

Effects of Phosphorus-Containing Flame Retardants on Pyrolysis of Cotton Cellulose

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Synopsis

Unmodified cotton and cottons finished with high levels of seven different phosphorus-containing flame retardants were pyrolyzed in a temperature-programmed solid probe of a mass spectrometer, and mass spectra were recorded continuously throughout the pyrolyses. The spectra at the maximum rates of volatiles evolution during the pyrolyses were analyzed to determine relative amounts of water, carbon monoxide, carbon dioxide, furfural, furyl hydroxymethyl ketone, hydroxymethylfurfural, levoglucosan, and 1,6-anhydro- β -glucofuranose. These volatile materials accounted for 64% to 90% of the total ionization in the spectra. The flame retardants increased the fractions of nonfuel volatiles (water and carbon dioxide) and decreased those of anhydroglucoses, but had less effect on the carbon monoxide and furan derivatives. The flame retardant fabrics differed greatly in the fractions of anhydroglucoses (from 1% to 23%) and water (from 19% to 57%) in their pyrolysis products. These results indicate that mechanisms of flame retardant action differ among phosphorus-containing finishes.

INTRODUCTION

Flaming combustion is by definition a gas-phase reaction. In the flaming combustion of polymers, the polymer must first be converted to a gas or volatile fuel. The first step in flaming combustion of polymers in general and textiles in particular is a pyrolysis or fuel-supplying reaction in which large polymer molecules are broken down into smaller, volatile fuel compounds. As the fuel compounds are formed, they volatilize, mix with air, and burn. The energy required for the solid-phase pyrolysis step and the volatilization of the fuel is supplied by the gas-phase flame. To understand the flaming combustion of textiles, it is therefore necessary to understand the chemistry of the critical pyrolysis step. The pyrolysis and combustion of cellulose have been studied by several methods, and reviews of cellulose pyrolysis have been published.^{1,2}

Previous studies of the pyrolysis of cellulose have concentrated on physical changes such as weight loss as measured by thermogravimetric analysis, or on collection, isolation, and identification of pyrolysis or combustion products. These studies led to a generally accepted theory^{3,4} which states that the primary pyrolysis product is levoglucosan and that this compound is the primary volatile fuel for the flaming combustion of cotton cellulose.

Studies of pyrolysis reactions are complicated by the fact that compounds that are isolated consist both of (1) primary products of the pyrolysis process and (2) secondary products from thermolysis of the primary products and from interactions among the pyrolysis products in the gas phase or in condensed phases.² Because of such complications, a great deal of pyrolysis work has been done under vacuum.⁵ The conclusions drawn from vacuum pyrolysis measurements apply to flaming combustion because the pyrolysis step (after ignition) takes place

behind the flame front, as can be seen in a burning match or strip of fabric, where charring occurs behind and below the front of the flame. Since the space behind the flame front is deficient in oxygen, the pyrolysis step very probably will not involve oxygen. The primary pyrolysis reactions are therefore very likely non-oxidative and thermal in nature,^{6,7} although the precise details of the pyrolysis reaction are still a matter of discussion.

Less work has been done on the pyrolysis of flame retardant cellulosic fabrics and on mechanisms of flame retardants, although most reviews do mention the subject.^{1,2,8,9} Although there is some evidence¹⁰ for gas-phase flame retardant action by halogen-containing flame retardants and additive phosphorus flame retardants in thermoplastics such as polyesters, it is generally agreed that the reactive phosphorus-containing flame retardants used in durable finishes for cotton act exclusively in the solid phase.^{2,8} Flame retardants reduce the pyrolysis temperature of cellulose, increase the yields of char and water, and decrease the yields of tar (volatile fuel). However, the chemical processes by which phosphorus flame retardants cause these effects are still the subject of much discussion and speculation.^{11,12} Indeed, the existence or nature of the widely accepted synergism between phosphorus and nitrogen in flame retardant action is open to question.⁸ An assumption which seems implicit in most studies of solid-phase flame retardant action, although it is rarely stated, is that all phosphorus flame retardants act by the same or similar mechanisms, despite the wide variety in structural types among the reactive phosphorus flame retardants used.

The technique described in this work gives continuous and instantaneous analyses of the primary pyrolysis products from cellulose and thus provides direct information on the mechanisms of action of phosphorus flame retardants, eliminating the complications from gas- and condensed-phase reactions leading to the numerous secondary pyrolysis products usually observed. Pyrolyses of cotton fabrics finished with phosphorus flame retardants of several structural classes are compared to determine if all of these flame retardants act by the same or similar mechanisms.

