Pyrolysis and Combustion of Cellulose.   III. Mechanistic Basis for the Synergism Involving Organic Phosphates and Nitrogenous Bases*

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Synopsis

The flame retardation mechanisms for cellulose treated with systems based on aromatic phosphates and phosphoramides have been investigated through pyrolysis studies on cellulose and related model compounds.   Pyrolysis of cellulose treated with phosphates or phosphoramides proceeds through formation of cellulose phosphate or phosphoramide esters, followed by subsequent ester pyrolysis to yield a dehydrated cellulose char.   Formation of phosphoramides during pyrolysis of flame retardants containing phosphorus and nitrogen constitutes a possible basis for reported phosphorus–nitrogen synergistic effects observed in commercial flame retardants.   Efficiency of ester formation is higher, and subsequent pyrolysis is lower for phosphoramides than for phosphate esters.   The build-up of a thermally stable crosslinked matrix in the residue occurs on pyrolysis of cellulose treated with phosphoramides.   Such crosslinking seems to be effective in enhancing flame retardation.

INTRODUCTION

Thermal data obtained for the pyrolysis of cellulose in mixtures with phenyl phosphates as model flame retardants[1] provide strong support for a hypothesis that interactions between these compounds involve thermally induced transphosphorylation reactions yielding cellulose phosphate esters, which subsequently decompose to dehydrated cellulose chars.   An alternative hypothesis requiring the phenyl phosphates to decompose to some intermediate species such as P_2O_5 before it could exert its effect on the cellulose substrate can be discounted in light of the previous study.   Degradation reactions for both treated and untreated cellulose occur at temperatures below that where pure triphenyl phosphate decomposes.   Addition of nitrogenous bases enhances the flame-retardant effectiveness of

triphenyl phosphate to produce efficiencies intermediate between the pure phosphate and a comparable phosphoramide, diphenyl amidophosphate. The complex nature of the cellulose substrate and pyrolytic reactions involved, however, prohibited unambiguous elucidation of the mechanisms responsible for the observed flame retardation.

Investigation of the thermal degradation of methyl α-D-glucopyranoside, a cellulose model of intermediate complexity, in analogous mixtures with these model flame retardants afforded greater insight into the mechanisms involved. Data indicated very strongly that an intermediate, probably a phosphoramide, was formed during pyrolysis of the phosphate/nitrogenous base mixtures, and that the flame retardant effectiveness of the mixed systems was related to the extent to which these intermediates were formed.[2]

This work is directed toward more conclusive definition of the reactions occurring during pyrolysis of cellulose treated with model flame retardant systems, the nature of the phosphorus-nitrogen synergism recently confirmed for these systems,[2] and its relation to retardation of flaming.

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.[3]

Differential Thermal Analysis (DTA). All curves were obtained in a static air atmosphere using a duPont 900 differential thermal analyzer equipped with 2-mm capillary 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 either neat or as KBr discs on a Perkin-Elmer Model 237B grating infrared spectrophotometer.

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

Fabric. Bleached and mercerized 100% cotton print cloth, 80 × 80, was used.

Fabric Treatment. Model flame retardants were applied to the fabric by pad-squeeze techniques described previously.[1]

Large-Scale Pyrolysis. All 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 at approximately 10°C/min to 300° ± 5°C and allowed to cool to 240°C. The tubes were
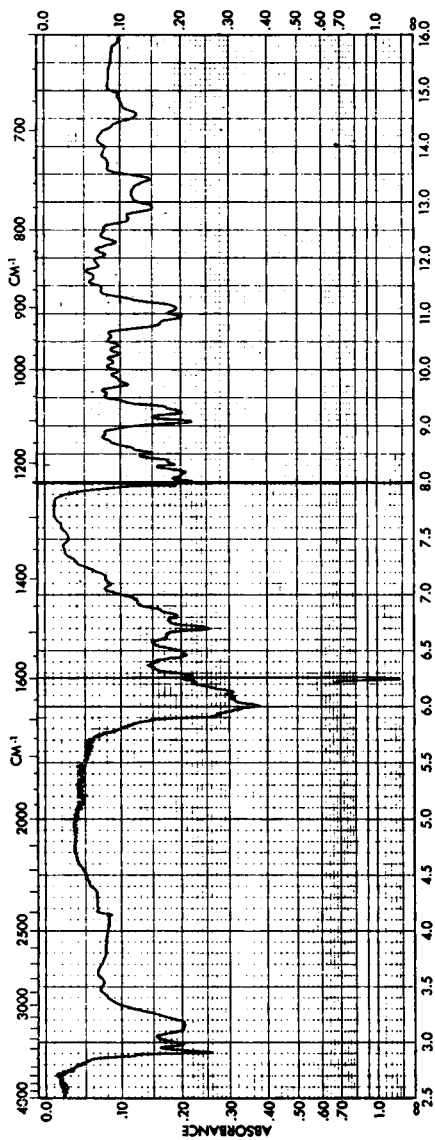
Fig. 1. Infrared spectrum of triphenyl phosphate/guanidine carbonate pyrolysis product.

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.

