Pyrolysis and Combustion of Cellulose. VII. Thermal Analysis of the Phosphorylation of Cellulose and Model Carbohydrates During Pyrolysis in the Presence of Aromatic Phosphates and Phosphoramides*†

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Synopsis

Thermal gravimetric analysis, differential scanning calorimetry, and derivative thermal gravimetric analysis were utilized to characterize the thermal interactions between cellulose, 1-6, anhydro β-D-glucopyranoside, and D-glucose and model phosphate and phosphoramide flame retardants. The phosphoramides induced higher char yields than the phosphates during the pyrolysis of the mixtures of carbohydrates and organophosphorus compounds. Exothermic reactions attributed to phosphorylation and char formation were observed with each of the phosphoramide/carbohydrate mixtures and were absent with the phosphates. The individual phosphorus compounds studied showed similar thermal behavior with each of the carbohydrates indicating that the mode of interaction for these mixtures was similar. Isothermal gravimetric analysis of the organophosphorus/carbohydrate mixtures was used to measure the rate of decomposition weight loss from isothermal conditions. This weight loss was used as an indication of rate of fuel formation. The kinetics observed for these measurements indicated that the phosphoramide mixtures underwent a rapid weight loss to a final char with an effective E_{act} of about 55 kcal/mol while the phosphate mixtures exhibited effective E_{act}'s for decomposition lower than those observed for the pure carbohydrates. Mixtures of glucose with selected arylphosphoramide esters were pyrolysed in order to determine the effect of lability of the leaving group on char formation. Gas chromatographic analysis of the pyrolysis products indicated that phenol was the favored leaving group in comparison with aniline units, but char promotion appeared to be dependent on the number of P-N bonds present in the original phosphoramide. Electron spectroscopy for chemical analysis indicated that chemically similar chars were obtained from the different organophosphorus/carbohydrate combinations.

INTRODUCTION

One of the textile materials most frequently implicated in fire injuries is cotton cellulose. Fortunately it is easily rendered flame resistant with the application of proper condensed phase-active flame retardants. Typically some of the most successful commercial flame retardants for cellulose have been the organo-phosphorus compounds. These have been the subject of numerous studies in recent years, and it has been shown that these compounds exhibit varying levels of effectiveness depending on their chemical structures. Their most probable mode of action seems to involve phosphorylation of the cellulose at the primary

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hydroxyls. This is presumed to block the depolymerization of the cellulose and thus reduce the amount of flammable gaseous fuel produced on thermal degradation while at the same time allowing competing reactions such as dehydration and crosslinking to become more important. The net effect is thus a decrease in volatile fuel production accompanied by an increased yield of char.[1]

Of those compounds which are effective in promoting these processes, a large portion is found to contain both phosphorus and nitrogen. This had led to proposals of synergistic interactions involving the two elements. Tesoro and co-workers,[2,3] Willard and Wondra,[4] and Reeves and co-workers[5] have evaluated this interaction on a quantitative basis. Results from further studies by Hendrix and co-workers[6-8] have been interpreted as indicating that the enhanced flame retardant efficiency of P/N systems is related to their high efficiency in phosphorylating the cellulose substrate. The chemistry of the P/N effect has been reviewed in detail by Weil[9]; the corresponding cellulose degradation chemistry has been compiled by Shafizadeh.[10]

EXPERIMENTAL

Chemicals Used

The cotton cellulose used in this work was Testfabrics 80 × 80 mercerized print cloth ground to 60 mesh with a Wiley mill. The levoglucosan was a previously prepared laboratory sample and was used without further purification: mp 172°C, lit.[11] 172°C.

The N,P,P-triphenylphosphinic amide was prepared by the method of Audrieth and Toy.[12,13] A solution of 56 g (0.24 mol) of diphenylphosphinic chloride and 38 ml (0.48 mol) of pyridine in 150 ml of chloroform was slowly added to 43.5 ml (0.48 mol) of aniline in 80 ml of chloroform. The reaction temperature was maintained at $0 \pm 2°C$ during the addition. The resulting solution was refluxed for 2 hr. The precipitate which formed on cooling was washed with cold chloroform, yielding 39.9 g (56.7%) of product with a melting point of 235–235.5°C, lit.[14] 231–233°C.

ANAL. Calcd. for $C_{18}H_{16}NOP$: C, 73.7; H, 5.5; N, 4.8; O, 5.5; P, 10.6. Found: C, 73.7; H, 5.3; N, 4.8; O (diff.), 5.3; P, 10.8.

The triphenylphosphoric triamide was prepared by the same procedure by adding pyridine and phosphorus oxychloride to excess aniline: mp 213°C, lit.[13] 211–214°C.

ANAL. Calcd. for $C_{18}H_{18}N_3OP$; C, 66.9; H, 5.6; N, 13.0; O, 5.0; P, 9.6. Found: C, 66.8; H, 5.8; N, 12.8; O (diff.), 4.8; P, 9.8).

Likewise, the N,N'-diphenylphenylphosphoric diamide was prepared from phenylphosphoryl dichloride and aniline: mp 178°C, lit.[12] 178–179°C.

ANAL. Calcd. for $C_{18}H_{17}N_2O_2P$: C, 66.7; H, 5.2; N, 8.6; O, 9.9; P, 9.6. Found: C, 66.6; H, 5.3; N, 8.6; O (diff.), 9.7; P, 9.8.

The N,N',P triphenylphosphoric diamide was prepared from phenylphosphoric dichloride and aniline: mp 226°C, lit.[14] 211.5°C.

ANAL. Calcd. for $C_{18}H_{17}N_2OP$: C, 70.1; H, 5.5; N, 9.1; O, 5.2; P, 10.1. Found: C, 70.0; H, 5.6; N, 9.2; O (diff.), 5.1; P, 10.1.

And the N-phenyldiphenylphosphoric amide was prepared from diphenyl-phosphoryl chloride and aniline: mp 128°C, lit.[12] 129–130°C.

ANAL. Calcd. for $C_{18}H_{16}NO_3P$: C, 66.5; H, 4.9; N, 4.3; O, 14.8; P, 9.5. Found: C, 66.2; H, 5.0; N, 4.2; O (diff.), 15.1; P, 9.5.

Tridodecylphosphate was prepared using a standard Schotten-Bauman procedure[15] by adding 11 g (0.07 mol) of phosphorus oxychloride in 40 ml of chloroform to a solution containing 56 g (0.30 mol) 1-dodecanol and 35 g (0.35 mol) triethylamine. The reaction temperature was maintained at 40°C by controlling the rate of addition of phosphorus oxychloride. The precipitated amine hydrochloride was filtered and discarded and the solvent removed on a steam bath. The resultant brown oil was recrystallized from ethanol/diethyl ether, yielding a white crystalline material, mp 65°C. Elemental analysis indicated that the material collected was 97% tridodecylphosphate with dodecylphosphoric acid impurities. The triphenylphosphate used was Eastman reagent-grade material recrystallized from ethanol/water: mp 51°C, lit.[16] 50–51°C.

ANAL. Calcd. for $C_{18}H_{15}O_4P$: C, 66.3; H, 4.6; O, 19.4; P, 9.6.

The triethyl phosphate was Fisher reagent grade and was repurified by distillation. The fraction boiling at 38.5°C at 0.05 mm Hg was collected and used experimentally.

ANAL. Calcd. for $C_6H_{15}O_4P$: C, 39.6; H, 8.2; O, 35.2; P, 17.0. Found: C, 39.5; H 8.3; O (diff.), 35.5, P, 16.7.