EXPERIMENTAL

Materials

The fabric was a 71 × 63 cotton sheeting weighing 3.8 oz/yd² (129 g/m²) which was desized, scoured, and bleached. It was treated with flame retardants by procedures recommended by the manufacturers.¹³ The treated fabrics were machine washed with AATCC detergent, tumble dried, and equilibrated to ambient conditions before use.

Known compounds for reference spectra were obtained from the following sources: 2-furfural from Eastman Kodak Co.; 5-hydroxymethyl-2-furfural from Aldrich Chemical Co.; 1,6-anhydro- β -D-glucofuranose from Dr. Richard Reeves of Louisiana State University Medical School; and levoglucosan, synthesized by Dr. David J. Stanonis of Southern Regional Research Center by the method of Ward.¹⁴

Pyrolysis-Mass Spectrometric Measurements

The pyrolyses were carried out in the solid probe of a Perkin-Elmer MS 270 mass spectrometer, modified by inserting an FM Model 240 power-proportioning temperature programmer in the ac power supply to the solid-probe heater circuit.

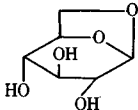
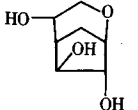
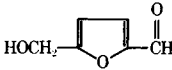
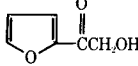
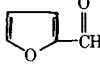
The solid-probe thermocouple controlled the temperature programmer through an appropriate external resistance. The MS 270 solid-probe control was adjusted as necessary throughout the programs to prevent temperature lag or overshooting and cycling. The temperature in the sample chamber of the solid probe was calibrated by monitoring an external thermocouple substituted for the sample while the probe was heated in temperature programs in an auxiliary vacuum system. The calibration equation for the temperature programs used in this study was: $T = 1.40T_{\text{obs}} - 30.0$, where T_{obs} is the temperature indicated by the probe thermocouple.

Warp yarns 6 mm long weighing approximately 85 μg were held in 1.7×15 mm Pyrex capillaries placed in the probe which was inserted into the source of the mass spectrometer and heated to 174°C at a pressure of 3×10^{-6} torr. Background spectra were obtained at this temperature, and the temperature was then programmed up to 460°C at a rate of 5.6°C/min. Mass spectra were measured continuously during the temperature program. Additional background spectra were obtained as the probe cooled. The mass spectrometer was operated at 70 eV electron energy, 2000 V accelerating voltage, and a source temperature of 250°C. The source pressure rose to about 8×10^{-6} torr at the peaks of the pyrolyses. The magnetic scan of the mass spectrometer was controlled by an Incos 2000 GC-MS data system, which also recorded the spectra on magnetic discs. The scan parameters were: quadratic scan function up from 1 to 500 amu in 20.0 sec down in 5.0 sec, hold at 1 amu for 5.0 sec; 30.0 sec total for each scan. The scan parameters for some runs were half of these times, totaling 15.0 sec. A total of 120 or 240 spectra were recorded for each run. Three to six replicate runs were made on each sample. Reproducibility of individual ion intensities was generally $\pm 2\%$ of total ionization or better in replicate runs.

Data Treatment

The data for each run consisted of a series of mass spectra that were characteristic of the composition of the volatile products being evolved at a specific point in the pyrolysis run. The scan with the highest total ionization in each run was chosen as being characteristic of the sample undergoing pyrolysis. This scan, which represents the peak of the pyrolysis curve, was the basis for calculating the fractions of the various pyrolysis products after subtracting the background. This analysis is possible because the mass spectrum of a mixture consists of additive contributions of the spectra of each component of the mixture. The mass spectra were resolved with the aid of reference spectra obtained from authentic samples or recalculated from collections of mass spectra. Table I lists the names, structures, and intensities of the ions used in calculations of fractions of pyrolysis products. The intensities are given as percentage of total ionization above m/e 10 ($\% \Sigma_{10}$) rather than the usual percentage of the most intense ion. Fractions of pyrolysis products were calculated as percentages of the total ionization and are related to the mole fractions (or partial pressures) of the pyrolysis products in the ion source.

TABLE I
 Identified Volatile Pyrolysis Products

Name	Structure	Mass spectrum ^a <i>m/e</i> (%Σ ₁₀)
Levoglucofan		97(1), 73(7), 60(20), 44(3), 28(7)
1,6-Anhydro-β-D-glucofuranose (AGF)		97(1), 73(22), 60(3), 44(5), 28(3)
5-Hydroxymethyl-2-furfural (HMF)		126(12), 97(18), 95(1), 28(8), 18(1)
2-Furyl hydroxymethyl ketone		126(11), 97(1), 95(23), 28(4)
Furfural		97(1), 95(31), 28(12), 18(1)
Carbon dioxide	CO ₂	44(76), 28(7)
Carbon monoxide	CO	28(92)
Water	H ₂ O	18(82)

^a Intensities of ions used in calculations of fractions of pyrolysis products.

