

A STUDY OF THE THERMAL DEGRADATION KINETICS OF TRIS DIBROMO ALKYL PHOSPHATES

Potential flame retardants for poly(ethylene terephthalate)*

M. Day, J. D. Cooney and D. M. Wiles

DIVISION OF CHEMISTRY NATIONAL RESEARCH COUNCIL OF CANADA
OTTAWA, CANADA, K1A 0R6

(Received July 6, 1987; in revised form August 29, 1987)

The thermal decompositions of a series of tris dibromo alkyl phosphates similar to tris(2,3-dibromopropyl) phosphate (T23DBPP), alone and incorporated in poly(ethylene terephthalate) (PET) fabric have been studied by non-isothermal thermogravimetry. Kinetic evaluation revealed that the decomposition rate for tris(2,3-dibromo-3-methyl butyl) phosphate (T23DB3MBP) was the fastest followed by tris(2,3-dibromo-2-methyl propyl) phosphate (T23DB2MPP). Tris(3,4-dibromobutyl) phosphate (T34DBBP) and tris(2,3-dibromo butyl) phosphate (T23DBBP) had only marginally faster decomposition rates than T23DBPP itself. Measured decomposition rates for PET treated with the chemicals were only marginally faster than those for the untreated fabric, except during the initial weight loss stages where some decomposition of the chemicals appears to be occurring. Calculated kinetic parameters using an isoconversional method, along with regression coefficients of compensation effect plots suggest that all the chemicals behave similar to T23DBPP in having an apparent detrimental effect on the condensed phase decomposition kinetics while relying on their combustion inhibition effects to act as gas phase flame retardants.

In the early 1970's tris(2,3-dibromopropyl) phosphate (T23DBPP) was extensively used as a flame retardant finish for 100% polyester fabrics where it could be easily "fixed" to give materials which would pass the U.S. Federal requirements for children's sleepwear, including the multiple laundering requirements. In 1977, however, the use of this chemical was banned as a result of tests [1] which showed it to be mutagenic and carcinogenic. Recently a series of alternate tris dibromo alkyl phosphates has been synthesised and evaluated for carcinogenic response, with

* Issued as NRC #28075

encouraging results [2]. Flammability evaluations in our laboratory [3], meanwhile, suggest that these compounds have excellent flame retardant characteristics when applied to polyester fabrics. This initial investigation indicated that the release of the combustion inhibitor hydrogen bromide (HBr) played a significant role in the flame retardation process, along with indications that the thermal stability of the chemicals could be playing some role. The present study was therefore undertaken to obtain more information on the kinetics and mechanisms of the thermal decomposition reactions of these chemicals.

In the first part of the study, the weight loss kinetics of the thermal decomposition of the individual chemicals were analysed. The second part was concerned with the decomposition of the chemicals in the presence of poly(ethylene terephthalate) (PET) fabric. The weight loss kinetics were determined by non-isothermal thermogravimetry (TG) in air using multiple heating rates between 0.2 and 20 deg/min. The kinetic parameters were then estimated from the thermogravimetric data according to the methods of Kissinger [4] and Flynn [5].

Experimental

The following dibromo alkyl phosphates were prepared and purified using previously published procedures and their purity checked by TLC [6, 7]:

tris(2,3-dibromopropyl) phosphate (T23DBPP)
tris(2,3-dibromo-2-methyl propyl) phosphate (T23DB2MPP)
tris(2,3-dibromobutyl) phosphate (T23DBBP)
tris(2,3-dibromo-3-methyl butyl) phosphate (T23DB3MBP)
tris(3,4-dibromobutyl) phosphate (T34DBBP)

The PET fabric used as a substrate was a 100% spun Dacron Type 54 (127 g/m²) obtained from Testfabrics, Middlesex, N.J., U.S.A. The fabric was treated by immersion in an appropriate solution of the chemical in methylene chloride. The wet fabric was then squeezed through "nip" rollers and dried. The percentage weight "add-on" was determined on the basis of quantitative analysis for bromine. Although treatment levels of approximately 10% were the goal, the following % add-on's (w/w) were achieved:

T23DBPP	9.1%
T23DB2MPP	8.7%
T23DBBP	7.1%
T23DB3MBP	7.8%
T34DBBP	9.3%

A DuPont 950 Thermogravimetric Analyzer was used to measure sample weight loss as a function of linearly increasing temperature with the data being analysed by a DuPont 1090 Thermal Analyzer. Sample weights of 18 ± 0.25 mg were used throughout the study at heating rates of 0.2, 0.5, 1, 2, 5, 10 and 20 deg/min. All experiments were performed in air at a flow rate of 50 mL/min.

