

Pyrolysis and Combustion of Cellulose. II. Thermal Analysis of Mixtures of Methyl α -D-Glucopyranoside and Levoglucosan with Model Phosphate Flame Retardants

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Synopsis

The thermal degradation of methyl α -D-glucopyranoside, a cellulose model of intermediate complexity, was investigated in an attempt to gain insight into the pyrolytic reactions of analogous cellulose systems. The pure glucoside pyrolysis proceeds through formation of an intermediate of higher thermal stability. Nitrogenous bases bring about decomposition of the glucoside at lower temperatures and without formation of a detectable intermediate. Phenyl phosphates and phosphoramides induce thermal degradation of methyl α -D-glucopyranoside at lower temperatures than observed for the pure glucoside. The postulated degradation mechanism involves esterification of the glucoside followed by dehydration and skeletal rearrangements. Nitrogenous bases assist the dehydration process but reduce the yield of residue and bound phosphorus. Levoglucosan, the cellulose degradation product responsible for flaming combustion, was pyrolyzed in the presence of model flame retardants. Nitrogenous bases were found to inhibit thermal polymerization of levoglucosan and to induce its decomposition at lower temperatures. Zinc chloride exerted its effects in two stages: acid-catalyzed polymerization at lower temperatures and dehydration at higher temperatures. Phenyl phosphates and phosphoramides alter levoglucosan pyrolysis by action as Lewis acids in a manner similar to zinc chloride.

INTRODUCTION

In part I of this study,¹ the flammability properties of cellulose treated with selected phenyl phosphates, alone and in conjunction with nitrogenous bases, were reported. These combustion data were tentatively interpreted in terms of thermal analysis parameters.

Effective flame retardants were shown to promote endothermic substrate decomposition at temperatures lower than that of untreated cotton. This was accompanied by increased yields of nonvolatile char. Nitrog-

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enous bases were found to exert their lesser flame retardant effects exothermically at temperatures greater than that of the uncatalyzed cellulose degradation and without accompanying residue increases.

Mixtures of triphenylphosphate with nitrogenous bases were shown to be more effective in retarding flaming than either constituent alone, as shown by increased char yields, decreased decomposition temperatures, and slower rates of flame propagation. These observations were interpreted in terms of possible synergistic interactions between the phosphate and the nitrogenous bases; however, due to the complex nature of the cellulose substrate and the wide diversity of the pyrolytic reactions which may occur in these systems, detailed explanations of the interactions were not attempted.

In an effort to gain a better insight into the action of flame retardants on cellulose during burning, a study was made of the thermal degradation of methyl α -D-glucopyranoside, a cellulose model of intermediate complexity, and of levoglucosan, a major product from cellulose pyrolysis.^{2,3} The results of this study are reported herein.

EXPERIMENTAL

Chemicals. All chemicals were reagent-grade commercial samples with the exception of diphenyl amidophosphate and triphenyl phosphate, which were prepared by the methods of Audrieth and Toy.⁴

Differential Thermal Analysis (DTA). All curves were obtained in a static air atmosphere using a du Pont 900 differential thermal analyzer equipped with microcapillary tubes for both sample and reference. The reference material was glass in all cases. A constant heating rate of 20°C/min and a scale sensitivity of 0.5°C/in. were used.

Thermogravimetric Analysis (TGA). The measurements were made in a dynamic atmosphere of nitrogen using a du Pont 950 thermogravimetric analyzer at a constant heating rate of 5°C/min and a scale sensitivity of 2 mg/in.

Infrared Analysis (IR). Infrared spectra were run as KBr discs on a Perkin-Elmer Model 237B grating infrared spectrophotometer.

Elemental Analysis. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Large-Scale Pyrolysis. Pyrolyses were performed in a static air atmosphere in 13 × 100-mm test tubes which were heated in a silicone oil bath. The bath was heated from room temperature to 300 ± 5°C at approximately 10°C/min and allowed to cool to 240°C. The tubes were then removed from the bath and allowed to cool to room temperature. The residues were extracted with benzene, acetone, ethanol, and water, each at the boil, and dried for 2 hr at 105°C.

Preparation and Pyrolysis of Mixed Methyl O-(Diphenylphosphoryl)- α -D-glucosides. To a solution containing 25.0 g of methyl α -D-glucopyranoside (1.0 mole) dissolved in pyridine (125 ml), 34.5 g of diphenyl-

chlorophosphate (1.0 mole) was added dropwise. The reaction was highly exothermic, necessitating the slow addition of diphenyl chlorophosphate. The resulting solution of mixed methyl O-(diphenylphosphoryl)- α -D-glucopyranosides was stirred for 24 hours, evaporated to a viscous syrup, and extracted twice with benzene (see Fig. 6 for infrared spectrum).

After evaporation of residual benzene, 7.4 g of the syrup was pyrolyzed, extracted with benzene, ethyl alcohol, acetone, and water (each at the boil), and dried for 2 hr at 105°C. A black lava-like residue (1.3 g) was obtained (found: 69.41% C, 4.02% H and 3.76% P) (see Fig. 5 for infrared spectrum).

Preparation of Levoglucosan. The method of Wolfrom and Whistler⁵ was modified using techniques developed by Dimler⁶ for the preparation of 1,6-anhydro- β -D-glucopyranose(levoglucosan).

Commercial unhydrolyzed starch (150.0 g) was washed with 2% acetic acid, rinsed with pure water, dried with acetone, and conditioned for 12 hr at 105°C. The purified starch was ground to a fine powder and pyrolyzed with a propane flame under reduced pressure (0.1 mm). A brown tar, consisting of levoglucosan and other starch degradation products, was collected as the distillate at 0°C. The distillate was dissolved in 200 ml of acetone and evaporated to dryness to remove excess moisture.

This tar was acetylated in pyridine (5 parts) with acetic anhydride (3 parts) at 0°C for 15 hr. The solution was then concentrated on a rotary evaporator at 80°C under reduced pressure (15 mm) to yield a thick syrup. Distillation of the syrup at reduced pressure (0.1 mm) over the boiling range 110–150°C gave a bright yellow liquid. This distillate was dissolved in hot isopropyl alcohol from which crystals of levoglucosan triacetate, mp 108–109°C (literature⁶ 108–109°C), formed upon cooling.

