

Combustion and Pyrolysis of Poly(ethylene Terephthalate). III. The Effect of Tris(2,3-Dibromopropyl) Phosphate on the Products of Pyrolysis*

M. DAY, V. PARFENOV,[†] and D. M. WILES, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9*

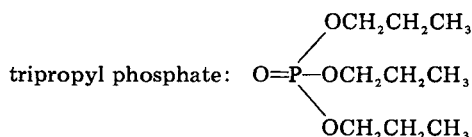
Synopsis

The influence of the flame retardant chemical tris(2,3-dibromopropyl) phosphate, and the related chemical species, tripropyl phosphate and 2,3-dibromopropanol, on the products of pyrolysis of poly(ethylene terephthalate), has been examined as a function of chemical concentration. The species containing phosphorus only and bromine only had little effect on the composition and concentration of the pyrolysis products. The tris(2,3-dibromopropyl) phosphate had a significant effect upon the pyrolysis product distribution, and is capable of influencing the decomposition reactions of poly(ethylene terephthalate).

INTRODUCTION

A fundamental understanding of the pyrolysis process occurring during the burning of poly(ethylene terephthalate) (PET) greatly assists in the evaluation of the effectiveness of flame retardant chemicals. In a previous paper,¹ we examined the role of several commercial flame retardants using a flash pyrolysis/gas chromatography technique to determine if they are capable of altering the pyrolysis. Although this earlier study examined several commercial flame retardants of proven effectiveness only one compound, tris(2,3-dibromopropyl) phosphate (Tris), was capable of producing changes in the composition of the volatile products of pyrolysis. Since there is the possibility of a concentration dependence with this flame retardant, it was decided to investigate several topically treated PET fabrics with different add-on levels of Tris present. Tris has the phosphorus and bromine present in the same molecular structure. In view of the possible interaction of these two elements when present in the same structure alternative species containing phosphorus and bromine only were also investigated.

The compounds chosen were

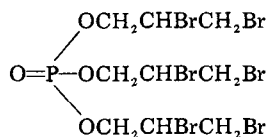


and 2,3-dibromopropanol: $\text{HOCH}_2\text{CHBrCH}_2\text{Br}$.

* Issued as NRCC 19854.

[†] Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow, USSR.

These two compounds were chosen since both the phosphorus and bromine atoms were in similar molecular environments to those encountered in the tris(2,3-dibromopropyl) phosphate:



The burning process associated with polymeric materials is a highly complex system, further complicated by variations in the surrounding fire environments. The polymeric material involved in the burning process can therefore experience temperatures ranging from ambient in the bulk of the material up to around 1000°C in the flame. In order to reflect this wide range of temperatures and heating rates encountered in the burning process, this investigation was conducted using a commercial flash pyrolysis system.

EXPERIMENTAL

Materials

The PET employed in this study was 100% spun dacron type 54 yarn woven fabric obtained from Testfabrics Inc. (Style 767).

The tris(2,3-dibromopropyl) phosphate was obtained from K and K Chemicals. Analysis for total bromine content indicated 68.3% (theoretical = 68.8%).

The tripropyl phosphate was obtained from Chemical Procurment Laboratories, Inc. Analysis for total phosphorus content indicated 13.4% (theoretical = 13.8%).

The 2,3-dibromopropanol was from Aldrich Chemicals and reported to be 96% pure. Analysis for bromine content indicated 70.8% (theoretical = 73.4%).

All the above chemicals were used as received without further modification. They were applied topically to the polyester fabric by padding the cloth with an appropriate solution of the chemical in methylene chloride. The wet cloth was then squeezed gently between blotting paper and dried under ambient conditions. The percentage chemical pickup of phosphorus and bromine on the fabrics was determined by appropriate quantitative methods.² Table I lists all the materials treated and tested in this investigation.

Pyrolysis System

The flash pyrolysis system employed was a Chemical Data Systems Pyroprobe 120 with a coil probe attachment interfaced to a Hewlett-Packard Model 5730A gas chromatograph. Fiber samples weighing 0.2–0.4 mg were pyrolyzed at nominal temperatures of 700°C and 900°C for 10 s and the pyrolysis products separated according to the procedure employed previously.¹ It should be noted that the Pyroprobe settings of 700°C and 900°C do not give instantaneous heating of the sample due to heat transfer delay and the thermal mass of the quartz sample tube. With the 900°C setting the sample temperature is approximately 600°C after 5 s and 700°C at the end of the heating period.

TABLE I
Polyester Fabrics Examined

| Chemical additive | % P on fabric | % Br on fabric | % Chemical loading (w/w) |
|-----------------------------------|---------------|----------------|--------------------------|
| Tris(2,3-dibromopropyl) phosphate | 0.15 | 2.29 | 3.33 |
| | 0.24 | 3.68 | 5.35 |
| | 0.34 | 5.26 | 7.65 |
| | 0.45 | 6.86 | 9.97 |
| Tripropyl phosphate | 0.16 | — | 1.16 |
| | 0.30 | — | 2.17 |
| | 0.44 | — | 3.19 |
| 2,3-dibromopropanol | — | 3.67 | 5.00 |
| | — | 4.92 | 6.70 |
| | — | 6.19 | 8.43 |

Employing the 700°C nominal temperature setting, meanwhile the temperatures are 450°C and 500°C at the 5- and 10-s intervals, respectively.