Fabric Treatments

A series of seven different flame-retarding finishes was selected for study to learn whether different types of durable phosphorus-based flame retardants for cotton act by the same or different mechanisms. The same finishes were studied recently to compare textile properties.¹³ The finishes are based on three types of phosphorus-containing reagents, i.e., Fyrol 76 (an oligomeric vinylphosphonate), Pyrovatex CP (N-methyloldimethylphosphonopropionamide), and tetrakis(hydroxymethyl)phosphonium chloride (THPC). The actual finishes consisted of (a) Fyrol 76,¹⁵ (b) Fyrol 76/N-methylolacrylamide (NMA),¹⁶ (c) Proban (a THPC-urea condensate)/NH₃,¹⁷ (d) Pyrovatex CP/methylolmelamine (MM),¹⁸ (e) THPC/urea/Na₂HPO₄,¹⁹ (f) THPOH (neutralized THPC)/NH₃,²⁰ and (g) THPOH/urea/trimethylolmelamine (TMM).²¹

In the form in which the finishes are deposited in cotton fibers, the structures of the reagent residues are believed to be phosphonates in (a), (b), and (d) and phosphine oxides in (c), (e), (f) and (g). The reagent residues represent vinyl polymers in (a) and (b), condensation polymers in (c), (e), (f), and (g), and a relatively nonpolymeric product in (d). Indications are that finishes (a), (c), (e), and (f) are deposited as network polymers in cotton fiber pores, whereas the others form covalent bonds to the cellulose. With the exception of (a), all finishes involve substantial amounts of bound nitrogen. This series of finishes represents reagent systems that are or have been considered commercial candidates for treating cotton fabrics. The flame retardants were applied at relatively high add-ons to a lightweight sheeting to emphasize the effects of the flame retardants. Add-ons were as follows: Fyrol 76, 28%; Fyrol 76/NMA, 38%; Proban/NH₃, 28%; Pyrovatex CP/MM, 22%; THPC/urea/Na₂HPO₄, 25%; THPOH/NH₃, 33%; and THPOH/urea/TMM, 27%.

RESULTS AND DISCUSSION

Method

Small samples of yarn were pyrolyzed in the solid probe of a mass spectrometer. The temperature of the probe was programmed at $5.6^{\circ}/\text{min}$ from 180° to 460°C . The rate and temperature range are similar to those commonly used in thermal analyses of cellulose and will facilitate ultimate comparison with results from thermal analytical methods, especially thermogravimetric analysis. In the mass spectrometer, pyrolyses take place under high vacuum, and evolved volatile materials pass from the solids probe into the ionization chamber and to the total ion monitor, which provides a readout of total ion current versus time (or programmed temperature). The dedicated computer controlled the magnetic scan of the mass spectrometer, collected data from the electron multiplier, and converted the data into mass spectra. The scan time for these experiments was 30 or 15 sec, with independent spectra of volatile pyrolysis products being obtained every 2.8° or 1.4°C during the temperature program.

The attractive feature of this method lies in the fact that the mass spectra are essentially instantaneous and that they measure the *primary* products from the pyrolysis. There is no opportunity for the products to interact with each other to form secondary products, as is common when products of pyrolysis are collected prior to separation and analysis.

Experimental Results

A typical pyrolysis curve used to estimate peak temperatures for pyrolyses is shown in Figure 1, and spectra used to calculate abundances of pyrolysis products are shown in Figures 2 and 3. Figure 1 is a plot of total ionization versus scan number for the pyrolysis of cotton finished with THPOH/urea/TMM. The peak of the curve corresponds to 329°C . Figure 2 is the spectrum at the peak