The trimethylphosphoric triamide was obtained by chloroform extraction of an aqueous solution of Monsanto MCC 100. The material used was recrystallized twice from chloroform/carbon tetrachloride: mp. 101°C, lit.[17] 102–103°C.

ANAL. Calcd. from $C_3H_{12}N_3OP$: C, 26.3; H, 8.8; N, 30.7; O, 11.7; P, 22.6. Found: C, 26.2; H, 8.9; N, 30.6; O (diff.), 11.8; P, 22.6.

Gas Chromatography

Gas chromatography was performed using a Perkin-Elmer model 900 chromatograph equipped with a flame ionization detector. Analysis of the D-glucose mixture pyrolysates was accomplished using a Carbowax K20M, 10% on 80–100 mesh Chromosorb W, column (0.125 in × 6 ft). The temperature-programmed chromatograms were performed under the following conditions:

Injector: 275°C
Manifold: 300°C
Column program
    Initial: 80°C, 3 min
    Heating rate: 13°C/min
    Final: 180°C, 5 min
Helium carrier flow: 40 ml/min

Thermal Gravimetric Analysis (TGA)

The TGA and differential scanning calorimetry (DSC) thermograms were obtained using a du Pont 950 TGA attached to a du Pont 990 thermal analyzer.

Samples were prepared by mixing requisite amounts of pure compounds in powder form. Intimate mixing was assured by grinding with a glass rod followed by tumbling for 48 hr in a rock tumbler. The TGA curves were run under a nitrogen atmosphere flowing at 60 ml/min and a scale sensitivity of 0.5 mg/in. The dynamic TGA measurements were made at a constant heating rate of 20°C/min. Isothermal TGA curves were run for a period of 10 min after the desired temperature was reached. It required 4.5 min to reach isothermal conditions, due to the relatively large mass of the Pyrex envelope covering the samples. The isothermal analyses were obtained over the desired temperature range of decomposition at 10°C increments.

Differential Scanning Calorimetry

The thermograms were obtained from a du Pont DSC Base Module II attached to a du Pont 990 thermal analyzer. The samples for these measurements were taken from the mixtures prepared for the TGA experiments. The calorimetry curves were obtained with the samples enclosed in covered aluminum pans with an empty covered pan as the reference. All DSC thermograms were run under a nitrogen flow rate of 60 ml/min. A heating rate of 20°C/min and a ΔH scale sensitivity of 1 mcal/sec/in. were used.

RESULTS AND DISCUSSION

Since previous work had indicated the importance of P-N bonds in determining the efficiency of cellulosic flame retardants, a study was undertaken to determine the nature of this effect. A series of aromatic derivatives with structures of ϕ_n-$P(O)(NH\phi)_{3-n}$ and $(\phi O)_n P(O) (NH\phi)_{3-n}$ was prepared with varying numbers of P-N, P-C, and P-O bonds. These were evaluated for flame retardant efficiency in 100% cotton fabric using the method of Yeh and Barker.[18] In this way the fraction of the cellulose converted into flammable gases during burning can be estimated. This value is designated as $Y/(1 - x)$, and its dependence on the amount of flame retardant present in the fabric can be used to show the degree to which the flame retardant efficiencies can vary as a function of the structure about the phosphorus. In this series the effects were found to be quite pronounced. For example, as shown in Figure 1, at approximately 1% P in the sample, triphenylphosphate-treated cellulose releases about 88% of its mass as volatile fuel, whereas the triphenylphosphoric triamide reduces the fuel formation to about 50%.

In an attempt to provide fundamental information needed to explain the increased flame retardant efficiency observed in compounds containing the P-N bonds, a series of selected model compounds was examined by thermal analysis. Their thermal interactions with pure cellulose, levoglucosan, and D-glucose were examined, since these are the species with which the retardants might be expected to react in a propagating flame environment.

Each of the three carbohydrates had been previously studied and was known to exhibit a distinctive manner of decomposition.[6-8] The relatively complex thermal behavior of D-glucose is shown by TGA, DTGA, and DSC in Figure 2. The two minor weight losses with maxima at 80 and 120°C were attributed to the loss of water of hydration of the α-D-glucose monohydrate and free water,
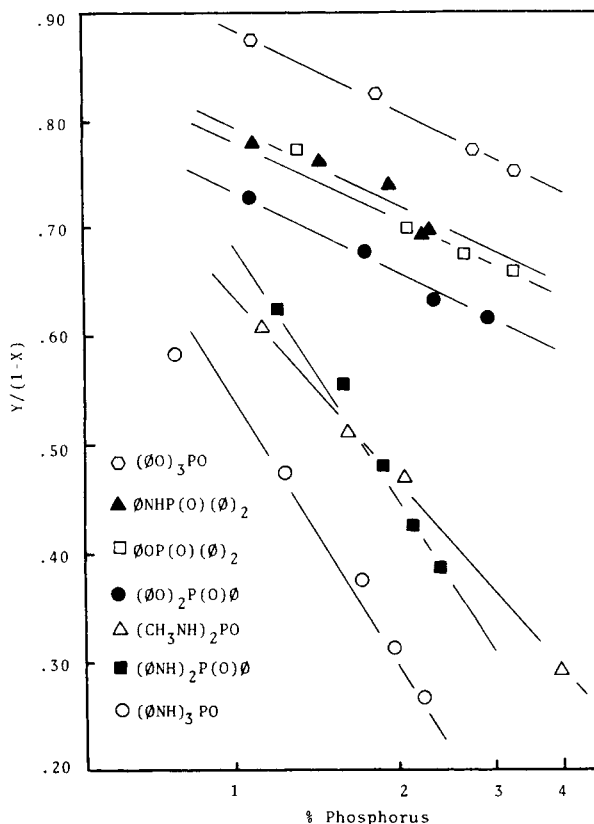
Fig. 1. Relative flame retardant efficiencies for a series of model flame retardants on cotton.

respectively. The next weight loss occurring was that with a maximum at 230°C and was attributed to dehydration reactions of the glucose. The major decomposition weight loss occurred with two overlapping maxima at 290 and 302°C. This weight loss was attributed to C-O and C-C bond cleavage reactions leading to a final char formation of 10.3% at 475°C. The DSC showed an endotherm at 82°C due to the melting of the α-D-glucose monohydrate. The endotherm occurring at 156°C without a weight loss represented the D-glucose melting. The final broad endotherm shows the decomposition of the substrate.

In contrast to the D-glucose behavior, levoglucosan exhibited relatively simple decomposition thermograms (Fig. 3). The TGA curves exhibited a single weight loss with a maximum at 302°C, which led to a 14.2% char yield at 475°C. This maximum appeared in the temperature range of the major decomposition for D-glucose, suggesting that the levoglucosan and D-glucose decompose thermally by similar mechanisms. The DSC indicated melting at 172°C and endothermic decomposition between 224 and 314°C. The thermally induced polymerization of levoglucosan suggested in earlier work[19] appeared at 280°C and was superimposed on the decomposition endotherm.