The triacetate was deacetylated in a solution containing 5% sodium methoxide in methyl alcohol, treated with Rexyn I-300 (H-OH) ion exchange resin to remove residual sodium, filtered with decolorizing carbon, and evaporated to dryness. The resulting syrup was dissolved in hot ethyl alcohol from which crystals of levoglucosan, mp 172–173°C (literature⁶ 172°C), formed upon standing. The yield of levoglucosan was 12.5 g (0.080 mole, or 8.3%) (see Fig. 11 for infrared spectrum.)

RESULTS AND DISCUSSION

The study of thermally induced chemical reactions for the cellulose substrate is difficult because a large percentage of the substrate exists as crystalline regions which may not be penetrated by the reagent being studied. The problem is further complicated by secondary reactions which may occur with primary degradation products or intermediates resulting from disintegration of the gross polymeric structure. It was advantageous, therefore, to select a monomeric model system and the major cellulose pyrolysis byproduct as bases for further investigations of thermally induced reactions occurring between cellulose and flame retardants. The

model selected was methyl α -D-glucopyranoside, which is readily available and similar to the basic cellulose unit except for anomeric form and a free C-4 hydroxyl.

Methyl α -D-Glucoside

The DTA thermogram for methyl α -D-glucopyranoside (Fig. 1) exhibits four major regions of thermal activity. The first, an endotherm near 160°C, corresponds to melting of the pure compound. Melting is followed by volatilization of the sample over the range 180–270°C and endothermic decomposition from 270–310°C. At 310°, exothermic activity attributable

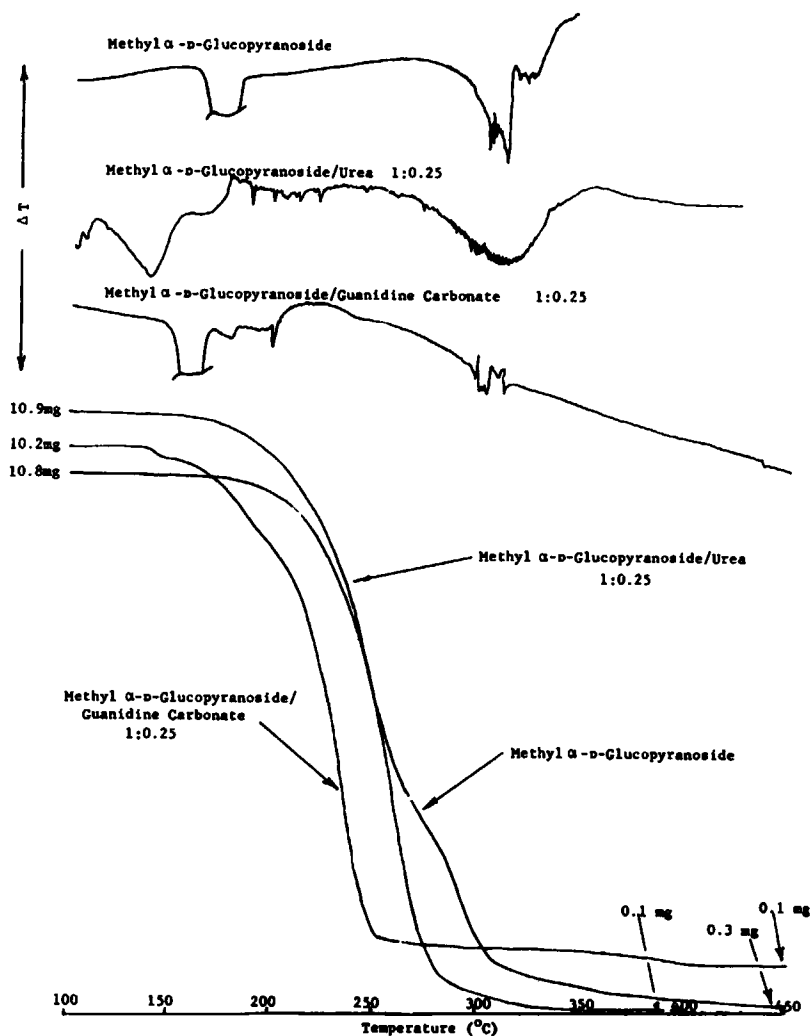


Fig. 1. DTA and TGA thermograms of methyl α -D-glucopyranoside in mixtures with urea and guanidine carbonate.

to condensation and rearrangement of the decomposition products becomes dominant and is followed by further endothermic decomposition. This interpretation of the thermal decomposition of methyl α -D-glucopyranoside is further illustrated by the inherent characteristics of its TGA thermogram. No weight loss is observed prior to melting, after which weight loss begins with a rate which increases to a maximum corresponding to the first region of endothermic decomposition. The rate then decreases as expected for the formation of condensates of lower volatility, after which the rate of weight loss increases again until essentially all of the sample is volatilized.

Mack and Donaldson⁷ reported catalyzed decomposition of cellulose by alkali metal bases, which resulted in lowered decomposition temperatures and increased residues. The effects of nitrogenous organic bases were reported in part I of this series.¹ Urea and guanidine were shown to have flame retardant properties and to change the nature of the reaction energetics for cellulose in the 300–450°C region from endothermic to exothermic. Because of the complex nature of the cellulose system, identification of the pyrolytic reactions occurring was not possible.

The thermograms for methyl α -D-glucopyranoside/nitrogenous base mixtures (Fig. 1) were somewhat more definitive. The DTA thermogram for the mixture with urea exhibits endothermic activity in the 100–170°C region due to loss of water of hydration from the urea and melting of the mixed solids. This is followed by exothermic activity and volatilization of decomposition products over the 170–250°C region and endothermic activity from 250° to 330°C. This latter activity is attributable to decomposition and volatilization of products formed in the exothermic reaction. The TGA supports this interpretation and illustrates further that no detectable intermediate product of lower volatility is formed with urea present. It can also be seen that the endotherm for the urea-to-cyanuric acid conversion near 250°C is absent from the DTA thermogram for the composite mixture. This would indicate that the exothermic activity involves reactions between methyl α -D-glucopyranoside and urea.

Examination of the thermogram for the methyl α -D-glucopyranoside/guanidine carbonate mixture reveals an endotherm due to melting of the mixed solids near 150°C followed by exothermic activity over the 170–320°C region. In view of the corresponding weight loss in the TGA thermogram (at 150°C) and the absence of thermal activity attributable to a guanidine-to-melamine interconversion, the exothermic activity may be attributed to formation and decomposition of a model glucoside-guanidine adduct with decomposition occurring at a temperature 30° lower than that observed for pure methyl α -D-glucopyranoside or its urea mixture.