Vapor Phase Chromatography (VPC). A 101 Silicon Rubber SE 30 (30%) on 45/60 Chromosorb P column (0.38 in × 20 ft) was used in all analyses. Qualitative analyses were performed isothermally on a Varian Aerograph Autoprep under the following conditions: helium flow, 60 ml/min; injector port, 280°C; column, 230°C; detector block, 280°C;
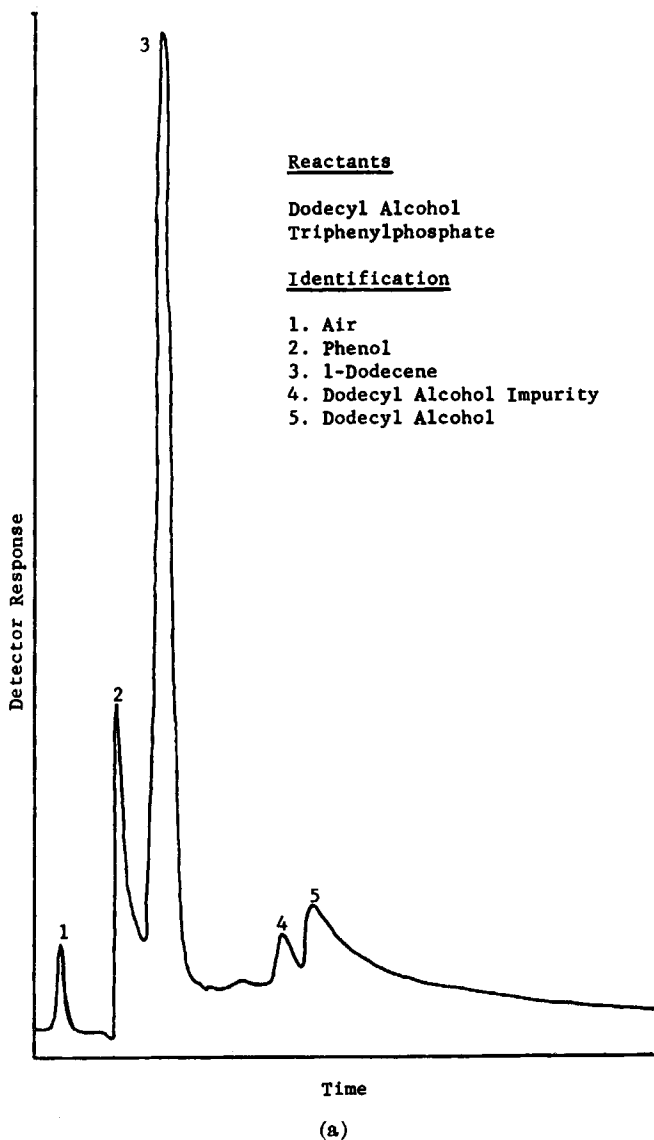

Reactants

Dodecyl Alcohol
Triphenylphosphate

Identification

1. Air
2. Phenol
3. 1-Dodecene
4. Dodecyl Alcohol Impurity
5. Dodecyl Alcohol

Time

(a)

Fig. 2 (*continued*)

bridge current, 160 Ma. In all cases, 5.0-μl samples were analyzed. The recorder integrator was calibrated using known quantities of dodecyl alcohol in benzene.

Identical conditions were employed for both preparative chromatography and qualitative analysis, except that for preparative treatment 0.5-ml samples were automatically injected "on-column" after 5-min cooling cycles. Samples were collected in Aerograph 10-ml condensers immersed in a reservoir containing Dry Ice and isopropyl alcohol.

Pyrolysis of Diphenyl Amidophosphate. Samples of diphenyl amidophosphate were pyrolyzed in the DTA to 225°C and to 300°C. Infrared
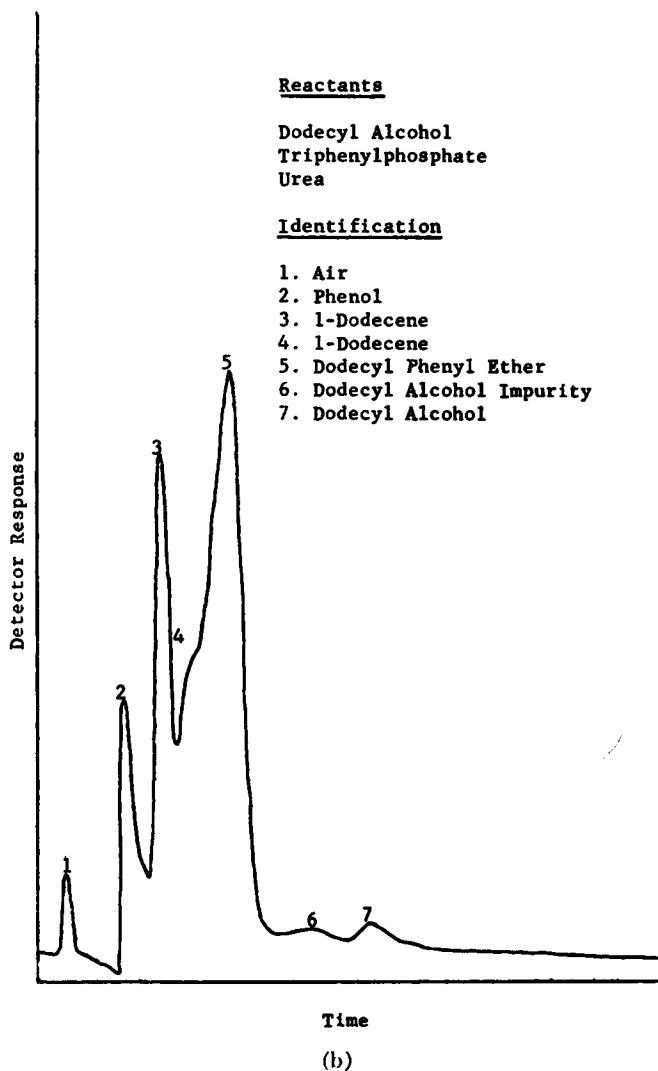
Reactants

Dodecyl Alcohol
Triphenylphosphate
Urea

Identification

1. Air
2. Phenol
3. 1-Dodecene
4. 1-Dodecene
5. Dodecyl Phenyl Ether
6. Dodecyl Alcohol Impurity
7. Dodecyl Alcohol

Time

(b)

Fig. 2 (*continued*)

spectra obtained from pyrolysis residues indicated decomposition of the parent compound between 225°C and 300°C.

A sample of diphenyl amidophosphate was pyrolyzed in an oil bath in the usual manner. The residual oil was dissolved in a minimum quantity of cold benzene and allowed to crystallize. Attempts to obtain a second crop of crystals from hot benzene resulted in separation of a brown oil from which clusters of tan needles formed on standing for two weeks. Infrared spectra of both crystal crops were similar to that of pure diphenyl amidophosphate.