Cellulose decomposition also exhibits relatively simple decomposition thermograms (Fig. 4). A single weight loss occurred with the maximum at 363°C to yield a char of 11.1% at 475°C. This value was close to the observed char yields for D-glucose and levoglucosan and suggested that the thermal degradation
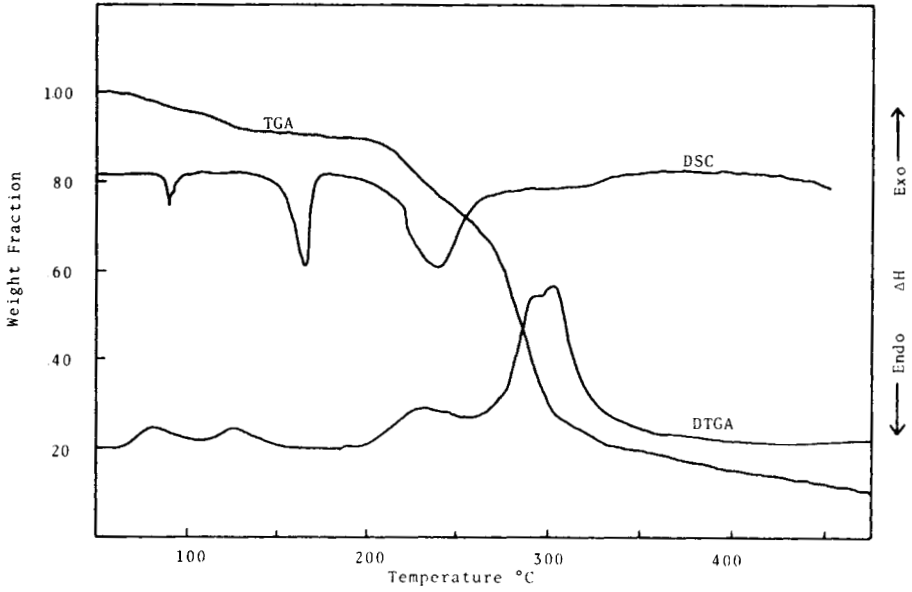
Fig. 2. Thermal analyses of glucose.

proceeded through similar routes to form a stable char. The DSC of cotton showed a broad endotherm centered at 100°C representing the loss of water. Decomposition appeared as an endotherm between 330 and 375°C and was followed by a slight exotherm at 380°C, which is attributed to char crosslinking reactions.
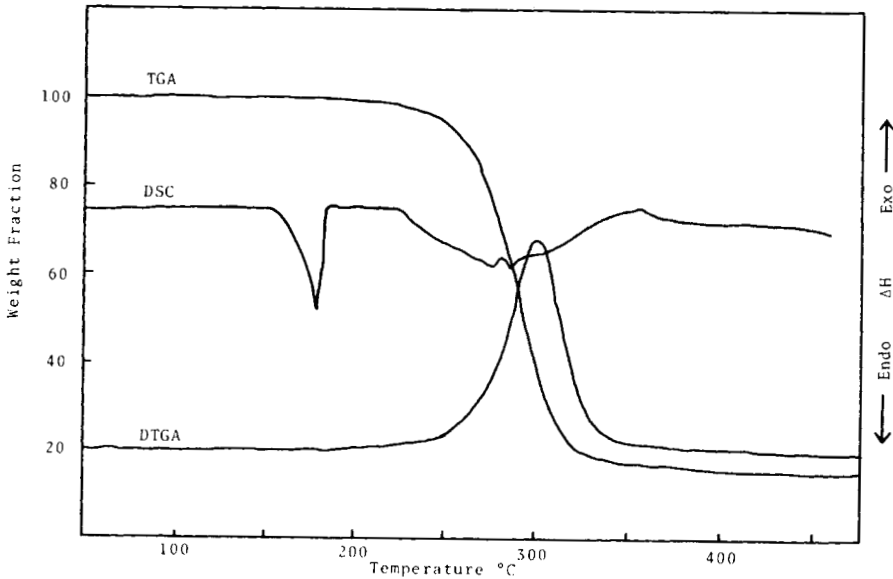

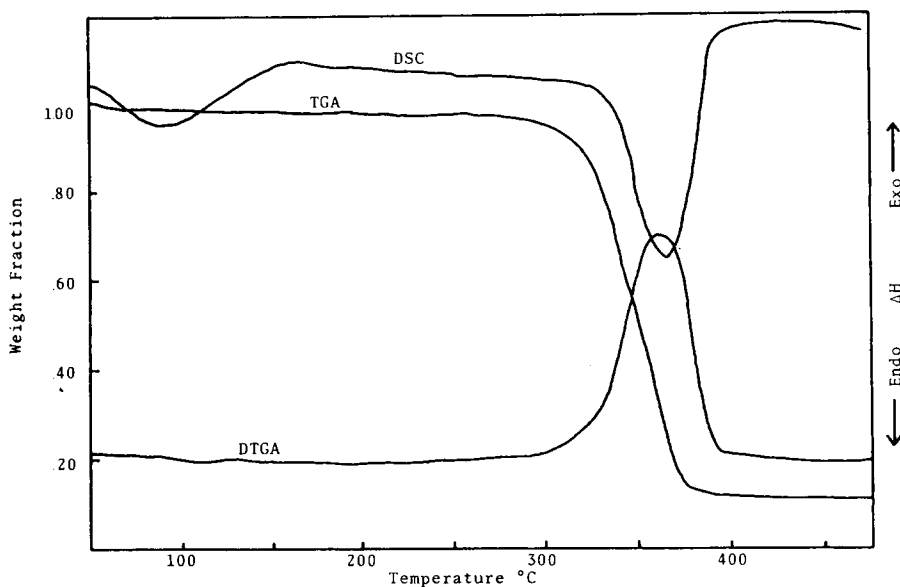Fig. 3. Thermal analyses of levoglucosan.

Fig. 4. Thermal analyses of cellulose.

Thermal Analysis of Model Flame Retardants

The model flame retardants chosen for this study were triphenylphosphate, tridodecylphosphate, triphenylphosphoric triamide, and trimethylphosphoric triamide. These were selected as representative alkyl and aryl phosphates and phosphoramides. The thermal analysis of these compounds was carried out as with the carbohydrate models.

The TGA curve of tridodecylphosphate as shown in Figure 5 exhibited one weight loss with a rate reaching a maximum at 287°C and resulting in a char yield of 22.5% at 475°C. The melting endotherm appeared at 65°C and was followed by endothermic decomposition at 300°C. A slight exotherm was observed at 320°C, which may have resulted from polymerization of phosphates in the residue.

As expected, the weight loss of triphenylphosphate appeared to proceed predominantly through volatilization with very little decomposition, as indicated by the 1.7% residue at 300°C (Fig. 6). The DSC indicated melting at 56°C, followed by a broad volatilization endotherm from 155 to 285°C. The differences in residues of these two compounds were attributed to β-elimination in the alkyl phosphate to form olefins and phosphoric acid derivatives. This type of mechanism was not available to triphenylphosphate, so the weight loss was assumed to proceed predominantly through volatilization.

