NOTES

Thermal Properties of Some Bromine-Containing Aromatic Fire Retardants*

INTRODUCTION

The pervasive and promising use of bromine-containing compounds as fire retardants in selected fibers, films, and plastics is well documented.[1,2] Particularly in aromatic compounds, the substitution of one or more hydrogens by bromine increases the resistance to flammability of systems where the bromine-containing compounds may be either nonpolymeric additives or where they are an integral part of the polymer structure.

In an attempt to correlate a common thermal property suitable for the screening of bromine-containing aromatic compounds as fire retardants, an investigation was made of the thermogravimetry and differential scanning colorimetry of an unrelated series of five compounds which have been reported to be useful as fire retardant chemicals and monomers.

EXPERIMENTAL

The thermal analyses curves were recorded on a du Pont model 990 thermal analyzer having a model 951 thermogravimetry and quantitative differential thermal analysis accessories.

Reagent-grade o-xylene and heptane and Spectroquality methanol (Matheson, Coleman, and Bell) were used for the recrystallizations. The 4,4'-(1-methylethylidene)bis(2,6-dibromophenol) (tetrabromobisphenol A), 2,2'-((1-methylethylidene)bis(2,6-dibromo)-4,1-phenyleneoxy)bisethanol (the bis(hydroxyethyl ether) of tetrabromobisphenol A), and 1,1'-oxybis(2,3,4,5,6-pentabromobenzene) (decabromodiphenyl ether) were obtained from the Dow Chemical Company. The 4,4'-sulfonylbis(2,6-dibromophenol) (tetrabromobisphenol S) and the dimethyl ester of 2,5-dibromo-1,4-benzenedicarboxylic acid (dimethyl 2,5-dibromoterephthalate) were obtained from Great Lakes Chemical and American Enka Company, respectively.

Purification of Compounds

The tetrabromobisphenol A (TBBPA, mp 183–185°C), tetrabromobisphenol S (TBBPS, mp 290–292°C), bis(hydroxyethyl ether) of TBBPA (ETBBPA, mp 118–119°C), and dimethyl 2,5-dibromoterephthalate (DBDMT, mp 328–330°C) were purified by successive recrystallizations from Spectroquality methanol. The decabromodiphenyl ether (DBDPE, mp 300–306°C) was purified by successive recrystallizations from an o-xylene/heptane mixture.

Thermogravimetry

Samples of the brominated compounds, ranging from 10.9 to 15.0 mg, were placed in the platinum sample pan of the thermobalance. The balance had a dynamic atmosphere of nitrogen flowing at a uniform rate of 30 ml/min. The thermogravimetry (TG) curves were recorded over the range of 25 to 500°C at a uniform rate of 10°C/min. The sensitivity of the TG recording pen was 2 mg/in., while that of the derivative TG (DTG) pen was 1 mg/min/in.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) curves were run following two methods. The first was a direct measure of the differential temperature (ΔT) versus the temperature of the block (T) to discern the position of the endo- and/or exotherms and the temperature of decomposition. The

TABLE I
Data for Calculating Thermal Decomposition Energies

| Compound	Peak temperature, °C	E	A, in.^{2}	B, min/in.	Δqs, mcal/sec/in.	m, mg	c_p, cal/°C/g
Tetrabromobisphenol A	338	0.4410	6.8033	0.5	1.0	8.800	0.2651
Tetrabromobisphenol S	339	0.4420	5.1230	2.0	0.1	0.343	0.2652
Dimethyl 2,5-dibromoterephthalate	424	0.4765	8.5667	1.0	1.0	8.000	0.2740
Bis(hydroxyethyl ether) of tetrabromobisphenol A	368	0.4510	1.9333	1.0	2.0	8.200	0.2685
Decabromodiphenyl ether	467	0.4948	0.7140	1.0	2.0	1.596	0.2777
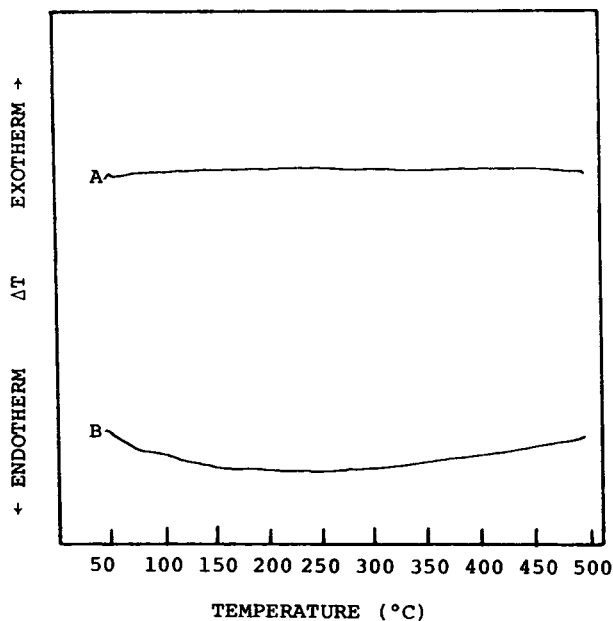
Fig. 1. Differential scanning calorimetry curve of sapphire standard: A = sample pan empty; B = sample pan containing sapphire.

second method recorded ΔT vs. time (t) with one pen and T vs. t with the other pen simultaneously. These time-based curves were recorded for quantitative measurements of the peak area for use in calculating the energy of decomposition.

