny.

During the past 50 years, a substantial amount of research has been done to understand the mechanism of inhibition of the gas-phase combustion of hydrocarbons by brominated compounds. It has been established that brominated fire-suppressing agents (such as CF_3Br) act as scavengers of reactive radicals (chemical mode of action) and as heat capacity energy sinks and diluents (physical mode of action) [1]. Dependences of burning velocity on the concentration of the agents have been analyzed and the inhibitors have been ranked in terms of their efficiency [2]. However, the mechanism of action of brominated flame retardants used in plastics is not so well developed because the gas-phase (flame) and condensed-phase (solid) processes of flaming combustion are highly coupled and difficult to isolate. While it is known that the flame retardants affect both the condensed-phase degradation of a polymer and the gas-phase combustion of the degradation products [3], the relative importance of these effects remain unclear.

In the present study, the heats of combustion of blends of bisphenol-A epoxy, brominated bisphenol-A epoxy, and brominated bisphenol A were calculated from the known atomic compositions and compared to the heats of combustion measured in flaming and nonflaming combustion. A quantitative analysis of the factors responsible for the reduction in heat release imparted by bromine is presented.

MATERIALS

Materials used in this study were prepared by blending diglycidylether of bisphenol A (DBA) with tetrabromodiglycidylether of bisphenol A (BDBA) or with tetrabromobisphenol A (BBA). A range of blends containing up to 80 wt.% of BDBA and up to 40 wt.% of BBA was made. The blends were cured at 120°C using 1-2 wt.% of 2-ethyl-4-methylimidazole.

METHODS

Flammability of the materials was evaluated using the cone calorimetry (CC), pyrolysis-combustion flow calorimetry (PCFC), and pyrolysis-flaming combustion calorimetry (PFCC). The CC and PCFC methods are described in references 4 and 5, respectively. PFCC is a new method. A schematic diagram of the PFCC setup is shown in figure 1. In this method, a small sample of material (about 30 mg) is pyrolyzed at a constant heating rate ($2\,K\,s^{-1}$ was used in this study). Gaseous products of pyrolysis are swept by a flow of methane ($0.8\,cm^3\,s^{-1}$) feeding a laminar diffusion flame, which is open to the atmosphere. The heat released as a result of combustion is measured by means of oxygen consumption [6].
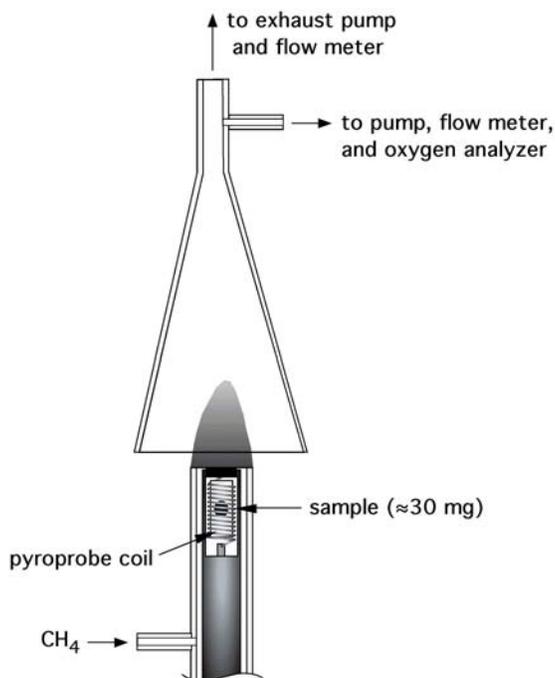
FIGURE 1. PYROLYSIS-FLAMING COMBUSTION
CALORIMETRY APPARATUS

RESULTS

All experimental methods used in this study rely on the oxygen consumption technique for the measurement of heat released by materials. This technique is based on the fact that for a large number of organic compounds, the heat released per gram of oxygen consumed in the combustion is constant and equal to 13.1 kJ [6]. To make sure that this approach is still valid when applied to brominated materials, the heat release constant was used to calculate heats of combustion of 20 small (6-20 atoms) brominated organic compounds, for which experimental heats of formation are available [7]. The amount of oxygen consumed by a unit amount of compound was determined from the stoichiometry of a complete combustion reaction:

$$C_xH_yO_zBr_k \;+\; (x+(y-k)/4-z/2)\,O_2 \;=\; x\,CO_2 \;+\; (y-k)/2\,H_2O(gas) \;+\; k\,HBr$$
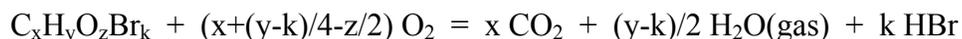
The calculated heats of combustion were found to be, in average, within 3% of those determined from experimental heats of formation (the maximum deviation was 8%). This means that the accuracy of the oxygen consumption technique is not compromised by the presence of bromine.

