Some Theoretical Aspects of Bromine-Containing Triazine Flame Retardants

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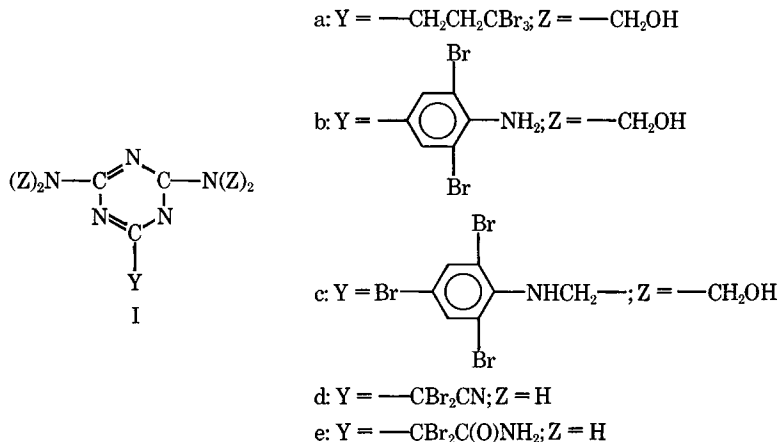
Synopsis

We studied flame retardancy of cotton fabric treated with five diaminotriazines containing bromine—three compounds with the bromine on aliphatic groups and two with the bromine on phenyl groups. Flame retardancy, as measured by oxygen index and FF3-71 flammability standards, was better on the fabrics containing aliphatic bromine than on the fabrics containing aromatic bromine. Thermogravimetric analyses (TGA) and differential thermogravimetric analyses (DTG) were obtained on the fabrics, results of which supported the theory that HBr liberated during burning lowers the ignition temperature and decomposition point of the cellulose causing a reduction in flammable gases and an increase in residual char. Since C–H and C–Br bond strengths are stronger on aromatic groups than on aliphatic groups, our results agree with the theory that flame retardancy increases as the C–Br bond strength decreases. In other words, since bromine inhibits oxidation reactions in the gas phases, the heat evolved is expected to become less as the C–Br bond strength decreases.

INTRODUCTION

Chance and Timpa[1-3] reported an effective, durable flame retardant for cotton, one with a relatively low bromine content, based on tetramethylol-2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine (TM-DABT). Continuing this work, Chance[4] described in detail the synthesis of several other diaminotriazines with groups containing both aliphatic and aromatic bromine. These compounds were used in the current investigation to study their effect on the flame retardancy of cotton fabric. There was a marked difference in the flame retardancy of cotton fabric treated with the aliphatic bromine compounds and that of fabric treated with aromatic bromine compounds. Thermogravimetric analysis (TGA) was used to try to explain the difference. Perkins et al.[5] used differential thermal analysis (DTA) and TGA in studying the thermal degradation of cotton fabrics treated with several different organophosphorus flame retardants. They concluded that DTA curves are unique for each flame retardant and that DTA defines the temperature or temperature range at which various physical and chemical changes take place. They also showed how TGA was used to determine exothermic and endothermic changes caused by the flame retardant during combustion. Similar studies were carried out by Neumeyer et al.[6] on polyester/cotton fabrics.

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Compounds of the following structures were used in this investigation:

a: Y = ―CH₂CH₂CBr₃; Z = ―CH₂OH

b: Y = (aryl) ―NH₂; Z = ―CH₂OH

c: Y = Br― (aryl) ―NHCH₂―; Z = ―CH₂OH

(Z)₂N―C―N(Z)₂ triazine ring Y

I

d: Y = ―CBr₂CN; Z = H

e: Y = ―CBr₂C(O)NH₂; Z = H

The compounds are listed by name as follows:

Ia—Tetramethylol-2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine;

Ib—Tetramethylol-2,4-diamino-6-(3,5-dibromo-4'-aminophenyl)-1,3,5-triazine;

Ic—Tetramethylol-2,4-diamino-6-(2',4',6'-tribromoanilinomethyl)-1,3,5-triazine;

Id—2,4-Diamino-6-(dibromocyanomethyl)-1,3,5-triazine;

Ie—2,4-Diamino-6-(dibromocarbamoyl)-1,3,5-triazine.