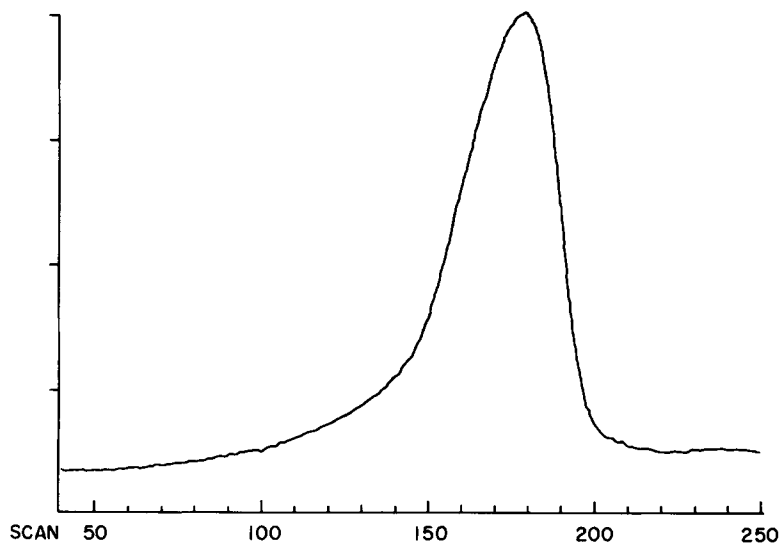


Fig. 1. Plot of total ionization vs scan number for the pyrolysis of cotton fabric finished with THPOH/urea/TMM.

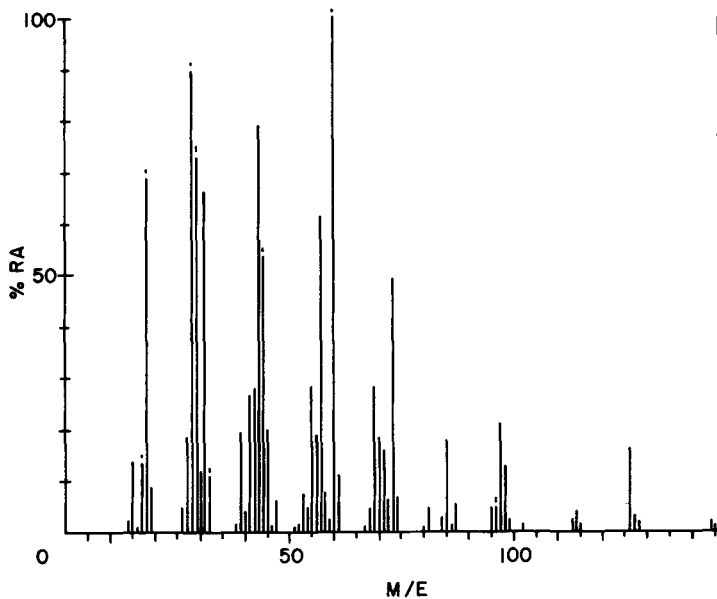


Fig. 2. Mass spectrum from pyrolysis peak of unmodified cotton.

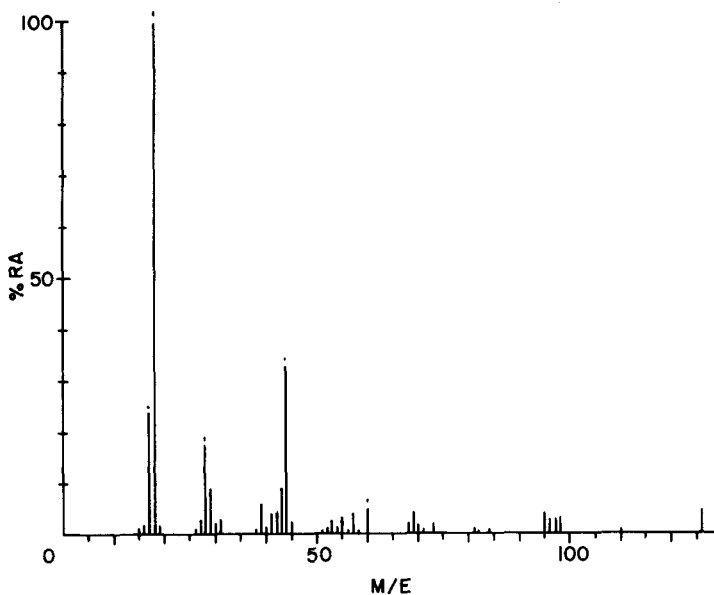


Fig. 3. Mass spectrum from pyrolysis peak of cotton fabric finished with THPOH/urea/TMM.

of the pyrolysis curve for unmodified cotton, and Figure 3 is for cotton finished with THPOH/urea/TMM. Backgrounds have been subtracted from both spectra. The two spectra differ greatly in appearance and illustrate the general difference in composition between pyrolysis products from unmodified cotton and a representative flame-retarded cotton. The spectrum for unmodified cotton is relatively complex. The most intense ion is at m/e 60, and there are 27 other ions with intensities greater than 10% of that of the most intense ion.

