Flame-Retardation Studies of Poly(ethylene Terephthalate) Fabrics Treated with *tris* Dibromo Alkyl Phosphates*

M. DAY and T. SUPRUNCHUK, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada*; J. G. OMICHINSKI[†] and S. D. NELSON, *Department of Medicinal Chemistry, University of Washington, Seattle, Washington, 98195*

Synopsis

The flammability characteristics of *tris*(2,3-dibromopropyl) phosphate (TRIS-BP), a known carcinogen, has been compared with other *tris* dibromo alkyl phosphates which show reduced mutagenic responses in experimental studies. The effectiveness of these alternative chemicals in releasing hydrogen bromide (HBr), a recognized combustion inhibitor, has been measured and the results compared with flammability evaluation of polyester fabrics treated with these chemicals. Results indicate that *tris*(2,3-dibromo-3,3-dimethyl propyl) phosphate, while having reduced mutagenicity and nephrotoxicity in comparison to TRIS-BP, exhibits excellent flame-retardant characteristics when applied to polyester fabrics. Meanwhile, other chemicals studied show comparable flame retardation to TRIS-BP, but with substantial reduced mutagenicity.

INTRODUCTION

The chemical *tris*(2,3-dibromopropyl) phosphate was, until it was banned in the U.S. in 1977, the most often used flame-retardant treatment for textile fabric, especially polyester and cellulose acetate materials. This chemical proved to be a convenient, practical solution for treatment of fabrics in compliance with the U.S. flammability standards for children's sleepwear.[1] Toxicological studies of this chemical, however, showed it to be mutagenic[2,3] and carcinogenic.[4-6] Consequently, on April 7, 1977, the U.S. Consumer Product Safety Commission banned the use of *tris*(2,3-dibromopropyl) phosphate-treated garments[7] and later (May 3, 1977) the use of the chemical itself.[8]

Although the ban raised much discussion in the industry regarding the technological evidence and its significance,[9] the potential health hazard has been clearly established. Toxicological studies have revealed the mechanistic role of *tris*(2,3-dibromopropyl) phosphate as a mutagen[10] and led to the design of dibromo alkyl phosphates with reduced mutagenicity and nephrotoxicity.[11,12]

The present study is concerned with an evaluation of the potential effectiveness of these chemicals as flame retardants for poly(ethylene terephthalate) (PET). The approach that we have taken is essentially the same as those

---

*Issued as NRCC No. 27692.

[†]Present address: Department of Toxicology, Statens Institutt for Folkenhelse, Oslo, Norway.

CCC 0021-8995/88/020529-07$04.00

that were applied in the study of *tris*(2,3-dibromopropyl) phosphate-treated PET.[13, 14] These include the monitoring of the effectiveness of the chemicals to release hydrogen bromide,[13] an evaluation of the combustibility of the gaseous pyrolysates,[14] and the determination of the limiting oxygen index (LOI) of the treated fabric samples.

EXPERIMENTAL

Chemicals

The following dibromo alkyl phosphates were prepared using previously published procedures.[12, 15]

Tris(2,3-dibromopropyl) phosphate (TRIS-BP)
Tris(2,3-dibromo-2-methyl propyl) phosphate (TRIS-2M-BP)
Tris(2,3-dibromo-3-methyl propyl) phosphate (TRIS-3M-BP)
Tris(2,3-dibromo-3,3-dimethyl propyl) phosphate (TRIS-33DM-BP)
Tris(3,4-dibromobutyl) phosphate (TRIS-BB)

Fabric Treatment

The PET fabric was a 100% Spun Dacron Type 54 (127 g/m^2) obtained from Testfabrics, Middlesex, NJ (Style 767). Topical treatment of the fabric with the chemical was achieved by immersion of the fabric in a solution of the chemical in tetrahydrofuran. Because of the small quantities of chemical available, approximately 4 g of fabric were immersed in the minimum amount of a 3% solution [15 mL] and the wet fabric squeezed through "nip" rollers and dried. Using this treatment "add on" levels of 10% were anticipated. Actual treatment levels, determined by quantitative bromine analysis however, were found to be slightly lower than 10% (see Table 1). These treatments are also likely to be nonhomogeneous due to the omission of a washing step which would have minimized surface deposits.

Flammability Measurements

Oxygen index measurements were performed using the Textile Research Institute flammability apparatus.[16] Small strips of the fabric (5 × 100 mm) were supported on a nonwoven fiber glass support and ignited at the 3 o'clock position on the wheel. An average LOI value was obtained from at least five observations.