EXPERIMENTAL

Syntheses. Compounds Ia–e were prepared by methods previously reported.[1,4]

Fabric Treatment. The compounds were applied to samples of a cotton flannelette (4.0 oz/yd²) by a typical padding operation followed by drying and curing. Because all of the compounds were insoluble in water, they were applied to the fabric from either a solution of DMF or a mixture of DMF and water. In the experiments where water was used, the compounds were dissolved in DMF, and just enough water was added to avoid precipitation of the compounds. In other experiments, only DMF was used because even a small amount of water caused the compound to precipitate. Water was used in the pad bath when possible because this caused the chemical to penetrate into the cotton fiber better. Data on fabric treatment are summarized in Table I.

Compounds Ia–c are N-methylol compounds which form thermosetting resins when used on the fabric. No catalyst was required for compounds Ia and Ib, but one was needed for Ic to obtain an adequate resin add-on. Methylol derivatives of compounds Id and Ie were not prepared because the bromine atoms in these molecules were so labile as to be removed by the alkali used in the methylolation; these compounds were deposited on the fabrics simply by padding the monomer

TABLE I
Data on Fabric Treatment

Compound	Pad bath, % (compd./DMF/H$_2$O)	Dried, min/°C	Cured, min/°C
Ia	20/60/20	5/85	3/140
Ib	25/70/5	5/85	5/165
Ic	22/78/0[a]	5/85	3.5/150
Id	17.5/82.5/0	5/85	no cure
Ie	18.3/81.7/0	5/85	no cure

[a] Contained 0.15% NH$_4$Cl catalyst based on total weight of pad bath.

from DMF solutions and drying. There was no polymer formation as was the case with compounds Ia–c. All of the fabric samples contained between 8 and 9% bromine.

Fabric Test Methods. Thermogravimetric analyses (TGA) of the cotton fabric samples and the pure compounds were obtained as described by Neumeyer et al.[6] A du Pont 990 Thermal Analysis system with an attached 951 Thermogravimetric Analyzer was used. Fabric samples of 5–10 mg were heated from ambient to about 650°C at a rate of 10°C/min in a 100% nitrogen atmosphere. A du Pont 915 Computer Interface converted the data to digital form for later processing by a digital computer. The TGA data were differentiated, and resulted in a differential thermogravimetric analysis (DTG). Both TGA and DTG data were normalized to a dry weight of 1. Oxygen index (OI) values were obtained on a Michigan Chemical Instrument according to a modified procedure of the American Society for Testing and Materials, ASTM Designation D-2863-70. The oxygen index is a measure of the minimum volume concentration of oxygen in a flowing stream of oxygen and nitrogen that will just support combustion. Flame retardancy was also determined by the FF3-71 Standard for the flammability of Children's Sleepwear.[7] Bromine analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. HBr evolved during combustion of the fabric samples was analyzed by Boeing Commercial Airplane Company using Boeing Specification Support Standards BSS 7238, BSS 7239, and BSS 7242. Combustion gases from fabric containing aliphatic bromine had about 5 ppm HBr and those from fabric containing aromatic bromine, about 3 ppm HBr.

RESULTS AND DISCUSSION

In the TGA curve, the temperature is plotted against the normalized weight. When the TGA curve is differentiated in time and the rate of weight loss (expressed in mg/min/mg) is plotted as a function of temperature, the result is the DTG curve. The temperature at which the maximum rate of weight loss occurs is referred to as the peak temperature. The TGA and DTG curves for the untreated control fabric and the treated fabrics are shown in Figures 1–6. TGA and DTG curves were also obtained on the pure compounds used to treat the fabric. These curves are not shown, but the peak temperatures were used in interpretation of the results. The major weight loss for the control fabric occurred between 270 and 370°C, and the maximum rate of weight loss occurred at 349°C (Fig. 1).
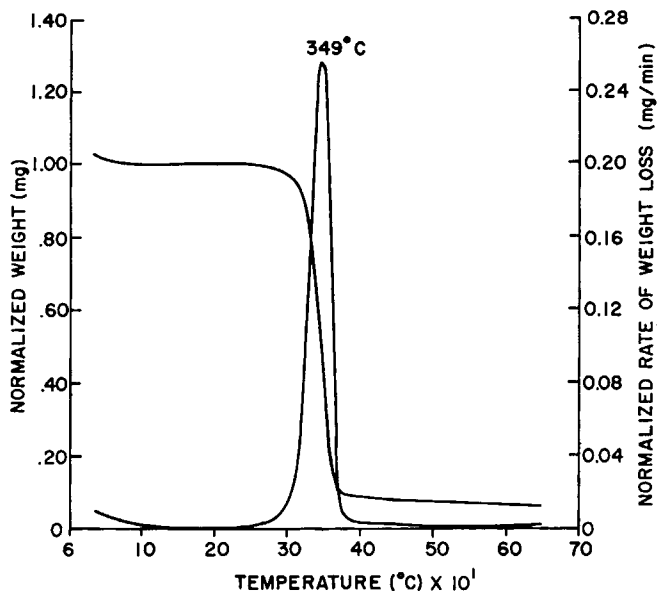
Fig. 1. TGA and DTG curves for untreated cotton, heating rate = 10°/min, 100% nitrogen atm.

