

The Role of Flame-Retardant Chemicals in the Thermal Degradation of Poly(ethylene Terephthalate). Studies with the Model Ester *n*-Propyl Pyrene-1-Carboxylate*

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Synopsis

The pyrolysis of *n*-propyl pyrene-1-carboxylate, a model ester for poly(ethylene terephthalate), has been studied using pyrolysis mass spectrometry. The major mode of decomposition has been identified as the formation of propylene and pyrene-1-carboxylic acid as a result of a cyclic intramolecular rearrangement. When phosphorus or bromine containing compounds are blended with the model ester, no significant changes are observed in the kinetics of the overall pyrolysis, while relatively small changes are observed in the mode of decomposition with the phosphorus compound. The results suggest that the role played by phosphorus and bromine in flame-retarding polyesters is predominately restricted to the gas phase.

INTRODUCTION

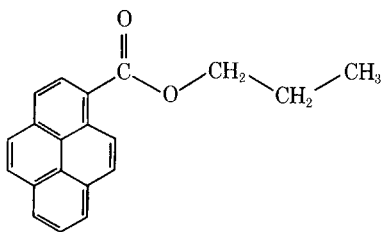
The application of chemical substances to reduce the fire hazard of materials has been known for a long time.¹ In the last two decades, however, there has been a great upsurge in research activity in this area, partly because of the rapid expansion in the utilization of synthetic materials, but mainly because of involvement of governments in establishing flammability standards.^{2,3} Despite this increased effort in flammability research and development, little detailed work has been undertaken regarding the specific chemical mechanisms involved in the flame retardation of polymeric materials. Most of the studies have been conducted on the melt-drip phenomenon, measurement of char length and amount of char residue, changes in rate of weight loss during decomposition, and limiting oxygen indices, etc. Unfortunately, these measurements only give the superficial consequences of the presence of a flame retardant, not the basics of the mechanisms of flame retardancy. Furthermore, many of the thermal studies pertaining to mechanistic evaluation have been carried out at relatively low heating rates ($\sim 20^\circ/\text{min}$) which are far slower than those encountered under real burning conditions.

This article presents some of our findings on the role of phosphorus and bromine compounds on the mechanisms of flame retardancy. Specifically, it con-

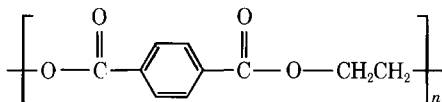
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siders the role of these elements on the pyrolysis of



(I)



(II)

n-propyl pyrene-1-carboxylate (I), a model ester for poly(ethylene terephthalate) (II).

This model compound was chosen for the relatively nonreactive nature of the bulky polynuclear group which served to reflect the restrictive motion of the esters in the polymer. The thermal properties of the material also made it ideally suitable for the pyrolysis studies under the rapid heating conditions employed in our work.

EXPERIMENTAL

Materials

n-Propyl pyrene-1-carboxylate (I) was prepared by refluxing 2.46 g (0.01 mol) of pyrene-1-carboxylic acid and 1.56 g (0.01 mol) of boron trifluoride etherate in 50 ml of *n*-propanol overnight. The clear, light-yellow solution was then cooled down and diluted with 100 ml of aqueous 5% sodium bicarbonate solution. The precipitate was collected and recrystallized from *n*-propanol yielding 2.3 g (94%) of *n*-propyl pyrene-1-carboxylate as yellow needles, mp 78°C. λ_{\max} (KBr) 2060, 2980, 2890, 1700, 1605, 1260, 1145, 855 cm^{-1} ; ^1H NMR (CDCl_3 , internal standard was tetramethylsilane) δ 8.88 (AB quartet, 2H, $J = 10$ Hz), 7.97 (m, $J = 7$ Hz), 4.38 (*t*, 2H, $J = 7$ Hz), 1.89 (m, 2H, $J_1 = J_2 = 7$ Hz), 1.13 (*t*, 3H, $J = 7$ Hz); mass spectrum (70 eV) m/e 288 (M^+ , 70) 246 (58), 202 (26), 201 (100), 42 (11).