TABLE I
LOI's of Treated Polyester Fabrics

Chemical additive	Br on fabric (%)	Chemical loading W/W (%)	LOI
None	0	0	20.0
TRIS-BP	6.2	9.1	23.5
TRIS-2M-BP	5.6	8.7	24.8
TRIS-3M-BP	4.6	7.1	24.8
TRIS-33DM-BP	4.8	7.8	27.5
TRIS-BB	6.0	9.3	23.5

Thermal Release of Hydrogen Bromide

The gaseous pyrolysate products from the thermal degradation in air were analyzed for hydrogen bromide (HBr), as a function of weight loss, using a special degradation procedure described previously.[13] Essentially, the apparatus consists of a Cahn electrobalance in a closed air-flow system and a radiative furnace to decompose the sample. The gases evolved are then bubbled through a buffered aqueous solution and the HBr formed during the thermal decomposition monitored continuously by a specific bromide ion electrode.

Combustibility of Gaseous Pyrolysates

In the case of gases or vapors which form flammable mixtures with air or oxygen, there is usually a minimum concentration of vapor in air below which flame propagation does not occur when ignition is attempted. In the same way there is usually a maximum concentration limit as well. These limits are usually known as the "lower and upper flammability limits." Below the lower flammability limit the gas/air mixture is said to be too "lean" and above the upper flammability limit it is said to be too "rich." The range of combustible gas/air mixtures between the two limits is known as the "flammable range." In our previous studies we have used special equipment to measure the flammability limits of the gaseous pyrolysates produced from the chemical decomposition of polymeric materials[17] and have applied the technique to the study of flame-retarded polyesters.[14, 18] The technique involves the thermal decomposition of the sample in a closed bomb containing a known volume of air. The gaseous pyrolysate/air mix is then subjected to a spark discharge to determine if a combustible mixture has been obtained. By performing the experiments as a function of pyrolysis time, a range of gaseous pyrolysate concentrations can be evaluated based upon the percentage weight loss enabling the flammability limits to be determined.

RESULTS

Oxygen Index Data

The results of the LOI determination for the treated PET fabrics are presented in Table I. These data identify all the chemicals as having some flame-retardation action on PET in terms of their ability to cause an increase in the LOI above that of the untreated PET. In comparison to the conventional TRIS-BP, all the alternative species appear to show beneficial effects with some showing more improvement than others.

Thermal Degradation and HBr Release Data

The weight loss and HBr release relationships for the neat chemicals and the PET-treated fabrics are summarized in Tables II and III, respectively. From these data, it can be seen that the thermal stabilities of all the chemicals are similar although clear and distinct trends appear. For example, the introduction of a terminal methyl group (in the 3 position) appears to be clearly responsible for an accelerated weight loss and HBr evolution. The introduction of the second methyl group further enhances this degradative

TABLE II
% Weight Loss and HBr Release for Neat Chemicals

Chemical		TRIS-BP	TRIS-2M-BP	TRIS-3M-BP	TRIS-33DM-BP	TRIS-BB
Time to reach the	10	1.00	0.40	0.60	0.31	0.90
following %	20	1.15	0.46	0.65	0.36	1.02
weight losses	40	1.40	0.56	0.75	0.40	1.08
(min)	60	1.62	0.66	0.84	0.48	1.12
	80	1.81	0.80	0.97	0.57	1.20
	90	2.05	2.22	1.33	0.63	1.70
Liberated HBr as a	10	0.05	0.05	0.04	0.23	0.01
% of total HBr	20	0.13	0.08	0.15	1.12	0.02
available at the	40	0.59	0.47	0.50	2.15	0.04
following %	60	1.33	0.94	1.40	3.77	0.10
weight losses	80	2.22	1.56	2.27	5.82	0.58
	90	2.72	3.31	4.03	6.88	2.17

weight loss and HBr evolution. Thus, based upon HBr evolution from the neat chemical, TRIS-33DM-BP obviously has a good potential to act as a combustion inhibitor, an observation in keeping with its high LOI value in comparison to the other chemicals when added to PET.

It is interesting to note the enhanced HBr evolution from all chemicals when applied to PET. Although chemical interaction is a possible explanation, a more likely rationale is the physical interaction between the polymer and the chemical which could result in a reduction in the free volatilization of undecomposed retardant. This is especially noticeable with the TRIS-33DM-BP-chemical which exhibits an exceptionally high release of HBr during the degradation of the PET (see Table III).

TRIS-3M-BP- and TRIS-BB-treated fabrics also show interesting behavior. Both materials are less prone to weight loss than the other treated samples in that they tended to give greater char residues at the conclusion of the experiments than is normally found with the TRIS-BP fabrics and conventional PET.