For fabric treated with compound Ia (Fig. 2), peaks occurred at 185 and 260°C. The DTG for pure Ia had a peak at 131°C, which corresponded to the initiation of polymerization, and a decomposition range beginning at about 180°C and peaking at 202°C. The temperature of 180°C corresponded to decomposition at 185°C of polymer Ia on the fabric. The peak rate of weight loss on Ia occurring at 260°C was much lower than that of the control (349°C) and indicates the point at which the HBr formed during combustion was most effective in lowering the
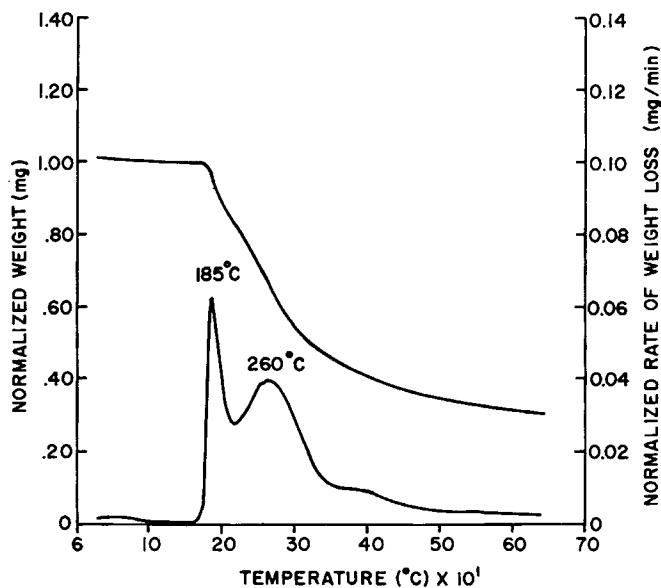
Fig. 2. TGA and DTG curves for cotton treated with Ia, heating rate = 10°/min, 100% nitrogen atm.
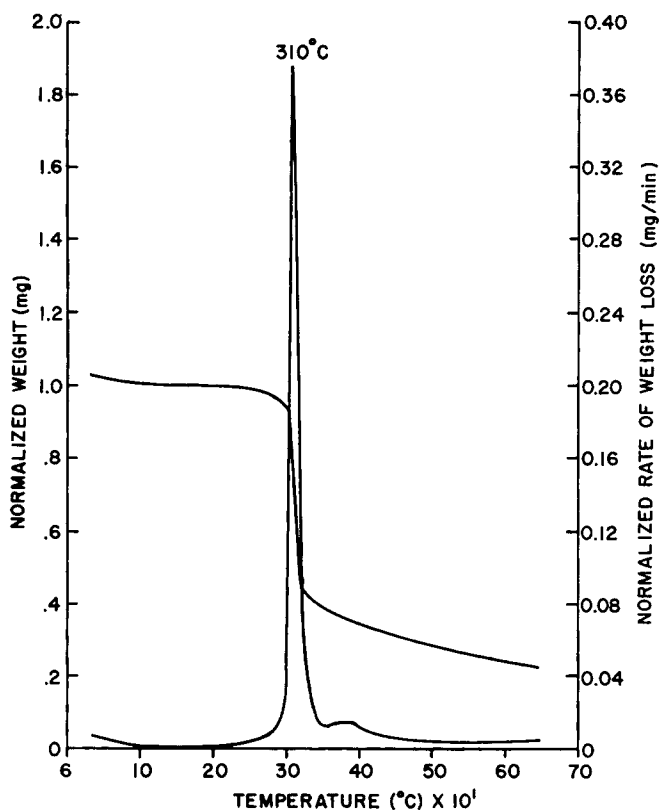
Fig. 3. TGA and DTG curves for cotton treated with Ib, heating rate = 10°/min, 100% nitrogen atm.

decomposition point of the cellulose and in minimizing the formation of flammable gases.