RESULTS

The pyrolysis of PET leads to the formation of numerous products, the relative quantitative distribution of which are greatly dependent upon the pyrolysis conditions. In the case of untreated PET we have identified close to 40 of the pyrolysis products.¹ However, from a mechanistic evaluation point of view it is necessary to consider only the 10 major products listed in Table II. The tripropyl phosphate and dibromopropanol treated fabrics did, however, give peaks associated with the volatilization of these compounds as well (confirmed by GC Mass Spectrometer). A quantitative evaluation of their concentrations revealed that these materials were simply being volatilized without decomposition under the pyrolysis conditions employed.

In the case of the Tris-treated polyesters, no new peaks associated with the flame retardant were detected.

This raises the question of the fate of the phosphorus and bromine present

TABLE II
The Major Pyrolysis Products of Untreated PET

| Pyrolysis temp (°C) % wt loss | 700 | | 900 | |
|----------------------------------|-------------------|----------------------|-------------------|----------------------|
| | 23.1 | | 89.8 | |
| | % wt pyrolyzed | % total volatiles | % wt pyrolyzed | % total volatiles |
| Carbon monoxide | 1.06 | 4.59 | 6.90 | 7.68 |
| Carbon dioxide | 4.27 | 18.48 | 10.68 | 11.89 |
| Methane | 0.02 | 0.09 | 0.25 | 0.28 |
| Acetylene | 0.65 | 2.81 | 2.20 | 2.45 |
| Acetaldehyde | 2.89 | 12.51 | 3.69 | 4.11 |
| Benzene | 0.05 | 0.22 | 3.14 | 3.50 |
| Vinyl benzoate | 2.30 | 9.96 | 12.87 | 14.33 |
| Benzoic acid | 1.89 | 8.18 | 14.42 | 16.06 |
| Divinyl terephthalate | 3.80 | 16.45 | 14.16 | 15.77 |
| Ethylene dibenzoate | 2.46 | 10.65 | 3.13 | 3.49 |
| Total | 19.39 | 83.94 | 71.44 | 79.56 |

in the flame retardant. A sample of Tris-treated asbestos fabric (preburnt to remove contaminations) was therefore pyrolyzed under the same pyrolysis conditions and the pyrolysis products determined by gas chromatography/mass spectrometer using the technique used previously. The results of this experiment are presented in Table III. It will be noted that the majority of these products are those found in the pyrolysis of standard PET, i.e., carbon monoxide, carbon dioxide, acetylene, etc. However, some aliphatic bromides are also formed, although not in large enough concentrations to explain the fate of the bromine present in the Tris. The presence in the pyrolysis gases of relatively large concentrations of the unsaturated species, however, indicate the possibility of unimolecular elimination of HBr occurring to give the olefins.

Okamoto,³ who studied the pyrolysis of tris(2,3-dibromopropyl) phosphate at 250–260°C observed that 1,2,3-tribromopropane was the major gaseous species formed along with *cis*- and *trans*-1,3-dibromopropene, 2,3-dibromopropene-1 and 3-bromopropene-1. Similarly pyrolysis at 430°C not only gives the bromopropanes but also some bromomethane.⁴ Paciorek,⁵ meanwhile, found hydrogen bromide in addition to the brominated propenes and propanes. At the higher temperature encountered in our pyrolysis studies it can be anticipated that these bromopropanes and propenes would further degrade to give HBr as a result of dehydrobromination a favorable reaction at 500°C. For example, based upon the existing data for other alkyl halides,⁶ a good estimate of the activation energy and log *A* factor for the dehydrobromination of these species are 52 kcal and 13.5 s⁻¹, respectively. Applying these figures to a reaction time of 10 s would give an estimated yield of HBr of 90% at 525°C. This therefore helps to explain the lack of organo bromides in the pyrolysis gases.