ANAL. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2$: C, 83.3; H, 5.6. Found: C, 83.4; H, 5.7.

Ammonium dibasic phosphate and decabromodiphenylene oxide, which were used as the phosphorus and bromine-containing species, were used as received. The ammonium dibasic phosphate was from Allied Chemical Canada, Ltd.'s B and A quality reagent grade ACS. The decabromodiphenylene oxide was supplied

by the Dow Chemical Co., and reported to be 95% pure as determined by liquid chromatography.

Pyrolysis System

The pyrolysis experiments were performed using a Chemical Data Systems (CDS) Pyroprobe 120 with the ribbon probe attachment. This probe was interfaced with a Finnigan 4000 GC/MS using a short 250 × 3-mm stainless-steel tube. Helium at a flow rate of 20 ml/min was used to sweep the products of pyrolysis to the sampling valve of the mass spectrometer. The ribbon probe was heated from 25 to 865°C using a heating rate of 60°/sec. Two mass ions in the pyrolysis stream were analyzed, namely, 42 and 60 using a 16-eV electron voltage.

Experimental Procedure

The model ester was mixed with different portions of ammonium dibasic phosphate or decabromodiphenyl oxide using an a "Wig-L-Bug" (Spex Industries) to obtain the uniformly blended test samples listed in Table I. Approximately 10 mg of the test mixture was melted on the platinum ribbon probe by warming the ribbon to 75°C for 2 sec. The probe was then loaded into the CDS interface and the helium flow turned on. Once the system was stabilized, the power to the probe was switched on and the formation of propylene (mass 42) and *n*-propanol (60) monitored continually on the mass spectrometer using the single ion monitoring technique. Figure 1 shows a curve obtained for the mass ion 42 monitored during a typical run. This graph represents the rate curve for formation of propylene from the thermal degradation of the *n*-propyl pyrene-1-carboxylate. It has been shown by Kleineberg, Geiger, and Gormley⁴ that a

TABLE I
Variation of the Ratio of Propylene to Propanol Mass Peaks as a Function of the Flame-Retardant Chemical in the Test Sample

FR chemical	% wt in sample	% FR elements		Propylene/Propanol
		P	Br	
None	0	0	0	167
Ammonium dibasic phosphate	1.00	0.27	—	13
Ammonium dibasic phosphate	1.86	0.50	—	14
Ammonium dibasic phosphate	3.84	1.04	—	14
Ammonium dibasic phosphate	7.09	1.90	—	20
Decabromodiphenyl oxide	0.73	—	0.61	125
Decabromodiphenyl oxide	0.73	—	1.36	167
Decabromodiphenyl oxide	4.00	—	3.34	167
	15.50	—	13.00	143