Pyrolysis of Triphenyl Phosphate. Triphenyl phosphate was heated in the DTA to 300°C. The infrared spectrum of the residue was identical to that of the pure compounds.
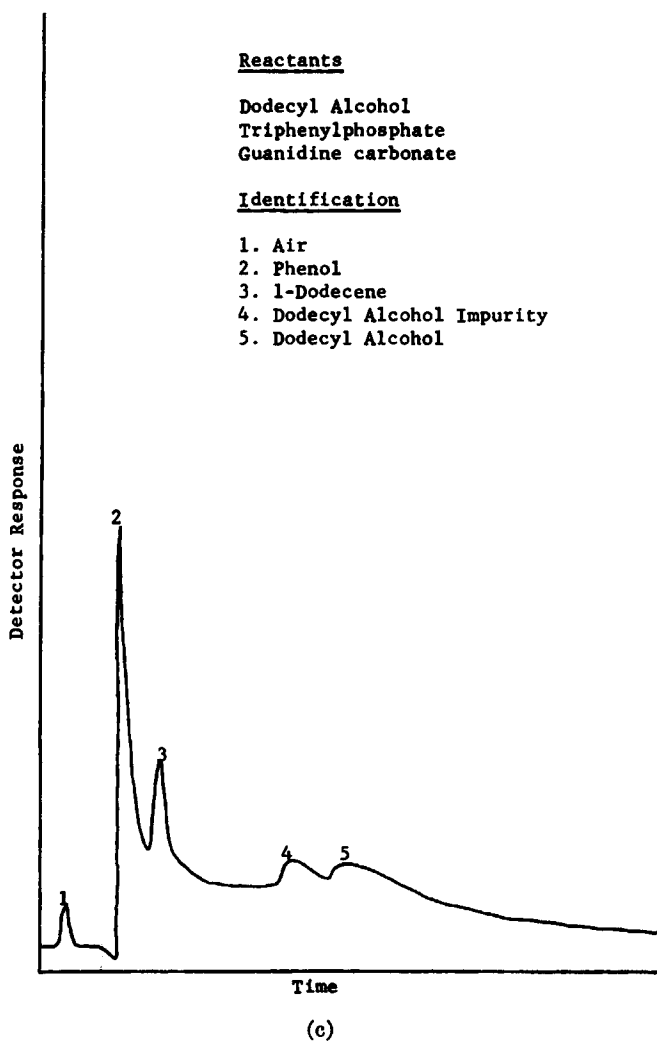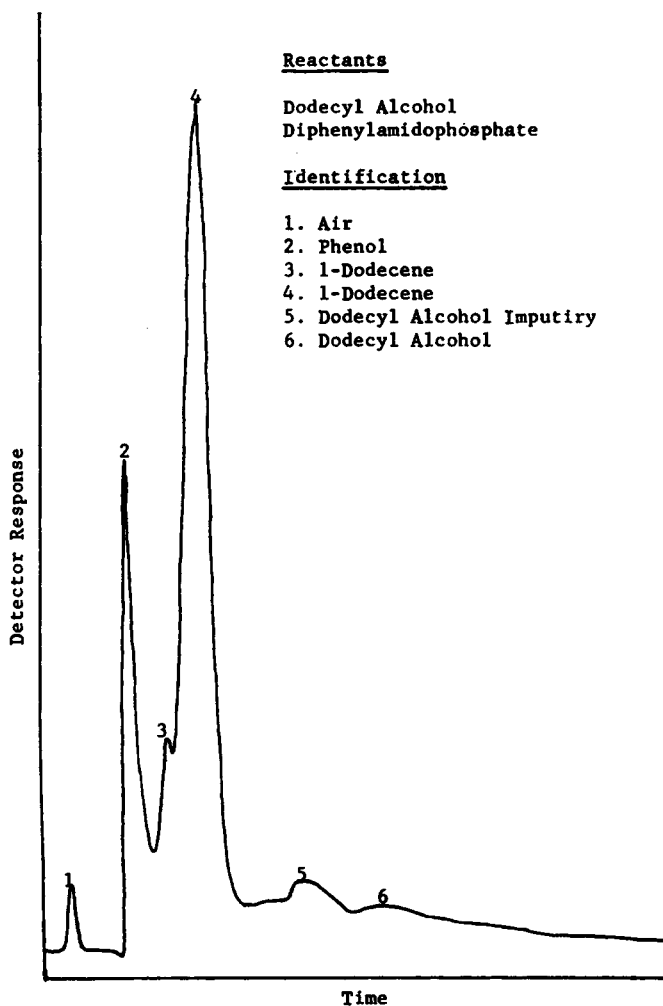

Reactants

Dodecyl Alcohol
Triphenylphosphate
Guanidine carbonate

Identification

1. Air
2. Phenol
3. 1-Dodecene
4. Dodecyl Alcohol Impurity
5. Dodecyl Alcohol

(c)

Fig. 2 (*continued*)

Reactants

Dodecyl Alcohol
Diphenylamidophosphate

Identification

1. Air
2. Phenol
3. 1-Dodecene
4. 1-Dodecene
5. Dodecyl Alcohol Imputiry
6. Dodecyl Alcohol

Detector Response

Time

(d)

Fig. 2. Vapor phase chromatograms of dodecyl alcohol pyrolytic reactions.

A 1.0-g sample of triphenyl phosphate was pyrolyzed in an oil bath in the usual manner to give 0.96 g of essentially pure triphenyl phosphate as indicated by IR spectroscopy and melting point.

Pyrolysis of Nitrogenous Bases. Samples of pure urea and guanidine carbonate were pyrolyzed both on a microscale in the DTA and on a macro-scale (1.0 g) in a heated oil bath. Under these conditions, cyanuric acid was obtained from the urea, and melamine was obtained from the guanidine carbonate, as would be expected from previously reported pyrolyses under a variety of other conditions.