Unfortunately, attempts to detect HBr in the pyrolysis gases from the pyroprobe were unsuccessful presumably due to absorption or reaction with the materials in the separating system. However, by the use of larger samples pyrolyzed in a tubular furnace maintained at 500°C HBr was readily detected in gaseous pyrolysis products of Tris-treated PET. Tests for phosphorus in the same gaseous pyrolysis products were negative. Chemical analysis of the residual

TABLE III
Volatile Pyrolysis Products of Tris-Treated Asbestos [18.6% Chemical Add-on]^a

| Product | % wt pyrolyzed | % total volatiles |
|------------------|----------------|-------------------|
| Carbon monoxide | 2.3 | 13.3 |
| Carbon dioxide | 2.7 | 15.8 |
| Methane | 0.3 | 1.7 |
| Acetylene | 1.7 | 9.8 |
| Ethane | 0.1 | 0.4 |
| Water | 2.9 | 16.9 |
| Propylene | 0.9 | 5.2 |
| Propyne | 0.2 | 1.2 |
| Acetone | 0.8 | 4.7 |
| Vinyl bromide | 0.3 | 1.9 |
| Propenal | 0.3 | 1.6 |
| Propenaldehyde | 1.0 | 5.6 |
| 2-Bromopropene-1 | 0.3 | 1.7 |
| 3-Bromopropene-1 | 0.5 | 3.1 |
| Total | 14.3 | 82.9 |

^a Pyrolysis temp setting = 900°C; Pyrolysis time = 10 s; % wt loss = 17.2%.

chars, however, revealed the presence of phosphorus but not bromine. It would thus appear that under the pyrolysis conditions employed in our study the bromine contained in the Tris is liberated as HBr while the phosphorus remains in the residue. The product distribution of the major pyrolysis products as a function of the treatment chemicals are shown in Figures 1–10. These figures, representing the variation of carbon monoxide, carbon dioxide, methane, acetylene, acetaldehyde, benzene, vinyl benzoate, benzoic acid, divinyl terephthalate, and ethylene dibenzoate, respectively, as a function of weight percentage of phosphorus and bromine on the fabrics. The values presented in these figures represent the mean calculated from at least four determinations. The uncertainty of these values are of the order of 10% for the major species ($\geq 10\%$ of total volatiles) while the other species have a slightly larger degree of uncertainty (15%).

The positive influence of Tris is clearly evident in the formation of CO (Fig. 1), which is enhanced by this chemical's presence. This effect is especially noticeable with the 900°C pyrolysis conditions when Tris causes a twofold increase in the CO formation over that obtained with the untreated fabric. It will be noted that in the case of the tripropyl phosphate and 2,3-dibromopropanol treatments no significant changes are observed in the CO production.

The data for CO₂ formation (Fig. 2) show a varied concentration dependence. However, in all cases the concentration of CO₂ produced at higher temperatures is always less than that produced at the lower temperatures. This variation in CO₂ concentration with chemical retardant concentration is largest with the Tris-treated material pyrolyzed at the 700°C setting. This additive apparently causes a marked increase in the CO₂ at the lower treatment levels of 3–4% but at higher levels the CO₂ percentage in the pyrolysis gas mixture is reduced, ultimately reaching a concentration less than that obtained with the untreated fabric. The other two chemical retardants, however, can be regarded as having little effect on the formation of CO₂.

Methane (Fig. 3) is obviously one of the gaseous products whose concentration is greatly dependent upon the concentration of Tris in the system. While the

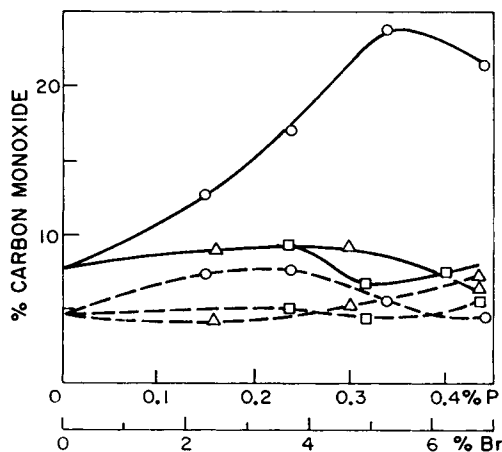


Fig. 1. Variation of percentage carbon monoxide formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-bibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

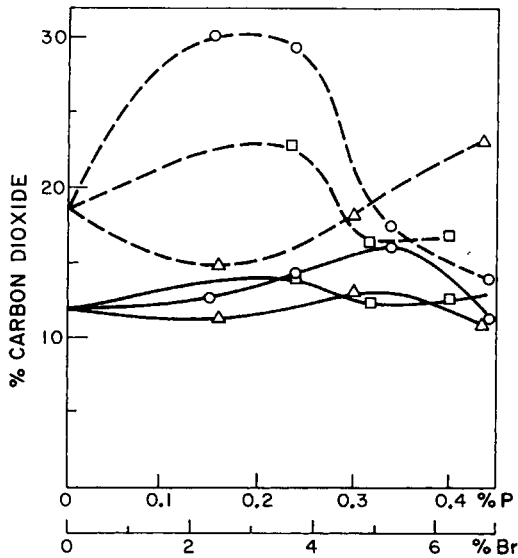


Fig. 2. Variation of percentage carbon dioxide formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

tripropyl phosphate and 2,3-dibromopropanol clearly have negligible effects on methane formation, Tris is capable of markedly enhancing the percentage of methane in the pyrolysis gases. This increase is most marked at 900°C but even at 700°C is still very pronounced.