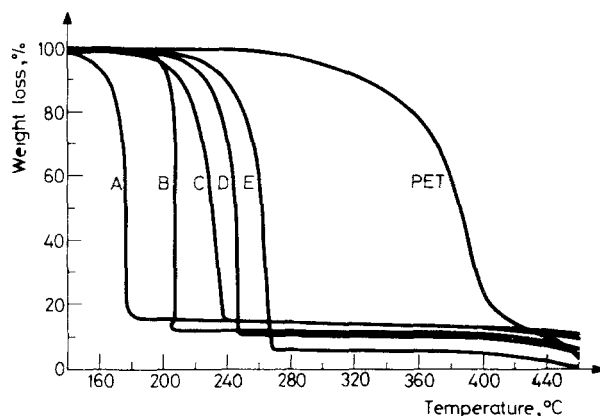


Fig. 1 Weight loss curves in air at 1 deg/min for T23DB3MBP (A), T23DB2MPP (B), T34DBBP (C), T23DBBP (D), T23DBPP (E) and standard untreated PET

Thermal analysis of the tris dibromo alkyl phosphates

The different thermal stabilities of the five chemicals are evident by examining the weight loss curves determined at a heating rate of 1 deg/min (see Fig. 1).

From these curves, it can be seen that the thermal stability increases as follows; T23DB3MBP < T23DB2MPP < T34DBBP < T23DBBP < T23DBPP. This order also agrees with the ranking of temperatures to achieve 50% weight loss and the measured peak rate temperatures shown in Table 1. However, it should be noted that all these chemicals are less stable than the polymer into which they are to be incorporated as defined by the onset of decomposition and the measured peak rate temperature (i.e. 397.8° at 1 deg/min for PET).

The measured peak rate temperatures determined at several heating rates allowed the apparent activation energy to be determined by the Kissinger method [4]. Applying this approach to our data, using the procedure described in detail in an earlier paper [8], enabled the values presented in Table 1 to be calculated. Although these values are based upon only one single value from each weight loss curve, they have been found to provide a reasonable estimate of a first order activation energy (E).

However, of the various methods that have been reported for the estimation of overall kinetic parameters from non-isothermal TG data, the method developed by Flynn [5] has been the most widely used. In this approach, the apparent Arrhenius activation energy (E) for the degradation process is calculated from the following expression:

$$\log F(\alpha) = \log(AE/R) - \log(\beta) - 2.314 - 0.4507 E/RT$$

by plotting the log of the heating rate (β) against the reciprocal of the absolute temperature ($1/T$) for a fixed degree of conversion (α). The slope of the resultant line is given by $-0.4507 E/R$ enabling E to be obtained. In addition, a value of $\log A$ can be found from the intercept on the $\log \beta$ axis.

The results of these calculations are presented in Table 2. From these data, it can be clearly seen that although the differences in apparent activation energies are not

Table 1 Maximum rate temperatures, maximum rates and first order activation energies for chemicals using Kissinger's method

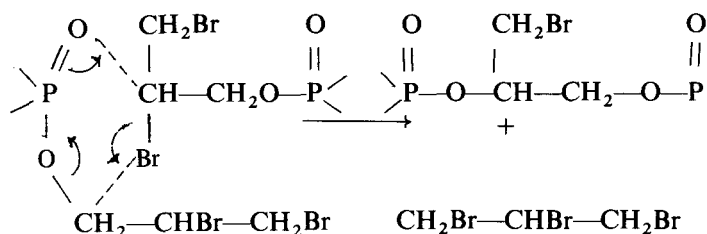
Chemical	T23DBPP	T23DB2MPP	T23DBBP	T23DB3MBP	T34DBBP
Measured values from 1 deg/min curves					
Peak temperature, °C	262.9	207.0	245.3	175.9	232.5
Peak rate, % min	14.5	104.7	69.8	35.8	9.84
Temp. of 50% wt. loss	261.1	206.9	244.8	175.9	230.6
Activation energy, kJ/mol	121 ± 4.3	131.4 ± 4.6	128.7 ± 4.2	123.4 ± 3.1	117.1 ± 3.0

Table 2 Kinetic parameters for the thermal decomposition of the tris dibromo alkyl phosphates as determined by the method of Flynn [5]