The spectrum of products from the flame retardant cotton is apparently much simpler and is dominated by a very intense ion at m/e 18; there are few other ions of even moderate intensity. Only three other ions have intensities greater than 10% of the most intense ion.

Even though the spectra have drastically different general appearances, they are basically similar. All of the intense ions in the spectrum from unmodified cotton are represented in the spectra from the flame retardant cottons, although in some cases the intensities are greatly reduced and the relative intensities are changed. This similarity indicates that the reactions occurring during the pyrolysis of unmodified cotton also occur during pyrolysis of flame retardant cottons, although the relative importance of the reactions occurring during the pyrolysis of the flame retardant cottons may be changed, and the fractions of some of the products may be depressed by the flame retardant finishes. All of the intense ions from unmodified cotton are at least detectable in the spectra from the flame retardant cottons. This shows that the formation of none of the major pyrolysis products from unmodified cotton is completely suppressed, although some of those from unmodified cotton are formed only in trace amounts from some of the flame retardant cottons. This finding was possible because mass spectrometry is highly efficient in detecting trace amounts of materials and because collection and fractionation of mixtures of pyrolysis products is not required.

Another, and possibly more significant, similarity between the spectra from unmodified and flame retardant cottons is that no ions, even of moderate intensities, that were absent in the spectra from the pyrolysis peak of unmodified cotton were found in the peaks of the flame retardant cottons. This strongly suggests that the mixtures of pyrolysis products from the flame retardant cottons contained only compounds that are formed in pyrolysis of unmodified cotton. This in turn suggests that the chemical processes occurring during the pyrolysis of flame retardant cottons are very similar to those occurring during pyrolysis of unmodified cotton. The differences in the relative intensities of the ions between the spectra from flame retardant cottons and unmodified cotton show that there are significant differences in the relative importance of the chemical reactions during pyrolysis. In particular, the dominance of the ion at m/e 18 of the spectra from the flame retardant cotton shows that a solid-phase dehydration reaction is the predominant process in the pyrolysis of the flame retardant cottons.

Another significant factor is the higher temperature required to pyrolyze the unmodified cotton as compared to the flame retardant cottons, even though the same ions were detected in all of the spectra. The ions characteristic of the anhydroglucoses and furan derivatives either were not detectable or were at the threshold of detection when unmodified cotton was heated at temperatures (300°C) characteristic of pyrolysis peaks for the flame retardant cottons. This observation indicates that flame retardant finishes enhance all of the chemical processes leading to the products from unmodified cotton.

To summarize, the flame retardant finishes behave as catalysts for all of the processes involved in the pyrolysis of unmodified cotton, but they enhance the various reactions occurring in the pyrolysis of unmodified cotton to different extents. Although previous theories^{1,6,8,9} state that phosphorus-containing flame retardants lower the pyrolysis temperatures and promote dehydration in char-

forming processes, our conclusions are not in conflict if it is remembered that the processes promoted are the same as or similar to those that occur at higher temperatures in the pyrolysis of unmodified cotton. Thus, an effective phosphorus-containing flame retardant is one that preferentially enhances the dehydration and char-forming processes so that they compete successfully with the other pyrolysis processes, which are also enhanced, but to a lesser extent, by the phosphorus-based flame retardants.

Pyrolysis Temperature

The temperatures corresponding to the peak intensities in the pyrolysis curves for the unmodified and flame retardant cotton fabrics are given in Table II, along with the results of analyses for the individual pyrolysis products for each fabric. The temperatures listed in the table refer to the scans with the highest total intensity in the runs for that fabric. The temperatures therefore correspond to that at which the rate of evolution of pyrolysis products is greatest under the conditions of the experiment. These data are similar to those obtained in temperature-programmed thermal analysis methods. The temperatures of the pyrolysis peaks depend upon the temperature programming rates. If all other factors are constant, a pyrolysis peak at a lower temperature indicates a lower activation energy for that reaction. The lower temperatures of the pyrolysis peaks for the flame-retardant cottons therefore indicate lower activation energies for the pyrolysis of the flame retardant cottons and catalysis of the pyrolysis by the flame retardant finishes.

The pyrolysis peak temperatures of four of the flame retardant fabrics are quite consistent at 299–304°C. The two fabrics finished with Fyrol 76 have peaks at lower temperatures than the other fabrics, and the peak for the fabric finished with THPOH/urea/TMM has a higher temperature than those of the other flame retardant fabrics. Thus, these data indicate that the Fyrol 76-containing finishes are more efficient and that the THPOH/urea/TMM finish is less efficient than the other flame retardant finishes in catalyzing the overall pyrolysis processes. The different peak temperatures of the pyrolyses of these fabrics indicate differences in mechanisms of flame retardance among these finishes.

