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Volatile Products from Kinetic Stages in the Pyrolysis of Cotton Fabrics Finished with THPS-Urea-Phosphate

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ABSTRACT

Volatile product fractions were measured for the three kinetic stages in the cellulose pyrolysis of cotton fabrics finished with ten add-ons of THPS-urea-phosphate flame retardant. Three classes of volatile products were distinguished: anhydroglucoses, "furans," and nonfuels. The classes of volatile products each showed different patterns of response to add-on in each of the kinetic stages. The main cellulose pyrolysis reaction was similar to the entire cellulose pyrolysis, and the flame retardancy of the fabrics was determined by the molar fraction of water evolved in the main reaction. The two initial stages were distinct both from each other and from the main reaction in the response of their fractions of volatile products to add-on of the flame retardant. The results are discussed in terms of proposed mechanisms for the kinetic stages of the pyrolysis.

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INTRODUCTION

It is generally believed that most flame retardants for cotton cellulose act in the solid phase by changing the pyrolysis reaction so that it cannot furnish volatile fuels to the flame. There is extensive literature on cellulose pyrolysis reactions, including a number of recent reviews [1-5]. The present series of studies combines two approaches to understanding mechanisms of cellulose pyrolysis and effects of flame retardants on the pyrolysis. One approach uses thermogravimetry (TG) to measure kinetic parameters of cellulose pyrolysis reactions. The other approach uses pyrolysis-mass spectrometry (PMS) to identify and measure the primary products of the pyrolyses. A wide range of add-ons of flame retardants or additives was used and identical samples were measured by both techniques.

Differential TG (DTG) plots for cotton finished with THPOH-ammonia [6], THPS-urea-phosphate [7], and high add-ons of seven reactive, phosphorus-containing flame retardants [8] showed single maxima in the cellulose pyrolysis region (240-350°C) and one or more wide peaks in the char pyrolysis region (450-900°C). DTG data for fabrics finished with THPOH-ammonia [9] was the basis for the proposal that a process involving disruption of cellulose crystallites was the rate-determining step of the cellulose pyrolysis. Kinetic analyses of the DTG data [6, 7] confirmed this proposal and showed that the volatile pyrolysis products are formed in rapid reactions following the rate-determining step. A detailed examination of the kinetic data showed that the cellulose pyrolyses occurred in a series of two initial stages followed by the main cellulose pyrolysis reaction [10]. This sequence was also characteristic of cotton cellulose finished with other reactive, phosphorus-containing flame retardants [8]. It was proposed that the rate-determining step of the first initial stage is a random cellulose chain scission and that of the second initial stage is an unzipping (orderly depolymerization) of the cellulose chains. Both stages were associated only with the less ordered ("amorphous") cellulose regions. In no case did the two combined initial stages cause a weight loss greater than 11%.

PMS data on fabrics finished with high levels of seven reactive, phosphorus-containing flame retardants [11], with THPOH-ammonia [9], and with THPS-urea-phosphate [12] showed that the primary volatile products were evolved simultaneously or almost so and that all the volatile products originated from cellulose. The only exceptions were small amounts of ammonia and phosphorus-containing products evolved during the second initial cellulose pyrolysis stage of fabrics containing very high levels of some flame retardants and some phosphorus-containing compounds evolved at very high temperatures during char pyrolyses [13, 14]. The primary volatile pyrolysis products from cotton finished with THPOH-ammonia were classified as anhydroglucoses, "furans," and nonfuels on the basis of how the individual pyrolysis product fractions responded to the add-on of the flame retardant [9]. Similar results were obtained on pyrolysis of fabrics finished with another flame retardant, THPS-urea-phosphate [12], except that one of the primary volatile products, 1,4:3,6-dianhydro-α-D-glucopyranose, behaved like a "furan" in this series, while it behaved like an anhydroglucose in the THPOH-ammonia series. The flame retardancy was best correlated with the total nonfuel fraction in the THPOH-ammonia series and with the water fraction in the THPS-urea-phosphate series.

In contrast, DTG plots for cotton fabrics containing moderate or high amounts of additive, inorganic flame retardants showed series of two or more distinct reactions separated by minima [15]. In all cases, the DTG data showed a peak in the range of 250 to 320° C. PMS data showed that volatile products derived from cellulose were evolved in this temperature range in fractions not greatly affected by the add-on above 5-10% of the inorganic additive. The earlier, lower temperature DTG peaks were shown to mark the evolution of nonfuels: water in the case of magnesium chloride, carbon dioxide in the case of potassium carbonate [15], and both water and carbon dioxide in the case of diammonium phosphate [8], again in fractions not greatly affected by the add-on of the inorganic flame retardant. The amount of inorganic additive in the fabric determined the relative amounts of weight loss or volatile product evolution in the various peaks. It was possible to obtain a good correlation between flame retardancy and nonfuel fractions only by calculating volatile product fractions over the entire temperature range from the beginning of the first peak to 320°C.

