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# Thermogravimetric Analysis and Pyrolysis Kinetics of Cotton Fabrics Finished with THPOH-$NH_3$

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# Thermogravimetric Analysis and Pyrolysis Kinetics of Cotton Fabrics Finished with THPOH-NH$_3$

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## ABSTRACT

Unmodified cotton and cotton fabrics finished with eight add-ons of THPOH-NH$_3$ were subjected to thermogravimetric analysis in a vacuum and in nitrogen. Nitrogen had no effect on the thermogravimetric data. THPOH-NH$_3$ up to 6% add-on lowered temperatures of maximum pyrolysis rates and decreased the weight loss per unit weight of cellulose. Additional add-on had little further effect. Arrhenius plots showed that the cellulose pyrolysis occurred in consecutive stages, the initial stage and a main stage. These stages were followed by a char pyrolysis. The main pyrolysis stage followed a first-order rate law. THPOH-NH$_3$ up to 6% add-on increased the energy of activation for this stage from 62 to 97 kcal/mol and the entropy of activation from 29 to 104 cal/deg·mol. Again, additional add-on had little further effect. These thermogravimetric and kinetic data are interpreted in terms of a model for the main cellulose pyrolysis stage.

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## INTRODUCTION

Reactive phosphorus-based flame retardants used with cellulose are generally believed to act primarily or solely in the solid phase. They affect the pyrolysis reactions in which cellulose is converted into gaseous fuel, which is oxidized in the flame [1]. Although pyrolyses of unmodified and flame-retardant celluloses have been extensively investigated [2, 3], the mechanism of the chemical reaction or reactions leading from solid cellulose to volatile fuels is still unclear. Even less clear [4] are the mechanistic details of the chemical reactions by which phosphorus-containing flame retardants affect the pyrolysis processes so as to decrease the fraction of fuels in the volatile products.

The kinetics of cellulose pyrolysis have been extensively investigated and have been reviewed recently [5, 6]. The many methods for rate measurements applied to cellulose pyrolysis have resulted in a correspondingly varied set of kinetic values for the reaction. Reported activation energies range from 22 to 150 kcal/mol. Basch and Lewin [7] concluded that the activation energy for pyrolysis of the less ordered regions of cellulose is approximately 30 kcal/mol and that for the pyrolysis of cellulose crystallites it is approximately 60 kcal/mol. There have been few reports of preexponential factors or entropies of activation. Most reports that mention the order of the cellulose pyrolysis reaction assume it to a be first-order reaction. There have been few reports on effects of flame retardants on the kinetic parameters of cellulose pyrolysis, although the well-known effects of flame retardants in decreasing pyrolysis temperatures and increasing char yields have been mentioned frequently. Cellulose impregnated with various inorganic salts has a lower activation energy for pyrolysis than does unmodified cellulose [8-11]. However, there has been no definitive study of the ways in which reactive, phosphorus-based flame retardants for cotton textiles affect the kinetic parameters of cellulose pyrolysis over a wide range of add-ons.

In previous work on mechanisms of flame retardancy, we concentrated on identification and measurement of volatile pyrolysis products [12, 13] by a pyrolysis-mass spectrometric method [14]. During that research, thermogravimetric (TG) analyses were performed on a series of fabrics differing only in add-on of a single flame retardant [13]. The TG data were used primarily to calculate weight yields of volatile pyrolysis products (from char residues) and for temperature calibration of the mass spectrometric data. However, some qualitative conclusions were drawn from the mass spectrometric total ion pyrograms, which correspond to derivative TG (DTG) curves. This report provides more detail about the TG data for those fabrics and the results of kinetic analyses of the DTG curves.

TABLE 1. THPOH-$NH_3$ Finishes on Cotton Printcloth

| $THPOH_3$ in pad bath (%) | Add-on of THPOH-$NH_3$ (%) | Phosphorous content (%) | Oxygen index |
|---|---|---|---|
| 0 | 0.0 | 0.00 | 0.183 |
| 5 | 3.0 | 0.57 | 0.205 |
| 10 | 6.1 | 1.22 | 0.232 |
| 15 | 8.9 | 1.86 | 0.250 |
| 20 | 11.2 | 2.31 | 0.272 |
| 25 | 15.6 | 3.13 | 0.292 |
| 30 | 18.3 | 3.59 | 0.301 |
| 35 | 21.3 | 4.07 | 0.313 |
| 40 | 24.8 | 4.37 | 0.314 |

## EXPERIMENTAL

TG analyses were performed by the method of Neumeyer et al. [15]. A DuPont* Thermal Analysis System with an attached 951 Thermogravimetric Analyzer and a 915 Computer Interface was used, and the computations were done with a CDC 1700 system. The samples were pieces of cotton printcloth weighing approximately 3 mg. They were heated from 100 to 500°C at a rate of 5°C/min. Most analyses were performed in a vacuum of 1 torr or less, but some were run in nitrogen at atmospheric pressure and a flow rate of 70 mL/min. Oxygen index values were measured by the ASTM procedure [16]. Fabrics were analyzed for phosphorus by x-ray fluorescence [17].