Samples ranging from 0.3 to 8.8 mg were placed in aluminum pans that were then sealed hermet-
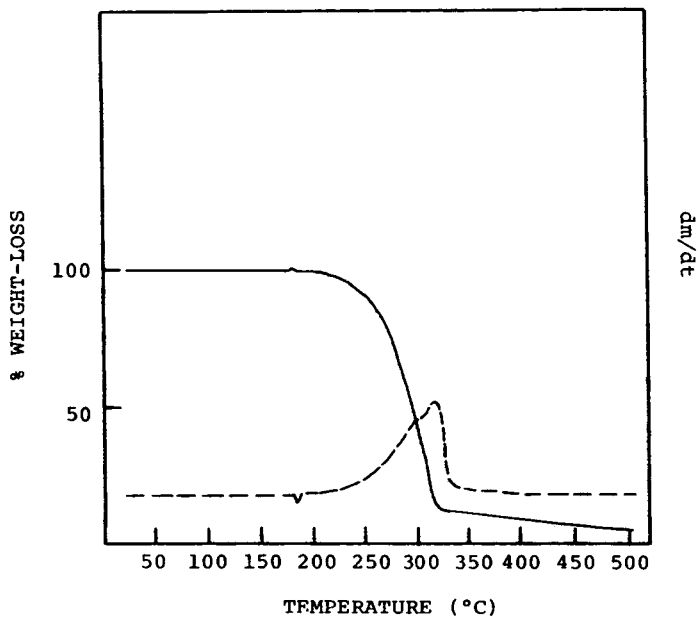

Fig. 2. Thermogravimetry and derivative thermogravimetry curves of tetrabromobisphenol A: (—) thermogravimetry curve; (- - -) derivative thermogravimetry curve.
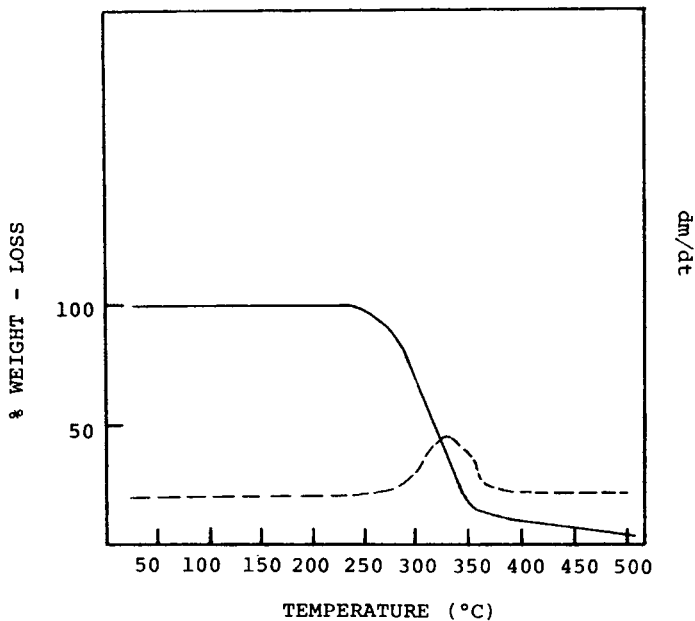
Fig. 3. Thermogravimetry and derivative thermogravimetry curves of tetrabromobisphenol S: (—) thermogravimetry curve; (- - -) derivative thermogravimetry curve.

ically.   Each sample was placed in the DSC cell along with an empty hermetically sealed aluminum pan used as a reference.   The cell had a dynamic atmosphere of nitrogen flowing at a uniform rate of 30 ml/min.