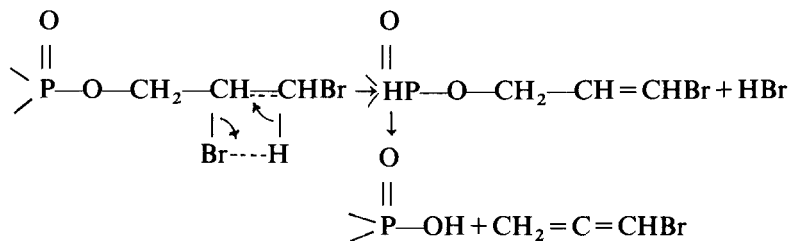
	Activation energy, kJ/mol	Log A , sec ⁻¹	Relative rate constants at 250 °C
T23DBPP	123.6 ± 1.3	13.3 ± 0.2	1
T23DB2MPP	133.1 ± 0.4	15.8 ± 0.1	33
T23DBBP	129.5 ± 1.5	14.3 ± 0.2	2.6
T23DB3MBP	121.8 ± 1.7	15.5 ± 0.3	221
T34DBBP	114.6 ± 1.2	13.2 ± 0.2	6.2

appreciable, major differences in the relative rate constants are evident. Clearly, as far as the decomposition of these dibromo alkyl phosphates are concerned, the presence of methyl groups in the basic tris(2,3-dibromopropyl) phosphate structure influences the thermal stability and decomposition rate. In order to understand the reasons for this effect, the thermal decomposition mechanism must be examined.

According to Okamoto et al. [9], T23DBPP decomposes mainly through an intermolecular transfer process according to the following scheme:



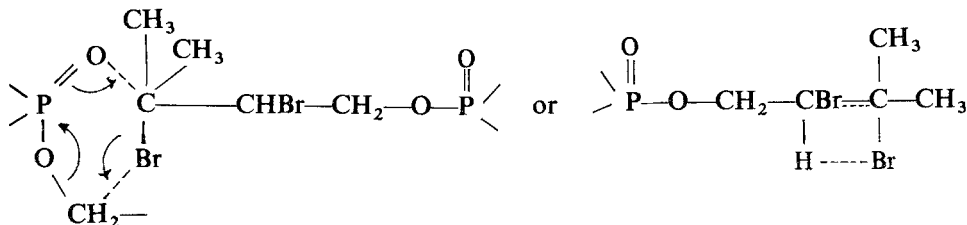
to account for 1,2,3-tribromopropane as the major product. Paciorek et al. [10] meanwhile have speculated that the dehydrobromination of T23DBPP is the first stage in the decomposition followed by the liberation of phosphoric acid and 1-bromo-allene formation.



Subsequently, hydrogen bromide additions to the 1-bromo-allene is then speculated to account for the major products of pyrolysis, the bromopropenes and 1,2,3-tribromopropane.

Unfortunately, both of the above decomposition mechanisms are dependent upon reactions centered around the 2-bromo atom and as such methylation on the 2 position rather than the 3 position would be expected to cause a larger increase in rate according to the data presented by Maccoll [11]. This arises from the inductive effect of the methyl group causing enhancement of the resonance stability of the 4 centred transition state. This enhancement of the degradation by 2-methyl substitution over that of 3-methyl substitution is clearly evident in comparing the results of T23DBBP and T23DB2MPP with those of T23DBPP.

When the data for the T23DB3MBP are considered, the observed enhanced rate clearly does not fit either of the above two mechanisms as written, since the two methyl groups are in a β position with respect to the 2-bromo, and the inductive effect is known not to be as effective in this position [11] (i.e. compare the T23DBBP and T23DB2MPP rates). The fast rate of decomposition for the T23DB3MBP therefore suggests that with this compound the 3-bromo becomes the active centre, i.e.:



Clearly, the presence of these two methyl groups on the active carbon to which the bromine is attached would be anticipated to enhance the stability of both these transition states and could account for the high rate of decomposition experienced with this compound. Measurements of hydrogen bromide evolution on these chemicals have revealed that T23DB3MBP liberate more HBr (2–10 times more) than any of the other compounds [3], suggesting that the four centred intramolecular transition state is the favoured process.

Thermal analysis of tris dibromo alkyl phosphate treated PET

The weight loss curves obtained at 1 deg/min for PET treated with these chemicals are shown in Fig. 2. Also included in this figure are the calculated curves obtained from the individual weight loss data for PET and each chemical. These curves were computed using the DuPont File Modification Utility software program. Comparison of the calculated curves with the actual experimental weight loss curves gives a clear indication of any actual interaction between the chemical and the PET.