Fabric samples were desized, scoured, and bleached cotton printcloth weighing approximately 108.5 g/m$^2$ and treated with tetrakishydroxymethylphosphonium hydroxide-ammonia (THPOH-$NH_3$) according to the method of Beninate et al. [18]. The fabrics were treated with solutions of THPOH in concentrations from 5 to 40% in 5% increments, dried, ammoniated, oxidized with hydrogen peroxide, and washed in distilled water (Table 1).

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*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.

## RESULTS AND DISCUSSION

The fuel-generating pyrolysis step in the flaming combustion of cotton cellulose is unaffected by the composition of the atmosphere, except for feedback of thermal energy from the gas-phase flame [1, 12]. This assumption seems reasonable on two bases: (a) The solid polymer undergoing pyrolysis is surrounded by an atmosphere of volatile pyrolysis products (the "reducing portion" of the flame) that excludes oxygen from the pyrolyzing polymer [19], and (b) TG or DTG curves in nitrogen and in air are generally similar in shape and in temperature positions for flame-retardant cottons [15]. Differences in cellulose pyrolyses between nitrogen and air have been observed [5, 6]. These differences are generally seen only in experiments at relatively low temperatures and slow heating rates where slow gas-solid reactions can compete with the pyrolysis processes, which are even slower at these temperatures, or in experiments at fast heating rates for unmodified cellulose, where ignition of flaming combustion changes the thermal environment of the sample.

Our previous work was primarily concerned with cellulose pyrolyses in vacuum [12-14]. It was of interest to compare TG data for vacuum and nitrogen atmosphere pyrolyses of unmodified and flame-retardant cotton celluloses. Figure 1 is an example of the TG data measured in this work. The rate (DTG) curve shows a characteristic peak for the cellulose pyrolysis, followed by a gradually decreasing rate of weight loss with continued heating of the char (char pyrolysis). The volatile fuels are evolved during the cellulose pyrolysis, and only water, carbon dioxide, and a little carbon monoxide are evolved in the char pyrolysis. The temperature at the maximum rate of weight loss is characteristic for a given sample and heating rate and is determined from the DTG curve. The char residue is the weight remaining after the cellulose pyrolysis and is found from the intersection between the straightline portions of the weight curve representing the cellulose pyrolysis and the char pyrolysis.

TG data for the pyrolyses in vacuum and in nitrogen (Table 2) show a surprisingly good correspondence between the results in vacuum and in nitrogen. The two sets of experiments agree as well as, or better than, sets of replicate runs. This agreement also extends to the shapes of the DTG curves. It might be expected that instrumental variations, such as thermal conductivity by nitrogen, would cause some small systematic variations between the two sets of experiments. However, no such variation was found, except for a consistently higher noise level in the baselines of the DTG curves for the pyrolyses in nitrogen.

Pyrolysis-mass spectrometric measurements [13, 14] showed that the only nitrogen- or phosphorus-containing pyrolysis product evolved in the cellulose pyrolysis stage of the fabrics treated with THPOH-$NH_3$ was a small amount of ammonia evolved in the initial stages. The fractions of formaldehyde and methanol in the products from the

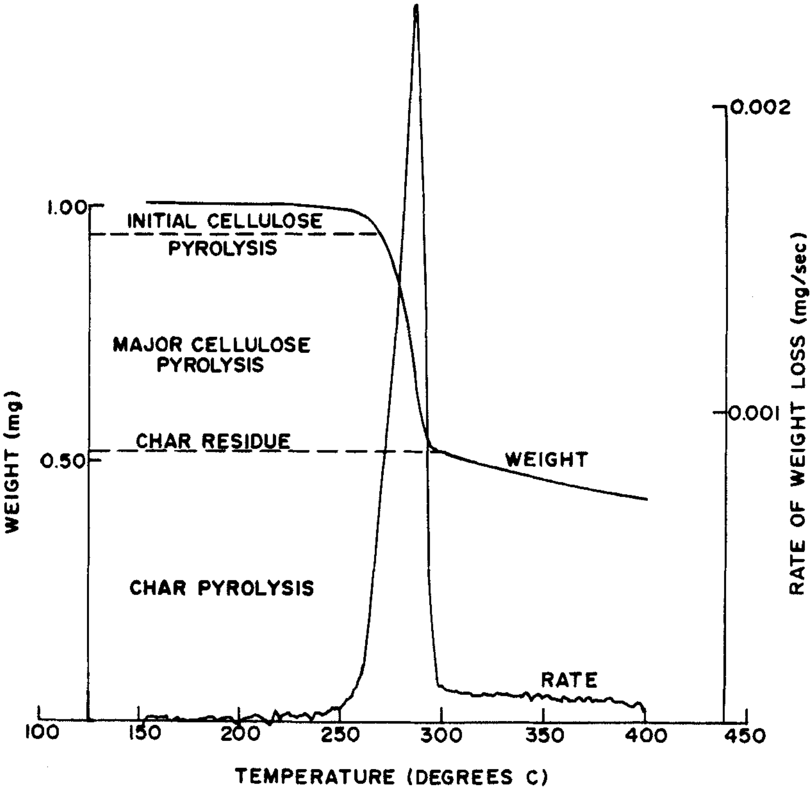

FIG. 1. Thermogravimetric data for vacuum pyrolysis of cotton printcloth finished with 8.9% of THPOH-NH$_3$. Weight (TG) and rate (DTG) indicated on respective axes. Char residue and pyrolysis reaction stages indicated on weight axis. Heating rate, 5° C/min.