The DTA thermogram for the methyl α -D-glucopyranoside/triphenylphosphate mixture (Fig. 2) is similar to that of the pure glucoside except for an additional endotherm near 250°C, which suggests that a reaction was achieved prior to volatilization of the glucoside. This endotherm imme-

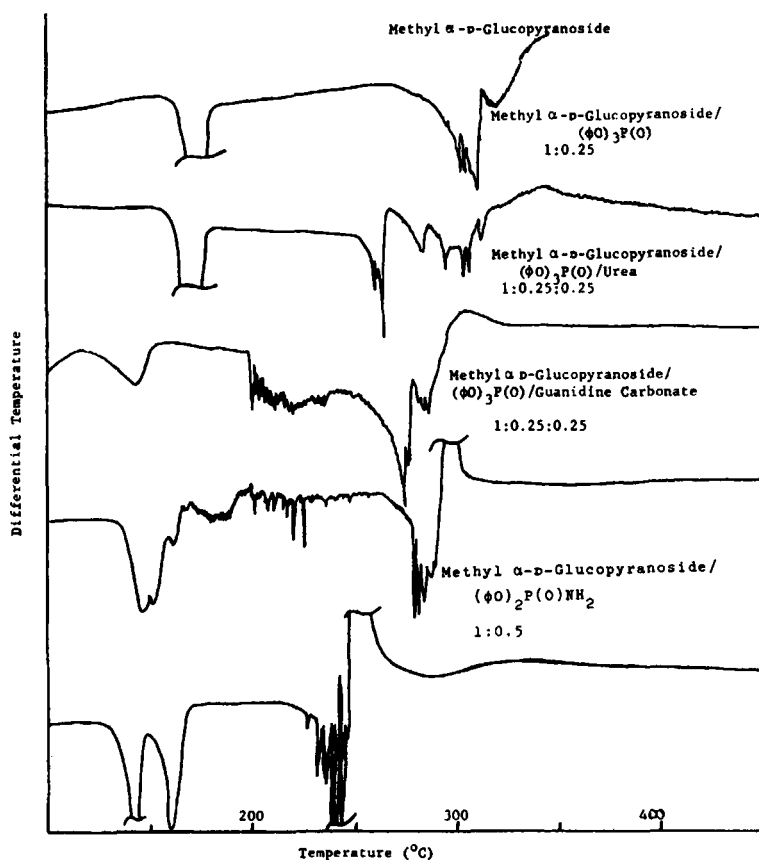


Fig. 2. DTA thermograms of methyl α -D-glucopyranoside mixtures.

diately precedes exothermic activity, upon which are superimposed volatilization endotherms over the range 280–350°C. Such a sequence of thermal activities would be expected for the thermally induced transesterification reactions (endothermic) followed by dehydration and skeletal rearrangements (exothermic), which were postulated to explain the thermal data for analogous cellulose systems.

Addition of urea to the methyl α -D-glucopyranoside/triphenyl phosphate mixture slightly increased the magnitude of the observed endothermic activity. Addition of guanidine to the system, however, greatly increased the magnitude of the endotherm near 250°C, making the immediately following exotherm very distinct. Identical thermal activity was observed with the methyl α -D-glucopyranoside/diphenyl amidophosphate mixture; however, the thermal activity with the latter is more vigorous and occurred at a temperature that was 50° lower. Thus it is not unreasonable to postulate that the active species for the guanidine/triphenyl phosphate and the diphenyl amidophosphate systems are very similar. Such an intermediate, probably complex polymeric phosphoramides resulting from

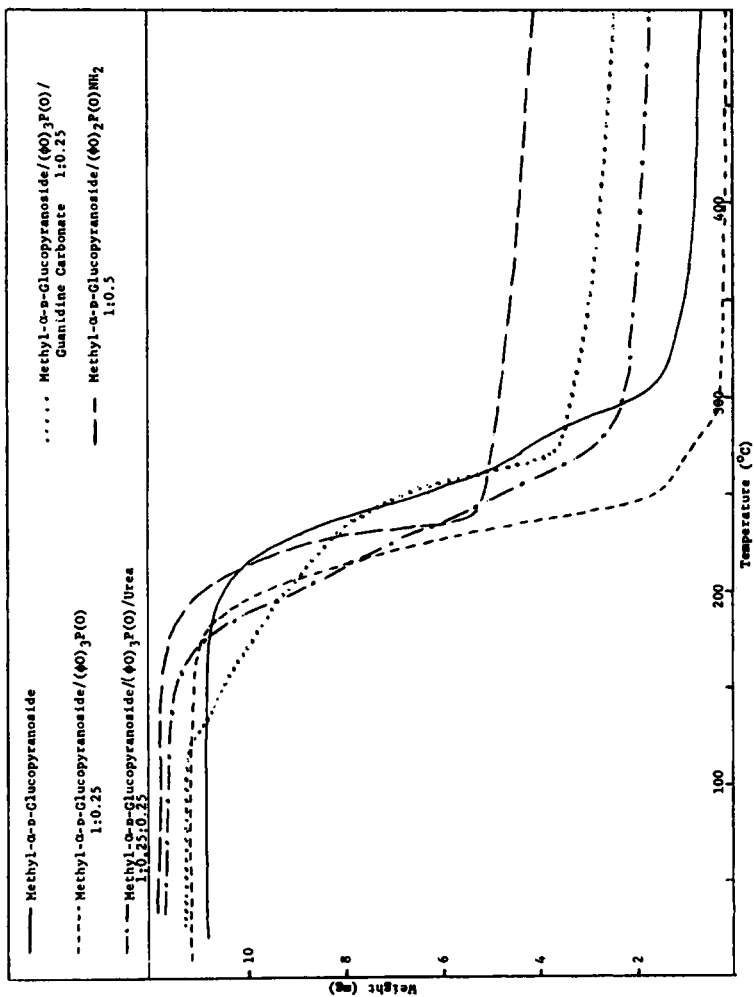


Fig. 3. TGA thermograms of methyl α -D-glycopyranoside mixtures.

condensation of guanidine and triphenyl phosphate, would not be formed as readily with the less nucleophilic urea. Analogous polymeric systems have been shown to result from the thermally induced reaction of triphenyl phosphate and guanidine carbonate in absence of carbohydrate substances.⁸