This study reports the volatile product fractions evolved in the kinetic stages of the cellulose pyrolysis of cotton fabrics finished with a reactive, phosphorus-containing flame retardant, THPS-urea-phosphate. The effects of add-on of the flame retardant on volatile product compositions from the three kinetic stages of the cellulose pyrolysis are reported, and implications of the data on possible mechanisms of the three stages are discussed.

EXPERIMENTAL

Cotton printcloth was treated with tetrakis(hydroxymethyl)phosphonium sulfate (THPS), urea, and disodium phosphate by a variation of the method of Donaldson et al. [16] as described previously [7]. Analysis of volatile pyrolysis product compositions was done by pyrolysis-mass spectrometry (PMS) as previously described [14]. PMS scan numbers were correlated with temperatures by matching scan numbers in total ion pyrograms with temperatures in DTG curves for the same samples. A calibration equation for PMS scan numbers and temperatures was derived by matching departures from the baselines, peaks, and returns to the baselines in DTG and PMS curves for each sample. This calibration equation was slightly different from that previously reported [14] because continued use of the solid probe had changed its thermal emissivity characteristics.

RESULTS AND DISCUSSION

Data Treatment

The PMS data consist of mass spectra acquired every 7.5 s as the sample is being heated in the solid inlet probe at approximately 5°C/min, which corresponds to the 5.0°C/min used in the TG experiments. The data can be manipulated to obtain composite mass spectra from any selected range in the pyrolysis, and thus to obtain information on the composition of the volatile products being evolved in that range. The data can also be manipulated to obtain plots of the total mass spectral intensity or of intensities of selected ions throughout the pyrolyses. A total intensity plot has the same shape as the DTG plot for the same sample because the former measures the rate of product evolution and the latter measures the rate of weight loss. The selected ion intensity plots for a single run in the present series are similar in shape to each other and to the total ion plot. Apart from irregularities caused by ion statistics in plots from very weak ions, the small differences in shape among the ion intensity plots occur at the beginning of the cellulose pyrolysis. This is in the region of the initial stages reported previously from the DTG data [10]. The small, but apparently real, differences in the ion intensity plots from the fabrics finished with THPS-urea-phosphate made it appear likely that the initial cellulose pyrolysis stages would show distinct responses to the add-on of the flame retardant, as was the case with the kinetic parameters measured from DTG data [10].

In order to investigate the volatile product compositions from each kinetic stage, it was necessary to have an accurate temperature calibration of the solid probe used in the PMS experiments. A calibration valid for each specific set of experiments performed consecutively is necessary because the relationship between the indicated temperature and the actual temperature of the probe changes as the probe is being used. In the present work, a temperature calibration of the PMS data was done with DTG curves for the same sample. A linear regression of corresponding DTG and MS probe indicated temperatures gave a correlation equation. This equation was used with the indicated starting temperature (usually 150°C) and the number of isothermal MS scans before the start of the temperature program to calculate the MS scan numbers for each kinetic stage in the pyrolyses. The temperature ranges of the kinetic stages were determined from Arrhenius plots of the DTG data [10]. Only the linear regions of the Arrhenius plots were used to generate mass spectra of a given kinetic stage, leaving gaps of two to fifteen scans between stages where the Arrhenius plots indicated a change from one stage to the next.

The spectra for a given stage were averaged and the MS background, from isothermal periods before and after the pyrolysis, was subtracted to obtain a composite mass spectrum for the products evolved in that stage. The ion intensities in the composite mass spectra were used to calculate the volatile product compositions [14]. The calculations were done by selecting ions characteristic of only one or two of the volatile products. Starting with the larger molecules, it was possible to subtract contributions of these larger molecules to ions characteristic of the smaller molecules. For example, contributions from all the anhydroglucoses and "furans" to the intensity of the ion at m/e 28 were subtracted from the measured intensities of this ion and the remainder used to calculate the fraction of carbon monoxide from a standard mass spectrum of carbon monoxide. The calculations of volatile product fractions were facilitated by the ability of the MS data system to list ion intensities as fractions of the total ion intensity in the spectrum and by scanning the mass range from m/e = 1 to m/e = 550 to include all ions formed in the MS ion source.