Pyrolysis of Triphenyl Phosphate/Urea Mixture. A mixture containing triphenyl phosphate (1.0 g, or 0.003 mole) and urea (1.0 g, or 0.017 mole)

was pyrolyzed in an oil bath in the usual manner. The resulting pyrolyzate (0.79 g) was extracted with hot benzene. An infrared spectrum of the insoluble residue (0.49 g or 0.003 mole; 53.5% yield) corresponded to the spectrum of pure cyanuric acid. The extract was evaporated to dryness to give crystals of essentially pure triphenyl phosphate (0.30 g, or 0.001 mole), as confirmed by its infrared spectrum.

Pyrolysis of Triphenyl Phosphate/Guanidine Carbonate Mixture. From a mixture of triphenyl phosphate (5.0 g, or 0.015 mole) and guanidine carbonate (9.2 g, or 0.051 mole), microsamples were pyrolyzed in the DTA to 200° and to 375°C, and infrared spectra were obtained from the pyrolysis residues. Examination of the spectra indicated that both residues differed from the unpyrolyzed mixture; however, the essential spectral features of both compounds were retained.

Pyrolysis of a macrosample of similar mixture of triphenyl phosphate (0.5 g, or 0.002 mole) and guanidine carbonate (0.5 g, or 0.003 mole) was performed in the usual manner to give 0.51 g of pyrolyzate. After extraction with benzene, 0.43 g of residue remained. This residue was crystallized from water and shown by its infrared spectrum to contain structural features related to melamine. No triphenyl phosphate was reclaimed.

Triphenyl phosphate (5.0 g, or 0.015 mole) and guanidine carbonate (5.0 g, or 0.028 mole) were mixed with grinding and pyrolyzed in the usual manner. The pyrolyzate was extracted with benzene, ethyl alcohol, acetone, and water (each at the boil), and the extracts were retained. On standing, a product precipitated from each extraction liquor. Infrared spectra of the precipitates indicated similar composition with varying degrees of purity, decreasing from the benzene extract to the water extract. Close examination of the precipitate from the benzene extract revealed that it was microcrystalline. Its insolubility in a wide variety of solvents was indicative of a crosslinked polymeric structure. Thermal properties, as determined by DTA and TGA, indicated the compound to be infusible and relatively stable at high temperatures. Elemental analysis indicated 46.13% C, 5.03% H, 26.77% N, and 7.26% P. (See Fig. 1 for infrared spectrum.) Yield of this compound in pure form was low (0.04 g); thus, further characterization was carried out on the fraction obtained from the ethyl alcohol extract.

A small portion of the ethyl alcohol precipitate was analyzed for pyrolytic liberation of ammonia by the method of Feigl.[4] This method, which involves hydrolysis with aqueous sodium hydroxide, gave a positive test when compared to an aqueous sodium hydroxide blank. A similar portion was analyzed for pyrolytic liberation of ammonia after hydrolysis with hydrochloric acid[5] and, in comparison to a blank containing melamine, also gave a positive test.

Thermal Reactions of Dodecyl Alcohol. Dodecyl alcohol was refluxed at the boil alone and in mixtures with phosphorus- and nitrogen-containing compounds for 1 hr. The pyrolyzates were allowed to stand overnight, were filtered, and the products were characterized through use of vapor
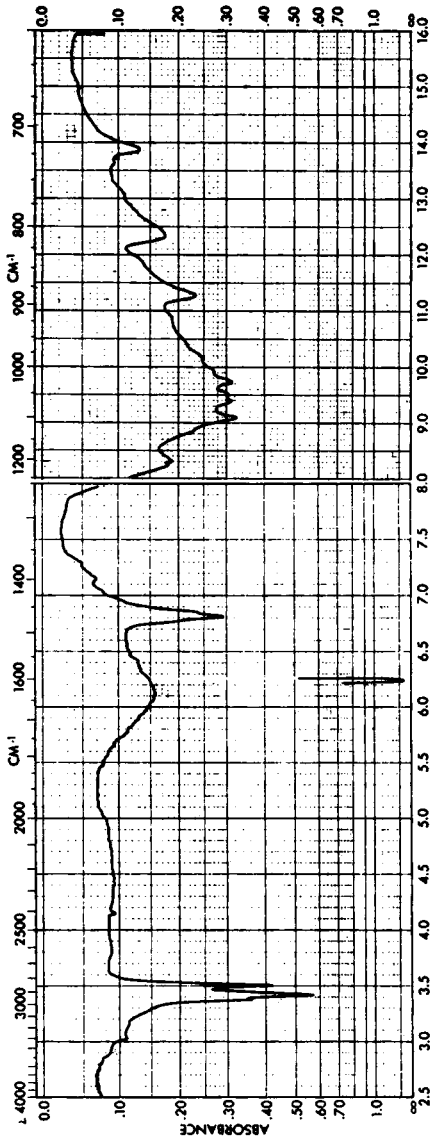
Fig. 3. Infrared spectrum of dodecyl alcohol/triphenyl phosphate pyrolytic reaction product.
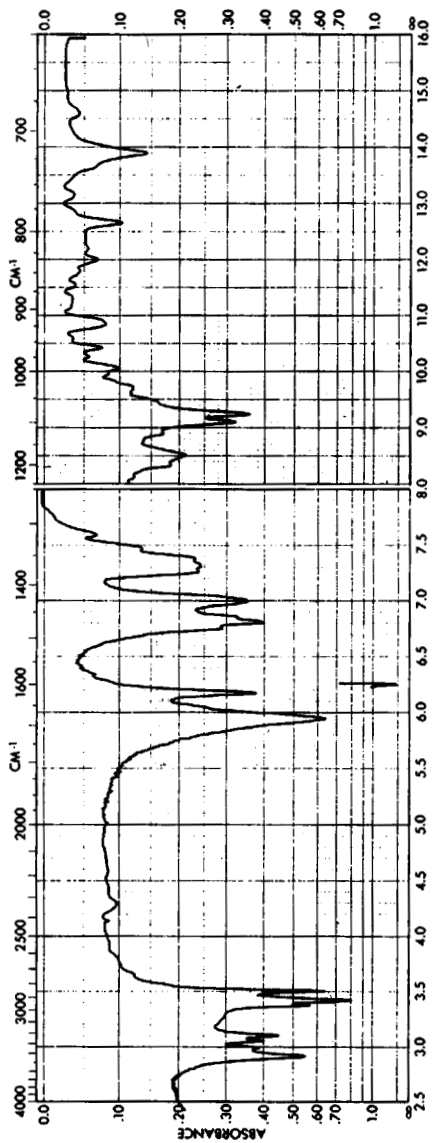
Fig. 4. Infrared spectrum of dodecyl alcohol/triphenyl phosphate/urea pyrolytic reaction product.