TGA thermograms for the methyl α -D-glucopyranoside mixtures (Fig. 3) give further evidence for the postulated sequence involving thermally induced transesterification reactions followed by dehydration and skeletal rearrangement occurring in these systems. A direct parallel also exists between the postulated tendency of the reactants toward phosphoramidate formation and the quantity of residue obtained. As was indicated by the DTA thermograms, the methyl α -D-glucopyranoside/triphenyl phosphate mixture undergoes essentially complete decomposition at temperatures 50° lower than was required for the pure glucoside, and without formation

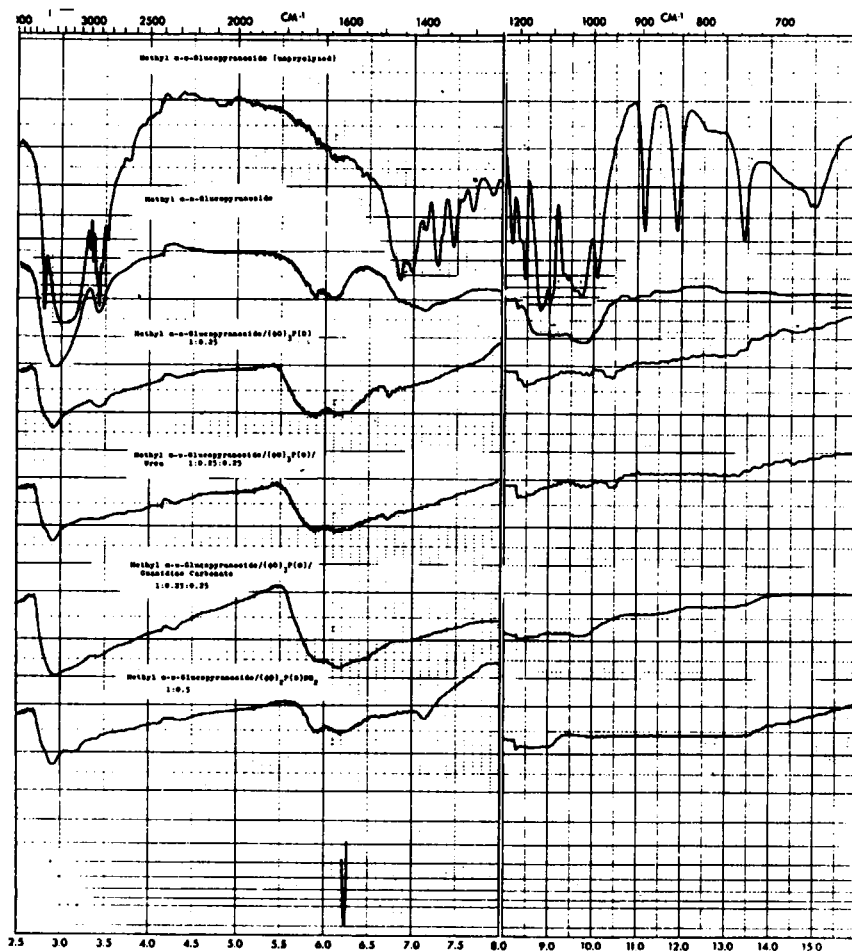


Fig. 4. Infrared spectra of methyl α -D-glucopyranoside and methyl α -D-glucopyranoside pyrolysis products.

of an intermediate displaying lower volatility. The mixture containing urea exhibited an increased residue characteristic of the phosphoramidate mixtures, but with a lesser effect in the onset decomposition temperature. This possibly illustrates the combined effects of triphenyl phosphate and the phosphoramidate formed from triphenyl phosphate and urea. The mixture containing guanidine was almost identical in the higher temperature region to that containing diphenyl amidophosphate, as was observed in the corresponding DTA thermograms.

Dehydration and skeletal rearrangement of methyl α -D-glucopyranoside during pyrolysis with organic phosphates and phosphoramidates is vividly illustrated in characterization of its respective pyrolysis residues. Infrared spectra (Fig. 4) show a decrease in absorptions attributable to hydroxyl O—H stretching (2.8–3.1 μ) and aliphatic C—H stretching (3.3–3.6 μ) when compared to the residue from the pure glucoside. Almost complete loss of the carbohydrate fine structure was also observed.

TABLE I
Pyrolytic Reactions of Methyl α -D-Glucopyranoside

Composition of pyrolysis mixtures	Ratios of components in mixtures	Elemental analyses of extracted residues ^a			
		%C	%H	%N	%P
Methyl α -D-glucopyranoside		46.05	6.28		
Methyl α -D-glucopyranoside Triphenylphosphate	1:0.25	68.54	4.64		0.00
Methyl α -D-glucopyranoside Triphenyl phosphate Urea	1:0.25:0.25	63.43	4.40	7.81	1.49
Methyl α -D-glucopyranoside Triphenyl phosphate Guanidine carbonate	1:0.25:0.25	55.65	4.85	9.74	2.47
Methyl α -D-glucopyranoside Diphenyl amidophosphate	1:0.5	51.69	3.78	3.17	7.14

^a Calculated for methyl α -D-glucopyranoside before pyrolysis: C, 43.30%, and H, 7.27%.

Elemental analyses of the corresponding residues (Table I) show increased carbon contents and decreased hydrogen contents when compared to the residue from the pure glucoside. These data again indicate that dehydration occurred during pyrolysis of the mixtures. Dehydration occurred to the greatest extent in the methyl α -D-glucopyranoside/triphenyl phosphate mixture and decreased as the tendencies toward phosphoramidate formation by the systems increased; however, residual chemically bound phosphorus in the residues increased with phosphoramidate formation. These data indicate that while the postulated transesterification reaction may increase with phosphoramidate formation, the dehydration reaction which follows is inhibited. Setterquist⁹ has shown that the phosphate ester pyrolyses are subject to acid catalysis; therefore, addition of nitrogenous bases to the pyrolysis system should decrease the overall

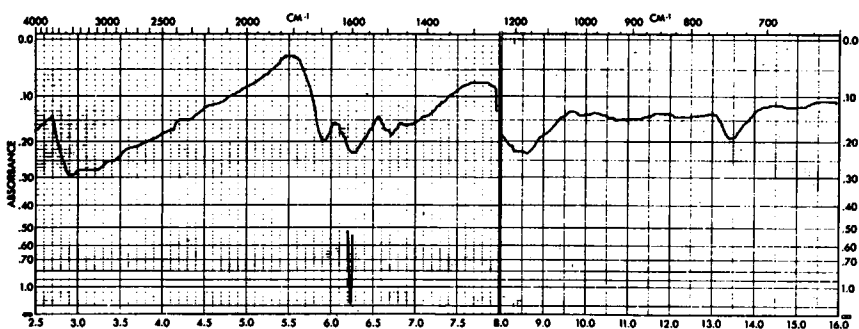


Fig. 5. Infrared spectrum of mixed methyl O-(diphenylphosphoryl)- α -D-glucopyranosides pyrolysis product.