The results of the CC, PCFC, and PFCC tests are summarized in tables 1 and 2. The average heat release rate (Avg.HRR) and total heat released (THR) decrease systematically with increasing amounts of brominated compounds. Addition of the compounds promotes formation of char. All methods indicate that on the wt.% basis, BBA is a more efficient flame retardant than BDBA.

TABLE 1. SUMMARY OF CONE CALORIMETRY DATA OBTAINED AT THE EXTERNAL HEAT FLUX OF 50 kWm^{-2}

Material[a]	Avg.HRR[b] kW m^{-2}	THR[c] kJ g^{-1}	Avg.MLR[b] g m^{-2} s^{-1}	Char wt.%
DBA	552	22.6	22.0	5.5
20 wt.% BDBA (9.3 wt.% Br)	541	16.0	37.1	7.4
40 wt.% BDBA (19.5 wt.% Br)	346	10.8	34.7	16.4
60 wt.% BDBA (29.2 wt.% Br)	228	9.3	28.4	13.4
80 wt.% BDBA (38.5 wt.% Br)	180	6.4	--	15.1
10 wt.% BBA (5.9 wt.% Br)	519	19.3	28.7	8.2
20 wt.% BBA (11.2 wt.% Br)	346	13.0	26.9	13.1
30 wt.% BBA (18.2 wt.% Br)	279	9.9	28.7	17.2
40 wt.% BBA (22.9 wt.% Br)	272	9.2	31.4	12.9

[a] 10×10×0.45(±0.10) cm samples were used in the measurements.

[b] The Avg.HRR and average mass loss rate (Avg.MLR) are obtained from the data collected during the time between the initial increase of the heat release rate above 150 kW m^{-2} and its final decrease below 150 kW m^{-2}.

[c] The value of the THR is divided by the initial weight of the sample.

TABLE 2. SUMMARY OF PCFC AND PFCC DATA

Material	PCFC THR[a] kJ g^{-1}	PCFC Char wt.%	PFCC THR[a] kJ g^{-1}	PFCC Char wt.%
DBA	25.7	5.3	19.2	9.6
20 wt.% BDBA (9.3 wt.% Br)	21.0	8.4	18.3	14.4
40 wt.% BDBA (19.5 wt.% Br)	18.2	11.3	16.7	18.7
60 wt.% BDBA (29.2 wt.% Br)	15.8	13.6	13.1	16.6
80 wt.% BDBA (38.5 wt.% Br)	12.9	14.9	9.6	20.0
10 wt.% BBA (5.9 wt.% Br)	23.0	7.7	19.4	13.5
20 wt.% BBA (11.2 wt.% Br)	21.3	8.7	17.6	13.5
30 wt.% BBA (18.2 wt.% Br)	19.3	8.5	15.7	17.2
40 wt.% BBA (22.9 wt.% Br)	17.7	10.7	14.5	14.8

[a] The value of THR is divided by the initial weight of the sample.

To analyze the THR and Avg.HRR trends, it is necessary to determine the heats of complete combustion (ΔH_c) of the materials under study. Since atomic compositions of the materials are known, the heats of complete combustion can be calculated from the stoichiometry of the corresponding reactions and the heat release constant (as described above). Assuming that the atomic compositions are not a significant source of uncertainties, these calculations should be at least as accurate as the measurements performed in this work because both approaches are based on the same empirical relation between the oxygen consumption and released heat. The results of the calculations are shown in table 3. The same approach was used to calculate ΔH_c of char (also given in table 3). The char was assumed to consist of pure carbon.