The thermal analysis of the triphenylphosphoric triamide indicated a relatively complex pyrolysis process (Fig. 7). The first weight loss occurred between 200 and 290°C, with a loss of about 28% of the original weight. The DTGA indicated two maxima in this temperature region, which were probably due to volatilization and intermolecular condensation reactions leading to dimers or higher oligomers. The second major weight loss occurred from 290 to 550°C, with a final residue of 1.95%. These observations were in line with the results obtained by Furukawa and Tanibuchi[20] in their studies of the thermal decomposition of polyphos-
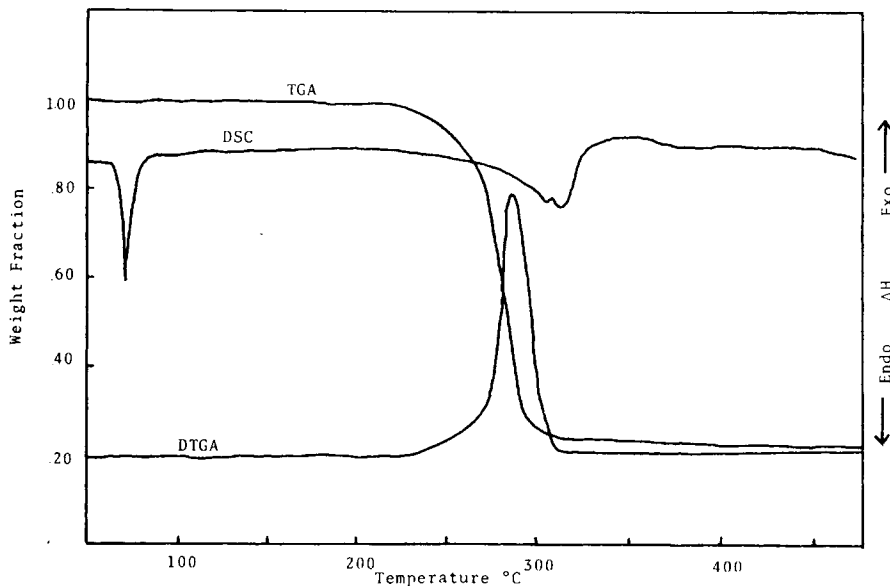
Fig. 5. Thermal analyses of tridodecylphosphate.

phonamides. They reported that phosphonamide polymers decomposed in two steps: the first involving elimination of amine between 200 and 350°C and the second resulting from main chain decomposition between 450 and 650°C. The complexity of the thermal behavior of triphenylphosphoric triamide was reflected in the DSC curve. The endotherm between 205 and 220°C represented the melting point and was followed immediately by the first weight loss endotherm. The second major weight loss was indicated by an endotherm from 320 to 380°C.
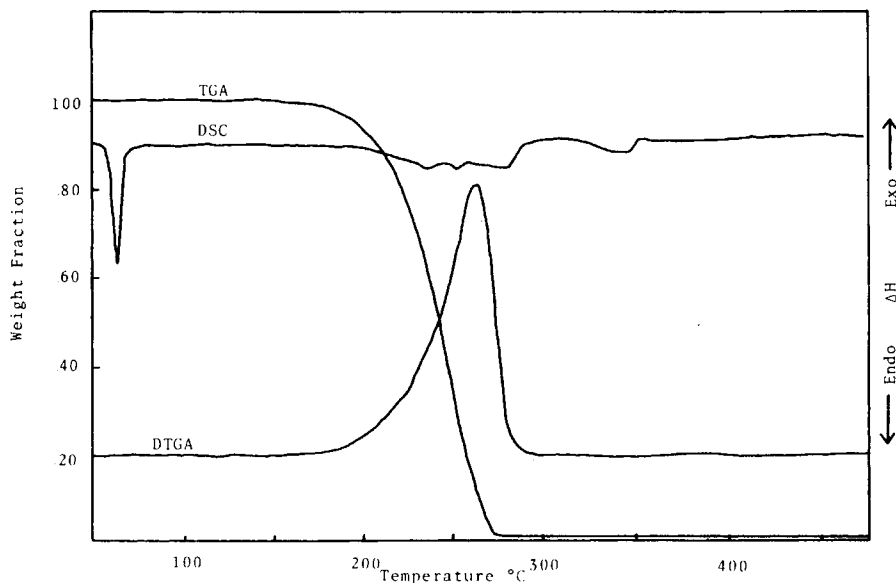

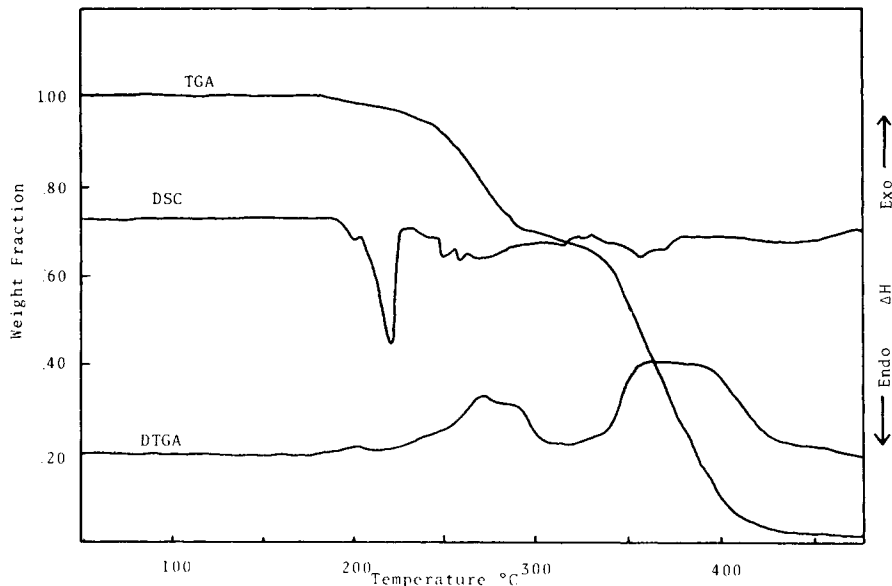Fig. 6. Thermal analyses of triphenylphosphate.

Fig. 7. Thermal analyses of triphenylphosphonic triamide.

The trimethylphosphoric triamide showed thermal behavior similar to its aromatic analog, the major difference being the temperature ranges of the decompositions. The major weight loss occurred from 110 to 225°C, and the DTGA indicated a broadened peak with two maxima in this range (Fig. 8). This was attributed to volatilization and intermolecular condensation, as with the phenylphosphoramide. A minor weight loss occurred from 225 to 280°C and yielded a char of 11.7% at 300°C. The high-temperature weight loss commenced above
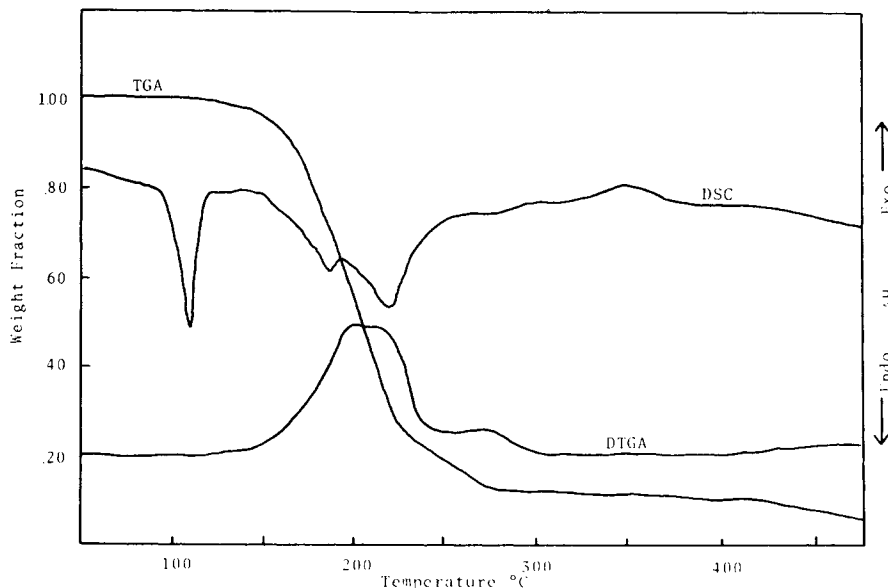