Nonfuels

The large increase in the fraction of water in the pyrolysis products from flame retardant fabrics compared with that from unmodified cotton agrees with the widely postulated enhancement of dehydration processes by phosphorus-containing flame retardants. However, there was wide variation in water fractions from the various flame retardant fabrics. Four of the flame retardant fabrics, those finished with Fyrol 76, Fyrol 76/NMA, Proban/NH₃, and THPOH/urea/TMM, gave between 26% and 33% water. In view of the observed variation in replicate analyses of 1% to 3%, there are no significant differences in water fractions among these four finishes. Two of the fabrics, those finished with Pyrovatex CP/MM and THPC/urea/Na₂HPO₄, gave much more water (50% and 57%, respectively); and one fabric, that finished with THPOH/NH₃, gave only 19% water. Thus, two of the finishes are much more efficient than the others in enhancing the dehydration process during pyrolysis, and one finish is significantly less efficient.

TABLE II
Volatile Products at Pyrolysis Peaks

Flame retardant	Peak temp., °C	Fraction, % of total ionization									
		Levoglucoosan	AGF ^a	HMP ^a	FHK ^a	Furfural	Carbon dioxide	Carbon monoxide	Water	Unidentified ionization	
Unmodified	368	30	8	9	6	tr	4	10	7	26	
Fyrol 76	266	9	2	10	4	3	8	5	32	27	
Fyrol 76/NMA	283	11	3	10	9	tr	7	5	30	25	
Proban/NH ₃	302	16	3	9	3	4	11	6	26	22	
Pyrovatex CP/MM	304	1	0	2	5	1	16	13	50	12	
THPC/urea/Na ₂ HPO ₄	299	2	0	2	3	1	18	7	57	10	
THPOH/NH ₃	300	20	3	10	5	tr	5	2	19	36	
THPOH/urea/TMM	329	6	1	6	7	tr	13	8	33	26	

^a See Table I for abbreviations of pyrolysis products; tr = trace, identified less than 0.5%.

The carbon dioxide fractions from the flame retardant cottons show similar trends, but to a lesser extent. These fractions were increased by all of the flame retardant finishes except one. Pyrovatex CP/MM and THPC/urea/ Na_2HPO_4 , which gave the highest yields of water, were also most efficient in enhancing the carbon dioxide fractions. The THPOH/ NH_3 finish was least efficient and did not enhance the carbon dioxide fraction to a significant extent.

Carbon dioxide and water are the only two noncombustible pyrolysis products identified in this work. Since all of the pyrolysis products discussed below are combustible and the unidentified ion intensities probably represent smaller organic molecules, the carbon dioxide and water can be classified as the nonfuel portion of the volatile pyrolysis products. The remaining volatile pyrolysis products are combustible and can be classified as the fuel volatiles. The fractions of water and carbon dioxide were combined and are listed in Table III under the heading of nonfuels.

The nonfuels constitute only a small portion of the volatile pyrolysis products from unmodified cotton; therefore it is quite understandable that unmodified cotton supports flaming combustion. The nonfuels constitute about 66% and 75% of the volatile pyrolysis products from cotton fabrics finished with Pyrovatex CP/MM and THPC/urea/ Na_2HPO_4 , respectively. Their nonflammability is also quite understandable on the basis of composition of volatile pyrolysis products. The relatively low fraction (24%) of nonfuel from cotton fabric finished with THPOH/ NH_3 makes it difficult to explain the nonflammability of this fabric solely on the basis of the composition of its volatile pyrolysis products.

Anhydroglucoses

The fractions of levoglucosan reported in Table II are in accord with previous theories of flame retardance by phosphorus-containing finishes. Levoglucosan is the major volatile pyrolysis product from unmodified cotton, and its fraction is decreased by the flame retardant finishes, as has been reported previously.^{1,2} However, the formation of levoglucosan was not completely suppressed by any of the flame retardants; indeed the rate of its formation is enhanced, since it was detected at lower temperatures from flame retardant cotton than from unmod-

TABLE III
Classes of Pyrolysis Products

Flame retardant	Fraction, % of total ionization			
	Nonfuels ^a	Anhydro-glucoses ^b	Furans ^c	Carbon monoxide
Unmodified	11	38	15	10
Fyrol 76	40	11	17	5
Fyrol 76/NMA	37	13	19	5
Proban/ NH_3	37	18	16	6
Pyrovatex CP/MM	66	1	8	13
THPC/urea/ Na_2HPO_4	75	2	6	7
THPOH/ NH_3	24	23	15	2
THPOH/urea/TMM	46	7	13	8

^a Nonfuels: water and carbon dioxide.