phase chromatography, infrared spectroscopy, and elemental analyses. (See Fig. 2 for chromatograms.)

Dodecyl Alcohol

Dodecyl alcohol (10.0 g) was heated at reflux for 1 hr and analyzed for degradation products. The vapor phase chromatogram of the pyrolyzate indicated that no reaction had occurred.

Dodecyl Alcohol/Triphenyl Phosphate Mixture

Dodecyl alcohol (5.0 g, or 0.027 mole) was allowed to reflux with triphenyl phosphate (1.75 g, or 0.005 mole). The pyrolyzate yielded a crystalline material (0.05 g), mp 61–61.5°C, which after washing with benzene was shown by elemental analysis to contain 67.61% C, 12.15% H, and 6.68% P and to have a mol wt of 949. (See Fig. 3 for infrared spectrum.) Attempts to obtain a NMR spectrum on the crystals were unsuccessful due to limited solubility. Vapor phase chromatography of the filtrate indicated the presence of phenol, 1-dodecene, and residual dodecyl alcohol.

Dodecyl Alcohol/Triphenyl Phosphate/Urea Mixture

Dodecyl alcohol (5.0 g, or 0.027 mole) was mixed with triphenyl phosphate (1.75 g, or 0.005 mole) and urea (1.75 g, or 0.029 mole) and allowed to reflux in the usual manner. Crystals which formed in the pyrolyzate on standing were recrystallized from benzene to give a yield of 0.42 g, mp 78–80°C. (Found: 66.83% C, 11.63% H, 5.05% N, and 2.63% P; mol wt 360.) (See Fig. 4 for infrared spectrum.) Attempts to obtain an NMR spectrum were unsuccessful due to limited solubility. Analysis of the filtrate by VPC indicated the presence of phenol, dodecene, dodecyl phenyl ether, and residual dodecyl alcohol.

Dodecyl Alcohol/Triphenyl phosphate/Guanidine Carbonate Mixture

Dodecyl alcohol (5.0 g, or 0.027 mole) mixed with triphenyl phosphate (1.75 g, or 0.005 mole) and guanidine carbonate (1.75 g, or 0.010 mole) was allowed to reflux in the usual manner. The pyrolyzate was filtered to remove solid material (0.38 g). No crystals formed in the filtrate on standing. Analysis of the filtrate using VPC revealed the presence of phenol, 1-dodecene, and residual dodecyl alcohol. A portion of the solid material (0.10 g) was extracted with benzene, air dried, and treated overnight with 50% aqueous sodium hydroxide (1.0 ml). The resulting solution was extracted with benzene (1.0 ml). Analysis of the extract using the VPC indicated the presence of dodecyl alcohol.

Dodecyl Alcohol/Diphenyl Amidophosphate Mixture

Dodecyl alcohol (5.0 g, or 0.027 mole) and diphenyl amidophosphate (1.34 g, or 0.005 mole) were allowed to reflux in the usual manner. The crystals which formed in the pyrolyzate on standing (0.15 g, mp 61–61.5°C) were washed with benzene. (Found: 64.28% C, 11.75% H, zero % N, and 7.76% P; mol wt 1023). The infrared spectrum of the crystals was identical to the spectrum shown in Figure 3 (crystalline pyrolyzate from the dodecyl alcohol/triphenyl phosphate reflux reaction). Attempts to obtain a NMR spectrum from the crystals were unsuccessful because of low solubility. Analysis of the pyrolyzate by VPC indicated the presence of phenol, 1-dodecene, and residual dodecyl alcohol.

Air Oxidation of Cotton Cellulose. A sample of bleached and mercerized cotton print cloth was heated in a muffle furnace at 290°C for 1 hr.
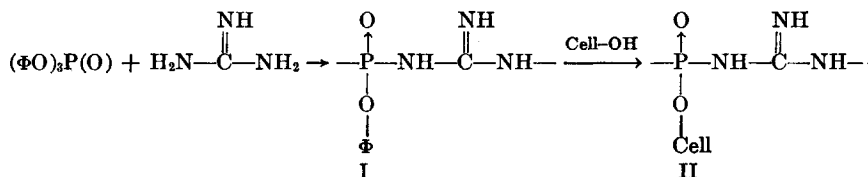
RESULTS AND DISCUSSION

The existence of a phosphorus-nitrogen synergism enhancing the effectiveness of model flame retardant systems for cellulose was confirmed in previous work.[2] In order to properly elucidate the mechanisms involved, however, it was necessary to first investigate the pyrolysis of the model systems in absence of a carbohydrate substrate.

Pyrolysis of Model Flame Retardants

Preparative-scale pyrolyses of diphenyl amidophosphate and of triphenyl phosphate, alone and in mixtures with nitrogenous bases, were carried out in an effort to isolate the actual species which altered the cellulose pyrolyses. The odors of phenol and ammonia were noted during the pyrolysis of diphenyl amidophosphate, and the infrared spectrum of the pyrolysis product indicated loss of aromatic and amide character. Complete characterization of the product was not possible; however, in view of the known reactions of compounds similar to diphenyl amidophosphate, it is reasonable to assume that condensation to oligomers containing P—N bonds had taken place during the pyrolysis.