The samples were measured over the temperature range of 25–500°C at a uniform heating rate of 10°C/min for ΔT vs. T.   The sensitivity of the recording pen was set at 2 mcal/sec/in.
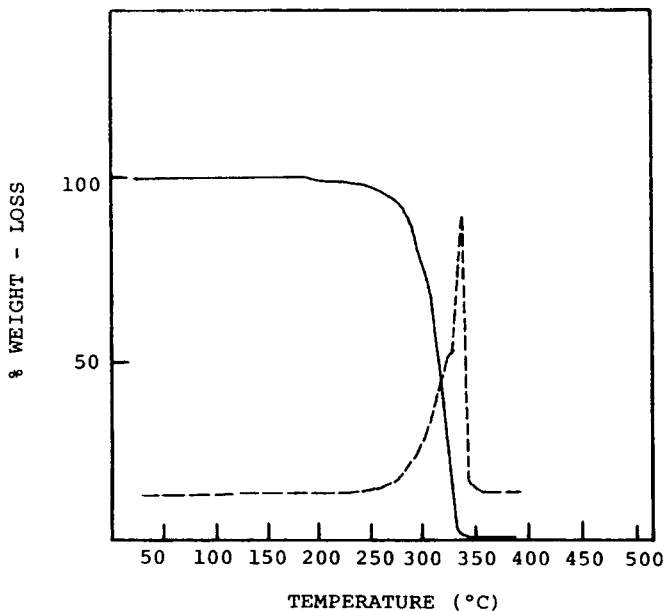

Fig. 4. Thermogravimetry and derivative thermogravimetry curves of dimethyl 2,5-dibromo-terephthalate: (—) thermogravimetry curve; (- - -) derivative thermogravimetry curve.
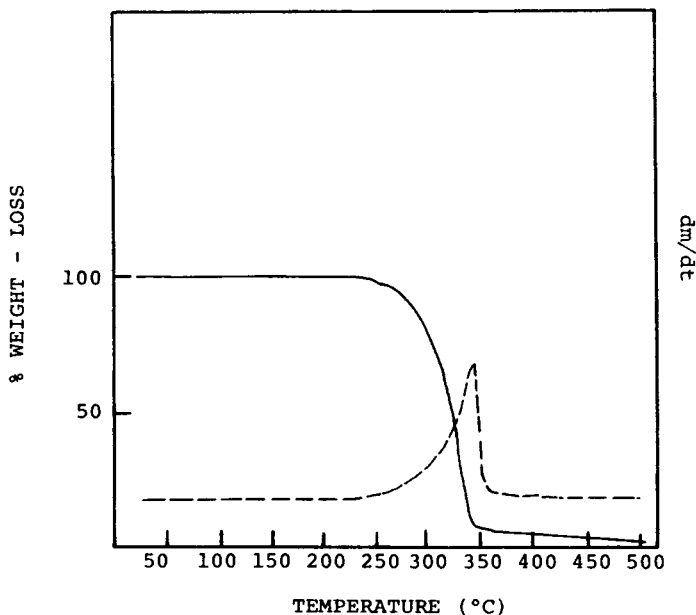
Fig. 5. Thermogravimetry and derivative thermogravimetry curves of the bis(hydroxyethyl ether) of tetrabromobisphenol A: (—) thermogravimetry curve; (- - -) derivative thermogravimetry curve.

The samples were also measured over portions of the DSC curve in which the decomposition occurred for ΔT and T vs. t. The temperature was increased at a uniform rate of 10°C/min. The sensitivity of the ΔT-vs.-t pen was set at 2 mcal/sec/in., while that of the T-vs.-t pen was set at 0.2 mcal/sec/in. (or approximately 100°C/in.). The time base of the curves varies from 0.5 to 2.0 min/in. depending on the size of the temperature range being recorded.

Determination of Decomposition Energy

The decomposition energy (ΔH) of each of the compounds was calculated using the equation

$$\Delta H = 60\, E\, A\, B\, \Delta gs/m$$

where E = the instrument quantitative calibration factor; A = the peak area (in.^{2}); Δgs = the pen sensitivity (mcal/sec/in.); m = the mass (mg); and 60 = a conversion factor (sec/min).

The calibration factor was determined from a DSC curve of a standard compound, sapphire. The peak areas were measured manually using a planimeter. The reported areas are the average of at least five measurements.

The necessary data for the calculation of the thermal decomposition energies are tabulated in Table I. The c_p values were interpolated from a table of the variation of c_p with temperature for aluminum oxide.[3] The E values were determined using the c_p and data obtained from Figure 1 from the equation