The composite mass spectra were used to calculate the fractions of nine specific compounds in the mixtures of volatile pyrolysis products. These compounds were divided into three classes of products on the basis of the response of their fractions to the add-on of THPS-urea-phosphate [12]. The anhydroglucoses consisted of levoglucosan (1,6-anhydro-β-D-glucopyranose) and 1,6-anhydro-β-D-glucofuranose (AGF). The "furans" are so named because the first identified members [9] of this class had a furan ring as a structural feature. They are classified together on the basis of the response of their fractions to add-on of THPS-urea-phosphate. However, they do have a common structural feature in having a six carbon atom chain and oxygen atoms in positions which can be formally derived from a glucose structure with the loss of two or three water molecules. The "furans" include 5-hydroxymethyl-2-furfural (HMF), 2-furyl hydroxymethyl ketone (FHK), levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose), and 1,4:3,6-dianhydro-α-D-glucopyranose (DAG). DAG had behaved as an anhydroglucose in the pyrolyses of fabrics containing THPOH-ammonia flame retardant [9]. In earlier work on this series of fabrics, DAG fractions were shown to respond to add-on of the flame retardant more like "furans" than anhydroglucoses [12]. The third class of pyrolysis products was the nonfuels, consisting of carbon dioxide and water. The carbon monoxide fractions were usually small and did not respond to add-on like any of the three major classes of primary pyrolysis products. In addition, a greater uncertainty is to be expected in the carbon monoxide fractions because the calculation of this product depends on the accuracy of the subtraction of the mass spectral background, which is dominated by a peak at m/e = 28 from atmospheric nitrogen.

Main Reaction

The volatile product compositions from the main cellulose pyrolysis reaction are reported as functions of the add-on of THPS-urea-phos-

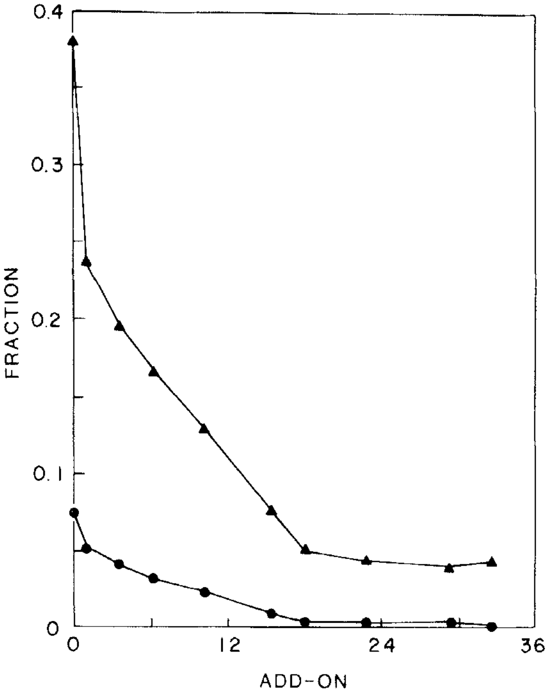

FIG. 1. Plot of anhydroglucose fractions evolved in main cellulose pyrolysis reaction against add-on of THPS-urea-phosphate. (▲) Levoglucosan, (●) anhydroglucofuranose.

phate. The fractions of anhydroglucoses (Fig. 1) show a continuous decrease with increasing add-on of the flame retardant. This response is similar to that of the anhydroglucose fractions from cotton finished with THPOH-ammonia [7] except that in the THPOH-ammonia series the DAG fractions also showed the typical anhydroglucose response to add-on of flame retardant.

The "furan" fractions (Fig. 2) show a different response to add-on. Small add-ons of THPS-urea-phosphate increase these fractions by either a small amount (HMF and DAG) or by a relatively large amount (levoglucosenone and FHK). The "furan" fractions do not begin to decrease until the add-on of flame retardant is 10% or higher, and, even at the largest add-on used in this work, the levoglucosenone and FHK fractions are larger than they are from unmodified cotton. This "furan" response to add-on is also similar to that reported previously for fabrics finished with THPOH-ammonia [7].

The fractions of nonfuels (Fig. 3) increase more or less continuously with increasing add-on of the flame retardant up to an add-on of

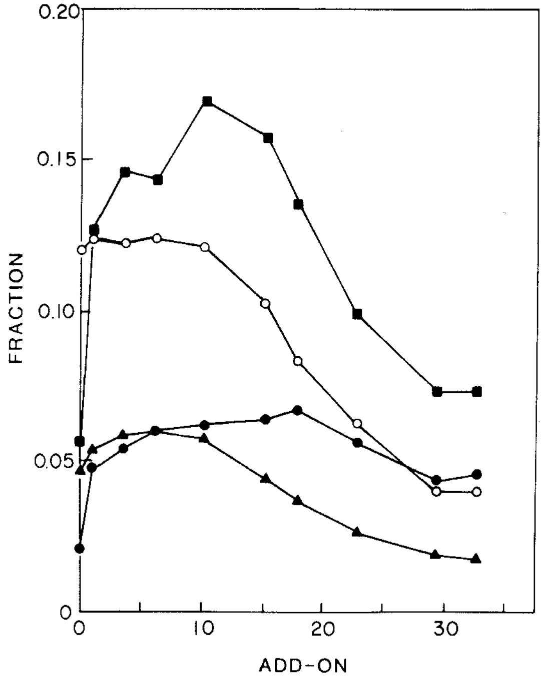

FIG. 2. Plot of "furan" fractions evolved during main cellulose pyrolysis reaction against add-on of THPS-urea-phosphate. (■) Levoglucosenone, (○) dianhydroglucose, (▲) hydroxymethyl furfural, (●) furyl hydroxymethyl ketone.