Air Oxidation of Cotton Cellulose

The large nonvolatile residues previously reported for cellulose treated with the triphenyl phosphate/guanidine carbonate mixture and with diphenyl amidophosphate[1] suggest that cellulose may be crosslinked during pyrolysis through ester formation (structure II) with the dehydrating agents. Rates of combustion of these treated celluloses are considerably lower than those of cellulose treated with triphenyl phosphate or triphenyl

$$(\Phi O)_3 P(O) + H_2N-\overset{\overset{\displaystyle NH}{\|}}{C}-NH_2 \rightarrow -\overset{\overset{\displaystyle \uparrow}{|}}{\underset{\underset{\displaystyle \Phi}{|}}{\underset{\displaystyle O}{|}}}{P}-NH-\overset{\overset{\displaystyle NH}{\|}}{C}-NH- \xrightarrow{\text{Cell-OH}} -\overset{\overset{\displaystyle \uparrow}{|}}{\underset{\underset{\displaystyle Cell}{|}}{\underset{\displaystyle O}{|}}}{P}-NH-\overset{\overset{\displaystyle NH}{\|}}{C}-NH-$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad I \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad II$$

phosphate/urea mixtures, and the latter celluloses formed no appreciable residue on pyrolysis. These data thus indicate that crosslinking may be a significant factor in the flame retardation mechanism.

In an effort to determine the effects of combined dehydration and cross-linking on the flammability of cotton cellulose, a sample was oxidized by air in a muffle furnace at 290°C. This treatment is similar to the preoxidation step through which crosslinks are formed to decrease volatility so that the material may be subjected to high-temperature pyrolysis in preparation of graphite fibers.[6] This method was chosen to achieve crosslinking because introduction of chemical crosslinks would introduce entities which might possess flame retardant properties of their own. The resulting oxidation product was a black, brittle material which glowed when placed in a butane flame, but would not ignite. Its DTA thermogram was completely struc-tureless, while the TGA showed that the specimen retained 81% of its original weight at 500°C. Honeyman[7] determined that fabric temperature during combustion lies within the range of 410–450°C; therefore, these results would indicate that any substrate modification achieved at low temperatures which interferes with the formation of fuel for the combustion process should decrease the flammability of the material. Either dehydra-tion or crosslinking of the anhydroglucose units prior to onset of depolymer-ization can achieve the desired effect. Also, Byrne and co-workers[8] have shown that dehydrated celluloses containing aldehyde and enol groups may form crosslinks with adjacent chains through aldol-type condensations. Such crosslinks should interfere with levoglucosan formation, decrease the volatilization of low molecular weight fragments, and promote formation of a carbon-rich char.

Pyrolysis of Dodecyl Alcohol Mixtures

Data obtained from the pyrolyses of cellulose,[1] methyl α-D-glucopyrano-side, and levoglucosan[2] in mixtures with phosphates and nitrogenous bases indicated similar mechanisms to be operating in each system. The levo-glucosan mixtures, however, undergo additional reactions beyond those observed for cellulose and methyl α-D-glucopyranoside. These are at-tributable to acid-catalyzed polymerization of levoglucosan. Based on data presented thus far, the interactions of phenyl phosphates and phos-phoramides with cellulose, methyl α-D-glucopyranoside, and to some extent levoglucosan can be explained by the following sequence of events: (a) a thermally induced transphosphorylation reaction occurring between the phosphate ester and the alcohol groups of the carbohydrate substrate, (b) dehydration of the resulting phosphate ester of the carbohydrate through ester pyrolysis, and (c) skeletal rearrangements within the dehydrated sub-strate involving opening of the acetal rings, which would be expected to result in formation of completely carbocyclic systems through crosslinks with adjacent chains. If such a sequence of reactions does operate during phosphate-assisted pyrolysis of these complex carbohydrate systems, similar reactions would be expected to occur with simple aliphatic alcohols. With simple alcohols, the reaction products should be less complex; there-

fore, identification of these products and a more positive assignment of the mechanism involved might be possible.

In view of the numerous reports of preferential esterification at the C-6 position of the anhydroglucose units of cellulose,[9-11] the model selected should relate to the C-6 hydroxyls. Secondary hydroxyls of cellulose are much less reactive toward esterification than are primary hydroxyls; therefore, secondary hydroxyls are not a major factor for consideration in selecting a model. Since pyrolysis temperatures of simple alcohols are limited to the boiling points of their mixtures, selection of an alcohol which would boil above the temperature where reactions were observed to occur in cellulose systems was necessary. The requirements of high boiling point and similarity to the C-6 hydroxyl of cellulose were fulfilled by dodecyl alcohol (bp 255°C).

The reactions proposed to explain pyrolyses of cellulose and methyl α-D-glucopyranoside mixtures[2] would indicate that heating dodecyl alcohol at reflux temperatures with phosphates and nitrogenous bases should produce 1-dodecene in high yield. Dodecene production was, in fact, observed for each dodecyl alcohol mixture studied (Fig. 2).

Heating mixtures of dodecyl alcohol with triphenyl phosphate at reflux produced 1-dodecene in good yield along with phenol, unreacted dodecyl alcohol (Fig. 2a), and a trace amount of nonvolatile crystalline substance which contained phosphorus. The infrared spectrum (Fig. 3) of the crystals showed strong absorptions attributable to aliphatic C—H stretching (3.3–3.6 μ), which are most logically assigned to dodecyl groups. The molecular weight of 949 indicates that the compound is oligomeric.