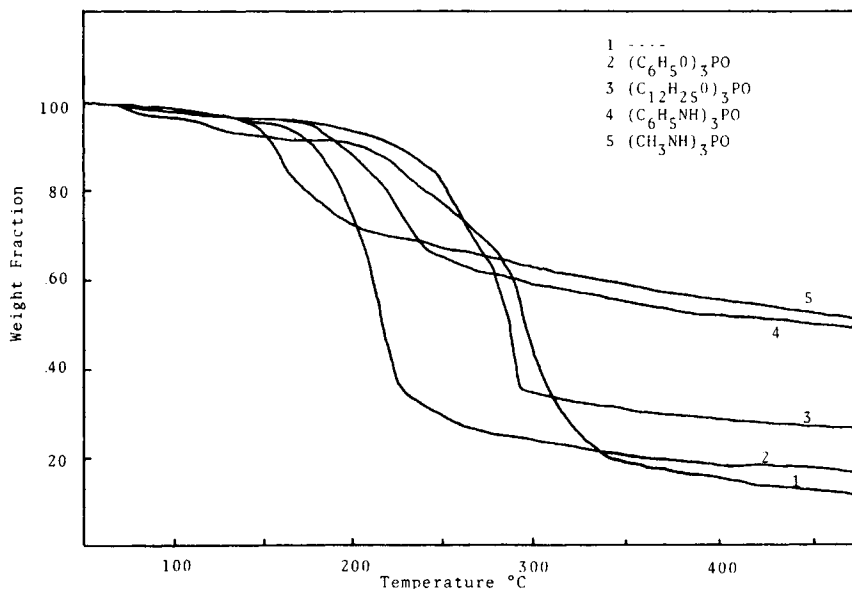Fig. 8. Thermal analyses of trimethylphosphonic triamide.

Fig. 9. TGA of glucose with organophosphorous compounds.

425°C and led to a final char of 5.7% at 475°C. These two weight loss reactions were attributed to further condensation reactions, with loss of amine followed by chain decomposition. The DSC curve showed the melting endotherm at 101°C, followed by a double-peaked endotherm from 154 to 300°C due to volatilization and condensation. A slight broad exotherm between 325 and 400°C preceded the high-temperature weight loss.

Effect of Model Flame Retardants on Carbohydrate Substrates

The presence of organophosphorus compounds during the thermal decomposition of D-glucose caused marked changes from the thermal behavior of the pure carbohydrate (Fig. 9). The onset temperature for the decomposition of pure glucose was 190°C, while this temperature was lowered in all cases of the mixtures. The residues at 475°C from all of the mixtures also increased over those observed from the untreated materials. Table I lists the mixtures and the observed char yields at 475°C plus the residues which would have been expected from the mixtures of pure compounds if there were no interaction. The order of the effect of the phosphorus substituent groups in increasing char formation was aryl amine > alkyl amine > aryl oxide > alkoxide. This type of ordering

TABLE I
TGA Char Yields for Carbohydrate/Organophosphorus Compound Mixtures at 475°C

	D-Glucose	Levoglucosan	Cellulose
$(C_{12}H_{25}O)_3PO$	26.2/11.7[a]	24.1/18.7	24.3/16.7
$(C_6H_5O)_3PO$	17.5/6.3	18.3/8.4	8.72/6.3
$(CH_3NH)_3PO$	50.3/14.5	33.6/10.2	46.0/9.6
$(C_6H_5NH)_3PO$	49.3/6.3	40.7/8.4	42.5/6.4

[a] % Char observed/% char expected.

was not surprising in light of the work of Hendrix[19] demonstrating the effect of phosphate–nitrogenous base mixtures on the thermal decomposition of selected carbohydrates. Striking differences in the thermal behavior of the model phosphorus compounds were further demonstrated by the DSC curves shown in Figure 10. In the case of both of the phosphoric triamides, a relatively large exotherm appeared, which was superimposed on and followed the glucose decomposition endotherm. The exotherm occurred at approximately 220°C for the trimethylphosphoric triamide and 260°C for the triphenylphosphoric triamide. Comparison of these temperatures with the TGA curves in Figure 9 shows that these exotherms occurred concurrently with the major weight loss reactions resulting in the final char. It appeared plausible that the observed exotherms could result from two causes: catalyzed decomposition of the phosphoramide or crosslinking reactions leading to the final carbonaceous char. Since the exotherms were absent in the pure compounds, they were assumed to be the result of some form of interaction between the decomposing substrate and the phosphoramide. The relative magnitudes of these exotherms corresponded to the relative amounts of char formed for the amides, aryl > alkyl.

The thermal reactions studied for the D-glucose mixtures indicated that a fundamental difference existed in the reactivities of phosphoramides and
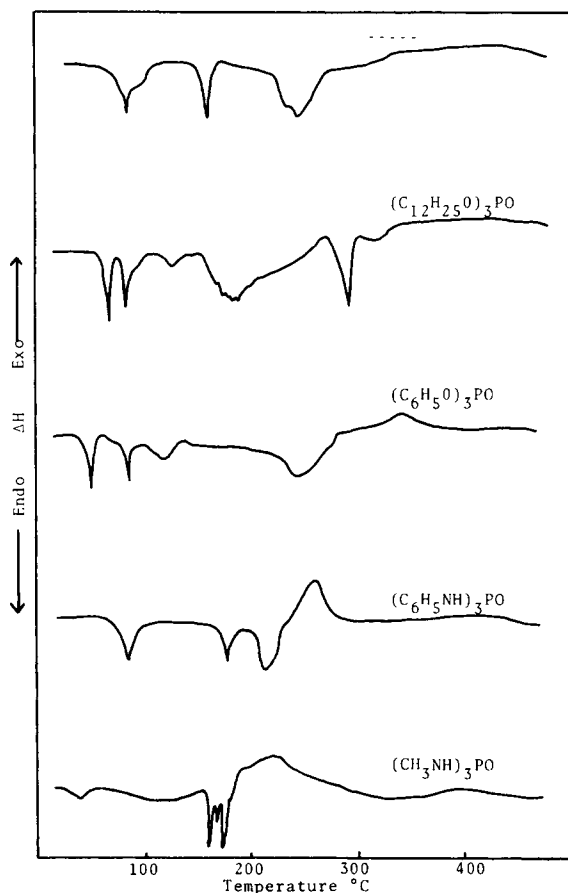

Fig. 10. DSC of glucose with organophosphorous compounds.

phosphates towards D-glucose. Further information about the thermal reactivity
of the selected model flame retardants was derived from thermal analysis of le-
voglucosan mixtures with these compounds. Since levoglucosan represents the
intermediate in cellulose pyrolysis, it was hoped that knowledge of the interaction
between the model flame retardants and this species might indicate whether the
flame retardants act on the original cellulose substrate or on its decomposition
products. The TGA of levoglucosan mixtures (Fig. 11) exhibited considerable
similarity to the D-glucose mixtures. The onset temperature for the decompo-
sition of pure levoglucosan was 195°C, while the temperature of decomposition
was lowered in all cases for the mixtures. Increased char yields were also ob-
served for the mixtures as compared to the pure compounds, as shown in Table
I and Figure 11. The observed order for char formation based on phosphorus
substituent was again aryl amine > alkyl amine > aryl oxide > alkoxide. The
DSC measurements on these reaction mixtures also showed similarities to the
D-glucose reactions (Fig. 12). The phosphoramides exhibited exothermic peaks
overlapping and following the substrate decomposition endotherm, while the
phosphates showed only relatively small or broad exotherms after the substrate
decomposition. As in the D-glucose systems the phenylphosphoramide exhibited
a more highly exothermic reaction than did the methylphosphoramide.