The retardant Tris also significantly influences acetylene formation (Fig. 4). However, unlike the situation that was observed in the case of methane, the greatest effect is observed at concentrations of Tris around 8% on the fabric: The

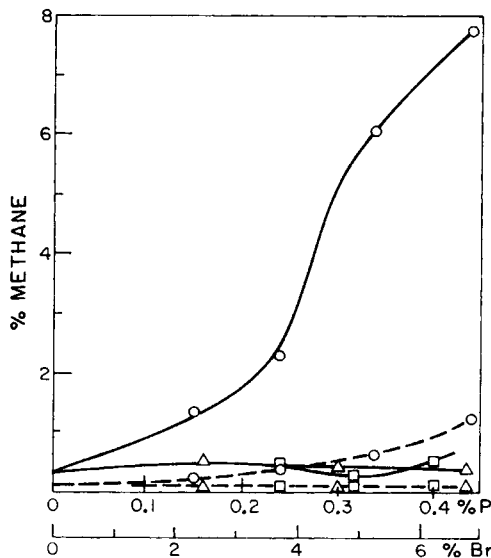


Fig. 3. Variation of percentage methane formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

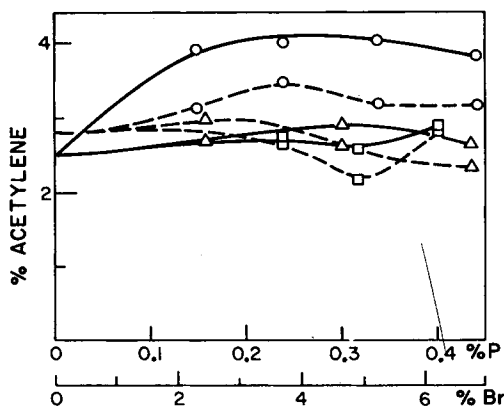


Fig. 4. Variation of percentage acetylene formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (O) is pyrolyzed at 700°C (---) and 900°C (—).

magnitude of the observed effect is also much less than that observed with methane. Meanwhile the other two retardants have little effect on the production of acetylene.

Acetaldehyde (Fig. 5) a product of major significance at the lower pyrolysis temperature is almost unaffected by the presence of the flame retardants. Tris, however, appears to be capable of causing some slight increase in the acetaldehyde concentration at 900°C as the amount of Tris on the fabric is increased.

The concentration of benzene (Fig. 6) in all samples pyrolyzed at 700°C was small and virtually independent of flame-retardant type and concentration. This would seem to suggest that it is being formed as a result of further fragmentation of the initial pyrolysis product. At 900°C, on the other hand, the concentration of benzene in the pyrolysis gases is reduced by the presence of Tris and 2,3-dibromopropanol, suggesting that they are both capable of retarding the decar-

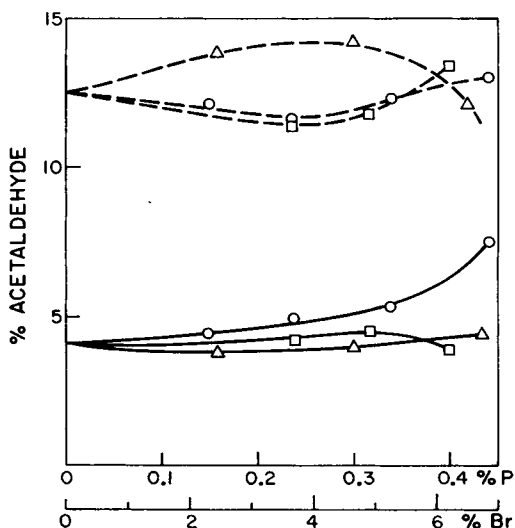


Fig. 5. Variation of percentage acetaldehyde formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (O) is pyrolyzed at 700°C (---) and 900°C (—).

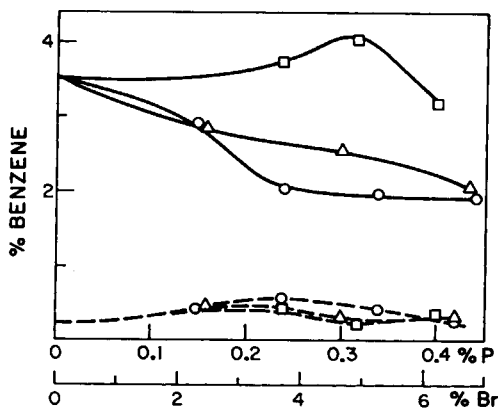


Fig. 6. Variation of percentage benzene formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

boxylation reactions required for its formation. Further pyrolysis of benzene at 900°C, however, is an alternative possibility which could lead to a reduced concentration of benzene in the pyrolysis gases.