flame-retardant fabrics were smaller than those in the products from unmodified cotton. In addition, the volatile products from the cellulose pyrolysis stage of the flame-retardant fabrics contained only products that were evolved from unmodified cotton [13]. The only likely volatile products from the flame retardant would then be some contribution to the water or carbon dioxide, which are major products from the pyrolysis of cellulose. Therefore, cellulose char yields were calculated by subtracting the add-ons from the char residues (Table 2). The response of cellulose char yields to add-on of THPOH-NH$_3$ is similar to the response of temperatures of maximum pyrolysis

TABLE 2. TGA Data for Vacuum and Nitrogen Pyrolyses

| Add-on (%) | Temperature of maximum pyrolysis rate (°C) |  | Char residue (%) |  | Cellulose char yield (%) |  |
|---|---|---|---|---|---|---|
|  | Vacuum | $N_2$ | Vacuum | $N_2$ | Vacuum | $N_2$ |
| 0.0 | 342 | 339 | 16 | 11 | 16 | 11 |
| 3.0 | 294 | 295 | 36 | 38 | 33 | 35 |
| 6.1 | 287 | 289 | 50 | 48 | 44 | 42 |
| 8.9 | 286 | 287 | 52 | 50 | 43 | 41 |
| 11.2 | 284 | 286 | 56 | 55 | 45 | 44 |
| 15.6 | 285 | 287 | 57 | 56 | 41 | 41 |
| 18.3 | 284 | 286 | 61 | 61 | 42 | 43 |
| 21.3 | 282 | 285 | 61 | 63 | 40 | 42 |
| 24.8 | 282 | 284 | 64 | 62 | 39 | 37 |

rates: Small add-ons cause large changes and the add-on of THPOH-$NH_3$ above 6% has little effect on the cellulose char yield or the temperature of maximum pyrolysis rate. This effect might be stated another way: The add-on of THPOH-$NH_3$ above 6% has very little effect on the weight loss per unit weight of cellulose. This statement suggests the observed lack of volatile pyrolysis products from the flame retardant, but it does not necessarily imply that the flame retardant remains unchanged during the cellulose pyrolysis stage.

## Kinetic Analysis

In our previous report on these fabrics [13], qualitative observations were made about the effect of add-on of THPOH-$NH_3$ on the kinetics of cellulose pyrolysis. The add-on affected the pyrolysis temperatures in a qualitatively different way than it affected the flammability and distribution of volatile pyrolysis products. It was proposed on the basis of the shapes of the pyrolysis-mass spectrometric and DTG curves that the lowering of pyrolysis temperatures was caused by an effect of the flame retardant on the entropy of activation ($\Delta S\ddagger$) rather than on the energy of activation ($E_a$). A kinetic analysis of the cellulose pyrolyses was therefore undertaken to clarify this point and to gain quantitative information on the rate-determining steps of the pyrolyses.

Although the pyrolysis-mass spectrometric data and the TG data contain equivalent kinetic information, the TG data were used because they were more accessible for computer manipulation. These data consisted of sets of weight, temperature, and rate of weight loss recorded simultaneously every 10 s throughout the TG runs. Each set of weight and rate measurements was used to calculate a rate constant at each temperature throughout a run. The calculations are based on Doyle's [20] general rate equation,

$$-dh/dt = kh^n \tag{1}$$

where h is the active weight fraction of the reactant at any instant in a reaction, and k is the specific rate constant. Doyle's derivation of an expression for h was used to derive Eq. (2), which was used in the calculations.

$$-dW/dt = (W_0 - W_f)^{n-1}k(W - W_f)^n \tag{2}$$

W is the weight, $W_0$ is the original weight, $W_f$ is the weight at the end of the reaction (the char residue), and -dW/dt is the rate of weight loss. W and -dW/dt refer to measured values at a specific time (and temperature) during a reaction, and $W_0$ and $W_f$ refer to values for an entire reaction (the cellulose pyrolysis) and are constants in Eq. (2). The values for k at each temperature (T) were used in the logarithmic form of the Arrhenius equation,

$$\ln k = \ln A - E_a/RT \tag{3}$$

to calculate $E_a$ and the preexponential factor (A) by a least-squares fit of the linear segments in Arrhenius plots (ln A against 1/T). $\Delta S\ddagger$ was calculated from Eq. (4) for a first-order reaction [21]:

$$\Delta S\ddagger = R(\ln A - \ln (\underline{k}T/\underline{h}) - 1) \tag{4}$$

There have been objections to the use of nonisothermal methods for measuring kinetic parameters, particularly of polymer degradations [22]. Objections about the fundamental validity of nonisothermal methods have been answered [23] and will not be further discussed except to state that the method used here was chosen to gain the maximum amount of information from the large amount of data obtained in a single TG run. Another objection to nonisothermal methods is that the reaction mechanism cannot be determined in the absence of a large amount of additional evidence and that the meanings of the kinetic parameters are therefore uncertain [22]. However, cellulose pyrolysis has been the subject of extensive investigation which has produced numerous and seemingly conflicting results and theories [5, 6]. The approach taken here is to calculate the kinetic parameters and to measure the effects of the flame retardant on the parameters. This evidence and other evidence, such as pyrolysis product distributions [13] and effects of cellulose fine structure on the pyrolysis [5], will be used as constraints on proposed mechanisms and transition states for the reaction. Even though there may be questions about the meaning of $\Delta S\ddagger$ values calculated for solid to gas reactions, the signs and approximate magnitudes of the values and the effects of the flame retardant on the values are expected to be indications of the degree of restraint or probability of transition states in the proposed mechanisms for the pyrolyses.