TABLE 3. HEATS OF COMPLETE COMBUSTION OF MATERIALS AND CHAR
NORMALIZED BY WEIGHT OR BY NUMBER OF MOLES OF
INITIAL COMPONENTS (DBA, BDBA, AND BBA)

Material	ΔH_c $\mathrm{kJ\,g^{-1}}$	ΔH_c $\mathrm{kJ\,mol^{-1}}$
DBA	30.8	10.7×10^3
20 wt.% BDBA (9.3 wt.% Br)	27.8	10.5
40 wt.% BDBA (19.5 wt.% Br)	24.4	10.4
60 wt.% BDBA (29.2 wt.% Br)	21.2	10.3
80 wt.% BDBA (38.5 wt.% Br)	18.1	10.1
10 wt.% BBA (5.9 wt.% Br)	29.0	10.5
20 wt.% BBA (11.2 wt.% Br)	27.3	10.2
30 wt.% BBA (18.2 wt.% Br)	25.1	9.8
40 wt.% BBA (22.9 wt.% Br)	23.6	9.5
char (carbon)	34.9	--

Knowledge of the heats of complete combustion makes it possible to determine the overall efficiencies of the gas-phase combustion processes that took place in the CC, PCFC, and PFCC tests.

$$\mathrm{Comb.Eff.} = \frac{\mathrm{THR}}{\Delta H_c (\mathrm{material}) - \Delta H_c (\mathrm{char}) * \mathrm{ch.yld.}} \text{,}$$

where ch.yld. is the mass fraction of char formed in a given experiment. Dependencies of the combustion efficiencies on the mass fraction of bromine (in the initial materials) are shown in figure 2. The CC dependencies are consistent with the notion that bromine acts as a suppressant of the gas-phase combustion. However, according to the PCFC and PFCC methods, addition of brominated compounds produces a slight increase in the combustion efficiency. The difference in the trends can be explained by differences in the combustion conditions. In particular, the temperatures in the PCFC and PFCC combustion zones are expected to be notably lower than the temperature in the CC combustion zone. According to the observations summarized in

reference 3, the role of bromine may change from an inhibitor of the gas-phase combustion to a promoter with decreasing temperature.
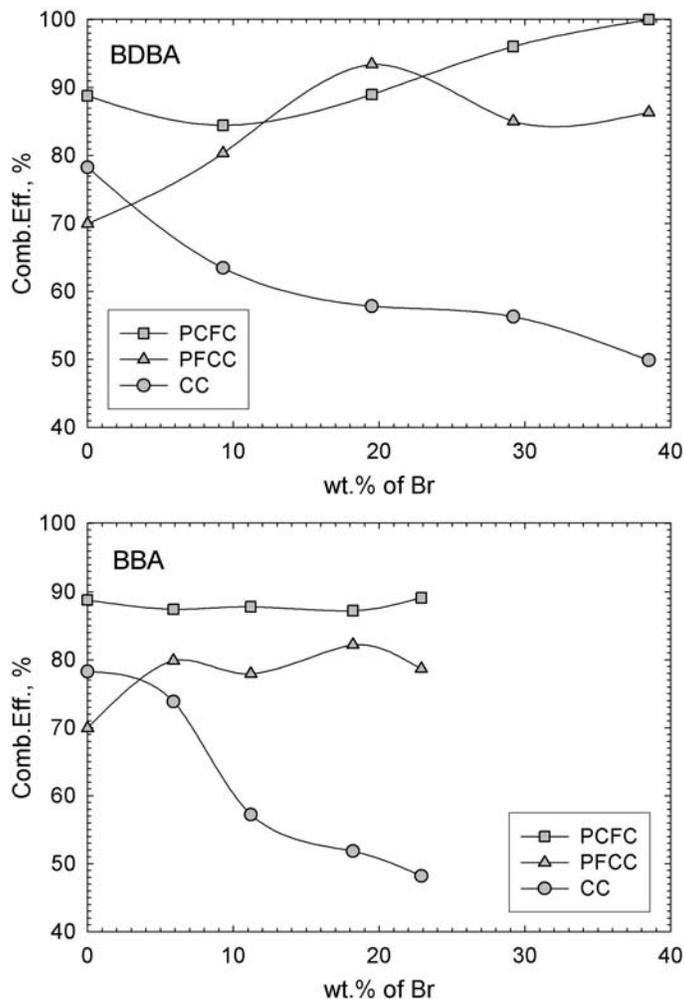
FIGURE 2. GAS-PHASE COMBUSTION EFFICIENCIES OF DBA-BDBA AND
DBA-BBA BLENDS