So far we have seen that the chemical Tris has enhanced the concentration of the nonaromatic species (CO, CO₂, methane, acetylene, and acetaldehyde). In the case of the aromatic systems, however, the situation is slightly different. For example with vinyl benzoate (Fig. 7), the Tris-treated material produces lower concentrations of this product as the amount of the flame retardant present on the fabric is increased. The changes observed with the other two systems are

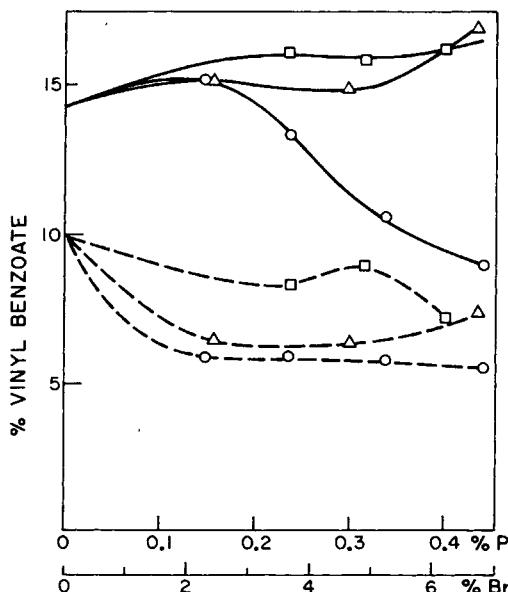


Fig. 7. Variation of vinyl benzoate formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

not nearly so marked, and appear to be dependent upon the temperature of pyrolysis, i.e., a slight increase at high temperatures, and reduction at the lower pyrolysis temperature.

Benzoic acid formation (Fig. 8) is significantly retarded by the Tris treatments, as well as by the other treatments, although to a much lesser extent. In the case of the Tris material, the reduction in benzoic acid concentration is of the order of 70% at both 700°C and 900°C.

The concentration of the aromatic product divinyl terephthalate (Fig. 9) is also reduced by increasing the concentration of Tris in the system. 2,3-Dibro-

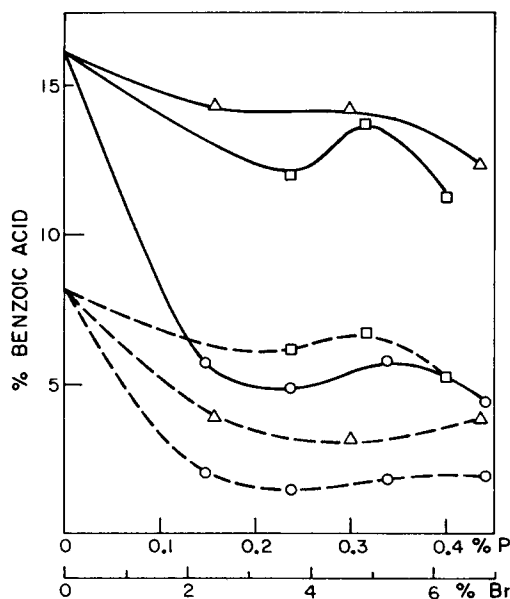


Fig. 8. Variation of percentage benzoic acid formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl)phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

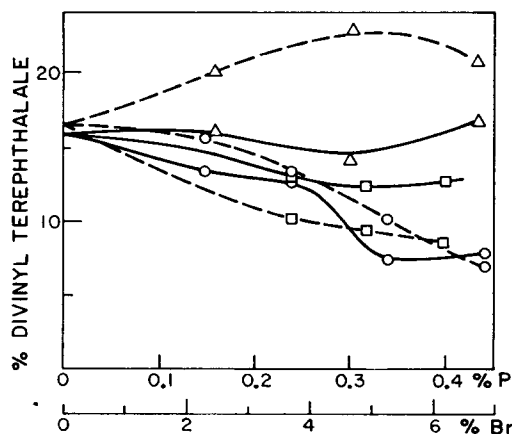


Fig. 9. Variation of percentage divinyl terephthalate formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

mopropanol produces a similar effect, which is contrary to that observed with tripropyl phosphate.

The concentration of ethylene dibenzoate (Fig. 10) appears to be unaffected by the presence of tripropyl phosphate and 2,3-dibromopropanol, irrespective of their concentration and the pyrolysis temperature. The Tris treatment, on the other hand, causes a drastic reduction in the concentration of ethylene dibenzoate as the Tris concentration in the fabric is increased. This reduction is particularly marked at the lower pyrolysis temperature, mainly because of its higher proportion in the pyrolysis gases at this temperature.

DISCUSSION

Based upon the data plotted in these graphs it can be clearly seen that the tripropyl phosphate and 2,3-dibromopropanol have little effect upon the major pyrolysis products of PET when present on the fabric in concentrations up to 3.2% and 8.4%, respectively. In view of the observed volatilization of these two compounds when pyrolyzed under the experimental conditions employed in this study, it is not too surprising that they have negligible effects upon the solid-phase pyrolysis reactions. Tris(2,3-dibromopropyl) phosphate, however, appears to have a significant influence upon the pyrolysis product pattern when present on the fabric in concentrations ranging from 3% to 10%. The major effect of Tris is to cause the concentration of the nonaromatic low-molecular-weight species to increase while at the same time causing the concentration of the volatile aromatic species to be reduced.