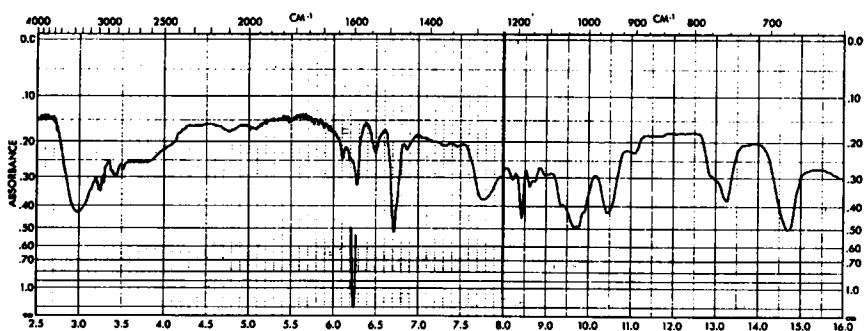


Fig. 6. Infrared spectrum of mixed methyl O-(diphenylphosphoryl)- α -D-glucopyranoside.

acidity of the system and inhibit dehydration of the carbohydrates involved.

Since esterification reactions occur predominantly at the C-6 hydroxyl of the glucoside unit of cellulose,¹⁰⁻¹² decreasing the extent of pyrolysis of the phosphorylated substrate should have little effect on the system's ability to retard burning. The unpyrolyzed ester at the C-6 position would prevent the formation of levoglucosan and therefore reduce the fuel supply necessary for combustion. In addition, the phosphates used are polyfunctional and therefore are capable of crosslinking low molecular weight fragments which may otherwise volatilize and enter into the combustion process as fuel.

As further confirmation of thermally induced transphosphorylation reactions occurring during phosphate-assisted pyrolyses of carbohydrates, mixed methyl O-(diphenylphosphoryl)- α -D-glucopyranosides were prepared by an unambiguous route and pyrolyzed in the usual manner. The infrared spectrum of the extracted residue (Fig. 5) showed decreased absorption attributable to hydroxyl O—H stretching (2.9–3.1 μ) and aliphatic C—H stretching (3.3–3.6 μ) when compared to the unpyrolyzed ester (Fig. 6). Carbon and hydrogen contents of the residue corresponded

closely to those of the residue obtained from in situ formation of the phosphate ester.

1,6-Anhydro- β -D-glucopyranose (Levoglucozan)

A major product resulting from the thermal degradation of cotton cellulose is a tar consisting primarily of 1,6-anhydro- β -D-glucopyranose (levoglucozan). It is this tar that provides fuel for the vapor phase process commonly referred to as flaming. Flame retardants presumably inhibit the formation of the tar by altering the primary mode of decomposition of cellulose to a path other than that which leads to levoglucozan formation.^{2,3} The resultant reduction in fuel for combustion leads to a subsequent retardation in burning. Complete elimination of levoglucozan

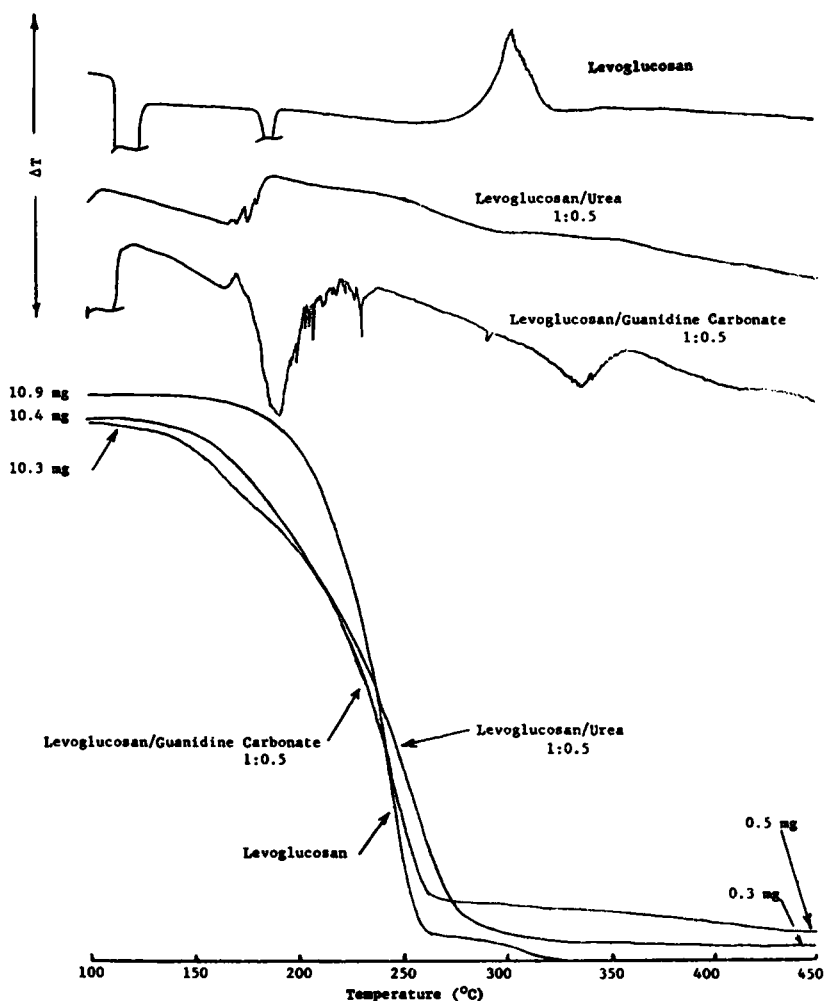


Fig. 7. DTA and TGA thermograms of levoglucozan in mixtures with urea and guanidine carbonate.

formation, however, may not be attained with all flame retardants which may be used; thus, it was of interest to determine what interactions might occur between flame retardants and levoglucosan itself.