Since CC is the most realistic flammability test used in this work, further analysis is focused on the CC data. By performing the ΔH_c and combustion efficiency calculations, all mechanisms by which addition of the brominated compounds reduces the THR were identified. The heats of complete combustion of BDBA and BBA are lower than that of DBA. Thus, when one of the brominated compounds is added to DBA, the heat of complete combustion of a unit amount of material decreases (see table 3). In this report, this effect is referred to as dilution. A more combustible material is diluted by a less combustible material. The brominated compounds also promote the formation of char (noncombustible residue). This constitutes the second mechanism by which the THR is reduced. Finally, brominated compounds also promote incomplete combustion (i.e., decrease the gas-phase combustion efficiency), which constitutes the third mechanism.

5

The dilution contributes most to the reductions in the THR. This is not unexpected because the THR is a weight-based value. The reductions in the THR are caused primarily by increases in the average molecular weight of structural units of material, which is the reason why the weight-based THR is not an objective measure of flammability for the polymeric systems under study. To correct this deficiency, the total heats released in the CC tests were renormalized by the total numbers of moles of DBA, BDBA, and BBA used to make the test samples. Subsequently, the THR reductions caused by dilution, char, and incomplete combustion were recalculated on the molar basis. The results of these calculations are shown in figure 3. According to these results, suppression of the gas-phase combustion is the main mechanism by which the brominated compounds reduce the molar THR. The ability of the brominated compounds to promote the formation of char also has a significant effect on the THR value.
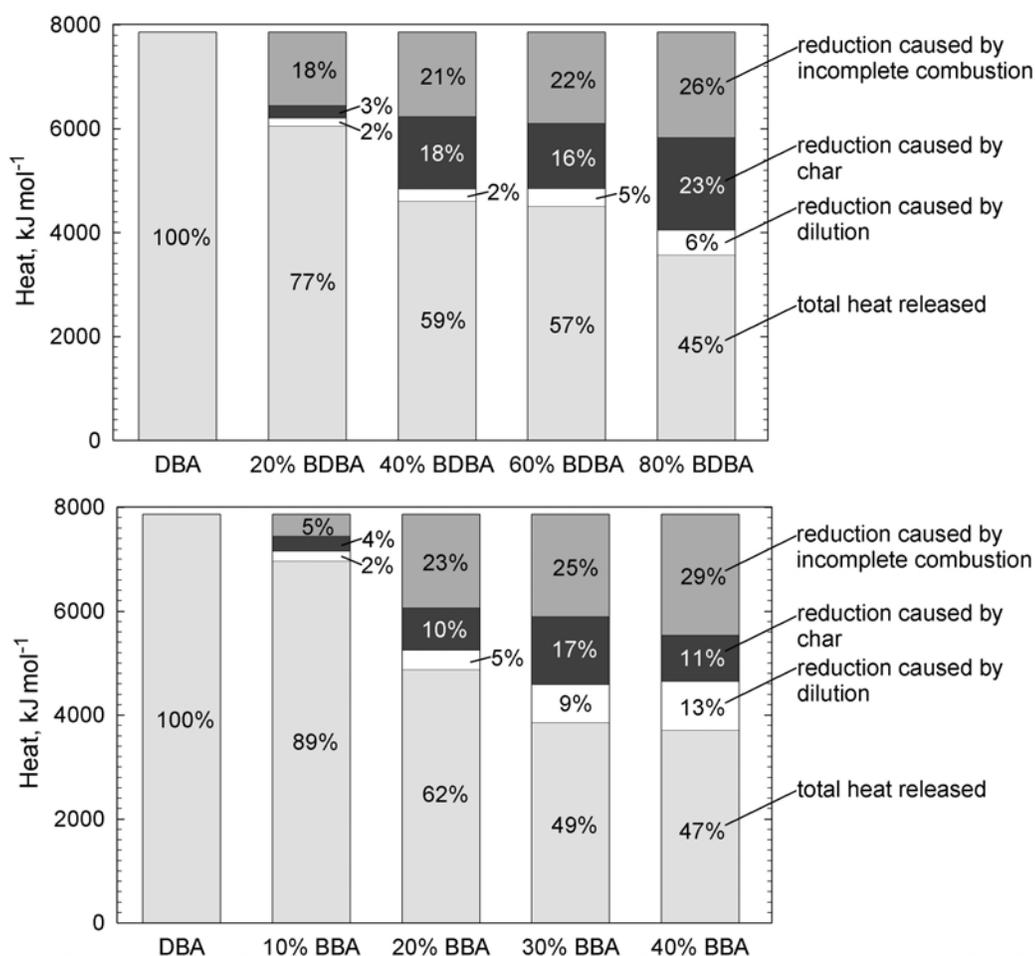
FIGURE 3. REDUCTIONS IN THE MOLAR THR ASSOCIATED WITH ADDITION OF BROMINATED COMPOUNDS