The thermal analysis of the cellulose mixtures with the phosphates and
phosphoramides showed that there were fundamental similarities in the reactions
of the model carbohydrates studied and that each substrate exhibited increased
char yields and exothermicity with the phosphoramides as compared with the
phosphates. The TGA thermograms of the cellulose mixtures in Figure 13
showed reduced onset temperatures of the decomposition from that of pure
cellulose (265°C) except in the case of triphenylphosphate mixtures, where the
cellulose decomposition appeared to be relatively unchanged. This was at-
tributed to volatilization of the triphenylphosphate, which takes place about
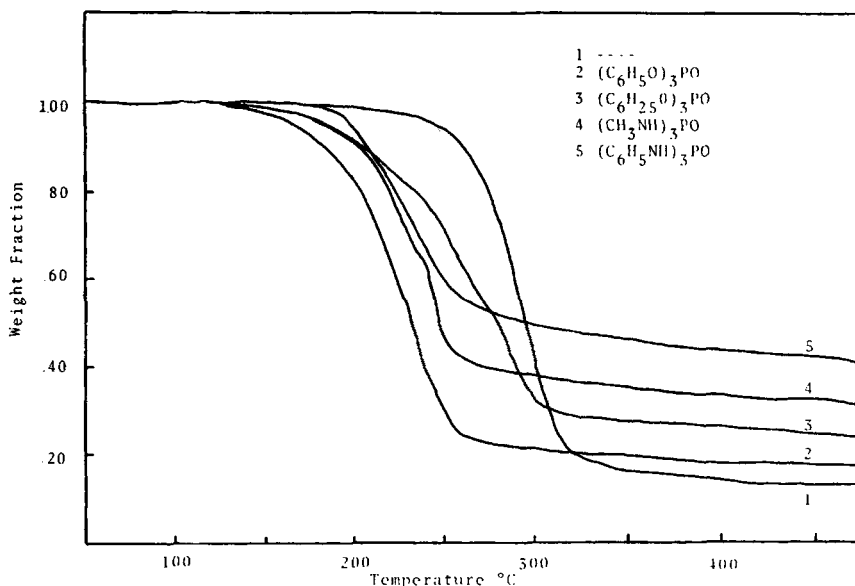

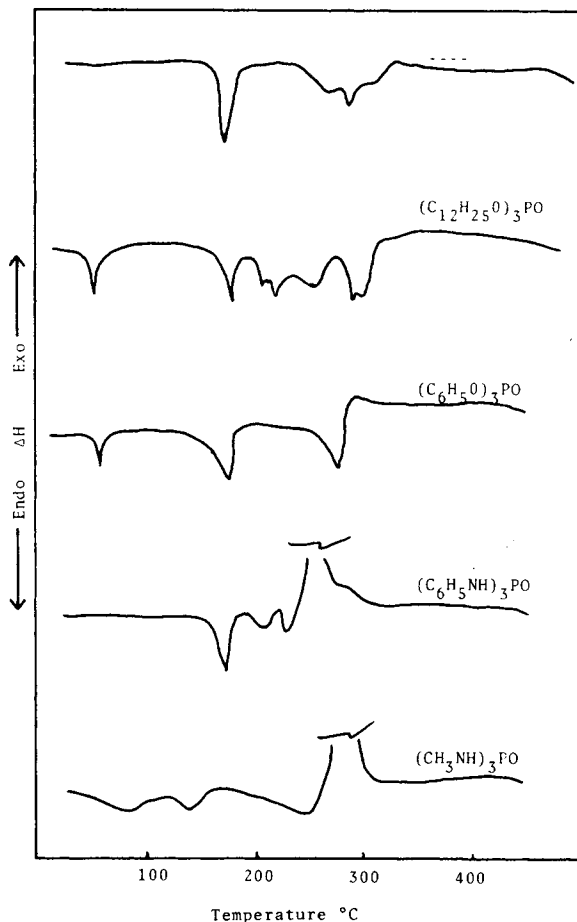Fig. 11. TGA of levoglucosan with organophosphorous compounds.

Fig. 12. DSC of levoglucosan with organophosphorous compounds.

100°C below the cellulose decomposition temperature. The char yields at 475°C (Table I) indicated the same effectiveness of char formation for the substituent groups as observed in the D-glucose and levoglucosan mixtures. The phosphoramides exhibited large exothermic peaks in the DSC measurements, which appeared superimposed on and following the cellulose substrate decomposition endotherm (Fig. 14). The relative magnitudes of these exothermic reactions are displayed in Table II.

The results of the thermal analysis indicated that the thermal decomposition for each of the carbohydrates was influenced in a similar manner by the presence of the organophosphorus compounds. The increased char yields with the phosphates and phosphoramides and highly exothermic decomposition with the phosphoramides were common to each of the carbohydrates studied. The lowered onset temperature of decomposition for the carbohydrates in the presence of the organophosphorus compounds indicated that the mode of action for condensed phase flame retardance is catalyzed decomposition of the initial carbohydrate structure regardless of its form.

The dynamic thermal analysis of the carbohydrate mixtures with the organophosphorus model compounds illustrated the complex nature of these reactions.
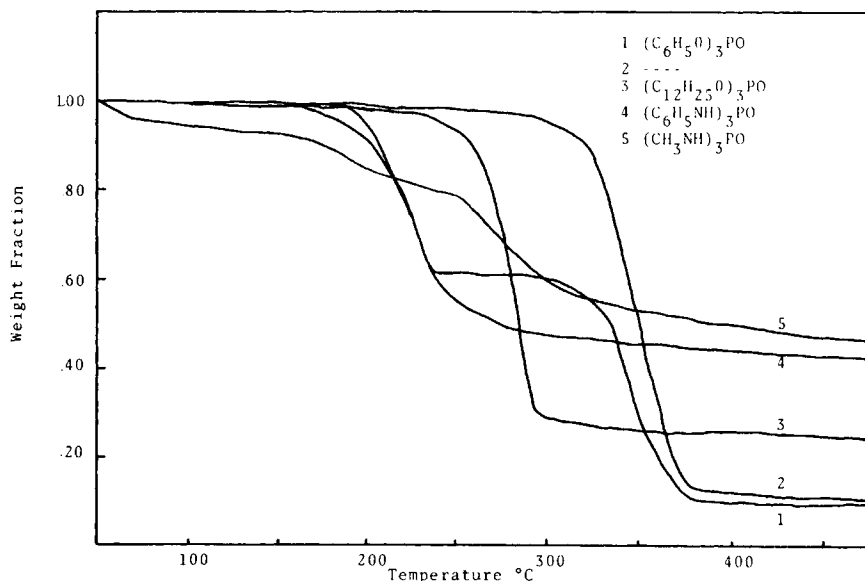
Fig. 13. TGA of cellulose with organophosphorous compounds.

TABLE II
ΔH^a Observed Values for the Exothermic Interaction Between Phosphoramides and Model
Carbohydrates at 5% Phosphorus

	D-Glucose	Levoglucosan	Cellulose
$(CH_3NH)_3PO$	0.65	1.40	1.99 (2.44)[b]
$(C_6H_5NH)_3PO$	1.99	1.93	2.64

[a] The observed ΔH values (as kcal/g cellulose/g P) represent a minimum value of heat evolution (Δq) of the reaction due to endothermic decomposition and volatilization competing with exothermic interactions. The phosphate reaction may, in fact, possess exothermic reactions with values small enough to be overshadowed by endothermic reactions. Therefore, the quantities expressed represent only relative exothermicity of reactions occurring.

[b] Value at 11% phosphorus.

Isothermal analysis of these compounds and mixtures was therefore performed in order to obtain more information about the thermal interactions between the carbohydrate substrates and the model flame retardants.