In order to explain these observations, the proposed mechanism¹ by which the primary and secondary chain scission reactions lead to the primary products of pyrolysis is considered in Scheme I.

These reactions explain the formation of the aromatic species vinyl benzoate, divinyl terephthalate, benzoic acid, and benzene, plus CO₂ produced by the decarboxylation reactions. With the Tris-treated materials the concentration of the aromatic components are reduced and the nonaromatic species are increased. This would suggest that alternative reactions to those already proposed must

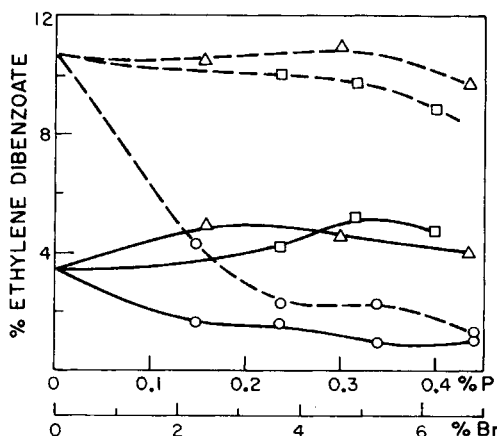
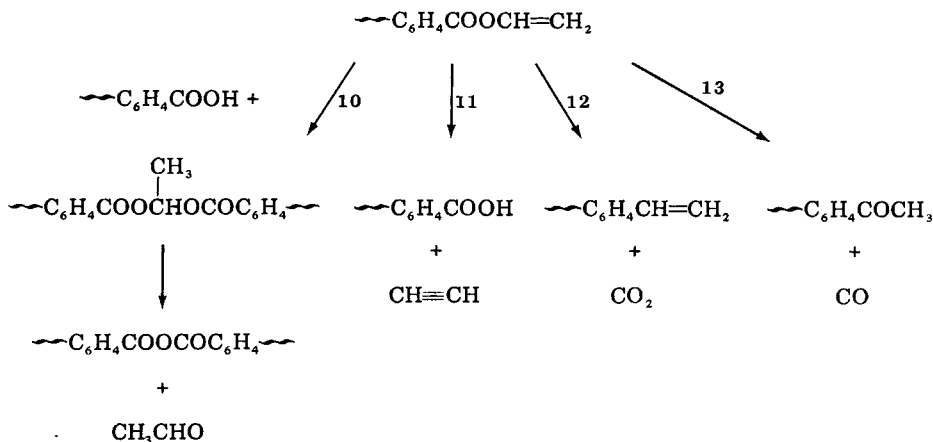


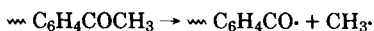
Fig. 10. Variation of percentage ethylene dibenzoate formed in pyrolyzed gases when PET containing tripropyl phosphate (Δ), 2,3-dibromopropanol (\square), and tris(2,3-dibromopropyl) phosphate (\circ) is pyrolyzed at 700°C (---) and 900°C (—).

be considered. In the case of untreated PET we have shown¹ that the vinyl-terminated species have alternative reactions to 4 and 5 above, namely:



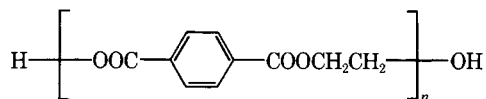
These reactions would thus enable the higher concentrations of acetaldehyde, acetylene, and CO to be accounted for.

Enhanced formation of methane from the Tris-treated materials, however, still remains to be resolved. In an earlier paper¹ we proposed that the most probable precursor to methane were the acetyl-terminated species produced by reaction 13 (above) which are capable of undergoing acetyl cleavage to give methyl radicals:



These radicals are then capable of numerous reactions, including hydrogen abstraction to give methane. The feasibility of this postulate can be established by performing a complete molar balance of the major products of pyrolysis.


PET, a condensation product of terephthalic acid and ethylene glycol, is frequently represented as follows:



With this structure we can identify the ester oxygen $-\text{O}-$, the carbonyl group $>\text{C}=\text{O}$, the aromatic ring, and the aliphatic carbons $-\text{CH}_2-$. Since the PET used in our investigation was known to have a molecular weight (M_n) of about 19,000, it follows then that n in the above structure must correspond to approximately 100. Thus if 1 mol of PET were completely pyrolyzed, it should be possible to account for 201 ester oxygens ($-\text{O}-$), 200 carbonyl entities ($>\text{C}=\text{O}$), 100 aromatic rings and 200 aliphatic carbons ($-\text{CH}_2-$) in the pyrolysis products. Using the proposed reactions (1-13 above) for the pyrolysis of PET, it is possible to analyze the pyrolysis data to determine if the product distribution obtained can be explained. These calculations have been performed using the pyrolysis data obtained for the standard untreated PET and the 10% Tris-treated PET at 900°C, and the results are presented in Tables IV and V, respectively.