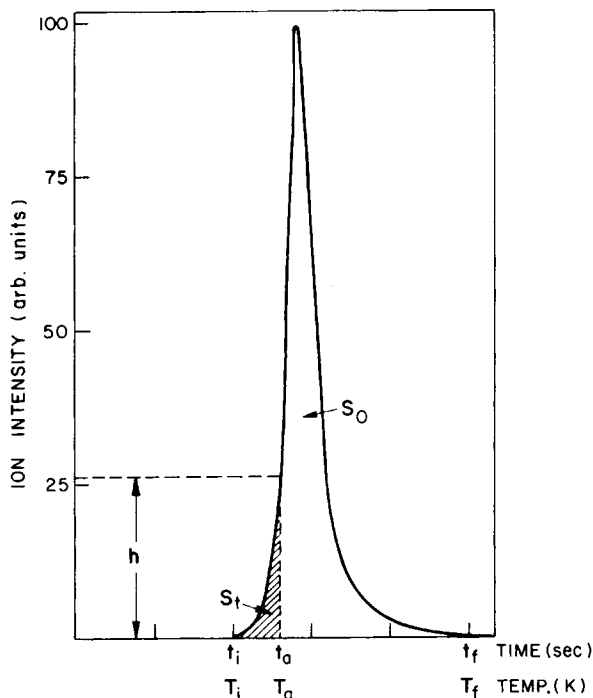


Fig. 1. Ion plot for m/e 42 as function of time showing propylene formation from n -propyl pyrene-1-carboxylate. T_i is temperature of initial decomposition after t_i sec heating (i.e., last data point at which $h = 0$). h is ion current at time t_a and temperature T_a . Total ion concentration at time t_a is proportional to S_t , the area under curve between T_i and T_a , while S_o is total area under curve and proportional to total ion concentration.

curve such as this may be interpreted by an equation of the type

$$\ln \frac{Kh}{(KS_o - KS_t)n} = \ln \frac{KA}{B} - \frac{E}{RT}$$

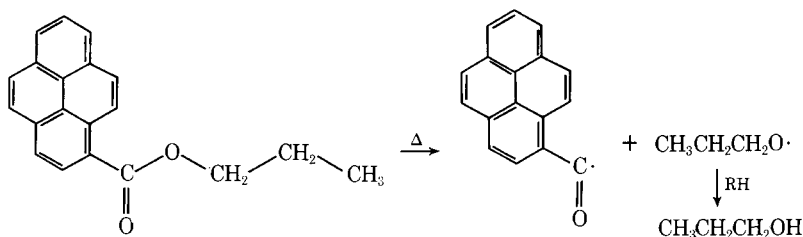
where h is the mass spectrometric ion current output at time t_a , S_o is the total area under the mass spectrometer ion current curve, S_t is the area under the curve between the initial temperature T_i and a given temperature T_a , E is the apparent activation energy, A is the frequency factor, B is the uncommitted constant which includes the heating rate, R is the universal gas constant, K is the proportionality constant, and n is the order of reaction.

The numerical values for h , S_o , S_t , and T , derived from graphs obtained with each system studied, were therefore inserted into the previous equation and the activation energies determined for trial values of n along with values for the correlation coefficients.

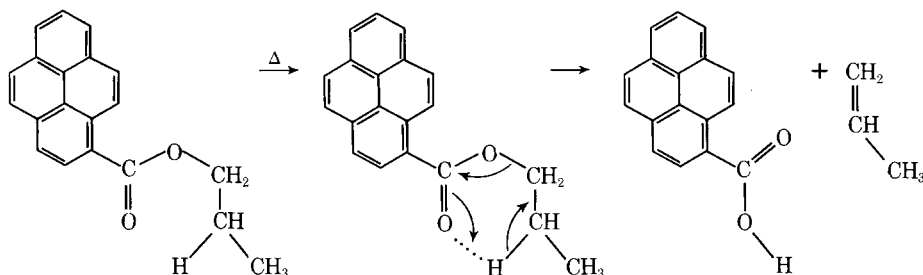
RESULTS AND DISCUSSION

With respect to the pyrolysis of the model compound n -propyl pyrene-1-carboxylate, two primary pyrolysis reactions can be postulated. (1) α cleavage

to give *n*-propanol as the major product:



and (2) an intramolecular cyclic elimination reaction to give propylene:



Of these two reactions the latter route is the one established as the most dominant in pyrolysis studies of aromatic esters.⁵⁻¹¹ However, all these studies were performed under isothermal conditions at relatively slow rates of reaction compared with the conditions employed in our studies in which samples were heated to temperatures of the order of 865°C.