Products from heating a dodecyl alcohol/triphenyl phosphate/urea mixture at the reflux temperature included phenol, 1-dodecene, unreacted dodecyl alcohol, dodecyl phenyl ether (Fig. 2b), and a crystalline solid containing phosphorus and nitrogen. The solid had a molecular weight of 360. Its infrared spectrum (Fig. 4) has absorptions attributable to aliphatic C—H (3.3–6.6 μ) and amide or amine N—H (2.8–3.2 μ) stretching frequencies. Since the crystalline material almost surely is an interaction product of dodecyl alcohol, triphenyl phosphate, and urea, and since 1-dodecene was observed, the solid probably is a mixture of unpyrolyzed esters of dodecyl alcohol. Subjection of the unpyrolyzed ester to VPC conditions would be expected to result in production of additional 1-dodecene by ester pyrolysis during the chromatographic process. This phenomenon was, in fact, observed to occur. From preparative-scale separation of products contained in the refluxed dodecyl alcohol/triphenyl phosphate/urea mixture, two compounds (peaks 3 and 4, Fig. 2b) proved to have infrared spectra identical to that of pure 1-dodecene. One of the compounds had exhibited a retention volume identical to that of 1-dodecene (peak 3), while the retention volume of the other (peak 4) was slightly greater. The latter compound was reinjected and this time gave a retention volume identical to that of 1-dodecene, thus supporting the hypothesis that 1-dodecene was formed during the chromatographic process by pyrolysis of phosphate esters of dodecyl alcohol.

TABLE I
Product Yields from Dodecyl Alcohol Reactions

Reactants	Phenol yield, %	1-Dodecene yield (prim.), %	1-Dodecene yield, (sec.), %	1-Dodecene total yield, %
Dodecyl alcohol + triphenyl phosphate	14	68		68
Dodecyl alcohol + triphenyl phosphate + urea	14	38	40	78
Dodecyl alcohol + triphenyl phosphate + guanidine carbonate	21	13		13
Dodecyl alcohol + diphenyl amido- phosphate	23	11	91	102

Phenol, unreacted dodecyl alcohol, and 1-dodecene were the only products isolated from the thermally induced reaction of a dodecyl alcohol, triphenyl phosphate, and guanidine carbonate mixture. VPC indicated a very low yield of 1-dodecene compared to previous cases (Fig. 2c). This discrepancy may be explained, however, since it was necessary to filter residual solid material before injection of the samples; thus, if the dodecyl phosphate moieties were incorporated into this insoluble material, it would be unavailable for pyrolysis in the chromatograph. The infrared spectrum of the solid material differed from that of the triphenyl phosphate/guanidine carbonate adduct primarily in the 3.3 to 3.5 μ region, which may be attributed to aliphatic C—H stretching absorptions; therefore, it seemed probable that the solid material is an unpyrolyzed ester of dodecyl alcohol and the triphenylphosphate/guanidine carbonate oligomeric adduct. To support this contention, the solid material was hydrolyzed with aqueous sodium hydroxide and extracted with benzene, and the extract was analyzed with the VPC. The chromatogram of the extract contained a peak whose retention time was identical to that of dodecyl alcohol. Dodecyl alcohol would result from hydrolysis of dodecyl phosphoramides.

The thermal reaction of dodecyl alcohol and diphenyl amidophosphate produced the same crystalline material which formed during pyrolysis of dodecyl alcohol and triphenyl phosphate. Other products included phenol and 1-dodecene. VPC again showed that 1-dodecene was produced during the chromatographic process by pyrolysis of undecomposed ester in the chromatograph (Fig. 2d).

Relative yields of volatile products from thermal reactions of dodecyl alcohol in mixtures with phosphates and nitrogenous bases are shown in Table I.

Since transesterification reactions of aryl phosphates involve displacement of the aryloxy groups, the yields of phenols constitute a comparison of the relative extents of reactions. In the dodecyl alcohol reactions, yields of phenol increase as the ability of the system to form P—N bonds increases (Table I). These data support the hypothesis that inclusion of amide groups should promote transphosphorylation reactions with aliphatic

alcohols.   Total yields of 1-dodecene give further support to this hypothesis.   Except in the case of guanidine carbonate, which forms polymer not amenable to VPC analysis, these yields also increase with tendencies of the systems to form P—N bonds.

"Primary" yields of 1-dodecene illustrate the relative ease of pyrolysis of aliphatic esters derived from triphenyl phosphate as compared to those from analogous systems containing nitrogenous bases (Table I).   The "primary" yields of 1-dodecene were obtained from the initial heating of the reaction mixtures.   Secondary yields are from pyrolysis of the phosphate esters in VPC.   During the initial heating of the reaction mixtures at reflux the phosphate esters formed should undergo pyrolysis to yield 1-dodecene and an aryl hydrogen phosphate.   The acid aryl hydrogen phosphate should both catalyze other phosphate ester pyrolyses[12] and form additional esters
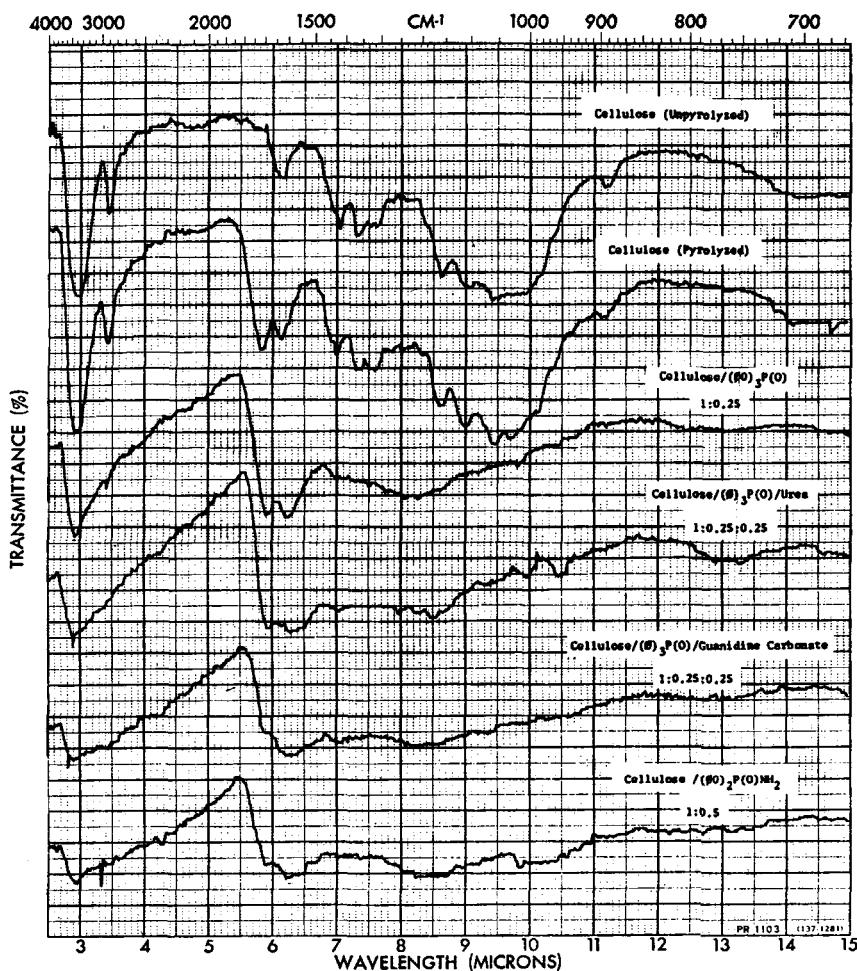