The isothermal decomposition of cellulose was studied over the temperature range of 275–312°C and the weight loss processes characterized in terms of apparent activation energies. No attempt has been made to interpret the chemical significance of these energy values because of the complexities of heterogeneous kinetics, as recently pointed out by Garn.[21] However, this limitation does not preclude the use of such apparent activation energies as indicators of the rate of the weight loss reactions. The pseudo-first-order Arrhenius activation energy for the decomposition was determined to be 49.0 kcal/mol. This value was in good agreement with the pseudo-first-order activation energy of 48.8 kcal/mol reported by Mack and Donaldson.[22] An activation energy of 34 kcal/mol has been reported by Smith and co-workers[23]; however, their work was carried out *in vacuo,* which would alter the observed rate of weight loss through increased volatilization of the decomposition products.
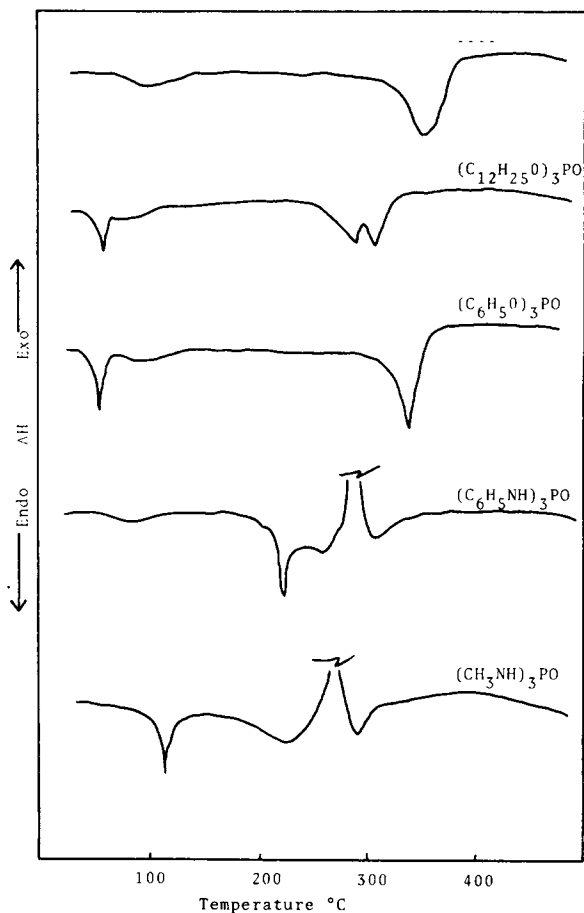
Fig. 14. DSC of cellulose with organophosphorous compounds.

The same treatment of levoglucosan yielded a psuedo-first-order activation energy of 40.3 kcal/mol over a decomposition range of 210–238°C. This activation energy was in the range to be expected for decomposition of cellulose and levoglucosan proceeding through similar transglycosylation-type reactions. Shafizadeh[24] has reported an activation energy of decomposition of 47 kcal/mol for the uncatalyzed decomposition of model glucosides.

D-Glucose exhibited an activation energy for isothermal decomposition of 20.2 kcal/mol over a temperature range of 217–270°C. This value was considerably lower than the activation energy observed for cellulose and levoglucosan and may be due to the weight loss reactions being able to take place without the initial heterolytic bond cleavage required for the cellulose and levoglucosan transglycoslation weight loss reactions to take place. The isothermal studies of mixtures of cellulose with the model phosphorus compounds provided some interesting results regarding the interactions between the phosphates and phosphoramides and cellulose. The activation energies for this set of samples are shown in Table III. The phosphates show some lowering of the activation energy of decomposition and the dodecylphosphate shows a lowering of the temperature range over which the decomposition occurs. This may be due to the increased lability of

TABLE III
Activation Energies for Isothermal Decomposition of Carbohydrate Mixtures

Substrate	Model flame retardant	E_{act}, kcal/mol	Sample correlation coefficient	Temp. range, °C
D-glucose		20.2	0.954	217–270
	$(C_{12}H_{25}O)_3PO$	26.2	0.982	188–230
	$(C_6H_5O)_3PO$	35.8	0.994	151–169.5
	$(CH_3NH)_3PO$	41.71	0.993	118–132
	$(C_6H_5NH)_3PO$	31.0	0.998	178–199
Levoglucosan		40.3	0.977	210–238
	$(C_{12}H_{25}O)_3PO$	41.7	0.953	230–249
	$(C_6H_5O)_3PO$	25.9	0.979	170–199
	$(CH_3NH)_3PO$	19.4	0.994	160–188
	$(C_6H_5NH)_3PO$	17.3	0.950	178–199
Cellulose		49.0	0.970	275–312
	$(C_{12}H_{25}O)_3PO$	43.6	0.987	217–249
	$(C_6H_5O)_3$	34.9	0.980	282–324
	$(CH_3NH)_3PO$	22.2	0.998	132–160
		55.2	0.979	225–241
	$(C_6H_5NH)_3PO$	13.7	0.969	178–199
		19.8	0.968	208–240

the tridodecylphosphate to form phosphoric acid derivatives, as was previously discussed. Under the isothermal analysis conditions, both of the phosphor-amides showed three distinct regions of weight loss. The first two regions were attributed to the initial decomposition weight loss of the phosphoramide, fol-lowed by catalyzed charring of the cellulose. In the triphenylphosphoramide mixtures, the weight losses occurred within a narrow temperature range, while these two weight losses were separated by 20°C with the trimethylphosphoramide mixtures. The third weight loss for both phosphoramide mixtures was a slow weight loss occurring over a broad temperature range and leading to formation of the final char. The reaction of interest was the second weight loss attributed to the major char-forming reactions. This reaction was easily resolved for the trimethylphosphoramide and yielded an activation energy of 55.2 kcal/mol for a rapid decomposition occurring in a relatively narrow temperature range of 225–241°C. Attempts to resolve the major charring reaction in the triphenyl-phosphoramide mixtures were foiled by the lack of separation of the first two weight loss reactions. The observed activation energies of 13.7 and 19.8 kcal/mol over a temperature range of 178–240°C represented the result of the two weight losses occurring in the overlapping temperature ranges.

The pseudo-first-order decomposition activation energies for the isothermal analysis of levoglucosan mixtures displayed values similar to those for the cel-lulose mixtures. The tridodecylphosphate–levoglucosan mixture showed an activation energy within 1.4 kcal/mol of that of pure levoglucosan, indicating essentially no alteration of the decomposition mechanism. The activation energy of 25.9 kcal/mol for the decomposition of the tridodecylphosphate–levoglu-cosan mixture resulted from completely overlapping weight losses and yielded no information concerning the kinetics of this reaction. Both of the phosphor-amide mixtures had activation energies within 2–3 kcal/mol of each other, and the high activation energy reactions that were observed in cellulose were not

observed in these mixtures due to the high rate of weight loss occurring over a very narrow temperature range.

The isothermal analysis of the glucose mixtures yielded very little information regarding the kinetics of the thermal reactions because of the existence of overlapping weight losses.