There has been discussion [24] of errors in kinetic data caused by experimental conditions in nonisothermal TG measurements. The major causes of such errors are effects of heat transfer causing nonuniform temperature distributions within the sample and effects of the sample configuration on rates of transfer of volatile products out of the sample. The experimental conditions used in this work are expected to minimize such errors. The samples were small (3 mg), single pieces of light-weight fabric supported only on two edges by the sample pan of the microbalance. The samples therefore had a small mass, a large surface-to-volume ratio, and a small distance for volatile products to travel before escaping into the environment. The heating rate affects the measured kinetic parameters (particularly A) only if the experimental errors described above are factors in the measurements. Varying the heating rate between 5 and 20°/min caused only random changes of 1-4% in the calculated values of both $E_a$ and ln A for unmodified and flame-retardant cottons. Since these changes are within the range of variation found for replicate experiments, it is concluded that the experimental errors described above do not affect the present measurements and that the calculated kinetic parameters represent real chemical processes occurring within cotton fibers.

Examples of Arrhenius plots of first-order pyrolysis rate constants for unmodified cotton and a flame-retardant cotton are given in Figs. 2 and 3. The Arrhenius plots for all pyrolyses in vacuum and in nitrogen had linear regions covering 85-97% of the weight loss in the cellulose pyrolysis region. The lower temperature regions of the Arrhenius plots deviate from this straight line and represent an initial weight loss of 3-7% of the original sample (3-15% of the weight loss in the cellulose pyrolysis) before the main pyrolysis occurred. The main pyrolysis stage generates 85-97% of the volatile fuel and nonfuel pyrolysis products and accounts for the flammability or nonflammability of the fabric. Therefore, only the main stage will be discussed here, and the initial stages will be discussed in a following report.

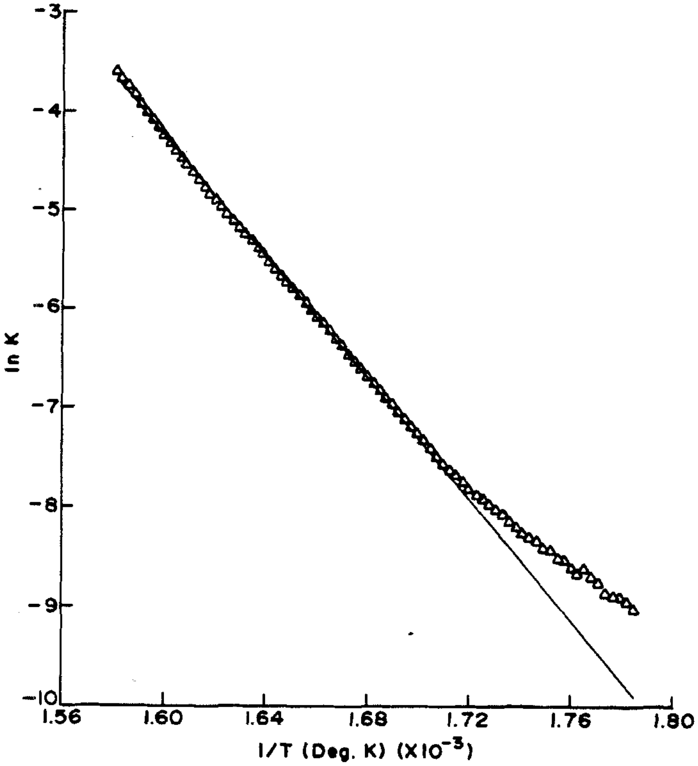

FIG. 2. Arrhenius plot for vacuum pyrolysis of unmodified cotton. Heating rate, 5°C/min. The points are the experimental points, and the line is the least squares fit for the main pyrolysis stage.

Occasional deviations from linearity in the Arrhenius plots at the highest temperatures (for example, the leftmost points in Fig. 3) were ascribed to the difficulty of accurate measurement of char residues, because the rate constants were quotients of two values (-dW/dt and $W-W_f$) rapidly approaching zero. Slight adjustments of the char residue values extended the linear portions of the Arrhenius plots to within 1-2% of the char residue.