^b Anhydroglucoses: levoglucosan and 1,6-anhydro- β -D-glucofuranose.

^c Furans: 5-hydroxymethyl-2-furfural, 2-furyl hydroxymethyl ketone, and 2-furfural.

ified cotton. The levoglucosan fractions were lowest from the cotton fabrics finished with Pyrovatex CP/MM and with THPC/urea/ Na_2HPO_4 , the finishes that enhanced production of carbon dioxide and water to the greatest extent. The fraction of levoglucosan from cotton finished with THPOH/ NH_3 was almost two thirds that from unmodified cotton, and the levoglucosan fraction from cotton finished with Proban/ NH_3 was one half that from unmodified cotton. The similarity in levoglucosan fractions from the last two fabrics may be due to the chemical similarity between the finishes. Levoglucosan was detected from all flame retardant fabrics in the present work, although previous workers sometimes failed to detect it. This is because there is no mixing or heating of pyrolysis products before analysis in the present method. Small amounts of levoglucosan would not be likely to be detected after heating and/or mixing numerous pyrolysis products; indeed, it has been suggested by Berkowitz-Mattuck and Noguchi²² that the hydrocarbon, carbonyl, and unsaturated compounds detected in pyrolyses of cellulose arise from secondary free-radical pyrolysis reactions, possibly in the gas phase and starting from levoglucosan. However, it is not believed that these secondary pyrolysis reactions lead to increased char formation, in view of the similarity in char yields of pyrolyses conducted under vacuum and in inert atmospheres.

1,6-Anhydro- β -D-glucofuranose (AGF) has been reported as a pyrolysis product from cellulose by Byrne⁶ and from starch by Dimler.²³ Evidence for its formation as a primary pyrolysis product from unmodified and flame retardant cotton fabrics was found in the ratios of the intensities of the ions at m/e 60 and 73 in the spectra from the pyrolysis peaks. The fractions of AGF calculated from these intensities are reported in Table II; they are decreased to very low levels by most of the flame retardants. The complete suppression of AGF formation by the Pyrovatex CP/MM and THPC/urea/ Na_2HPO_4 finishes may be real or may be apparent because of the difficulty of comparing two small ion intensities.

The fractions of levoglucosan and AGF were combined and are given in Table III as anhydroglucoses, since they represent the fractions of the more or less intact cellulose structural units which have not been fragmented or dehydrated. The fabrics finished with Pyrovatex CP/MM and THPC/urea/ Na_2HPO_4 give very small fractions of anhydroglucoses, and those finished with THPOH/ NH_3 and Proban/ NH_3 give relatively large fractions, compared to those from the other flame retardant cottons.

Carbon Monoxide

The fractions of carbon monoxide from the various flame retardant cottons (Tables II and III) are quite similar. The THPOH/ NH_3 finish is the only one that greatly reduced the fraction of carbon monoxide. This may indicate that the usual mechanisms of flame retardance have little or no effect on the processes leading to the formation of carbon monoxide in the solid phase, but not necessarily in the gas-phase processes of flaming combustion.

Furans

5-Hydroxymethyl-2-furfural (HMF) is well known as a product of acidic degradation of glucose, fructose, and other monosaccharides in aqueous solution and has been reported by Byrne⁶ and others² as a pyrolysis product from cellulose. The presence of HMF in the volatile materials from the pyrolysis of all unmodified and flame retardant cottons was well attested by moderately intense ions at m/e 97 and 126 in the spectra from the pyrolysis peaks. The effects of the flame retardant finishes on fractions of HMF are quite different from those on the fractions of anhydroglucoses. Three of the flame retardants (Fyrol 76, Fyrol 76/NMA, and THPOH/NH₃) slightly increased HMF, and only the THPC/urea/Na₂HPO₄ and Pyrovatex CP/MM finishes decreased the HMF fractions to a significant extent.

The spectra from the pyrolysis peaks showed a moderately intense ion at m/e 95 and an excess of intensity at m/e 126 that could not be accounted for by HMF. These ions could be accounted for by the presence of 2-furyl hydroxymethyl ketone (FHK) in the pyrolysis products. This compound was detected as a product from the pyrolysis of cotton cellulose by Byrne,⁶ but he gave no estimate of the amount of this compound. FHK is also formed in the aqueous acidic degradation of fructose, glucose, and other monosaccharides and has been detected by mass spectrometry from several sources.²⁵⁻²⁷ Since no authentic sample of FHK was available, a reference spectrum supplied by Dr. A. Ferretti of the Dairy Products Laboratory, USDA, is reported in Table I and was used to calculate the fraction of FHK. It was quite consistent throughout the series: in no case was it increased or decreased by more than 3% from that of unmodified cotton.