TABLE III
% Weight Loss and HBr Release for PET-Treated Fabrics

Chemical		TRIS-BP	TRIS-2M-BP	TRIS-3M-BP	TRIS-33DM-BP	TRIS-BB
Time to reach the	10	0.61	0.59	0.67	0.28	0.79
following %	20	0.80	0.72	1.28	0.50	1.71
weight losses	40	1.20	1.11	2.89	0.96	4.07
(min)	60	1.83	1.74	6.39	1.46	7.77
	80	3.94	3.52	—	2.73	—
	90	10.50	7.35	—	7.35	—
Liberated HBr as a	10	0.04	0.31	0.56	20.21	0.37
% of total HBr	20	0.30	0.72	4.16	25.91	3.26
available at the	40	1.98	1.89	9.21	29.23	6.74
following %	60	3.72	3.22	12.05	31.33	8.47
weight losses	80	5.46	4.38	—	34.56	—
	90	6.92	5.39	—	39.42	—

TABLE IV
Results of Flammability Limit Studies

| Chemical | Experimental condition | Flammability limit % by weight | | | Peak pressure on ignition (kPa) |
		Lower	Upper	Range	
None	—	11.6 ± 1.6	43.7 ± 0.3	32.1	269
TRIS-BP	Separated	15.2 ± 0.2	37.6 ± 0.2	22.4	191
	Combined	21.1 ± 0.6	44.7 ± 3.1	23.6	319
TRIS-2M-BP	Separated	20.0 ± 0.1	38.9 ± 1.1	18.9	236
	Combined	19.3 ± 0.1	42.5 ± 3.9	23.2	319
TRIS-3M-BP	Separated	19.1 ± 0.2	32.9 ± 1.7	13.8	269
	Combined	19.5 ± 0.7	32.7 ± 0.7	13.2	303
TRIS-33DM-BP	Separated	25.5 ± 0.6	42.0 ± 0.5	16.5	208
	Combined	18.4 ± 0.1	35.1 ± 1.5	16.7	303
TRIS-BB	Separated	25.4 ± 0.1	40.6 ± 3.8	15.2	212
	Combined	17.9 ± 0.7	38.4 ± 1.9	20.5	303

Flammability Limits of Gaseous Pyrolysates

The flammability limits of the gaseous pyrolysates were determined in two ways in an attempt to distinguish between gas phase combustion inhibition reactions and solid/solid phase interactions between the PET and the retardant. In order to identify the former, the PET and chemical were heated in a special crucible divided into two halves. Untreated PET (180 mg) was loaded into one half of the crucible and the neat chemical (20 mg) was loaded into the other half (i.e., equivalent to a 10% w/w add on). The results of these experiments are shown in Table IV. Also presented in Table IV are the results obtained with 200 mg of the topically treated fabrics (i.e., both retardant and PET are in intimate contact during pyrolysis).

Examination of these data reveals that all of the chemicals have the ability to increase the lower flammability limits of the gaseous pyrolysate and reduce the flammability range in comparison with the values recorded for the untreated PET sample. All the chemicals are therefore acting as combustion inhibitors, though to varying degrees.
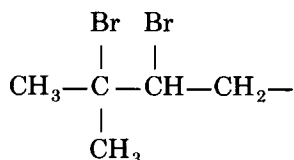
DISCUSSION

The utilization of alternative *tris* dibromo alkyl phosphates as potential flame retardants for PET appears to be a possible option compared to TRIS-BP. In terms of flame retardancy, the chemical *tris*(2,3-dibromo-3,3-dimethyl propyl) phosphate is the chemical of choice among those studied in this investigation. This chemical demonstrated the highest release potential of HBr although its thermal stability as measured by rate of weight loss was the lowest. Even when applied to PET, its rate of HBr generation was significantly faster than that of the other compounds. Although HBr generation is regarded as a precursor to combustion inhibition,[19] its fast release prior to the formation of the gaseous pyrolysate fuel is not always advantageous. However, with TRIS-33DM-BP, the LOI determination clearly indicates that actual inhibition is being achieved. In terms of flammability limit measurements, the neat chemical TRIS-33DM-BP can be seen to have the greatest

effect on the ignitability of the fuel gases being produced since it has caused the largest increase in the lower flammability limit of all the systems studied. However, interestingly, the upper limit is very similar to that of untreated PET. When combined with the fabric in a topical treatment however, the increase in the lower flammability limit with TRIS-33DM-BP, is not as marked, with its value being similar to that obtained with the other chemicals. This difference in the lower flammability limit between the separated and combined experiments suggests that some interactions are taking place in the condensed phase in addition to the gaseous phase inhibition processes. This observation of condensed phase interaction is also supported by a reduction in the peak pressure on ignition which suggests different gas/air compositions exist as a result of the separated and combined experiments.