29.3%, but the responses of the water and carbon dioxide fractions to add-on are not completely parallel. A 1.0% add-on of THPS-urea-phosphate causes a large increase in the water fraction, which continues to increase with add-on up to 29.3% add-on. On the other hand, a 1.0% add-on causes a slight decrease in the carbon dioxide fraction, which does not increase rapidly until an add-on of 10.2% is reached. The pattern of the response of the carbon dioxide fractions to add-on in Fig. 3 appears to be nearly the inverse of a typical "furan" fraction to add-on in Fig. 2. Similarly, the pattern of the response of the water fractions in Fig. 3 is nearly the inverse of the response of the anhydroglucose fractions in Fig. 1. These patterns may be an indication of two parallel and competing processes in the generation of the volatile products. One process would lead to the formation of anhydroglucoses or water in relative amounts determined by the add-on of the flame retardant. The other process would lead to the formation of "furans" or carbon dioxide, again in relative amounts determined by

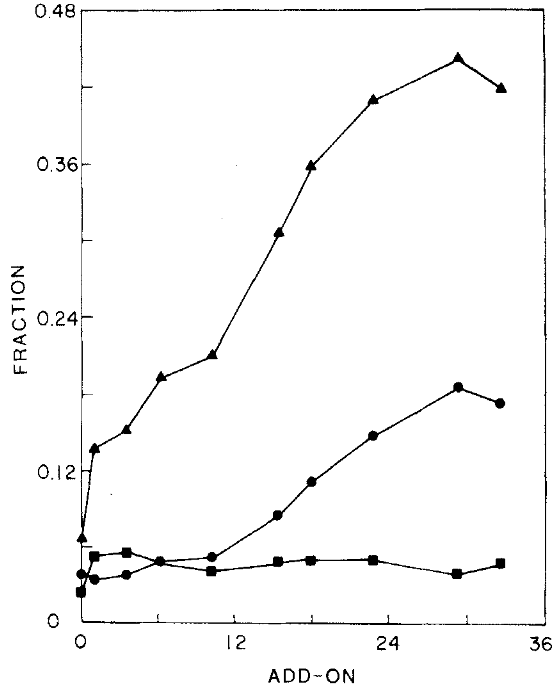

FIG. 3. Plot of nonfuel and carbon monoxide fractions evolved in main cellulose pyrolysis reaction against add-on of THPS-urea-phosphate. (▲) Water, (●) carbon dioxide, (■) carbon monoxide.

the add-on. It is, of course, obvious from the stoichiometry of the process that water must be evolved in the formation of the "furans" from cellulose anhydroglucose units. The slight decrease in both water and carbon dioxide fractions on increasing add-on from 29.3 to 32.6% is reflected by slightly increasing fractions of levoglucosan and FHK in the same add-on region. This behavior at very high add-ons had been noted also in the THPOH-ammonia series [7], and may be a result of the very high level (>45%) of solids in the finishing bath. The high viscosity of the pad bath may have hindered penetration of the reagent into the yarns and fibers or caused migration of the reagent out of the fibers. In either case, a larger part of the THPS-urea-phosphate polymer may have been deposited on the fiber and yarn surfaces, resulting in the very high stiffness observed for the fabric with 32.6% add-on. Earlier work [11] has shown that the distribution of THPOH-ammonia polymer in or around cotton fibers can affect both the volatile pyrolysis product compositions and the pyrolysis kinetics. The carbon monoxide fractions (Fig. 3) were affected to only a small extent by the add-on of THPS-urea-phosphate.

The data in Figs. 1-3 are similar to, but not identical with, the data for the entire cellulose pyrolysis [12]. This result is to be expected because the main reaction accounts for 84-91% of the weight loss in the entire cellulose pyrolysis [3]. Therefore, the correlations and conclusions discussed previously apply to the data on the volatile product fractions from the main reaction. In particular, the strong positive correlation between the oxygen indices and the water fractions and the strong negative correlations between the oxygen indices and the anhydroglucose fractions indicate that the THPS-urea-phosphate finish exerts its flame-retardant action during the main cellulose pyrolysis reaction. It appears from these correlations that the flame retardant is effective principally in suppressing anhydroglucose formation and promoting water formation. The effects of the THPS-urea-phosphate finish on "furan" and carbon dioxide formation contribute less to the flame-retardant action. In fact, the promotion of "furan" formation by the finish would be detrimental to flame retardancy at low and intermediate add-ons if anhydroglucose formation were not simultaneously suppressed.