Fig. 5. Infrared spectra of cotton cellulose and cellulose pyrolysis products.

with dodecyl alcohol. These processes should continue until dodecyl hydrogen phosphates constitute the only unpyrolyzed esters present, and they would be capable of mutual catalysis. Therefore, in absence of nitrogenous bases, the pyrolysis process would be autocatalytic. In the presence of bases, however, build-up of acid-rich systems could not occur; therefore, ester pyrolysis would be less favorable, and the initial yield of 1-dodecene should be decreased.

Pyrolysis of Cotton Celluloses

As a final confirmation of the proposed mechanism for the interactions of the model flame retardant systems with cellulose, treated fabric samples were subjected to preparative-scale pyrolysis, and the resultant residues (Fig. 5) were characterized. IR spectra of the residues show evidence of dehydration and skeletal rearrangements, as evidenced by decreases in absorptions attributable to hydroxyl O—H stretching (2.8–3.1 μ) and aliphatic C—H stretching (3.3–3.6 μ). Dehydration is also evidenced by elemental analysis of the residues (Table II). Residues from the treated celluloses are considerably more highly carbonaceous than those from the untreated material. Additionally, chemically bound phosphorus contents are considerably higher in residues from celluloses treated with diphenyl amidophosphate or with a triphenyl phosphate/guanidine carbonate mixture (which forms phosphoramides in good yield) than those treated with either of the other systems. These bound phosphorus contents parallel the effectiveness of these systems at retarding combustion of cellulose and are consistent with the mechanisms proposed.

TABLE II
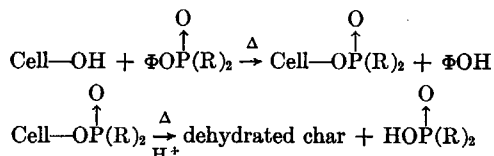Pyrolytic Reactions of Cellulose

Composition of pyrolysis mixtures	Ratios of components in mixtures	Elemental analyses of extracted residues[a]			
		C, %	H, %	N, %	P, %
Cotton cellulose		50.38	5.69		
Cotton cellulose + triphenyl phosphate	1:0.25	64.95	3.72		0.37
Cotton cellulose + triphenyl phosphate + urea	1:0.25:0.25	63.78	4.23	7.22	1.29
Cotton cellulose + triphenyl phosphate + guanidine carbonate	1:0.25:0.25	60.56	3.99	6.49	3.03
Cotton cellulose + diphenyl amidophosphate	1:0.5	62.89	3.44	1.00	2.73

[a] Calculated for cotton cellulose before pyrolysis: 44.44% C and 6.17% H.
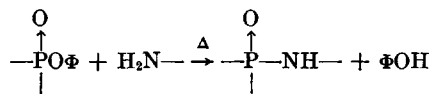
SUMMARY AND CONCLUSIONS

Investigations of interactions occurring between model flame retardants and cotton cellulose support the following conclusions:

1.   Pyrolysis of cotton cellulose treated with phenyl phosphates or phosphoramides proceeds through formation of cellulose phosphates or phosphoramide esters, followed by subsequent ester pyrolysis to yield a dehydrated cellulose char:

$$\text{Cell—OH} + \Phi O\overset{\overset{\displaystyle O}{\uparrow}}{P}(R)_2 \xrightarrow{\Delta} \text{Cell—O}\overset{\overset{\displaystyle O}{\uparrow}}{P}(R)_2 + \Phi OH$$

$$\text{Cell—O}\overset{\overset{\displaystyle O}{\uparrow}}{P}(R)_2 \xrightarrow[H^+]{\Delta} \text{dehydrated char} + HO\overset{\overset{\displaystyle O}{\uparrow}}{P}(R)_2$$

where Cell is cellulose substrate and R is phenoxy or amide group.

2.   Formation of phosphoramides during pyrolysis of flame retardants containing phosphorus and nitrogen is a possible basis for reported phosphorus-nitrogen synergism in commercial flame retardants:

$$-\overset{\overset{\displaystyle O}{\uparrow}}{\underset{|}{P}}O\Phi + H_2N- \xrightarrow{\Delta} -\overset{\overset{\displaystyle O}{\uparrow}}{\underset{|}{P}}-NH- + \Phi OH$$

3.   Efficiency of the ester formation is higher and that of the subsequent pyrolysis is lower for phosphoramide esters than for phosphate esters.

4.   The build-up of a thermally stable highly crosslinked matrix residue, such as is obtained on pyrolysis of cellulose treated with phosphoramides, leads to better flame retardation than is achieved by simply decomposing the substrate below normal decomposition temperatures through phosphate catalysis.

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