$$E = c_p H_r m/60\, \Delta gs\, \Delta Y$$

where c_p = the specific heat of aluminum oxide (cal/°C/g); H_r = the heating rate (°C/min); m = the sample weight of the sapphire (mg); Δgs = the sensitivity of the recording pan (mcal/sec/in.); and ΔY = the distance between the two curves for the sapphire standard (in.).
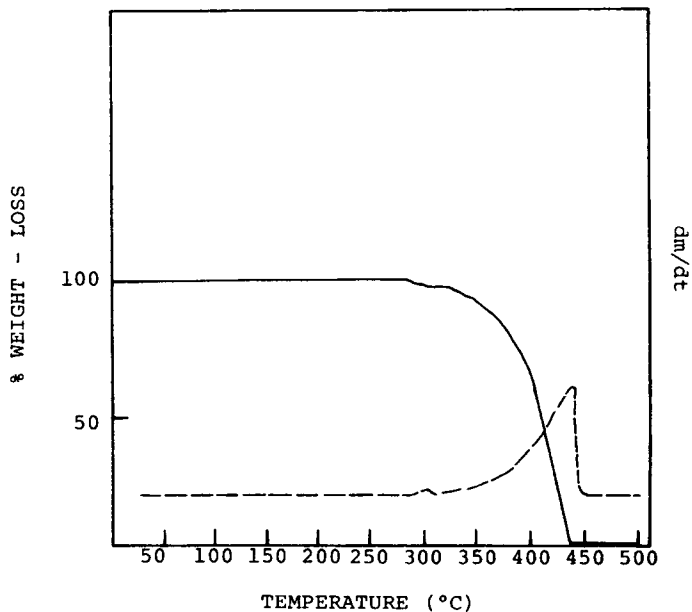
Fig. 6. Thermogravimetry and derivative thermogravimetry curves of decabromodiphenyl ether: (—) thermogravimetry curve; (- - -) derivative thermogravimetry curve.

DISCUSSION

Thermal Analysis

The thermogravimetry (TG) curves and the differential scanning calorimetry (DSC) curves of the five brominated compounds are shown in Figures 2–6 and Figures 7–11, respectively, and the
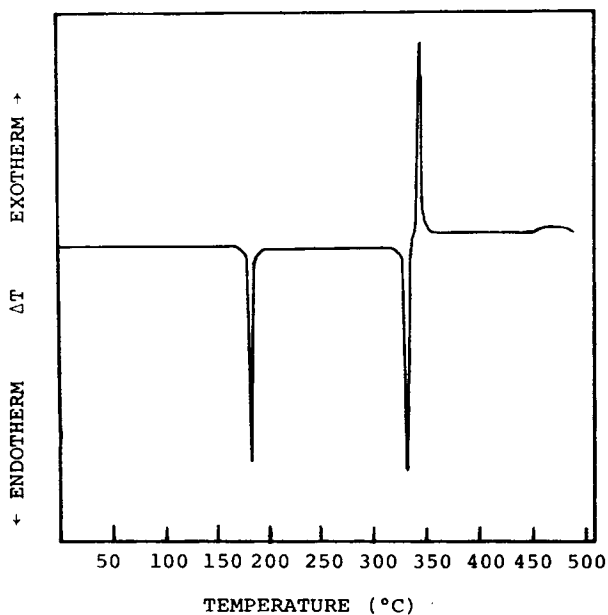

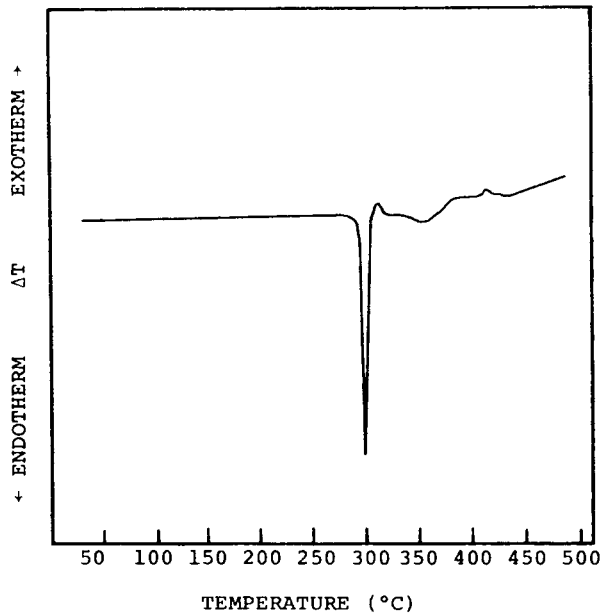Fig. 7. Differential scanning calorimetry curve of tetrabromobisphenol A.

Fig. 8. Differential scanning calorimetry curve of tetrabromobisphenol S.

data are tabulated in Tables II and III, respectively. From the TGs it can be seen that each of the compounds has only one region of major weight loss and that these regions all occur below 500°C. The TG of TBBPA showed a temperature range of weight loss of 225–325°C, which is in close agreement to that of the work reported by Factor,[4] although the final percent weight loss reported by Factor was not as low as that found in this study.