The data on the weight fractions and yields of volatile products are also similar to both the data on the molar fractions from the main reaction and to the data on the weight fractions and yields from the entire cellulose pyrolyses. In the main reaction, as well as in the entire cellulose pyrolysis, the oxygen index has a slightly stronger correlation with the molar fractions of water than with either the carbon dioxide fractions or the weight fractions or yields of either carbon dioxide or water.

Second Initial Stage

The patterns of response to add-on of all the volatile product fractions are quite different from those in the main reaction. The anhydroglucose fractions in the second stage (Fig. 4) are significantly increased by an add-on of only 1.0% of THPS-urea-phosphate, and further increases in add-on tend to lower the anhydroglucose fractions. This response to add-on is similar to that of the "furans" in the main reaction except for the large increases caused by 1.0% add-on and the continuous decreases above 1.0% add-on (levoglucosan) or 3.5% add-on (AGF).

There is an interesting parallel between the shape of the levoglucosan fraction versus add-on curve for the second initial stage and the activation energy versus add-on curve for the same stage [3]. This is the first such parallel response found for volatile pyrolysis product fractions and pyrolysis kinetic parameters for fabrics finished with reactive, phosphorus-containing flame retardants. This parallel response to add-on may be a further indication of the drastic change in the mechanism of the second initial pyrolysis stage caused by 1.0% of the flame retardant.

It was proposed previously [3] that the second initial stage in unmodified cotton is a cellulose chain unzipping process and that even small amounts of flame retardants restrict the mobility of the cellulose chains

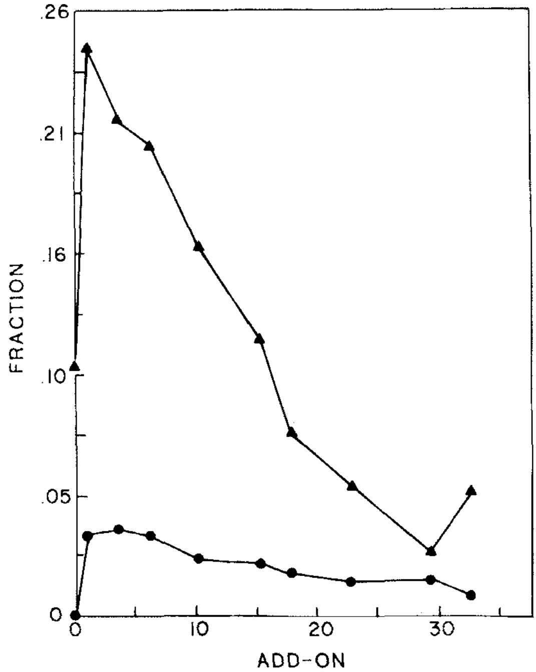

FIG. 4. Plot of anhydroglucose fractions evolved in second initial stage against add-on of THPS-urea-phosphate. See Fig. 1 for key to symbols.

in the less-ordered regions. The rate-determining step in the flame-retardant fabrics was proposed to be a process in which bonds are broken in the flame-retardant polymer so that the cellulose chains are mobile enough to undergo depolymerization in rapid steps after the rate-determining step. Small amounts of ammonia were evolved only during the second initial stage from the fabrics finished with THPS-urea-phosphate, and volatile products containing phosphorus were evolved only in the second initial stages of fabrics finished with other reactive, phosphorus-containing flame retardants. It is also possible that small amounts of the flame retardant can promote the depolymerization steps. The decrease in anhydroglucose fractions with increasing add-on may be a result of the lesser restraint in the less-ordered regions as proposed for the kinetic parameters of this stage [3]. It is more likely due to the same causes that decrease anhydroglucose fractions with increasing add-on in the main reaction.

The molar fractions of the "furans" in the second initial pyrolysis stage (Fig. 5) show a response to add-on of THPS-urea-phosphate

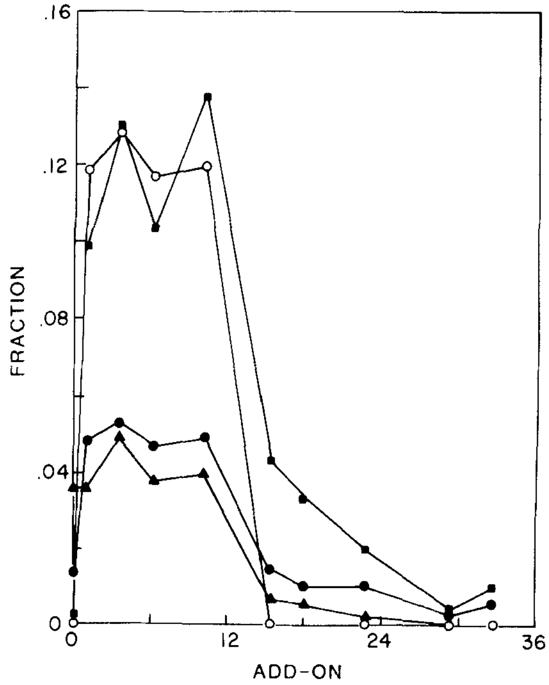

FIG. 5. Plot of "furan" fractions evolved in second initial stage against add-on of THPS-urea-phosphate. See Fig. 2 for key to symbols.