If no interaction was occurring between the chemical and the PET substrate, the calculated and experimental curves should coincide. However, differences are clearly evident in all cases indicating that interactions are occurring with the additive affecting the rate of weight loss of PET, a phenomena noted with other additives [12]. All the calculated curves have a relatively sharp weight loss zone at low temperatures associated with the loss of the chemical. The experimental curves on the other hand do not show this sharp region (with the exception of T23DB3MBP) although there does appear to be some early weight loss in all cases. This suggests that for the most part, the added chemical is not as free to loose weight when present in the PET as it was when heated alone. Another striking example of

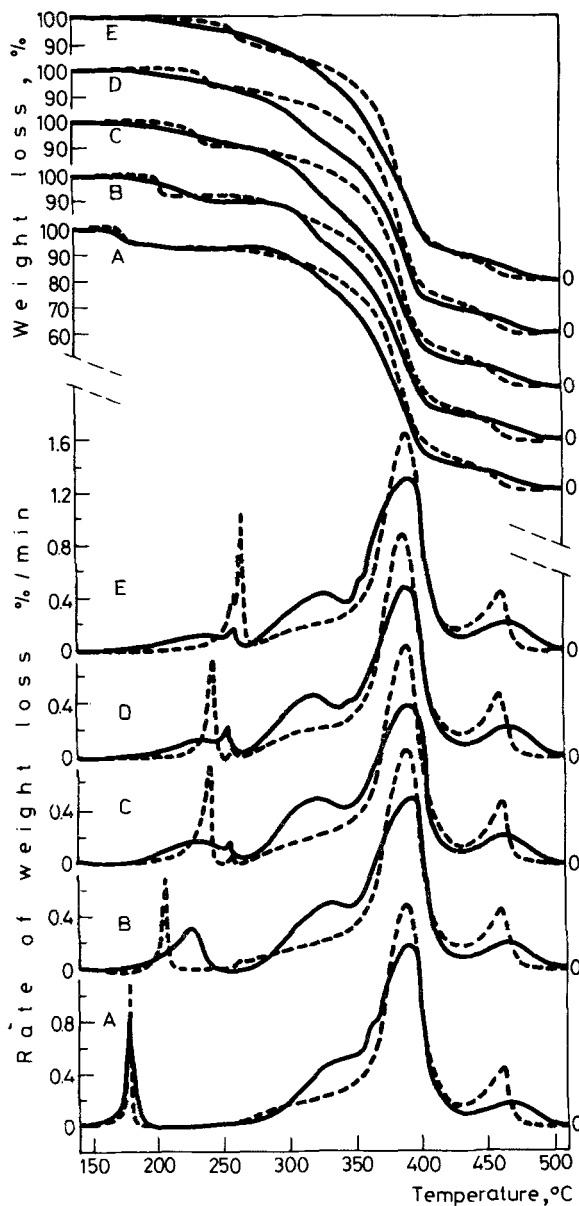


Fig. 2 Weight loss and derivative thermogravimetric curves in air at 1 deg/min for T23DB3MBP (A), T23DB2MPP (B), T34DBBP (C), T23DBBP (D) and T23DBPP (E) treated PET samples. Experimental curves shown (—) and simulated curves calculated from the chemical and PET shown (---)

chemical interaction between the chemicals and PET is the enhanced rate of weight loss noted in all experimental runs around 320° corresponding to the onset of the rapid weight loss of PET. Coupled with this earlier onset of PET weight loss is a reduction in the maximum rate. With respect to the high temperature oxidation of the char represented by the weight loss above 420°, all chemicals seem to be responsible for similar effects in causing a more gradual and prolonged weight loss.

The Kissinger kinetic analysis procedure [4] has been applied to each of these four stages of the decomposition and the results obtained are summarised in Table 3. Clearly, for the main weight loss region (3rd Stage) there are only slight differences in the activation energy as measured by this technique, while during the high temperature oxidation of the char (4th Stage), no significant differences could be detected. The main differences in the activation energies were associated with the early weight-loss regions (i.e. Stages 1 and 2) where the decomposition of the actual chemical is obviously playing a significant role in the calculated values. However, as was pointed out earlier, the Kissinger data are of limited value in that they just give information at the peak rates.