An ion at m/e 96 from unmodified cotton and from several of the flame retardant fabrics indicated the presence of furfural among the primary pyrolysis products, although only as a trace component in most of the pyrolyses. Furfural had been reported from unmodified and flame retardant cottons by Byrne⁶; therefore, the yields of furfural are reported in Table II, even though significant amounts were found from only two of the fabrics.

The fractions of the furan derivatives, HMF, FHK, and furfural, were combined and are listed in Table III as furans. They show a very different pattern from that of the anhydroglucoses. The furans were depressed significantly only by the THPC/urea/Na₂HPO₄ and Pyrovatex CP/MM finishes, and this was by a factor of 2 rather than 40, which was the case for the anhydroglucoses. Three of the flame retardant finishes increased the fractions of the furan derivatives. Since the furans were formed at low temperatures (and in some cases larger amounts) from the flame retardant cottons, compared with the unmodified cottons, the flame retardant finishes evidently promoted pyrolysis processes leading to the formation of furans. The promotion of furan-forming processes by the phosphorus-containing flame retardants is greater than for the anhydroglucose-forming processes but less than for processes leading to nonfuel volatiles. This may be rationalized on the theory² that phosphorus flame retardants behave as acids during pyrolysis of flame retardant celluloses. The role of acids in promoting dehydration and decarboxylation reactions in the solid phase is well known. The fact that acids promote furan formation in browning reactions^{24,25} and in aqueous decompositions of monosaccharides²⁶ may explain the behavior of phosphorus-containing flame retardants as acids in the pyrolysis

of cotton cellulose. The real but less effective role of these flame retardants in promoting the formation of levoglucosan and AGF during cellulose pyrolyses is less clear but may be analogous to the acid catalysis of acetalization and etherification reactions.

CONCLUSIONS

The composition of primary volatile pyrolysis products from unmodified cotton and from cottons finished with various phosphorus-containing flame retardants was analyzed by a method that involved vacuum pyrolysis in the solid probe of a mass spectrometer. Composition of the volatile products at the peaks of the pyrolyses (temperatures of the highest rates of volatile evolution) was measured without intervening mixing and fractionation of the products.

All major products from the pyrolysis of unmodified cotton were detected when the flame retardant cottons were pyrolyzed, and only products found in the pyrolysis of unmodified cottons were found at the pyrolysis peaks for the flame retardant cottons. Since these products were formed at lower temperatures from the flame retardant cottons than from unmodified cotton, it is concluded that the flame retardant finishes enhanced all pyrolysis processes in cellulose. Dehydration and char formation, however, were enhanced to a greater extent at the expense of pyrolysis processes leading to the formation of the volatile fuels that support flaming combustion.

Pyrolysis products consisted of nonfuel volatiles (H_2O and CO_2) and fuel volatiles—carbon monoxide, anhydroglucoses (levoglucosan and 1,6-anhydroglucofuranose), and furans (hydroxymethylfurfural, furyl hydroxymethyl ketone, and furfural). These materials constituted 67% to 85% of the volatile pyrolysis products from unmodified and flame retardant cottons, measured as percentages of total ionization in the mass spectra.

Two of the flame retardant finishes, Pyrovatex CP/MM and THPC/urea/ Na_2HPO_4 , greatly increased (by factors of 6 to 7) the fraction of nonfuel volatiles and almost completely suppressed the formation of anhydroglucoses. These finishes also significantly decreased the fractions of furans. Four of the finishes, Fyrol 76, Fyrol 76/NMA, Proban/ NH_3 , and THPOH/urea/TMM, increased the nonfuel fractions by factors of 3 to 4 but did not affect the furans. Three of these finishes (all except Proban/ NH_3) decreased the fractions of anhydroglucoses by more than 50%.

The THPOH/ NH_3 finish was unique in that it increased the nonfuels and decreased the anhydroglucoses to lesser extents than did the other finishes. The two finishes containing Fyrol 76 decreased the pyrolysis temperatures to a greater extent than did the other flame retardant finishes, and the THPOH/urea/TMM finish decreased the pyrolysis temperature to a lesser extent. These differences indicate that the flame retardant finishes have different mechanisms of action, which probably affect the efficiency of the processes that occur simultaneously during pyrolyses.

Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

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