The decomposition range for fabric treated with Ib (DTG curve, Fig. 3) occurred at 258–340°C, with a peak temperature of 310°C. It is obvious that Ib was not very effective in lowering the decomposition point of the cellulose, which was not unexpected because Ib contains aromatic bromine (which is more strongly bonded to carbon than bromine in the aliphatic compounds) and therefore was not as effective in preventing the formation of flammable combustion products. In pure Ib, peak temperatures occurred at 140, 168, and 342°C. The lower peaks probably correspond to the initiation of polymerization, because when Ib is placed in a bath at 140°C, a strong odor of formaldehyde is observed; and at 165–166°C, melting takes place with the liberation of additional formaldehyde and water and the formation of a product insoluble in boiling DMF.

The DTG curve for fabric treated with Ic (Fig. 4) had a peak temperature of 291°C, which was lower than that of Ib, but still much higher than that of Ia. DTG curves for pure Ic had peak temperatures at 137, 166, and 270°C. The peak at 137°C corresponds to the melting point of Ic, and 166°C probably indicates polymerization. The peak rate of decomposition occurred at 270°C. Again, the peak rate of weight loss occurred at a much higher temperature than that for Ia, which was also attributed to aromatic bromine.

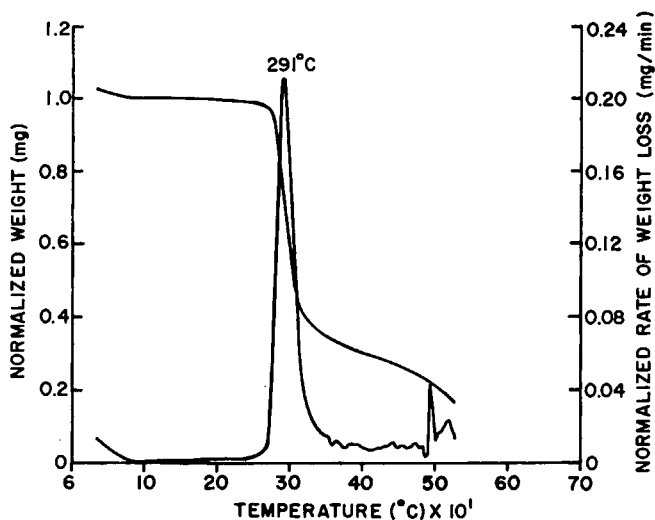The DTG curve (Fig. 5) of fabric treated with Id showed peak temperatures

Fig. 4. TGA and DTG curves for cotton treated with Ic, heating rate = 10°/min, 100% nitrogen atm.

of 197 and 260°C, and fabric treated with Ie (Fig. 6) had peaks of 207 and 259°C. Both Id and Ie contain aliphatic bromine, which results in much lower peak temperatures than those of the aromatic compounds.

DTG data (summarized in Table II) show again that the temperature at the maximum rate of weight loss (mg/min/mg) was lowest for the aliphatic bromine compounds. The percent residual char at 600°C was highest for Ia, Id, and Ie, which shows that aliphatic bromine is more effective in lowering the amount of flammable gases and increasing the amount of char. Flame retardancy, as measured by OI and char length, is also shown in Table II. Data from all the samples were obtained at approximately the same bromine content (8–9%) and
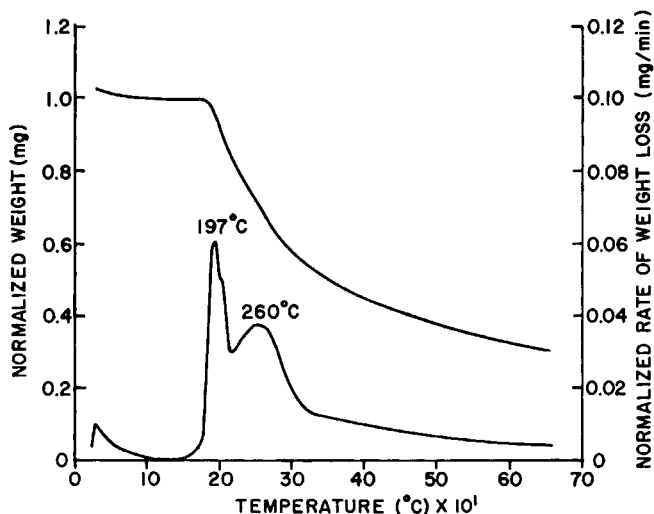