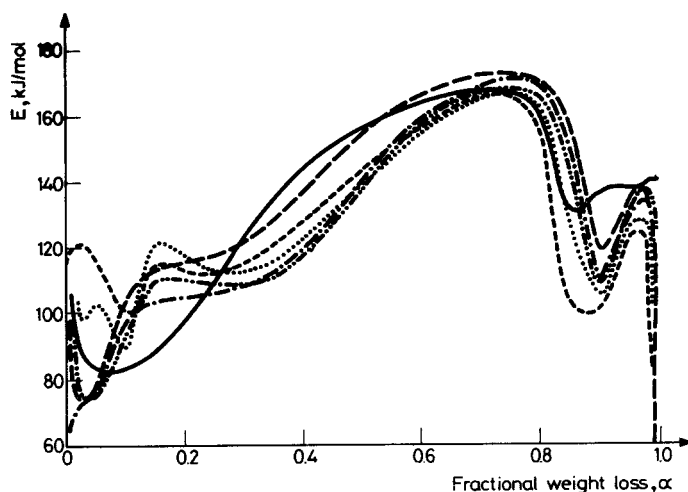


Fig. 3 Calculated activation energies as a function of fractional weight loss for T23DB3MBP (---), T23DB2MPP (...), T34DBBP (-.-), T23DBBP (-.-), T23DBPP (—) treated PET samples and standard untreated PET (—)

More informative kinetic data are obtained by the application of the Flynn [5] technique. This approach enables the kinetic parameters to be determined at various degrees of conversion (α). These data, for the activation energies (summarized in Fig. 3), enables four zones or stages of decomposition to be distinguished for the treated PET samples, corresponding approximately to the

Table 3 Peak values from the 1 deg/min heating rates and activation energies calculated according to the Kissinger method

	Sid PET	T23DBPP on PET	T23DB2MPP on PET	T23DBBP on PET	T23DBMBP on PET	T34DBBP on PET
<i>1st Stage</i>						
Peak temp., °C	247	246.0	228	238	181	238
Peak rate (%/min)	0.42	0.12	0.35	0.13	0.95	0.16
E_a , kJ/mol	—	—	113.9 ± 2.1	—	113.7 ± 1.5	—
<i>2nd Stage</i>						
Peak temp., °C	322	327	331	320	335	322
Peak rate (%/min)	0.24	0.43	0.54	0.46	0.51	0.52
E_a , kJ/mol	—	117.7 ± 6.2	159.7 ± 17.1	105.2 ± 10.0	132.5 ± 5.4	102.04 ± 4.9
<i>3rd Stage</i>						
Peak temp., °C	394	393	394	392	389	392
Peak rate (%/min)	1.82	1.35	1.30	1.29	1.35	1.22
E_a , kJ/mol	184.5 ± 3.7	194.6 ± 8.8	195.3 ± 9.1	195.8 ± 8.5	186.3 ± 4.5	205.2 ± 3.7
<i>4th Stage</i>						
Peak temp., °C	450	468	469	468	469	468
Peak rate (%/min)	0.40	0.22	0.20	0.21	0.19	0.21
E_a , kJ/mol	148.9 ± 4.5	142.5 ± 1.0	143.3 ± 0.6	142.0 ± 1.6	141.1 ± 4.8	144.8 ± 1.8

stages identified from the maximum rates according to the Kissinger method. These zones can now be further analysed to obtain "global" kinetic parameters for specific fractional weight loss regions of the decomposition. These parameters determined using a weighed mean statistical procedure, are presented in Table 4 for comparative purposes.

Interestingly, while all treated PET samples tended to show two early zones between 0.01 and 0.1 and between 0.15 and 0.4, the untreated PET instead has only one major zone between about 0.01 and 0.2, above which there is a progressive increase until the E starts to level off at about 0.6. Meanwhile, the calculated kinetic parameters over the main weight-loss region are very similar for each of the treatments and closely resemble those for the standard untreated PET. For example, for the main weight-loss region (0.5–0.8), the calculated values are close enough to suggest that the additive has only a very slight effect on the degradation rate. A similar observation can also be made with respect to the 4th Stage degradation process where once again the differences between the untreated and treated PET samples are not significant, especially in terms of the large uncertainty associated with these values. However, it should be noted that although the differences are not large, in all cases, without exception, the presence of the additive does cause an enhanced weight loss rate over that of the untreated PET.