The DTA thermogram for levoglucosan (Fig. 7) exhibits four major regions of thermal activity. These have been assigned by Shafizadeh¹³ essentially as follows: a physical transformation of the molecule, including a solid state transition near 120°C; melting near 190°C; evaporation over the region 190–270°C; and polymerization and degradation of levoglucosan above 270°C.

The effects of pure nitrogenous bases on the pyrolysis of levoglucosan were investigated by DTA and TGA (Fig. 7). Both urea and guanidine carbonate were effective at altering the thermally induced polymerization of levoglucosan. The exotherm observed at 270°C in the DTA thermogram of pure levoglucosan disappeared when urea or guanidine carbonate was present. The melting endotherm near 190°C was also absent. In-

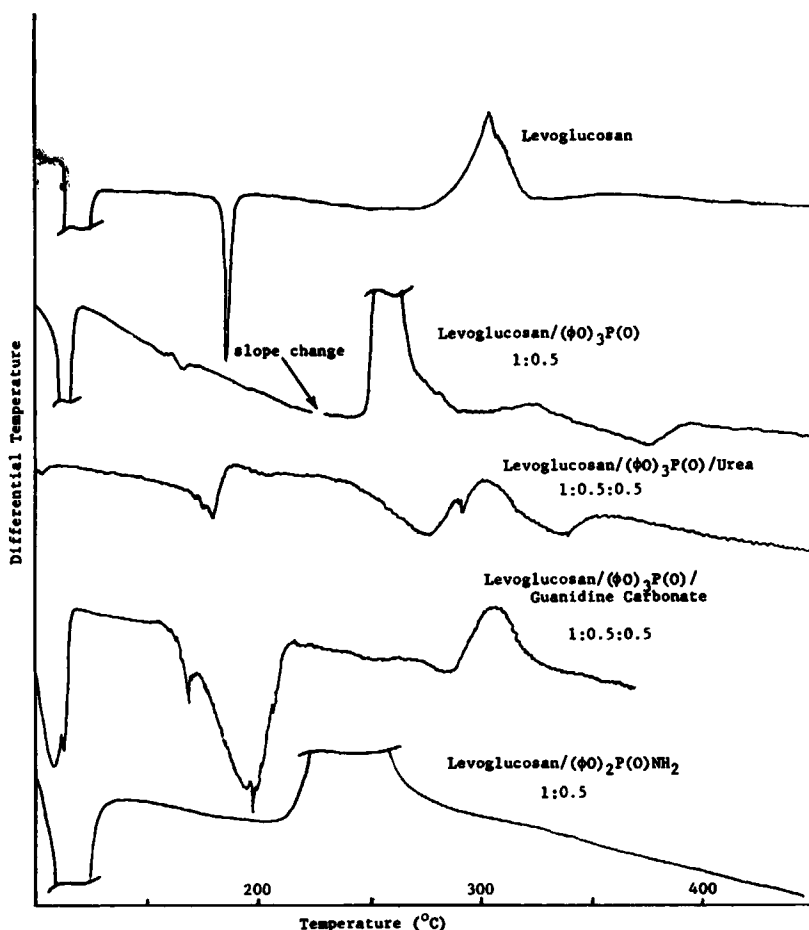
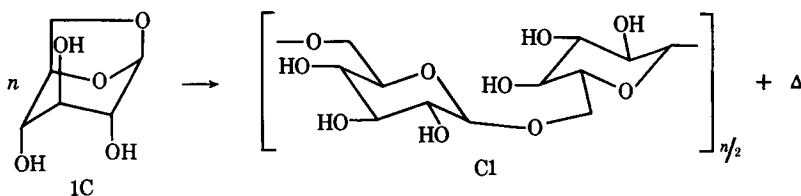


Fig. 8. DTA thermograms of levoglucosan mixtures.

stead, exothermic activity occurred for both systems with onset temperatures in the DTA thermogram near 170°C. For both nitrogenous base mixtures, the exotherm extends to near 300°C. The exotherm for the levoglucosan/guanidine mixture has a vigorous evaporation endotherm superimposed upon it over the range 180–240°C and is followed by a second exotherm beginning near 330°C which may be attributed to further degradation of the remaining residue. From the DTA thermograms it can be concluded, therefore, that these nitrogenous bases induced exothermic decomposition at lower temperatures than required for the pure compound. This induced decomposition was also evident in the TGA thermograms. The onset decomposition temperatures for the nitrogenous base mixtures occur some 50° lower than for the pure levoglucosan, and the decomposition proceeds at a much slower rate. The absence of levoglucosan polymerization in the presence of nitrogenous bases is probably due to the destruction of the levoglucosan before the temperatures necessary for polymerization are reached. It must also be noted, however, that levoglucosan polymerization is an acid-catalyzed process and that the overall acidity of the system would be reduced by the nitrogenous bases.

Vigorous exothermic activity was observed at 250° and 210°C in the curves from levoglucosan mixed with triphenyl phosphate and with diphenyl amidophosphate (Fig. 8), respectively. The DTA curves for levoglucosan mixed with triphenyl phosphate and nitrogenous bases were much less clearly defined. These latter curves were complicated by the nitrogenous bases and by exothermic interactions with volatilization endotherms; therefore, the curves appear deceptively structureless. Exothermic activity was discernible, however, in the 280–330°C region.

A question thus arises as to the origin of the exothermic activity observed for pyrolysis of the levoglucosan/phosphate mixtures. Levoglucosan exists in the thermodynamically unfavored 1C conformation in which all functional groups occupy axial positions. If cleavage of the acetal ring occurs, a tremendous amount of energy should be released, as shown in scheme I:



Scheme I

It is likely that the observed exothermic activity reflects this release of energy. Either polymerization or thermal degradation of levoglucosan would be accompanied by ring cleavage.