superficially similar to that in the main reaction. However, the increases in all the "furan" fractions (except the HMF fraction) caused by the first 1.0% of add-on are from very low values up to values typical of these fractions in the main reaction. Increasing the add-on from 1.0% up to 10.2% does not greatly affect the "furan" fractions in the second initial stage, as is the case in the main reaction. A further increase in the add-on to 15.3% drastically decreases the "furan" fractions by 69-100%. Further increases in add-on cause less drastic decreases in the levoglucosenone, HMF, and FHK fractions. It appears that very small add-ons make the second initial stage similar to the main reaction in terms of volatile product compositions. Very high add-ons are more effective in reducing "furan" fractions in the second initial stage than in the main reaction. In applying statistical multiple correlation tests to the data on the "furan" and anhydroglucose fractions, there was no clear grouping of the fractions of any single volatile product or group of products from the second initial stage, despite the difference in appearance between the curves in Figs. 4 and 5.

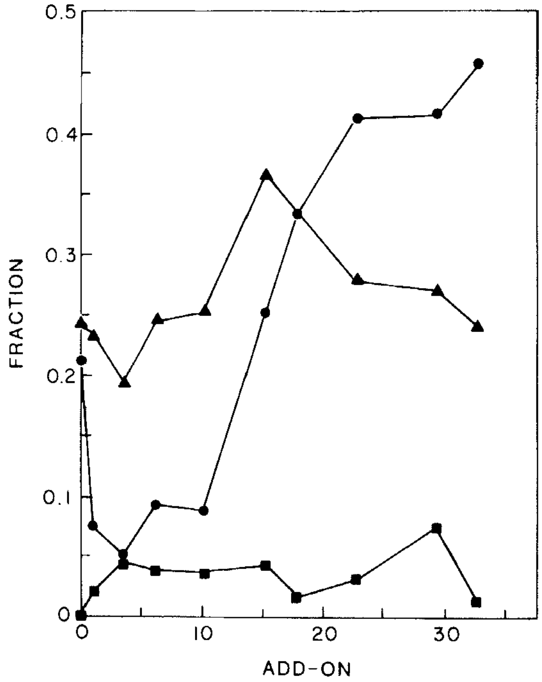

FIG. 6. Plot of nonfuel and carbon monoxide fractions evolved in second initial stage against add-on of THPS-urea-phosphate. See Fig. 3 for key to symbols.

The fractions of the nonfuels (Fig. 6) show a different and characteristic response to add-on of THPS-urea-phosphate in the second initial pyrolysis stage. The water fractions do not show the continuous increase with add-on seen in the main reaction. There seems to be no consistent pattern in the response of the water fractions except for a maximum somewhere around 15% add-on. Both the first three points and the last five points show decreases in the water fractions with increasing add-on. The carbon dioxide fractions show a characteristic response which is the inverse of the response of the "furan" fractions to add-on. The double maxima at 3.5 and 10.2% add-on in the "furan" fractions are seen in the carbon dioxide fractions as double minima at the same two add-ons. The water fractions could be interpreted as having a similar pattern up to 17.9%, where some other process decreases the water fractions with increasing add-on. At 22.8% and higher add-ons, carbon dioxide is the major volatile pyrolysis product. Again in this stage, the carbon monoxide fractions show no characteristic response to add-on, and carbon monoxide remains a minor primary pyrolysis product. There is no strong correlation of the oxygen indices to the fractions of any individual product or class of products. No such strong correlation would be required to explain the flammability data because of the small amount of weight loss in the second initial pyrolysis stage.

First Initial Stage

Since the weight losses in the first stage are quite small (1.2-3.1%, or 1-4 μg in the samples used in this work), the variation in the molar fractions of the individual volatile products is expected to be quite high. Nevertheless, some definite patterns can be seen in the responses of the volatile product fractions to add-on of THPS-urea-phosphate.