During the early stages of decomposition, the degradation rates are not only dependent upon the presence of the additive, but also its chemical structure. For example, during the first 10% weight-loss zone, the rates for the treated PET samples are significantly faster than those for the untreated PET. The fact that the relative rate constants for the five treatments closely resemble the relative rate constants for the neat chemicals suggests only a slight interfering action from the PET. Comparison of the calculated rate constants for the decomposition kinetics of the chemicals and the 1st Stage for the PET treated fabrics are presented in Table 5. From these data, it can be clearly seen that if the weight loss of the treated fabrics is assumed to be due to the degradation of the chemicals only, its rate is substantially reduced when present on the PET. Consequently, based upon release of HBr being the active source of combustion inhibition, the chemicals should be more effective when present in the fabric especially when the release of the combustion inhibitor coincides with the decomposition process of the polymer.

In previous kinetic studies of the thermal degradation of PET, the parameters of the kinetic compensation effect (CE)

$$\text{Log } A = a_0 E + a_1$$

have been utilised to indicate changes in the decomposition kinetics [13–16]. In these studies, all stages of the decomposition processes were combined together to calculate a_0 and a_1 . This same approach has been applied to the data obtained in

Table 4 Kinetic parameters for the thermal decomposition of PET treated fabrics

	Std PET	T23DBBP on PET	T23DB2MPP on PET	T23DBBP on PET	T23DB3MBP on PET	T34DBBP on PET
<i>1st Stage</i>						
α range (0.01-0.1) E_a , kJ/mol	84.7 \pm 2.3	88.9 \pm 9.7	102.8 \pm 2.1	80.6 \pm 8.7	118.5 \pm 2.1	85.3 \pm 9.0
Log A , sec ⁻¹	7.77 \pm 0.21	9.18 \pm 0.99	11.08 \pm 0.34	8.26 \pm 0.69	13.87 \pm 0.36	8.98 \pm 0.96
Relative rate constant @ 250 °C	1	9.5	31.3	7.2	514	14.1
<i>2nd Stage</i>						
α range (0.15-0.4) E_a , kJ/mol	115.4 \pm 19.8	116.4 \pm 4.5	116.4 \pm 3.5	106.1 \pm 2.7	115.2 \pm 3.7	110.8 \pm 2.4
Log A , sec ⁻¹	10.36 \pm 1.60	10.94 \pm 0.30	10.89 \pm 0.34	10.11 \pm 0.17	10.72 \pm 0.29	10.49 \pm 0.18
Relative rate constant @ 300 °C	1	3.1	2.8	4.0	2.4	3.5
<i>3rd Stage</i>						
α range (0.5-0.8) E_a , kJ/mol	163.1 \pm 3.0	170 \pm 3.1	160.8 \pm 5.5	164.9 \pm 6.7	158.0 \pm 5.6	161.9 \pm 6.6
Log A , sec ⁻¹	14.12 \pm 0.24	14.84 \pm 0.33	14.12 \pm 0.40	14.45 \pm 0.48	13.91 \pm 0.42	14.21 \pm 0.47
Relative rate constant @ 300 °C	1	1.1	1.6	1.5	1.8	1.6
<i>4th Stage</i>						
α range (0.85-0.98) E_a , kJ/mol	136.8 \pm 2.5	143.3 \pm 14.9	124.9 \pm 7.8	130.1 \pm 9.2	116.1 \pm 13.4	132.7 \pm 11.4
Log A , sec ⁻¹	11.63 \pm 0.11	12.2 \pm 1.39	10.67 \pm 0.44	11.05 \pm 0.67	10.09 \pm 0.77	11.31 \pm 0.90
Relative rate constant @ 300 °C	1	1.1	1.3	1.1	2.2	1.2

Table 5 Calculated rate constants from the kinetic parameters derived using the Flynn method

Chemical	k at 250 °C for neat chemical, sec^{-1}	k' at 250 °C for the 0.01–0.1 α range on PET, sec^{-1}	k/k'
T23DBPP	9.6	1.9	5.0
T23DB2MPP	319	6.4	49.6
T23DBBP	25	1.5	17.0
T23DB3MBP	2135	105	20.3
T34DBBP	60	2.9	20.8