In the case of the standard untreated PET (Table IV) with a 89.8% weight loss on pyrolysis the expected yield of benzene residues is 90, while the yield of the

TABLE IV
Moles of Pyrolysis Products and Mole Fragments Produced per Mole^a of Untreated PET Heated at 900°C (89.8% Pyrolysis)


| Compound | Moles | Mole fragments accountable | | | |
|---------------------------------|-------|----------------------------|-------|----------|---|
| | | $>C=O$ | $-O-$ | $-CH_2-$ |  |
| Carbon monoxide | 47 | 47 | — | — | — |
| Methane | 3 | — | — | 3 | — |
| Carbon dioxide | 47 | 47 | 47 | — | — |
| Acetylene | 16 | — | — | 32 | — |
| Propylene | 1 | — | — | 3 | — |
| Acetaldehyde | 16 | — | 16 | 32 | — |
| Acetone | 1 | 1 | — | 2 | — |
| Ethanol | 2 | — | 2 | 4 | — |
| Benzene | 8 | — | — | — | 8 |
| Toluene | 1 | — | — | 1 | 1 |
| Styrene | 1 | — | — | 2 | 1 |
| Acetophenone | 3 | 3 | — | 3 | 3 |
| Vinyl benzoate | 17 | 17 | 17 | 34 | 17 |
| Benzoic acid | 23 | 23 | 23 | — | 23 |
| <i>p</i> -Methyl vinyl benzoate | 1 | 1 | 1 | 3 | 1 |
| <i>p</i> -Ethyl vinyl benzoate | 1 | 1 | 1 | 4 | 1 |
| <i>p</i> -Vinyl vinyl benzoate | 1 | 1 | 1 | 4 | 1 |
| Diacetyl benzene | 1 | 2 | — | 2 | 1 |
| <i>p</i> -Acetyl vinyl benzoate | 3 | 6 | 3 | 9 | 3 |
| Divinyl terephthalate | 13 | 26 | 26 | 52 | 13 |
| <i>p</i> -Acetyl benzoic acid | 2 | 4 | 2 | 2 | 2 |
| Ethylene dibenzoate | 2 | 4 | 4 | 4 | 4 |
| Total | | 182 | 143 | 196 | 79 |

^a Based upon a sample weight of 19,200 g (i.e., 1 mol unit of PET).

$>C=O$, $-O-$, and $-CH_2-$ fragments should be 180. The value of 182 obtained for the $>C=O$ is obviously in very good agreement with the expected value of 180, while the values for the aliphatic carbon (196) and the aromatic ring (79) are also close to the expected values of 180 and 90, respectively. The value for the ester $-O-$, however is on the low side in that approximately 38 molecular units are still unaccounted for. While water, a pyrolysis product detected but not quantified, could account for some of this discrepancy, it is possible that some hydroxylation of the pyrolysis residue also occurred. Essentially, however, the molar balance for the standard untreated PET is very good (within the accuracy and precision estimated for the pyrolysis products), and the pyrolysis reactions proposed for PET enable the products to be accounted for based upon a random chain scission process.

The data obtained with the 10% Tris-treated material, (Table V) represents a slightly different situation. With this system, since the pyrolysis products of the flame retardant could not be separated from those derived from the polyester, the calculations have to take this into account. Assuming all the retardant is converted into pyrolysis products, it can be calculated that pyrolysis of the treated polymer at 80.2% weight loss would result in 70 mole fragments of the aromatic residue and 140 mole fragments of the $>C=O$, $-O-$, and $-CH_2-$ from the PET. Comparisons of these calculated values with those actually observed (Table V) reveals that only about one-half of the anticipated aromatic compounds have been accounted for in the pyrolysis products.

TABLE V
Moles^a of Pyrolysis Products and Fragments Produced from PET Treated with 9.97% Tris When Heated at 900°C (80.2% Pyrolysis)

| Compound | Moles | Mole fragments accountable | | | |
|---------------------------------|-------|----------------------------|-----|--------------------|---|
| | | >C=O | —O— | —CH ₂ — |  |
| Carbon monoxide | 118 | 118 | — | — | — |
| Methane | 75 | — | — | 75 | — |
| Carbon dioxide | 39 | 39 | 39 | — | — |
| Acetylene | 23 | — | — | 9 | — |
| Ethane | 4 | — | — | 8 | — |
| Propylene | 3 | — | — | 46 | — |
| Acetaldehyde | 26 | — | 26 | 52 | — |
| Ethanol | 2 | — | 2 | 4 | — |
| Benzene | 4 | — | — | — | 4 |
| Toluene | 2 | — | — | 2 | 2 |
| Ethyl benzene | 1 | — | — | 2 | 1 |
| Styrene | 1 | — | — | 2 | 1 |
| Acetophenone | 1 | 1 | — | 1 | 1 |
| Vinyl benzoate | 11 | 11 | 11 | 22 | 11 |
| Benzoic acid | 6 | 6 | 6 | — | 6 |
| <i>p</i> -Methyl vinyl benzoate | 1 | 1 | 1 | 3 | 1 |
| <i>p</i> -Ethyl vinyl benzoate | 1 | 1 | 1 | 4 | 1 |
| <i>p</i> -Vinyl vinyl benzoate | 1 | 1 | 1 | 4 | 1 |
| <i>p</i> -Acetyl vinyl benzoate | 2 | 4 | 2 | 6 | 2 |
| Divinyl terephthalate | 5 | 10 | 10 | 20 | 5 |
| Ethylene dibenzoate | 1 | 2 | 2 | 2 | 2 |
| Total | | 194 | 101 | 262 | 38 |

^a Based upon sample weight of 19,200 g.