The anhydroglucose fractions in the first initial stage (Fig. 7) show a pattern which seems to be somewhat similar to that for these fractions in the second initial stage. The levoglucosan fractions show a

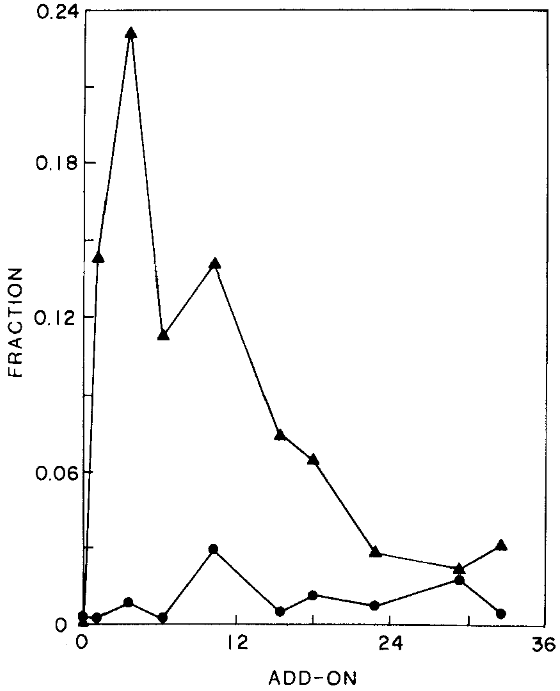

FIG. 7. Plot of anhydroglucose fractions evolved in first initial stage against add-on of THPS-urea-phosphate. See Fig. 1 for key to symbols.

large increase with add-on up to 3.2%, followed by a more or less continuous decrease with increasing add-on, and the same small increase from 29.3 to 32.6% add-on. The AGF fractions remain very small and do not show an obvious pattern except for a possible increase in the AGF/levoglucosan ratios, which may also occur in the second initial stage. The minimum at 6.2% add-on appears to be similar to the minimum for the "furan" fractions and the slight maximum for the carbon dioxide fractions in the second initial stage, and also may occur in the nonfuel fractions for the first initial stage. This response by the fabric with 6.2% add-on does not occur in the main reaction and no ready explanation is obvious.

The "furan" fractions (Fig. 8) are very small in the first initial stage. All except two are below 0.017, and more than half the points are below the detectable level (0.0001). The only pattern to be seen in the data on the "furan" fractions evolved in the first stage is a maximum at 3.5% add-on, although an isolated point at 10.2% add-on shows a higher fraction of DAG.

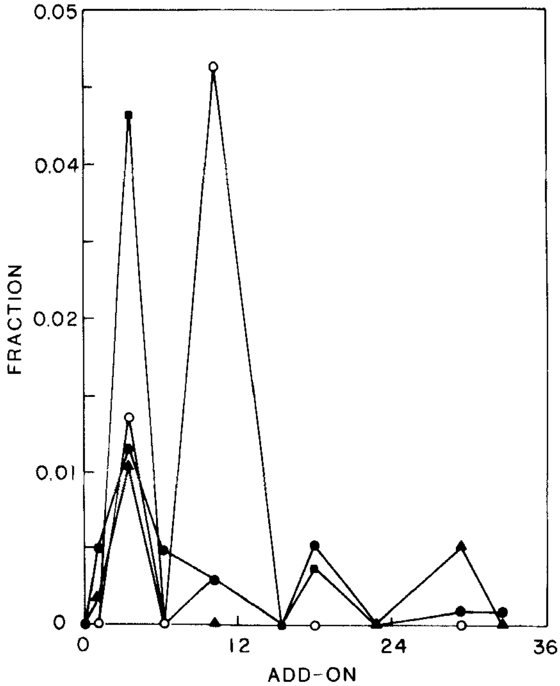

FIG. 8. Plot of "furan" fractions evolved in first initial stage against add-on of THPS-urea-phosphate. See Fig. 2 for key to symbols.

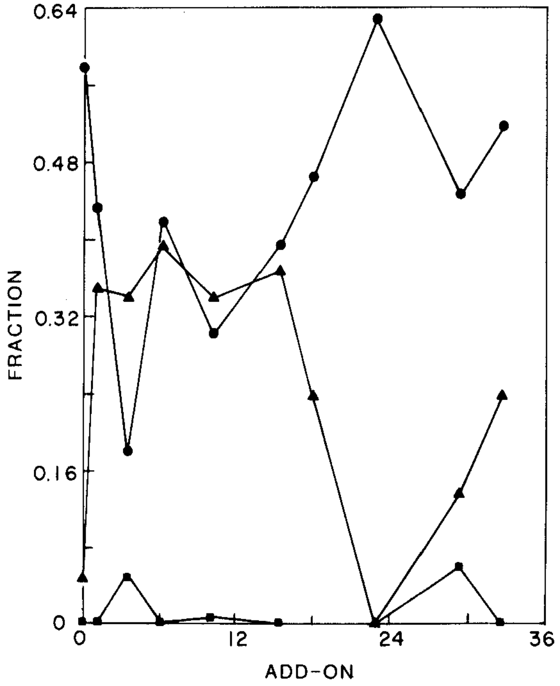

FIG. 9. Plot of nonfuel and carbon monoxide fractions evolved in first initial stage against add-on of THPS-urea-phosphate. See Fig. 3 for key to symbols.