Table 6 Regression coefficients of compensation effect plots of the kinetic data obtained from the Flynn method

	a_0	a_1	r
Std PET	-0.081 ± 0.001	0.95 ± 0.03	0.999
T23DBPP	-0.074 ± 0.002 (-0.077 ± 0.003)	2.16 ± 0.28 (1.71 ± 0.29)	0.991 (0.989)
T23DB2MPP	-0.065 ± 0.006 (-0.078 ± 0.003)	3.49 ± 0.71 (1.54 ± 0.37)	0.924 (0.981)
T23DBBP	-0.073 ± 0.002 (-0.076 ± 0.003)	2.17 ± 0.24 (1.85 ± 0.31)	0.992 (0.985)
T23DB3MBP	-0.070 ± 0.012 (-0.080 ± 0.003)	3.18 ± 1.56 (1.21 ± 0.30)	0.769 (0.988)
T34DBBP	-0.069 ± 0.003 (-0.073 ± 0.005)	2.76 ± 0.35 (2.19 ± 0.41)	0.982 (0.977)

Values in parenthesis obtained by rejection of the $\alpha=0.01-0.1$ data.

this study for the treated PET samples and the results obtained are summarized in Table 6.

From these data, it can be seen that all additives are responsible for changes in a_0 and a_1 , although not to the same degree but at least in the same direction. Unfortunately, this direction of change has been interpreted to correspond to a nonbeneficial effect in the condensed phase fuel producing reactions in flame retardation studies [17] a finding confirmed in our studies with commercial T23DBPP [14, 18].

Interestingly, the data presented for T23DB2MPP and T23DB3MBP in Table 6 show large errors and poor correlation coefficients " r ". Examination of the actual $\log A$ vs. E plots revealed that the data for the α values between 0.01–0.1 were

obviously outliers, i.e. they did not lie on the same line as the other data. When the data were re-evaluated omitting the data up to $\alpha=0.1$, the new a_0 and a_1 coefficients were more consistent. Clearly, therefore, the greatest differences in the behaviour of these chemicals on the thermal decomposition of PET lie in the early weight-loss stages. In the case of T23DB2MPP and T23DB3MBP, the kinetics of the earlier weight loss stage appear to be significantly different from those observed for the other chemicals. Not only are they responsible for discrepancies in the regression coefficients, but also marked differences in the apparent activation energies E for the 1st Stage decomposition (Table 4). Interestingly, these two compounds were also the only ones to provide sufficient data to enable peak E values to be determined for the 1st Stage according to the Kissinger method (Table 3). Although possible chemical and physical interaction may be occurring between the chemicals and PET, it would appear that in the case of T23DB2MPP and T23DB3MBP, the major cause of these different kinetic behaviours lies in the lower thermal stability associated with these two chemicals. T23DB2MPP and T23DB3MBP decompose at lower temperatures, consequently their effect on the regression coefficients, as noted in Table 6 are the least nonbeneficial once the earlier weight loss has been accounted for. Thus, in terms of actual flame retardation this observation may help in part to explain their relative effectiveness in comparison to the other compounds [3].

Conclusion

The incorporation of methyl substituents into the tris dibromo propyl phosphate structure reduces the thermal stability of the compounds. Kinetic measurements of the weight-loss decomposition rates have indicated that two methyl substituents in the 3 position result in the greatest effect followed by 1 methyl substituent in the 2 position. Incorporation of these chemicals into PET at an approximate "add on" of 10% resulted in only slight changes to the degradation of PET, similar to those observed previously for the commercial flame retardant T23DBPP.

* * *

The authors wish to express their appreciation to Dr. S. D. Nelson and Dr. J. G. Omichinski of the Department of Medical Chemistry, University of Washington, Seattle, Washington, 98195, U.S.A. for supplying the chemicals for this study.