It has generally been assumed that cellulose pyrolysis is a first-order reaction [5, 6], but the assumption has not been proved. Therefore, rate constants were calculated at each point in the pyrolysis of unmodified cotton and several flame-retardant cottons using various reaction orders between 0 and 2.5. Figure 4 illustrates the results for the main cellulose pyrolysis stage of unmodified cotton and reaction orders of 0, 1, and 2. Only the first-order rate constants

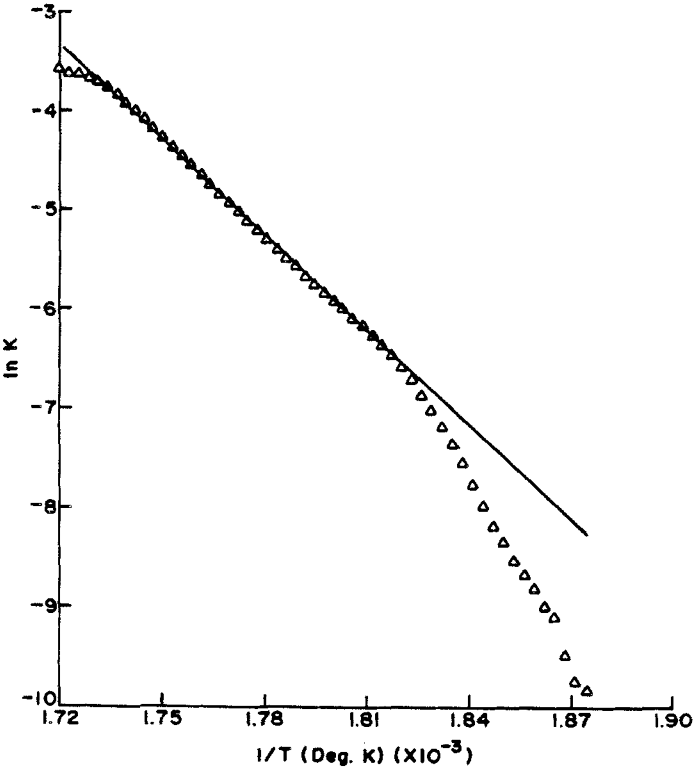

FIG. 3. Arrhenius plot for vacuum pyrolysis of cotton printcloth finished with 3.0% of THPOH-$NH_3$. Heating rate, 5°C/min. The points are the experimental points, and the line is the least squares fit for the main pyrolysis stage.

gave a linear Arrhenius plot of 50 points over a 45°C temperature range covering a weight loss of 78% of the sample or 93% of the total weight loss during the cellulose pyrolysis, exclusive of the char pyrolysis. The same results were obtained from calculations on pyrolyses of the flame-retardant samples. Therefore, the main pyrolysis stage both in unmodified cotton and in the flame-retardant cottons is kinetically a first-order process.

The kinetic parameters for the main cellulose pyrolysis stages are given in Table 3 along with the temperature ranges of the linear regions of the Arrhenius plots and the weight losses over those regions. Relative standard deviations for the slopes and intercepts ($E_a$ and ln A) were ± 0.5 to 1.0% for single plots covering 13 to 46°C temperature ranges (16 to 55 points). Replicate experiments agreed

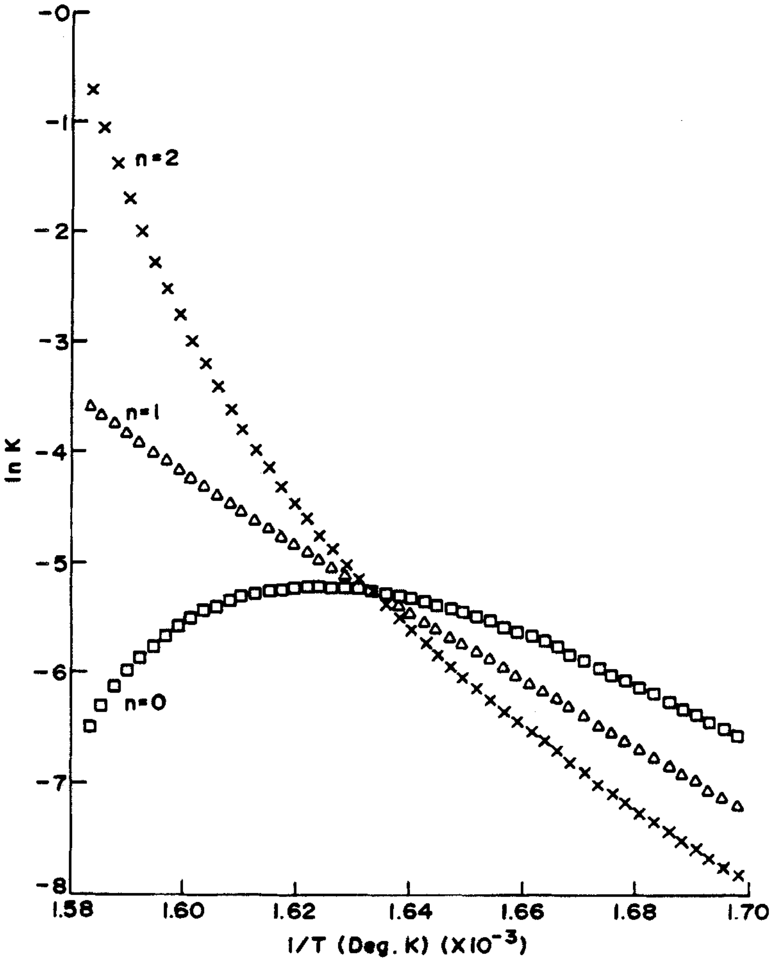

FIG. 4. Arrhenius plots for main cellulose pyrolysis stage of unmodified cotton printcloth in vacuum. Calculated for reaction orders 0 ( □), 1 ( △ ), and 2 ( X ).

to within ±2-3%. The kinetic parameters of the pyrolyses in nitrogen agreed closely with those in vacuum. The $E_a$ or ln A values for any add-on, including replicates and pyrolyses in vacuum and in nitrogen, can be considered as single sets of values with relative standard deviations of 4-5% and with random variation between the nitrogen and vacuum pyrolyses.