The nonfuel fractions in the first initial stage (Fig. 9) show a unique response to add-on of THPS-urea-phosphate. In contrast to the data from the main reaction and the second initial stage, the water and carbon dioxide fractions show an almost inverse relationship with each other in the first initial stage. The broad maximum in the water fractions between 1.0 and 15.3% add-ons is matched by an apparent broad minimum in the carbon dioxide fractions in the same add-on range. The minimum in the water fractions at 22.8% add-on is matched by a maximum in the carbon dioxide fractions at the same add-on. Both the water fractions and the carbon dioxide fractions increase as the add-on increases from 29.3 to 32.6%, which is opposite to the response seen in the other two stages. The carbon monoxide fractions are either missing or small at all add-ons in the first initial stage.

The response of none of the volatile pyrolysis product fractions in the first initial stage to add-on of THPS-urea-phosphate follows the pattern of response to add-on of the kinetic parameters [3]. The activation energies for the first initial stages of unmodified cotton and cotton with 1.0% add-on were very close, and the activation energies for that stage in all the fabrics were low but very similar. The rate-determining step of the first stage was proposed to be a chain scission process, followed by rapid decarboxylation and dehydration steps. It was proposed that the flame retardant causes the kinetic effects by polymerizing before the cotton fibers collapse completely while drying and keeping the fibers partially swollen. The volatile product fractions from unmodified cotton are consistent with the above mechanism, but the effect of add-on on the kinetic parameters does not explain its effects on the volatile product fractions. It appears that in the first initial stage, as in the main reaction, the flame retardant affects rapid reactions that occur after the rate-determining step. In the first initial stage, small add-ons of THPS-urea-phosphate can promote the formation of some levoglucosan and small amounts of other volatile fuels. Large add-ons suppress the fuel formation, possibly in rapid steps simultaneous with or following processes that would lead to fuel formation.

SUMMARY AND CONCLUSIONS

Volatile product fractions from each of the kinetic stages of the cellulose pyrolysis were measured from the pyrolysis-mass spectrometric data. The kinetic stages had been measured from thermogravimetric data. The volatile product fractions from the main pyrolysis reaction were similar to, but not identical with, the fractions from the entire cellulose pyrolysis. The anhydroglucose fractions showed a continuous decrease with increasing add-on of THPS-urea-phosphate up to an add-on of 17.9%, and were almost constant at higher add-ons. Small add-ons increased the "furan" fractions, and add-ons above 10.2% caused continuous decreases in the "furan" fractions. Water fractions continuously increased with increasing add-on up to 29.3%. Small add-ons decreased the carbon dioxide fractions, but add-ons from 10.2 to 29.3% caused a continuous increase in the carbon dioxide fractions. There appear to be inverse relationships between anhydroglucose and water fractions and between "furan" fractions and carbon dioxide fractions. These inverse relationships may indicate competing pathways to volatile products. One leads to anhydroglucoses or water. The other leads to "furans" or carbon dioxide. The relative amounts of all products are determined by the add-on of the flame retardant. These inverse relationships were not apparent in the data from fabrics finished with THPOH-ammonia. The molar fractions of water showed the best parallel with the oxygen indices (measurements of flame retardancy). This also contrasts with the data from fabrics finished with THPOH-ammonia, where the total nonfuel molar fractions showed the best parallel with the oxygen indices.

The volatile product fractions in the second initial pyrolysis stage showed patterns of response to add-on that were quite different from those in the main reaction. The lowest add-on caused a substantial increase in the anhydroglucose fractions. Further increases of the add-on to 29.3% decreased the anhydroglucose fractions. The "furan" fractions showed flat maxima between 1.0 and 15.3% add-on, and small or decreasing values at higher add-ons. The water fractions showed an inconsistent response to add-on. The response of the carbon dioxide fractions to add-on was nearly the inverse of that of the "furan" fractions. At high add-ons, carbon dioxide was the major volatile product evolved in the second initial stage. It is proposed that the rate-determining step in the second initial stage of cotton finished with THPS-urea-phosphate is the breakdown of the flame retardant, as indicated by the evolution of ammonia only in this stage. The presence of small amounts of flame retardant in the cotton seems to promote the evolution of both anhydroglucoses and "furans" in this stage.

The first initial pyrolysis stage is characterized by small weight losses, and therefore by small amounts of volatile products. Small add-ons of the flame retardant increase the anhydroglucose fractions and large add-ons decrease them almost to the values from unmodified cotton. The "furan" fractions are all very small, but seem to respond to add-on similarly to the anhydroglucose fractions in the first stage. Carbon dioxide is the major volatile product evolved in the first stage. The water fractions respond to add-on in a pattern almost the inverse of that of the carbon dioxide fractions. The rate-determining step of the first initial stage is proposed to be a chain scission process in the less-ordered cellulose regions. Small amounts of the flame retardant promote the evolution of some anhydroglucoses and small amounts of "furans" in this stage.

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