The DSC curves each show two regions of energy change. The first endothermic peak (or endo-
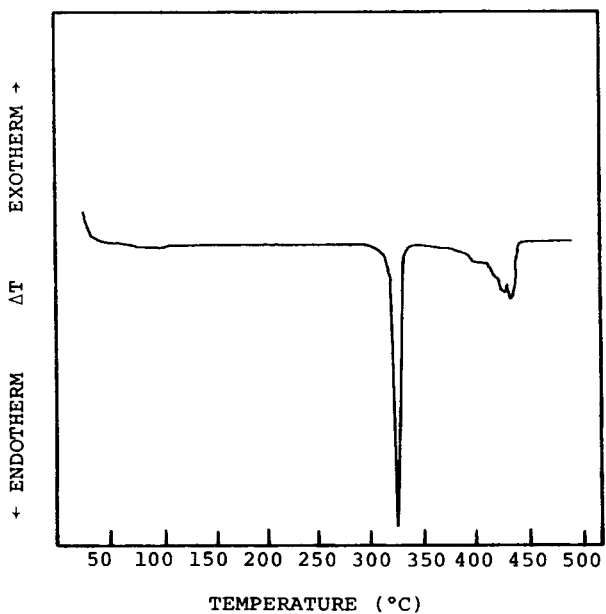

Fig. 9. Differential scanning calorimetry curve of dimethyl 2,5-dibromoterephthalate.
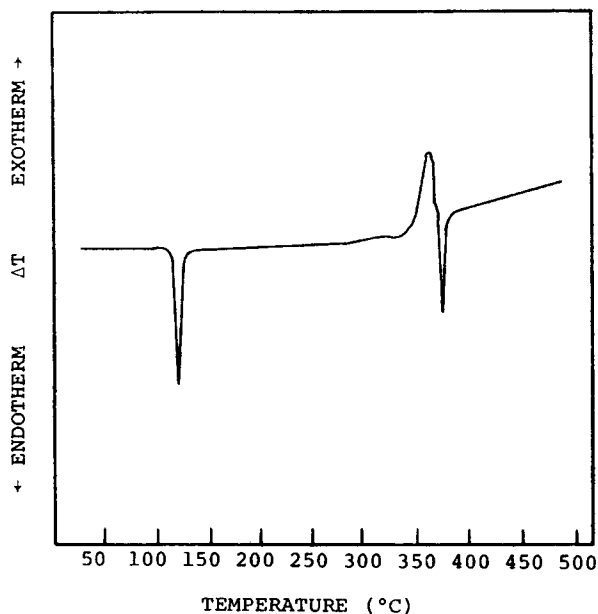
Fig. 10. Differential scanning calorimetry curve of the bis(hydroxyethyl ether) of tetrabromo-bisphenol A.

therm), which ranges from a peak temperature of 120°C for ETBBPA to 323°C for DBDMT, is caused by a phase transition, while the second region, which is either endothermic, exothermic, or a combination of both, is due, at least in part, to decomposition. This second region ranges from a peak temperature of 255°C for TBBPA to 478°C for DBDPE.

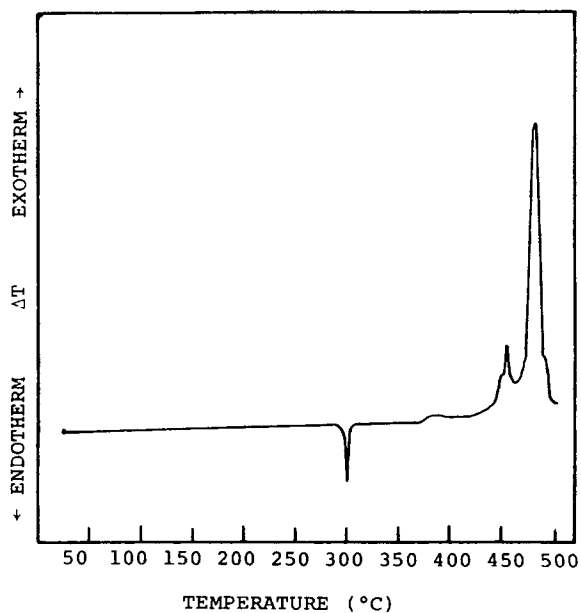The weight loss observed in the TG curves can be due to either decomposition or sublimation of