In order to assess the importance of these two reactions in our pyrolysis study, we have compared the total ion intensities for the propylene ion ($m/e = 42$) and the *n*-propanol ion ($m/e = 60$) for all the samples examined and the results obtained are given in Table I. Although the figures given in this table are only a measure of the relative intensities of the mass ions 42 and 60 as measured by the quadrupole mass spectrometer and as such are not directly related to the moles of propylene and *n*-propanol produced, they do give a clear indication of the importance of the propylene formation. Thus, in the case of the model ester with no added phosphorus or bromine compound, it can be concluded that the formation of propylene is the predominant reaction. This is consistent with the observation that ethylene formation predominates in the pyrolysis of ethyl benzoate.^{7,10,11} The addition of the organobromine compound has little, if any, effect on the ratio of the propylene to *n*-propanol formed. However, while the ratio of propylene to *n*-propanol has been reduced (by a factor of 10 in all cases) by the phosphorus compound, there is no apparent connection between this ratio and the amount of phosphorus present in the model ester, and the propylene formation is still dominant.

The calculated activation energies for the formation of propylene and *n*-propanol using the equation of Kleineberg⁴ are given in Tables II and III, respectively, as a function of *n* which is the order of reaction.

Considering first the calculated activation energies for the formation of propylene (Table II), it can be seen that irrespective of the choice of *n* (1, 2, or 3) the

TABLE II
 Activation Energies (kcal/mol) for Propylene Formation Calculated from the Rate Curves for
 Mass 42 using Kleineberg's⁴ Equation^a

Elemental FR in model ester		<i>n</i> order of reaction		
%P	%Br	1	2	3
0	0	15.63 ± 0.97 (0.980) ^b	<u>19.46 ± 0.89</u> (0.989)	23.30 ± 1.44 (0.973)
0.27	0	11.76 ± 2.32 (0.901)	16.64 ± 1.47 (0.977)	<u>21.52 ± 0.84</u> (0.995)
0.50	0	13.76 ± 1.64 (0.936)	18.66 ± 0.99 (0.986)	<u>23.57 ± 0.76</u> (0.995)
1.04	0	15.97 ± 1.18 (0.971)	18.61 ± 1.04 (0.983)	<u>21.25 ± 1.19</u> (0.983)
1.90	0	10.94 ± 1.86 (0.861)	17.19 ± 1.48 (0.976)	<u>23.45 ± 1.11</u> (0.997)
0	0.61	13.22 ± 2.13 (0.920)	16.67 ± 1.45 (0.975)	<u>20.13 ± 1.00</u> (0.991)
0	1.36	16.14 ± 1.38 (0.975)	<u>19.69 ± 0.97</u> (0.991)	23.24 ± 1.44 (0.987)
0	3.34	13.53 ± 1.53 (0.964)	<u>17.93 ± 0.92</u> (0.992)	22.33 ± 1.44 (0.988)
0	13.00	10.82 ± 1.69 (0.888)	17.06 ± 0.92 (0.984)	<u>23.29 ± 0.32</u> (0.999)

^a These data were calculated by measuring the values of h , S_0 , S_t , and T from the appropriate rate curve and then substituting these values in Kleineberg's equation with the above values for n .

^b Figures in parenthesis are the correlation coefficients for the Arrhenius plot with the underlined values representing the best fit of the data.

calculated activation energies for propylene formation are independent of the nature of the flame-retarding species and its concentration in the model ester. The only significant difference observed in this table is the apparent change in the order of the reaction (n) required to obtain the best kinetic fit of the data. The best fit of the kinetic data for the formation of propylene with the untreated model ester is $n = 2.0$. However, when the phosphorus species is present, $n = 3$ gives the best kinetic fit while $n = 2.5$ gives the best results for the bromine species.* This would suggest that, while the kinetics are not greatly altered by the presence of the phosphorus or bromine species, these could be having some slight influence on the mechanisms responsible for the propylene formation, with the phosphorus having the greater effect.

With respect to the data for n -propanol formation (Table III), it would appear that both the phosphorus and bromine compounds are having no effect on either the kinetics or mechanism of its formation. This is apparent since there are no changes in either the energies of activation or n , the order of reaction required to give the best fit of the experimental data, or between that observed with the model compound and the model compound treated with the flame-retarding species.