Meanwhile the concentrations of carbonyl and aliphatic carbon derived species are significantly higher than anticipated. However, in the above calculations we have neglected the contribution of the flame retardant to the aliphatic carbon and ester oxygen. Continuing the assumption that all of the organic portion of the Tris finds its way into the volatiles, its contribution to the pyrolysis products can be estimated as 27 mole fragments of —CH₂— and 12 of —O—. However, even after correcting for this contribution from the flame retardant, 235 mol of aliphatic —CH₂— and 182 mol of >C=O must still be accounted for from the polyester, of which only 140 are attributable to random scission of the polymer chain.

Even if all of the available methylene carbons in the PET were to manifest themselves in the volatile residues this would only provide 180 mole fragments which would still leave a discrepancy of 55 mole fragments of —CH₂—. The observed 182 moles for the >C=O, however, is close to the figure of 180, suggesting that in the case of the Tris-treated PET a complete breakdown of all of the ester groups are taking place. The low concentration of aromatic rings in the pyrolysis gases, however, coupled with a complete depletion of the carbonyl into the gas phase suggest that the residue must contain a relatively high proportion of polyphenyl species produced as a result of the further reactions of the aromatic species such as benzene under these conditions in the presence of the Tris material. In the pyrolysis of benzene at 700–900°C biphenyl is a major product⁷ but at higher temperatures quantities of methane and acetylene are

produced.⁸ Although energetically unlikely, it is possible that in the presence of Tris some of these aromatic pyrolysis products are undergoing ring fission to produce methane and acetylene. Although no direct evidence was found supporting these ring fission reactions, they do explain both the low aromatic totals observed in Table V and the surplus of aliphatic carbons produced.

In this study the product benzyl alcohol was not detected as a major pyrolysis product. This observation was a little surprising in view of the work of Inagake, et al.,⁹ who studied Tris containing PET pyrolyzed at 360–450°C, and found that this alcohol was a major product of the pyrolysis. Our work, however, would suggest that at the higher pyrolysis temperatures benzyl alcohol is being subjected to further degradation when Tris is present in the system.

CONCLUSIONS

Flame retardant chemicals tripropyl phosphate and 2,3-dibromopropanol appear to have little effect upon the products of pyrolysis of PET and hence can be regarded as having no effect upon the pyrolysis fuel producing reactions. The phosphorus and bromine-containing compound, tris(2,3-dibromopropyl) phosphate, is, however, capable of altering the pyrolysis reactions of PET. Since the same general products are being observed in the presence and absence of Tris, it would appear that this chemical does not alter the primary pyrolysis reactions but instead modifies (or enhances) the secondary fragmentation steps which lead to the increased formation of the low-molecular-weight nonaromatic species at the expense of the higher-molecular-weight aromatic compounds. Thus although the organic gases present in the fuel produced on the pyrolysis of PET in the presence and absence of Tris are the same, the relative composition is changed due to the presence of the flame-retardant tris(2,3-dibromopropyl) phosphate.

References

1. M. E. Bednas, M. Day, K. Ho, R. Sander, and D. M. Wiles, *J. Appl. Polym. Sci.*, **26**, 277, (1981).
2. H. B. MacPherson, V. P. Clancy, and D. S. Russell, *Anal. Chim. Acta*, to appear.
3. Y. Okamoto, N. Kimura, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **47**(5), 1299 (1974).
4. P. D. Gain and C. L. Denson, *Tex. Res. J.*, **47**, 485 (1977).
5. K. J. L. Paciorek, R. H. Kratzer, J. Kaufman, J. H. Nakahara, T. Christos, and A. M. Hartstein, *Am. Ind. Hyg. Assoc. J.*, **39**(8), 633 (1978).
6. A. Maccoll, *Chem. Rev.*, **69**, 33, 1969.
7. G. M. Badger and J. Rovotny, *J. Chem. Soc.*, 3400 (1961).
8. C. R. Kinney and R. S. Slysh, *J. Phys. Chem.*, **65**, 1044 (1961).
9. N. Inagaki, H. Onishi, H. Kunisada, and K. Katsuura, *J. Appl. Polym. Sci.*, **21**, 217 (1977).

Received December 3, 1980

Accepted June 30, 1981