Fig. 11. Differential scanning calorimetry curve of decabromodiphenyl ether.
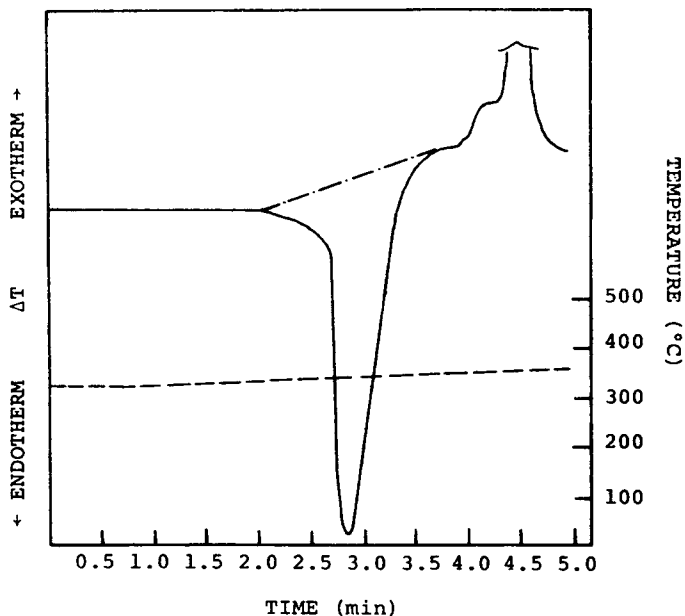
Fig. 12. Time-based differential scanning calorimetry curves of tetrabromobisphenol A: (—) ΔT vs. t; (- - -) T vs. t; (-·-) extrapolated baseline.

the sample, as these are the only possible mechanisms by which a sample that does not vaporize can undergo weight loss (assuming the sample does not react with anything under the conditions of the analysis). Since the sample is in an inert atmosphere of dry nitrogen, the above assumption is valid. Thus, whether the samples decomposed or sublimed can be determined by comparing the peak temperatures of the DTG curves to the peak temperatures of the DSC curves. For TBBPA, TBBPS, and ETBBPA, it was found that the weight losses recorded on the TG curves were due to decomposition of the sample, since the DTG peak temperatures were very similar to the peak temperatures of the decomposition areas of the corresponding DSC curves. For DBDMT and DBDPE, the weight loss was determined as due to sublimation. This was determined not only by correlation to the peak temperatures of the phase transitions, but also by the rapid weight loss to a final percentage of 100% weight loss. In the other samples, although the weight loss was rapid, it was not complete, as seen by the weight loss for TBBPA, TBBPS, and ETBBPA at 500°C, which are 93.7, 79.3, and 98.2%, respectively.

While the weight losses for DBDMT and DBDPE were determined to be due to sublimation, the weight losses for the other compounds were determined to be due to decomposition, and the activation energies for these decomposition weight losses were calculated. The activation energies E_a were calculated from areas measured on the TG curves of TBBPA, TBBPS, and ETBBPA, using the equation derived by Reich and Levi.[5] The values that were calculated, which are shown in Table II, ranged from approximately 28.5 to 30.5 kcal/mole. It is believed that these energies are truly activation energies for decomposition, although the real significance of these energies is not known at this time.

In order to calculate the energy of thermal decomposition, the decomposition peak was determined. In the cases of TBBPS and DBDMT, which only had a single broad endotherm above the phase transition endotherm, this determination was not difficult. For TBBPA, ETBBPA, and DBDPE, the determination was made by inspection of the contents of sample pans heated to a temperature between the two peak temperatures. In this way, the peak for initial decomposition was determined for TBBPA as the endotherm preceding the exotherm, and for DBDPE as the first of the two sharp exotherms. The ETBBPA was found, when heated to the intermediate temperature, to reverse the peaks, so that the exotherm occurred after the endotherm. This reversal is unexplainable at this time. Hence, the peak chosen for the ETBBPA decomposition energy determination was also
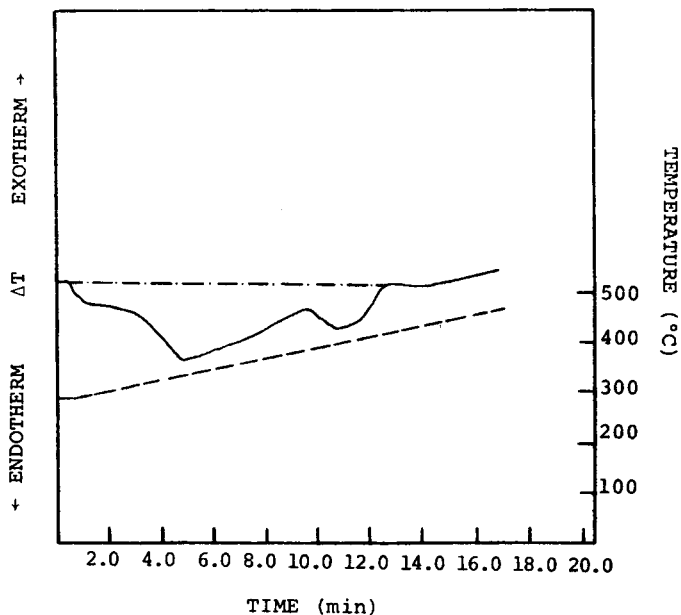
Fig. 13. Time-based differential scanning calorimetry curves of tetrabromobisphenol S: (—) ΔT vs. t; (- - -) T vs. t; (-··-) extrapolated baseline.

endothermic.   The occurrence of exotherms in the DSCs of TBBPA and ETBBPA and the second exotherm in the DSC of DBDPE are attributed to a reaction between the bromine liberated by the decomposition and either the aluminum sample pan or the silver heater block.   Brauman and Brolly used a gold sample pan to help eliminate the problem.