Analysis of Degradation Product

In an attempt to further define the chemistry of the phosphorus-modified glucose degradation reactions, a series of mixed phosphorus amide esters with D-glucose were pyrolyzed and the major decomposition products identified. Equal molar mixtures of D-glucose with triphenylphosphoric triamide, N,N'-diphenylphenylphosphoric diamide, N,N',P-triphenylphosphonic diamide, N-phenyl diphenylphosphonic amide, and N,P,P-triphenylphosphonic amide were chosen as model systems for this study. Gas chromatography was used to identify the aniline and phenol which were formed as the major products from these reactions (Table IV). No benzene was detected due to the stability of the phosphorus–aryl linkage. The results indicated that phenoxide was the favored leaving group when both phenoxide and anilide were present at the phosphorus center. This order of reactivity was not surprising, despite the higher bond strength of the P-O bond of 92 kcal/mol versus the P-N bond of 67 kcal/mol, and was attributed to the greater stability of the phenoxide anion leaving group.

Samples of each of the D-glucose mixtures were also converted to chars in crucibles held over an open propane burner. These chars were then submitted to electron spectroscopy for chemical analysis (ESCA) in an attempt to investigate the chemical nature of the char and the state of the phosphorus present in each char.

Spectra were obtained of the phosphorus $2p$, carbon $1s$, nitrogen $1s$, and oxygen $1s$ electrons for each of the samples. The results of these analyses are shown in Table V with the binding energies expressed in electron volts (eV).

The interpretation of absolute binding energy values obtained by ESCA is influenced to an appreciable degree by charging effects. However, the observed binding energies displayed in Table V indicated that the nature of the phosphorus species in the chars was chemically similar regardless of the phosphorus compound initially present.

The ESCA experiments also provided quantitative analysis of the elements scanned. The ratios of nitrogen, carbon, and oxygen to phosphorus in both the initial mixtures and final chars provided information about the final char structure (Table VI).

TABLE IV
Major Thermolysis Products of D-Glucose Mixtures

D-Glucose with	Product identified	Relative amount
$(C_6H_5NH)_3PO$	$C_6H_5NH_2$	27
$(C_6H_5NH)_2P(O)C_6H_5$	$C_6H_5NH_2$	27
$C_6H_5NHP(O)$ $(C_6H_5)_2$	$C_6H_5NH_2$	1
$(C_6H_5NH)_2P(O)OC_6H_5$	C_6H_5OH	0.01
$C_6H_5NHP(O)$ $(OC_6H_5)_2$	C_6H_5OH	2

TABLE V
ESCA Binding Energies for D-Glucose Pyrolysis Mixture Chars

D-Glucose with	P_{2p} BE(eV)	FWHH[a]	O_{1s} BE(eV)	FWHH	C_{1s} BE(eV)	FWHH	N_{1s} BE(eV)	FWHH
$(C_6H_5NH)_3PO$	132.4	2.5	530.8	3.3	283.5	1.9	398.3	3.5
$(C_6H_5NH)_2POC_6H_5$	132.5	2.3	530.9	3.1	283.0	2.3	398.5	2.9
$(C_6H_5NH)_2PC_6H_5$	133.9	2.3	532.2	3.2	284.3	2.3	399.1	3.7
$C_6H_5NHP(OC_6H_5)_2$	132.6	2.4	531.0	2.9	283.8	2.2	398.7	3.1
$C_6H_5NHP(C_6H_5)_2$	131.2	2.5	530.0	3.7	282.7	2.2	398.3	2.7

[a] Full width at half-height (FWHH) represents the distribution of species centered at the reported binding energy (BE) and is influenced by homogeneity of the sample, depth of x-ray penetration, and sample surface smoothness.

It can be seen from Table VI that the nitrogen to phosphorus ratio is approximately 1:1, which is in good agreement with results obtained by other workers from studies of similar systems with cellulosics.[25] The carbon to phosphorus ratio has decreased in all cases, which is attributed to retention of phosphorus in the char. The oxygen to phosphorus ratio was relatively unchanged for each of the samples and is in excess of the 4:1 ratio necessary for phosphate to be present in the char. This suggests a relatively highly oxidized char structure with the phosphorus species present as a phosphoric mono-amide.

SUMMARY AND CONCLUSIONS

Organophosphorus flame retardants alter the thermal decomposition of carbohydrates by lowering the onset temperature for decomposition and decreasing the formation of volatile combustibles through promotion of higher char yields.[1] Flame retardants possessing phosphorus–nitrogen bonds are generally more effective in increasing char production and reducing the flammability hazards of cellulosic materials.[1-10] The nature of the reported enhanced effectiveness of phosphoramide compounds has not been previously elucidated. Explanations for the increased effectiveness of phosphorus–nitrogen compounds as flame retardants are generally based on the increased reactivity of phosphoramides as compared to phosphates. In this work we investigated the thermal interactions of a series of phosphate and phosphoramide flame retardant models with cellulose and model carbohydrates.

TABLE VI
Elemental Ratios of D-Glucose Mixtures and Chars

D-Glucose with:	Initial sample[a] N/P	C/P	O/P	Final char N/P	C/P	O/P
$(C_6H_5NH)_3PO$	3	24	7	1.0	6.7	6.1
$(C_6H_5NH)_2P(O)OC_6H_5$	2	24	8	1.3	7.7	9.1
$(C_6H_5NH)_2P(O)C_6H_5$	2	24	7	0.9	3.9	6.6
$(C_6H_5NH)P(O)(OC_6H_5)_2$	1	24	9	1.2	10.2	9.7
$C_6H_5NHP(O)(C_6H_5)_2$	1	24	7	0.9	18.5	8.8

[a] Calculated values based on initial 1:1 molar ratio of D-glucose and organophosphorus compounds.

The thermal analysis studies of D-glucose, levoglucosan, and cellulose with model flame retardants showed that phosphoric triamides promote much higher char yields than analogous phosphates. The phosphoramides also exhibited relatively large exothermic reactions with the carbohydrates at decomposition temperatures, while the phosphate samples did not. These exotherms occurred concurrently with weight loss reactions and were assigned to direct interaction between the phosphorus derivative and the carbohydrate substrate.

The model flame retardants showed similar reactivity with each of the carbohydrates studied. Though it was not clearly determined whether the flame retardant models acted directly with the undecomposed carbohydrates or with decomposition products, the thermal analysis data indicated that they can react readily with similar structures capable of undergoing phosphorylation reactions.

While the isothermal weight loss studies were not interpretable in mechanistic terms, they showed that each of the flame retardant models altered the kinetics of decomposition to some extent for each of the carbohydrates studied. An extremely rapid weight loss took place with each of the phosphoramide mixtures but was measurable only for the methylphosphoramide and cellulose sample. Measurements for all of the glucose mixtures were complicated by overlapping weight losses. The activation energies for decomposition of the cellulose and levoglucosan mixtures were similar in magnitude, which probably indicates that the decomposition weight losses took place through similar mechanisms.

Studies of char formation from a series of mixtures of D-glucose with various phosphorus amide esters indicated that leaving group lability influences the thermolysis products formed during pyrolysis. ESCA showed that the final chars possess similar structures regardless of the original phosphoramide present. Nitrogen to phosphorus ratios of 1:1 were common to each of the char samples and indicated that the final structure at the phosphorus center retains one nitrogen bond, despite the oxidative nature of the char, which suggested a highly oxidized solid state, as expected from oxidative decomposition.

Although these thermal studies have been carried out at slow heating rates and in inert atmospheres, it seems probable that the chemistry is of the same general type as that encountered under conditions of flaming combustion. The relative abilities of the phosphates and phosphoramides to induce char formation and alter the carbohydrate pyrolysis chemistry parallel their flame retardant efficiencies. These findings tend to substantiate previously proposed mechanistic theories in which flame retardant efficiency has been correlated with its ability to thermally phosphorylate cellulose, pyrolyze to phosphoric acid derivatives and unsaturated carbohydrate residues, and provide clearage of glycosidic linkages.

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