Shafizadeh and co-workers¹⁴ reported that the presence of $ZnCl_2$ during pyrolysis of either levoglucosan or cellulose resulted in dehydration of the carbohydrate substrates. This observation is supported by thermal data

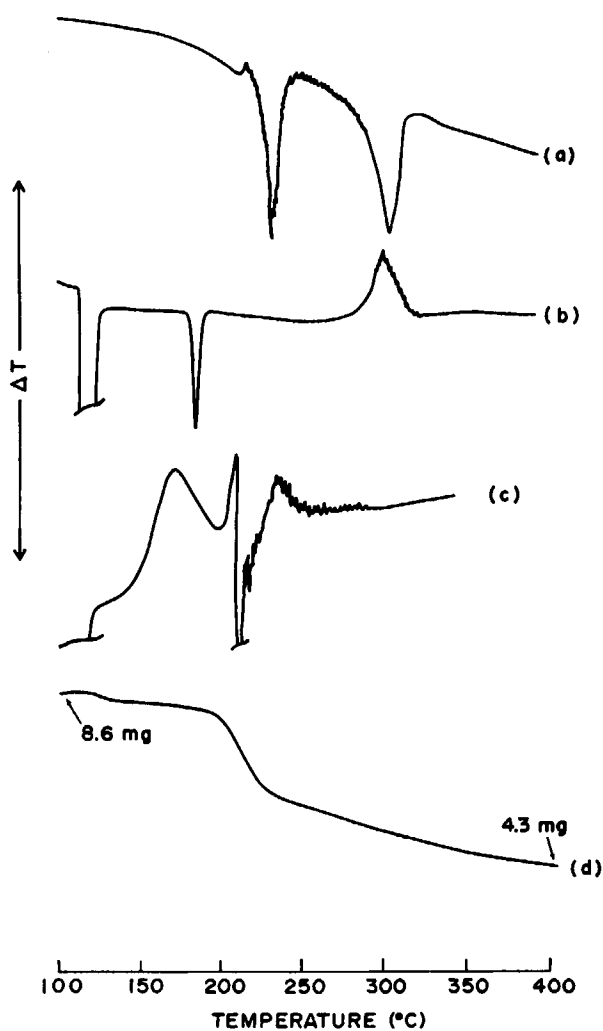


Fig. 9. Effect of zinc chloride on levoglucosan pyrolysis.

presented in Figure 9. It is apparent, however, that more than simple dehydration is occurring. Following the phase transition at 120°C observed with the levoglucosan/ ZnCl_2 mixture are two distinct regions of thermal activity. In the first of these, an exothermic process occurring over the 120–200°C range takes place with no accompanying weight loss. This may be attributed to a Lewis acid-catalyzed polymerization of levoglucosan, a process known to occur in solvent systems.¹⁵ The second area of thermal activity involves an exotherm over the 200–260°C range upon which is superimposed a strong evaporation endotherm. In view of the corresponding weight loss observed in the TGA thermogram, this activity may be ascribed to the dehydration reactions observed by Shafizadeh et al.¹⁴

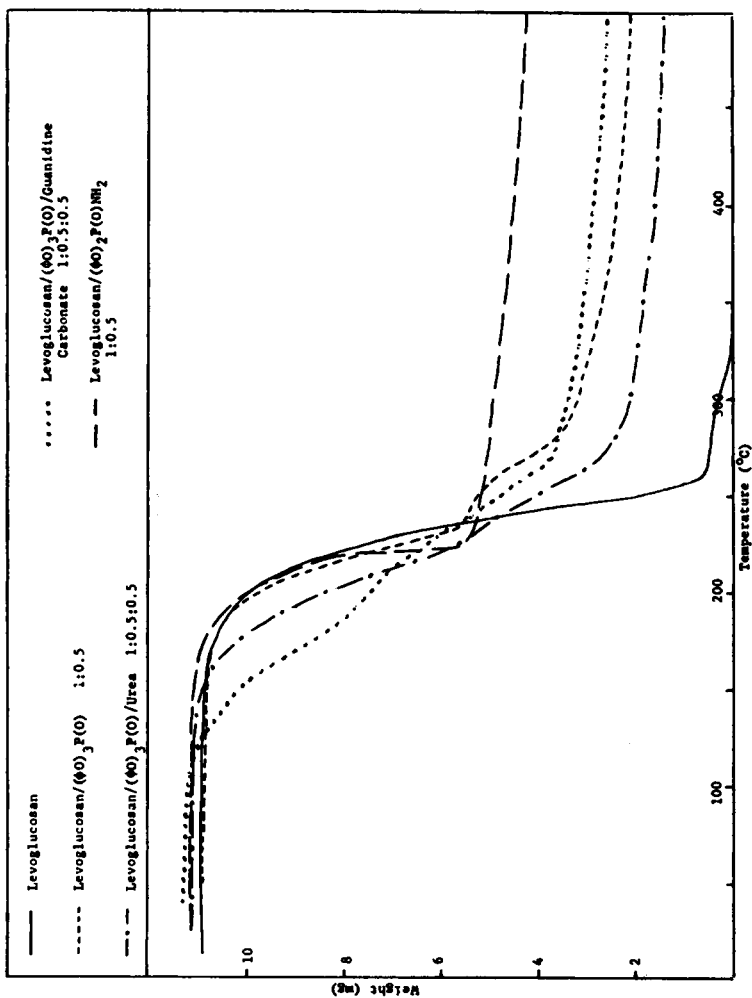


Fig. 10. TGA thermograms of levoglucosan mixtures.