Fig. 5. TGA and DTG curves for cotton treated with Id, heating rate = 10°/min, 100% nitrogen atm.
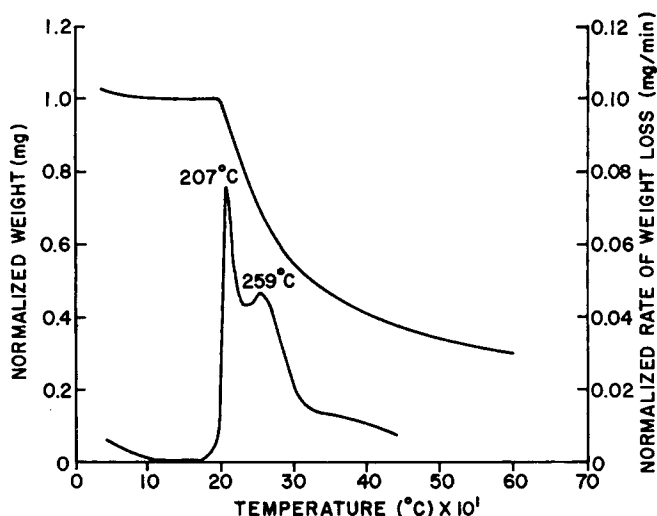
Fig. 6. TGA and DTG curves for cotton treated with Ie, heating rate = 10°/min, 100% nitrogen atm.

show that aliphatic bromine gave better flame retardancy. Slightly higher OI and percent residual char were obtained on Id than on Ie, which can be attributed to the fact that because the bromine atoms on Id are on a carbon adjacent to a nitrile group, they are more labile. This low C–Br bond strength is caused by the electron-withdrawing effect of the nitrile group. The bromine atoms in Ie are on a carbon adjacent to an amide group and are not as labile as the ones in Id.

CONCLUSIONS

The TGA and DTG data presented here are consistent with the theory, discussed by Prins et al.,[8] that chlorine- and bromine-containing flame retardants liberate HCl and HBr, which react with free radicals formed during burning and

TABLE II
Data on Cotton Flannelette Treated With Bromine-Containing Triazines[a]

Treatment	Temp. °C[b]	Rate[c]	Percent residue at 600°C	Oxygen index	FF3-71 Char length, in.
Ia	185	0.064	31.7	34.0	3.0
	260	0.040			
Ib	310	0.378	24.0	22.1	BEL[e]
Ic	291	0.212	15.8[d]	22.1	BEL
Id	197	0.061	32.4	33.8	2.7
	260	0.038			
Ie	207	0.076	29.7	31.0	2.7
	259	0.046			
Control	349	0.256	6.2	18.5	BEL

[a] DTG heating rate, 10°C/min; 100% N_2 atmosphere.
[b] Temp. at maximum rate of weight loss (°C).
[c] Normalized maximum rate of weight loss (mg/min/mg).
[d] Percent residue at 530°C.
[e] BEL= Burned entire length.

terminate the chain reaction with the end result of a lowering of the ignition temperature and decomposition point of cellulose, a reduction in the amount of flammable volatiles, and an increase in residual char. Schneider et al.[9] compared the effect of tetrabromophthalic anhydride and 2,2-bis(bromo-methyl)-1,3-propanediol on the fire retardant properties of polyesters and assumed that aliphatic bromine compound are approximately 1.5 times more effective than aromatic bromine compounds. From the data shown in Table II on OI and char lengths, it was concluded that triazines containing aliphatic bromine were more effective flame retardants for cotton than triazines containing aromatic bromine. Since both C–Br and C–H bond energies in the benzene rings are comparatively greater than the ones on the aliphatic groups, it appears that the TGA and DTG results support the theory that flame retardancy increases as the C–Br bond strength decreases,[10,11] i.e., since bromine inhibits oxidation in the gas phase, the value of the heat evolved is expected to become less as the C–Br bond strength decreases.

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