* For a unimolecular reaction of the type described in this article, it is anticipated that n should equal 1. However, owing to the computer manipulations only the best fit is reported.

TABLE III
 Activation Energies (kcal/mol) for Propanol Formation Calculated from the Rate Curves for
 Mass 60 using Kleineberg's⁴ Equation^a

Elemental FR in model ester		<i>n</i> order of reaction		
%P	%Br	1	2	3
0	0	11.25 ± 0.83 (0.971) ^b	<u>14.60 ± 0.48</u> (0.994)	17.96 ± 0.67 (0.992)
0.27	0	12.96 ± 1.16 (0.977)	<u>15.88 ± 0.72</u> (0.994)	18.80 ± 0.93 (0.993)
0.50	0	9.98 ± 1.15 (0.934)	14.92 ± 0.51 (0.994)	<u>19.87 ± 0.41</u> (0.998)
1.04	0	11.15 ± 0.42 (0.994)	<u>12.86 ± 0.44</u> (0.995)	14.57 ± 0.73 (0.990)
1.90	0	10.71 ± 0.56 (0.985)	<u>12.85 ± 0.30</u> (0.997)	14.98 ± 0.42 (0.996)
0	0.61	10.65 ± 0.79 (0.981)	14.34 ± 0.46 (0.996)	18.02 ± 1.17 (0.986)
0	1.36	9.53 ± 1.03 (0.966)	<u>14.49 ± 0.25</u> (0.999)	19.45 ± 1.10 (0.991)
0	3.34	10.59 ± 0.98 (0.971)	<u>13.63 ± 0.63</u> (0.993)	16.66 ± 0.93 (0.989)
0	13.00	13.08 ± 0.95 (0.972)	<u>16.81 ± 0.42</u> (0.997)	20.53 ± 0.59 (0.996)

^a These data were calculated by measuring the values of h , S_0 , S_t , and T from the appropriate rate curve and then substituting these values in Kleineberg's⁴ equation with the above values for n .

^b Figures in parenthesis are the correlation coefficients for the Arrhenius plot, with the underlined values representing the best fit of the data.

CONCLUSIONS

The model ester *n*-propyl pyrene-1-carboxylate decomposes under pyrolysis conditions reflective of the fire situation to give propylene and pyrene-1-carboxylic acid as the major reaction products, presumably via a six-centered intramolecular transition state as is observed with other esters. While some *n*-propanol is formed as a result of α cleavage, the contribution of this reaction to the overall decomposition appears to be insignificant.

The addition of decabromodiphenylene oxide to the model ester appears to have no significant effect on the solid-phase pyrolysis process. Thus, it can be concluded that for bromine containing compounds of this type to have an influence on reducing the flammability characteristics of polyesters, they must influence the gas-phase reactions.

The phosphorus containing compound utilized in this study, although not a candidate as a commercial flame retardant, was selected because of its ability to remain in the solid phase during pyrolysis (i.e., low volatility). In terms of its ability to influence the ratio of propylene to *n*-propanol the phosphorus compound certainly plays some role in the solid-phase pyrolysis of the model ester, although propylene formation still dominates the overall pyrolysis. Thus, it must be concluded that ammonium dibasic phosphate has little effect on the solid-phase reactions and presumably retards the flammability of the polyesters by a combined solid-gas phase interaction. This observation is not inconsistent with the findings reported by Hastie and McBee¹², who noted that triphenylphosphine oxide was ineffective as a condensed phase retardant for PET.

In view of these observations regarding the apparent lack of solid-phase interaction in the pyrolysis of *n*-propyl pyrene-1-carboxylate, a model compound for poly(ethylene terephthalate), the gas phase inhibition reactions of phosphorus and bromine compounds need to be investigated in greater detail.

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