Interestingly, even though differences between the monitored HBr, lower flammability limits, and flammability ranges are observed, with all the other chemicals studied, in comparison with the conventional TRIS-BP materials, their overall effect upon the flammability of PET as measured by the LOI values are not all that different. This would suggest that the decomposition reaction of these chemicals both in the presence and absence of PET are indeed complex processes. It is well known that the mechanism of the gas phase pyrolysis of bromohydrocarbons is a complex process dependent upon the strength of the carbon-bromine bond.[20] Information in the literature[21] indicates that bromohydrocarbons can undergo unimolecular four-centered elimination reactions, homogeneous radical reactions, as well as heterogeneous radical reactions with third bodies, depending upon structures of the chemical (i.e., nature of any α or β substitution). Based on this information, it appears that the introduction of methyl groups α and β to the bromine groups is capable of altering the nature of the decomposition mechanism and hence the gaseous pyrolysates produced and their flammability characteristics.

Based upon the chemicals examined, the structure:

$$
\begin{array}{c}
\quad\quad\text{Br}\quad\text{Br} \\
\quad\quad\;|\quad\;\;| \\
\text{CH}_3\text{—C—CH—CH}_2\text{—} \\
\quad\quad\;| \\
\quad\quad\text{CH}_3
\end{array}
$$

appears to be the one of choice for HBr liberation and combustion inhibition of PET. This finding coupled with known reduced mutagenicity and nephrotoxicity when compared with the TRIS-BP structure of:

$$
\begin{array}{c}
\text{Br}\quad\quad\text{Br} \\
|\quad\quad\;\;| \\
\text{CH}_2\text{—CH—CH}_2\text{—}
\end{array}
$$
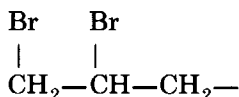
suggests that TRIS-33DM-BP could have some merit as a commercial flame retardant.

References

1. *Fed. Reg.*, **36**(196), 14062 (July 29, 1971).

2. A. Blum and B. N. Ames, *Science*, **195**, 17 (1977).

3. M. J. Prival, E. C. McCoy, B. Gutter, and H. S. Rosenkranz, *Science*, **195**, 76 (1977).

4. National Cancer Institute, Carcinogenesis Testing Program, National Cancer Institute Carcinogenesis Technical Report, Series no. 76, Washington, D.C. (1978).

5. G. Reznik, J. M. Ward, J. F. Hardistry, and A. Russfield, *J. Natl. Cancer Inst.*, **63**, 205 (1979).

6. E. Søderlund, E. Dybing, and S. D. Nelson, *Toxicol. Appl. Pharmacol.*, **56**, 171 (1980).

7. *Fed. Reg.*, **42**(68), 18850 (April 8, 1977).

8. *Fed. Reg.*, **42**(87), 22878 (May 5, 1977).

9. A. Q. Devereux, *Textile Ind.*, 84 (Oct. 1980).

10. S. D. Nelson, J. G. Omichinski, L. Iyer, W. P. Gordon, E. J. Søderlund, and E. Dybing, *Biochem. Biophy. Res. Comm.*, **121**, 213 (1984).

11. E. J. Søderlund, J. G. Omichinski, J. E. Dahl, S. D. Nelson, and E. Dybing, *Toxicol. Appl. Pharmacol* (in press).

12. J. G. Omichinski, E. J. Søderlund, J. Braussano, E. Dybing, and S. D. Nelson, *Mutagenesis* (1987) (in press).

13. M. Day and D. M. Wiles, *J. Fire Sci.*, **1**, 255 (1983).

14. M. Day, T. Suprunchuk, and D. M. Wiles, *Fire Mater.*, **7**, 150 (1983).

15. E. J. Søderlund, S. D. Nelson, and E. Dybing, *Toxicology*, **21**, 291 (1981).

16. B. Miller and C. H. Meiser, *Text. Chem. Col.*, **3**, 118 (1971).

17. M. Day, T. Suprunchuk, and D. M. Wiles, *J. Appl. Polym. Sci.*, **26**, 3085 (1981).

18. M. Day, T. Suprunchuk, J. D. Cooney, and D. M. Wiles, *J. Appl. Polym. Sci.*, **33**, 2041 (1987).

19. D. L. Chamberlain, in *Flame Retardancy of Polymeric Materials*, W. C. Karyla and A. J. Papa, Eds., Marcel Dekker, New York, Vol. 4, 1978, p. 109.

20. E. S. Swinbourne, in *Comprehensive Chemical Kinetics*, Vol. 5, C. H. Banford and C. F. H. Tipper, Eds., Elsevier, Amsterdam, 1972, Chap. 2.

21. J. H. Lippiatt and D. E. Wells, *Dyn., Mass. Spectrom.*, **4**, 273 (1976).