Under the assumptions that the average molar rate of decomposition of all the materials in the CC tests is the same (regardless of the composition) and that the decomposition is the rate-limiting step of the gasification process, the Avg.HRR should be proportional to the molar THR.

Dependencies of the Avg.HRR and molar THR, which were normalized by the corresponding values obtained for DBA, on the mass fraction of bromine are shown in figure 4. A good agreement between the Avg.HRR and molar THR observed for DBA-BBA blends indicates that for these systems, the assumptions are valid. It also means that all mechanisms by which addition of BBA affects heat release have been accounted for. Discrepancies between the Avg.HRR and molar THR observed for DBA-BDBA blends are probably caused by a combination of factors. According to the mass loss data shown in table 1, addition of 20 wt.% of BDBA to DBA sharply increases the average rate of mass loss. This suggests that the change in the composition reduces the thermal stability, which results in the Avg.HRR being about 20% higher than the molar THR (see figure 4). At the same time, high concentrations (60-80 wt.%) of BDBA probably cause a significant reduction in the rate of condensed-phase transport of volatile decomposition products, which results in the Avg.HRR being about 15% lower than the molar THR.
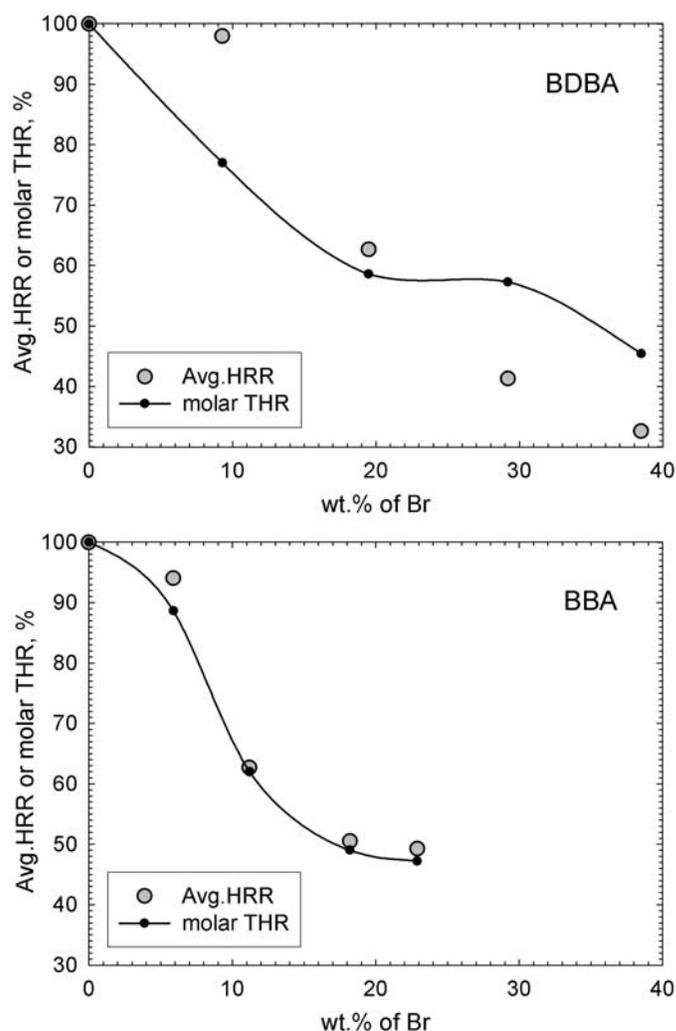
FIGURE 4. RELATIVE Avg.HRR AND RELATIVE MOLAR THR OF DBA-BDBA AND DBA-BBA BLENDS

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