The THPOH-$NH_3$ flame retardant increases both $E_a$ and $\Delta S\ddagger$ for

TABLE 3. Kinetic Parameters of Main Cellulose Pyrolysis Stage in Vacuum

| Add-on (%) | Temperature range (°C) | Weight loss (%) | $E_a$ (kcal/mol) | ln A (A in $s^{-1}$) | ΔS‡ (cal/deg·mol) |
|---|---|---|---|---|---|
| 0.0 | 309-355 | 78 | 62.2 | 46.1 | 29.4 |
| 3.0 | 281-307 | 59 | 63.7 | 51.8 | 41.1 |
| 6.1 | 277-290 | 44 | 97.2 | 83.1 | 103.5 |
| 8.9 | 277-292 | 43 | 97.7 | 83.6 | 104.5 |
| 11.2 | 278-290 | 38 | 99.9 | 85.9 | 109.1 |
| 15.6 | 276-290 | 38 | 99.7 | 85.7 | 108.4 |
| 18.3 | 276-290 | 35 | 94.2 | 80.8 | 98.6 |
| 21.3 | 273-288 | 36 | 90.7 | 77.8 | 93.0 |
| 24.8 | 274-287 | 32 | 90.5 | 77.6 | 92.6 |

the pyrolyses, but to different extents. At higher add-ons, the flame retardant increases the $E_a$ by 45-60% compared to unmodified cotton. This finding is contrary to previous results from cotton containing inorganic flame retardants [8-11] and also contrary to expectation, because an increased $E_a$ is usually accompanied by increased reaction temperature. The lower pyrolysis temperatures of the flame-retardant cottons are a result of the large (215-270%) increases in the ΔS‡ caused by the flame retardant. The moderately high positive ΔS‡ for unmodified cotton indicates that the transition state is more disordered, or has less restriction of thermal motion, than the initial state. The flame retardant increases the ΔS‡ to extremely high values. This increase indicates that the transition state for the pyrolysis of the flame-retardant cotton is very disordered, compared to the initial state, and also less ordered or restricted than the transition state for the pyrolysis of unmodified cellulose.

The changes in the kinetic parameters of pyrolysis caused by the flame retardant are not linear functions of add-on. The kinetic parameters are almost independent of add-on above 6%. At the higher add-ons the $E_a$ could be represented as 95.7 ± 4.0 kcal/m and the ΔS‡ as 101.4 ± 6.9 cal/deg·m. This finding can be seen more clearly in Fig. 5. The bottom four curves are superimposable except for the decrease in areas under the curves with increasing add-on, a result of normalizing the curves to the same initial sample weight (1 mg) rather than to the same initial weight of cellulose.

Despite the similarity in $E_a$ and ΔS‡ values for add-ons of 6% and higher, there seems to be a slight maximum at 11-15% add-on and a