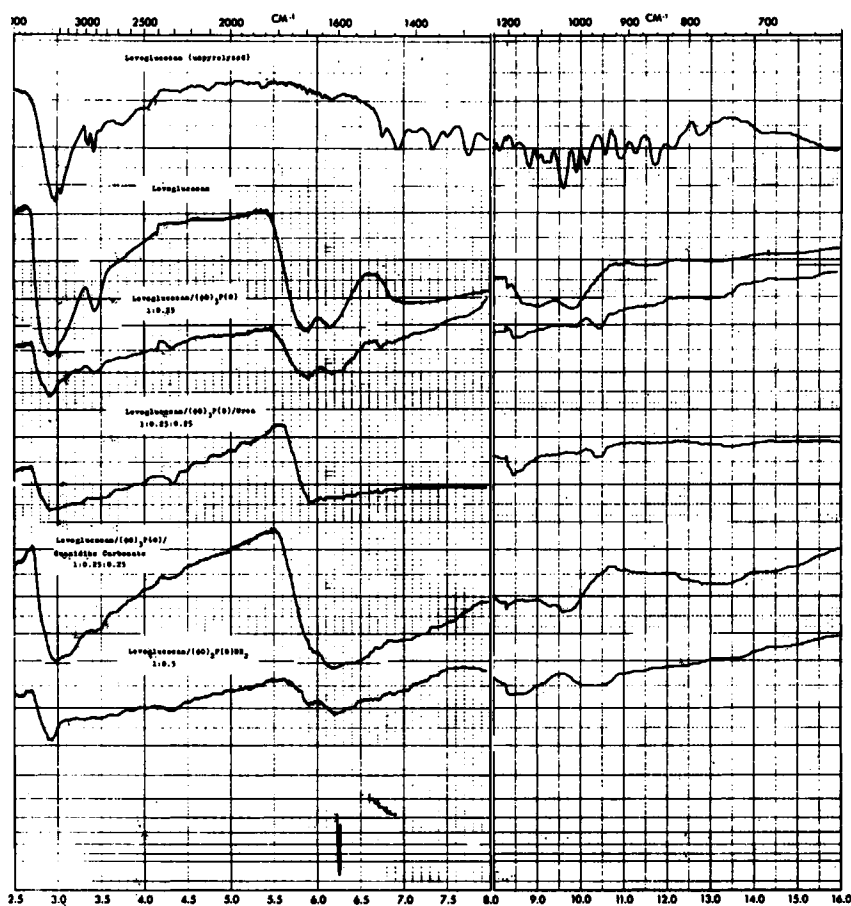


Fig. 11. Infrared spectra of levoglucosan and levoglucosan pyrolysis products.

The TGA thermograms for levoglucosan/organic phosphate mixtures (Fig. 10) provide information necessary for a more detailed explanation of the thermal activity observed in the corresponding DTA curves. Residues increase within the series progressing from pure levoglucosan to the levoglucosan/diphenyl amidophosphate mixture. This is the same order of residue increases which was observed on pyrolysis of analogous methyl α -D-glucopyranoside mixtures. It was postulated that these results are associated with transesterification reactions with phosphates having differing degrees of phosphoramidate character. Further substantiation of this postulate is given elsewhere.⁸ Prior to termination of weight loss for the levoglucosan mixtures, an intermediate of lower volatility can be observed. This intermediate shows up after about 50% of the weight has been lost and is attributable to polymerization. Similar intermediates were not observed in the analogous methyl α -D-glucopyranoside mixtures or in the levoglucosan/diphenyl amidophosphate mixture. This is consistent with the proposed interpretation, since methyl α -D-

glucopyranoside is not an anhydro sugar and would not be expected to polymerize. Any intermediate occurring with the levoglucosan/diphenyl amidophosphate mixture is obscured by the TGA temperature overshoot resulting from the vigorous exothermic interaction (presumably polymerization) between the components of the mixture.

These observations all tend to indicate that the pyrolysis of levoglucosan in mixtures with organic phosphates involves acid-catalyzed polymerization followed by transphosphorylation reactions leading to dehydration, crosslinking, and skeletal rearrangements. The extent to which each of these processes occurs varies with the degree of phosphoramidate character of the variable component in the mixture. Further support for this conclusion is gained from elemental analyses (Table II) and infrared spectra (Fig. 11) of the extracted pyrolysis residues. All of the phosphate systems are shown to promote dehydration and skeletal rearrangements as evidenced by decreased infrared absorptions attributable to hydroxyl O—H stretching (2.8–3.1 μ) and aliphatic C—H stretching (3.3–3.6 μ). Increased carbon contents and decreased hydrogen contents of the residues as compared to the residue from pure levoglucosan are also indicative of dehydration. Levoglucosan also showed evidence of dehydration on pyrolysis, but this is expected in view of reported pyrodextrin formation which results from heating levoglucosan at moderate temperatures.¹⁶

TABLE II
Pyrolytic Reactions of Levoglucosan

Composition of pyrolysis mixtures	Ratios of components in mixtures	Elemental analyses of extracted residues ^a			
		%C	%H	%N	%P
Levoglucosan		56.48	4.07		
Levoglucosan Triphenyl phosphate	1:0.25	61.57	4.60		0.56
Levoglucosan Triphenyl phosphate Urea	1:0.25:0.25	57.55	4.23	8.41	1.75
Levoglucosan Triphenyl phosphate Guanidine carbonate	1:0.25:0.25	47.45	4.38	10.77	2.54
Levoglucosan Diphenyl amidophosphate	1:0.5	57.16	4.15	2.74	5.71

^a Calculated for levoglucosan before pyrolysis: C, 44.44%, and H, 6.17%.

SUMMARY AND CONCLUSIONS

A study of the thermal degradation of methyl α -D-glucopyranoside, a cellulose model compound of intermediate complexity, was undertaken to gain insight into pyrolytic reactions of analogous cellulose systems. The thermal degradation of the pure glucoside proceeds through an intermediate of lower volatility. Nitrogenous bases effected the decomposi-

tion of the glucoside at lower temperatures and through a path not involving a detectable intermediate of lower volatility.

Phenyl phosphates, mixtures of phenyl phosphates with nitrogenous bases, and phosphoramides were shown by thermal analysis to interact endothermically with methyl α -D-glucopyranoside at temperatures below those necessary for its decomposition. As expected, these interactions were of a greater magnitude than those observed for cellulose mixtures probably because the monomer is more accessible to the phosphate. As in the case with cellulose, phosphoramides interacted with methyl α -D-glucopyranoside at lower temperatures and produced more char than did phenyl phosphates or mixtures of phenyl phosphates with nitrogenous bases. Infrared spectra and elemental analysis of the residues showed that dehydration was greater for methyl α -D-glucopyranoside in a binary mixture with triphenyl phosphate than with either phenyl phosphates and nitrogenous bases or phosphoramides; however, residual phosphorus was greater in the chars from mixtures with phosphoramides and ternary mixtures with phenyl phosphates and nitrogenous bases. These data indicate that, while interactions to form esters are more favored for phosphoramides, the phenyl phosphate esters of methyl α -D-glucopyranoside pyrolyze more completely.

The pyrolysis of levoglucosan, a major product from thermal degradation of cellulose, in mixtures with phenyl phosphates, nitrogenous bases, phenyl phosphate/nitrogenous base mixtures, and phosphoramides was investigated. Nitrogenous bases were shown to interact exothermally with levoglucosan prior to and in lieu of thermal polymerization. The strong base guanidine also lowered the onset decomposition temperature.

Zinc chloride induced exothermic activity at lower temperatures than that observed in pyrolysis of pure levoglucosan. This exothermic activity existed over two distinct temperature regions, the lower attributable to Lewis acid-catalyzed polymerization of levoglucosan and the higher to transesterification reactions concurrent with pyrolysis of the formed ester and subsequent skeletal rearrangements. Phenyl phosphates, phenyl phosphate/nitrogenous base mixtures, and phosphoramides were shown to alter the pyrolysis of levoglucosan in a manner similar to that observed for zinc chloride.

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