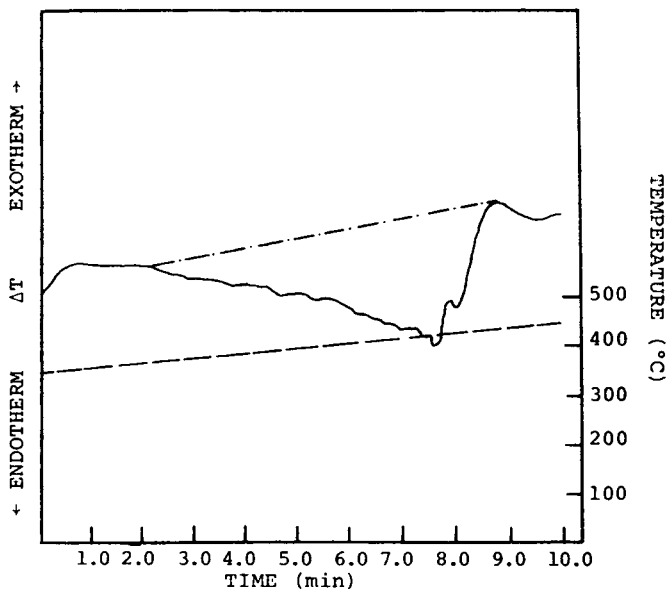By measuring time-based DSC (DSC–t) curves for the compounds (Figs. 12–16) heated through

Fig. 14. Time-based differential scanning calorimetry curves of dimethyl 2,5-dibromoterephthalate: (—) ΔT vs. t; (- - -) T vs. t; (-··-) extrapolated baseline..
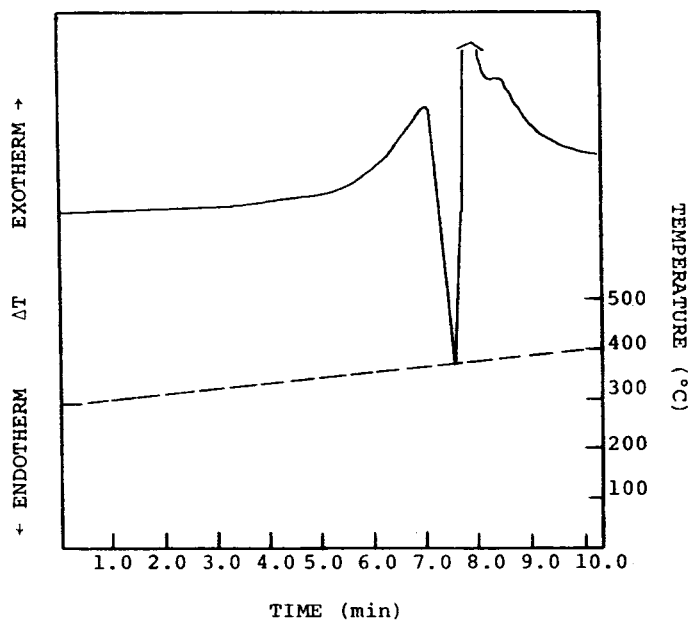
Fig. 15. Time-based differential scanning calorimetry curves of the bis(hydroxyethyl ether) of tetrabromobisphenol A: (—) ΔT vs. t; (- - -) T vs. t; (-·-) extrapolated baseline.

the chosen decomposition range, the heat of decomposition (ΔH) was obtained (see Experimental section) and converted from cal/g to kcal/mole.   The values of ΔH in both sets of units are shown in Table III.   The E values were calculated at each peak temperature from a DSC curve of a known weight of a sapphire standard.