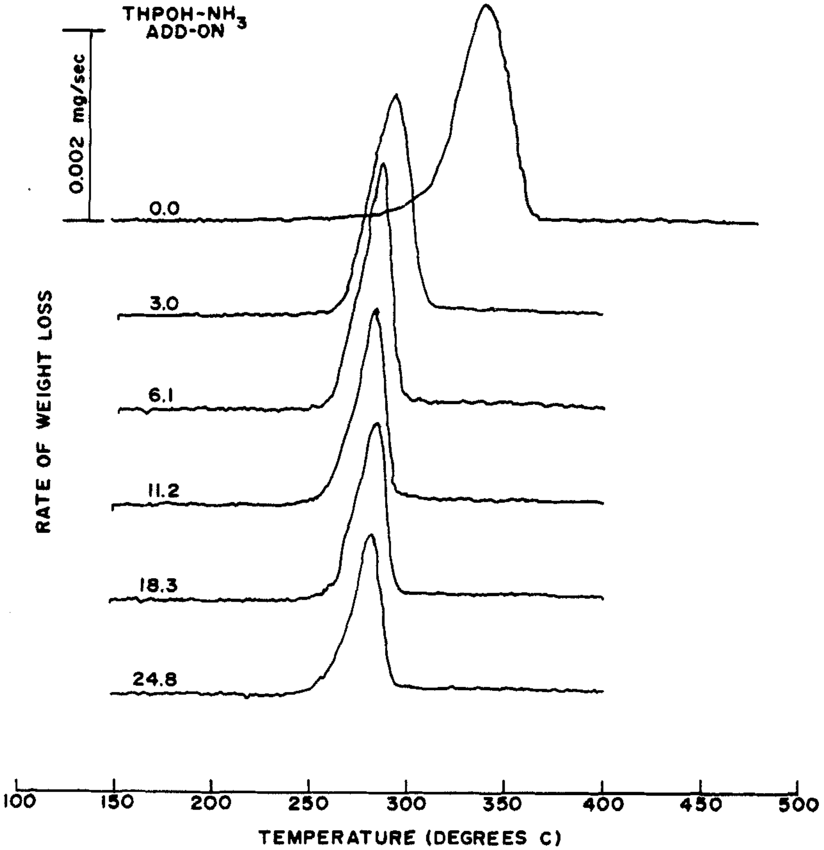

FIG. 5. DTG curve for vacuum pyrolysis of cotton printcloth finished with various add-ons of THPOH-NH$_3$. Heating rate, 5°C/min.

slight decrease at add-ons of 18% and higher. The decrease at the highest add-ons is probably real, because it is greater than the variation between replicate runs. This difference can be seen in Fig. 6. The cellulose char, also included in Fig. 6, has a sharp rise to 6% add-on, a possible maximum at 11% add-on, and decreases with additional add-on. This pattern is therefore similar to the kinetic parameters in response to add-on. Oxygen index, an inverse measure of flammability, increases continuously from that of the level of unmodified cotton to that of the second highest add-on. This relation is also shown in Fig. 6, which illustrates the contrast in response to add-on between the flammability on the one hand and the kinetic parameters and cellulose char on the other hand. Thus the decrease

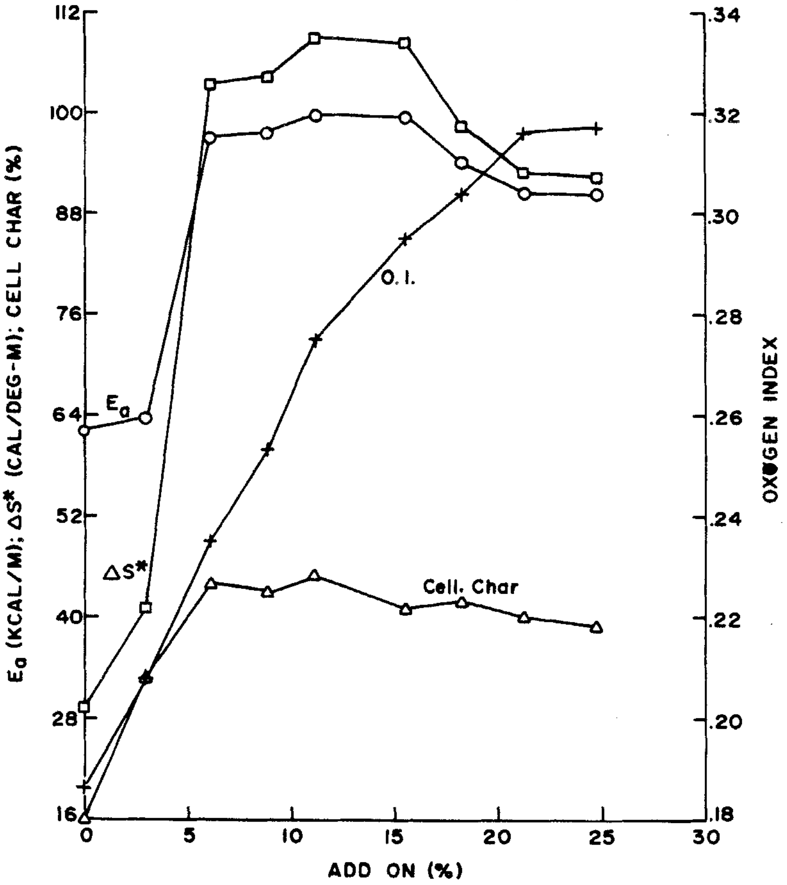

FIG. 6. Plots of energy of activation ( □ ), entropy of activation ( o ), cellulose char yield ( △ ), and oxygen index ( + ) against add-on of THPOH-$NH_3$ on cotton printcloth.

in flammability caused by the flame retardant is not directly related to the effects of the flame retardant on the kinetic parameters of the main cellulose pyrolysis stage. Furthermore, the flammability is not directly related to the amount of weight loss during pyrolysis, because the weight loss per unit weight of cellulose remains constant in the add-on range 6-21% and flammability decreases continuously in that range.

## Pyrolysis Mechanisms

The kinetic parameters for the main cellulose pyrolysis stage and the effects of THPOH-NH$_3$ on the parameters can be combined with other information about cellulose pyrolyses to propose a mechanistic model for the reaction. The difference between the effects of THPOH-NH$_3$ on the kinetic parameters and its effects on the volatile product composition and flammability suggests that these effects are exerted at different points in a complex reaction composed of distinct steps. The similarity in mass spectrometric ion pyrograms for all volatile pyrolysis products from the main cellulose pyrolysis stage [13, 14] indicates that all the products are formed by processes with a common rate-determining step. The usual methods of kinetic measurements, including the present method, give information on only the rate-determining step, which is the slowest step in a reaction consisting of a series of steps. The evidence given above strongly suggests that the rate-determining step in the main cellulose pyrolysis stage is the first step in a sequence of steps and that the individual volatile products are formed in fast, competing steps that occur after the slow, rate-determining step.