References

- 1 A. Blum and B. N. Ames, *Science*, 195 (1977) 17.
- 2 E. J. Soderlund, T. G. Omichinski, J. E. Dahl, S. D. Nelson and E. Dybing, Submitted to *Toxicol. Appl. Pharmacol.* (1987).
- 3 M. Day, T. Suprunchuk, J. G. Omichinski and S. D. Nelson, *J. Appl. Polym. Sci.*, 35 (1988) 529.
- 4 H. E. Kissinger, *Anal. Chem.*, 21 (1957) 1702.
- 5 J. H. Flynn, *J. Thermal Anal.*, 27 (1983) 95.
- 6 J. G. Omichinski, E. J. Soderlund, J. Brausano, E. Dybing and S. D. Nelson, *Mutagenesis* (1987) (in press).
- 7 E. J. Soderlund, S. D. Nelson and E. Dybing, *Toxicology*, 21 (1981) 291.
- 8 J. D. Cooney, M. Day and D. M. Wiles, *J. Appl. Polym. Sci.*, 28 (1983) 2887.
- 9 Y. Okamoto, N. Kimiara and H. Sakurai, *Bull. Chem. Soc. Japan*, 47 (5) (1974) 1299.
- 10 K. J. L. Paciorek, R. H. Kratzer, J. Kaufman, J. H. Nakahara, T. Christos and A. M. Harstein, *Am. Ind. Hyg. Assoc. J.*, 39 (8) (1978) 633.
- 11 A. Maccoll, *Chem. Rev.*, 69 (1969) 33.
- 12 P. J. Koch, E. M. Pearce, J. A. Lapham and S. W. Shalaby, *J. Appl. Polym. Sci.*, 19 (1975) 227.
- 13 Z. Adonyi and T. Korosi, *Thermochim. Acta*, 60 (1983) 23.
- 14 J. D. Cooney, M. Day and D. M. Wiles, *J. Appl. Polym. Sci.*, 29 (1984) 911.
- 15 A. I. Lesnikovich, S. V. Levchik and G. F. Levchik, *J. Appl. Polym. Sci.*, 31 (1986) 1943.
- 16 J. D. Cooney, M. Day and D. M. Wiles, *Thermochim. Acta*, 113 (1987) 105.
- 17 W. Micheva, S. Voynova, A. Cherneva and P. Petrova, "A Thermogravimetric Investigation of Modified Polyethylene Terephthalate Decomposition Kinetics", Hungarian Symposium on Thermal Analysis, Budapest, June 1981.
- 18 M. Day, T. Suprunchuk and D. M. Wiles, *Fire Mater.*, 7 (1983) 150.

Zusammenfassung — Für eine Reihe von Tris-dibrom-alkylphosphaten (ähnlich dem Tris-(2,3-dibrompropyl)-phosphat (T23DBPP) wurde mittels nichtisothermer Thermogravimetrie deren thermische Zersetzung separat bzw. eingebettet in Polyäthylenterephthalat- (PET) gewebe untersucht. Eine kinetische Analyse zeigte, daß Tris-(2,3-dibrom-3-methylbutyl)-phosphat (T23DB3MBP) vor Tris-(2,3-dibrom-2-methylpropyl)-phosphat (T23DB2MPP) die größte Zersetzungsgeschwindigkeit aufweist. Tris-(3,4-dibrombutyl)-phosphat (T34DBBP) und Tris-(2,3-dibrombutyl)-phosphat (T23DBBP) verfügen über eine nur schwach geringere Zersetzungsgeschwindigkeit als das T23DBPP selbst. Die zersetzungsgeschwindigkeit des mit den Chemikalien behandelten PET ist nur um ein geringeres höher als die des unbehandelten Gewebes. Ausnahmen bilden hier nur einige anfängliche Gewichtsverluste, die anscheinend auf den Zerfall der Chemikalien zurückzuführen sind. Die errechneten kinetischen Parameter lassen darauf schließen, daß sich alle obigen Substanzen ähnlich dem T23DBPP verhalten, nämlich in einer auffallend ungünstigen Beeinflussung der kinetischen Eigenschaften der Zersetzung in der kondensierten Phase, während sie auf Grund der entflammungshemmenden Wirkung als Entflammungshemmer in der Gasphase dienen können.

Резюме — Неизотермической термогравиметрией изучено термическое разложение ряда три(бромалкил)фосфатов, подобных три(2,3-дибромпропил)фосфату (T23ДВРР), как чистых, так и введенных в полиэтилентерефталат (PET). Кинетические определения показали, что скорость разложения была наибольшей для три(2,3-дибром-3-метилбутил)фосфата, а затем для три(2,3-дибром-2-метилпропил)фосфата. Скорости разложения три(3,4-дибромбутил)фосфата

и три(2,3-дибромбутил)фосфата были только немного выше по сравнению с самим три(2,3-дибромпропил)фосфатом. Скорости разложения полиэтилентерефталатов, обработанных этими соединениями, были только немного большими по сравнению с необработанными, за исключением начальных стадий потери веса, где происходило некоторое разложение фосфатов. Кинетические параметры, вычисленные на основе изоконверсионного метода совместно с графиками регрессионных коэффициентов компенсационного эффекта, предполагают, что все исследованные соединения ведут себя подобно три(2,3-дибромпропил)фосфату, имея в виду их кажущийся вредный эффект на кинетику разложения конденсированной фазы. Относительно их влияния на замедление горения, они действуют как замедлители воспламенения газовой фазы.