Fig. 16. Time-based differential scanning calorimetry curves of decabromodiphenyl ether: (—) ΔT vs. t; (- - -) T vs. t; (-·-) extrapolated baseline.
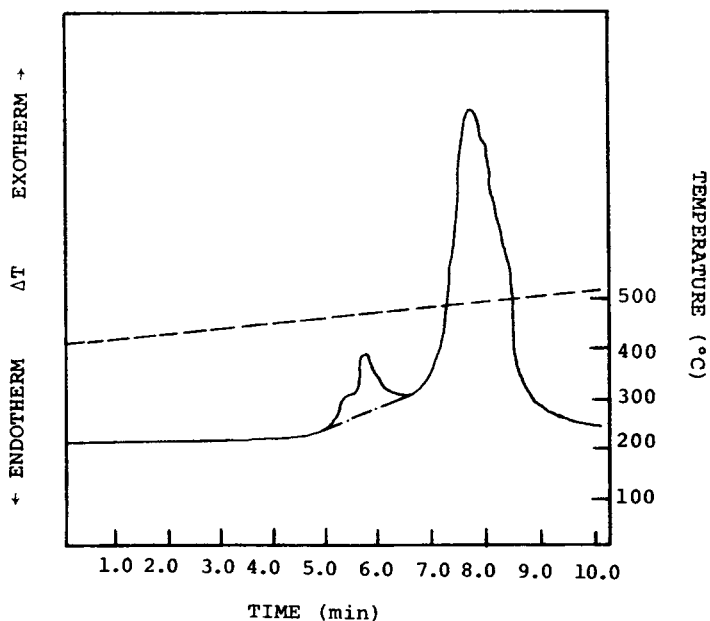
TABLE II
Thermogravimetric Analysis, in Nitrogen, of the Brominated Compounds

Compound	Weight Loss, %, at temperatures							E_a, kcal/mole
	200°C	250°C	300°C	360°C	400°C	450°C	500°C	
Tetrabromobisphenol A	0.0	9.0	58.6	90.1	91.0	92.8	93.7	28.46
Tetrabromobisphenol S	0.0	1.7	25.8	69.0	75.0	77.6	79.3	28.73
Dimethyl 2,5-dibromoterephthalate	0.0	2.0	26.2	100.0	100.0	100.0	100.0	
Bis(hydroxyethyl ether) of tetrabromobisphenol A	0.0	2.8	21.1	92.7	94.5	96.3	98.2	30.44
Decabromodiphenyl ether	0.0	0.0	3.8	8.5	37.7	1.0.0	100.0	

TABLE III

Differential Scanning Calorimetry Data and Thermal Decomposition Energies of the Brominated Compounds

Compound	Peak type	Peak temperature, °C	Transition	ΔH^a	
				cal/g	kcal/mol
Tetrabromobisphenol A	endotherm	182	fusion		
	endotherm	332	decomposition	10.23	5.56
	exotherm	346			
Tetrabromobisphenol S	endotherm	292	fusion		
	endotherm	255	decomposition	79.22	44.84
Dimethyl 2,5-dibromoterephthalate	endotherm	323	sublimation	30.62	10.78
	endotherm	430	decomposition		
Bis(hydroxyethyl ether) of tetrabromobisphenol A	endotherm	120	fusion	12.76	8.06
	exotherm	364			
	endotherm	374	decomposition		
Decabromodiphenyl ether	endotherm	302	sublimation	26.56	25.47
	exotherm	385			
	exotherm	452	decomposition		
	exotherm	478			

[a] The ΔH in cal/g was calculated from experimental data, while the value in kcal/mole was converted from the calculated ΔH value.

The thermal decomposition energies (ΔH) were compared to the bond strength of an aromatic C–Br bond. The ΔH values, ranging from approximately 5.5 to 45 kcal/mole, do not agree even closely to the C–Br bond strength of 72–80 kcal/mole. The large variance may be explainable by the release of the bromine during decomposition and subsequent reactions which overshadow the decomposition. Or, the lack of correlation may be due to the possibility that the measured decomposition energies may not truly be decomposition energies; they may be composite energies combining decomposition and some other, probably exothermic, reaction that causes the calculated energies to be lower than the actual decomposition energies.

It does appear, however, that these data on decompositions of the five bromine-containing fire retardants may be properly related to practical applied uses. That is, the ΔH values for the two tetrabromobisphenol A compounds (ΔH 5.56 and 8.06 kcal/mole) related well to their effectiveness in plastics and fibers, respectively.

CONCLUSIONS

The thermal decomposition of the five bromine-containing compounds varies over too large a range of values to be correlated to published aromatic carbon–bromine bond energies. This may be due to the fact that the decomposition energies measured are not truly decomposition energies, but composite energies combining a number of reactions, of which one is decomposition.

The activation energies for the decomposition of tetrabromobisphenol A, tetrabromobisphenol S, and the bis(hydroxyethyl ether) of tetrabromobisphenol A, obtained from thermal analysis studies, ranged from 28.46 to 30.44 kcal/mole. It is believed that these are effective and reasonable activation energies for the decomposition of the compounds.

References

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3. *Instruction Manual, 990 Thermal Analyzer and Modules*, E. I. du Pont de Nemours and Co., Inc., Instrument Products Division, Wilmington, DE, 1974, p. A-10.

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