Previous work on the effects of cellulose fine structure on pyrolysis kinetics [5, 7] shows that the $E_a$ found here for the main cellulose pyrolysis stage (60 kcal/mol) is characteristic only of very highly crystalline cellulose. It is therefore proposed that the rate-determining step of the main cellulose pyrolysis stage is associated only with the cellulose crystallites (highly ordered regions), and that less ordered regions (LORs, the "amorphous regions") are removed in the initial cellulose pyrolysis stages. The weight loss in the initial stages (12%) corresponds quite well with estimates of the fraction of cotton cellulose in the LORs from hydrolysis measurements. The behavior of the degree of polymerization (DP) during pyrolysis of cotton cellulose also supports the association of the main cellulose pyrolysis stage with cellulose crystallites. The DP of the remaining cellulose drops rapidly during the initial cellulose pyrolysis stages (below 300°C) to a leveling-off DP of 150-200 and remains at this value throughout the remainder of the pyrolysis (the main stage) [5, 6, 24]. This leveling-off DP is similar to the chain lengths in cotton cellulose crystallites as measured in hydrolytic experiments.

It is proposed on the basis of the above evidence that the rate-determining step of the main cellulose pyrolysis stage involves the disruption of cellulose crystallites, possibly by individual cellulose chains unpeeling from crystallite surfaces in a stepwise process. This proposal is plausible in view of the rigidity of cellulose chains in crystallites. It is unlikely that a significant amount of depolymerization or chain scission could occur within cellulose crystallites because the crystalline forces would prevent the conformational changes of individual anhydroglucose units necessary for productive chain scission reactions. Conformational changes in anhydroglucose units that could lead to depolymerization would be quite rapid at pyrolysis temperatures in free cellulose chains removed from disrupted crystallites.

The kinetic parameters and effects of the flame retardant may now be reconciled with the model for the major pyrolysis reaction. The $E_a$ is explained by the model as the energy required to overcome the crystalline forces, such as hydrogen bonding and nonbonded interactions holding the anhydroglucose units in a specific conformation. The increase in $E_a$ caused by the flame retardant may be a surface effect whereby the flame retardant stabilizes the crystallites by additional hydrogen bonding or other interactions with the exterior anhydroglucose units. The relatively high $\Delta S^\ddagger$ for unmodified cotton indicates an increased freedom of motion in the transition state as a result of an anhydroglucose unit being freed from restraints on motion caused by crystalline forces. The large increase in $\Delta S^\ddagger$ caused by the flame retardant may be a result of a greater disordering of the cellulose chains by the flame retardant as the anhydroglucose units move, or "unpeel," from the crystalline surface through the flame retardant. Such an increased disorder could come from the flame retardant disrupting hydrogen bonds, causing conformational changes, or partially dehydrating anhydroglucose units as the cellulose chains unpeel from crystallites containing flame retardants on their surfaces. Such complete disordering is not visualized in pyrolysis of unmodified cotton.

The foregoing model also accounts for observations that the kinetic parameters are affected to only a small extent by add-ons of flame retardant above 6%, and that flammability and product distributions [13] are affected strongly by add-on at all levels studied. The explanation of flame-retardant effects on kinetic parameters of the main cellulose pyrolysis stage as a surface effect on crystallites accounts for the observations reported above. This model also accounts similarly for the previous observation [13] that similar kinetic parameters are associated with the formation of all major primary pyrolysis products at add-ons of 6% or higher, even though relative amounts vary greatly with add-on in this range.

## SUMMARY AND CONCLUSIONS

Thermogravimetric analyses were performed on a series of cotton fabrics finished with add-ons of THPOH-$NH_3$ from 0 to 24.8%. Temperature of maximum pyrolysis rate and DTG curves were identical for a given sample pyrolyzed in nitrogen or in vacuum, indicating that the presence or absence of an atmosphere does not affect the course of the pyrolysis step, which is the initial, fuel-supplying step in flaming combustion of cotton. Temperatures of maximum pyrolysis rates and weight loss per unit weight of cellulose are unaffected by additional add-ons above 6%.

Kinetic analyses of the thermogravimetric data were performed to measure energies and entropies of activation for the pyrolyses. Arrhenius plots showed that each pyrolysis occurred in consecutive stages in the cellulose pyrolysis region, the initial stages causing 3-6% weight loss, and a main stage causing a weight loss of 32-78%. These stages were followed by a slow char pyrolysis. The main cellulosis pyrolysis stage followed a first-order rate law. An add-on of 6% of THPOH-$NH_3$ increased the energy of activation by approximately 50% and the entropy of activation by 215-270% over those of unmodified cellulose. The well-known decrease in pyrolysis temperature caused by phosphorus-containing flame retardants results from an entropic effect in the transition state. Above 6%, the add-on has little or no effect on the kinetic parameters of the main stage. This effect of add-on on the kinetic parameters parallels the effect on the cellulose char yield and contrasts with the effect on flammability and composition of volatile pyrolysis products.

A model was proposed for the main cellulose pyrolysis stage in which the rate-determining step is the "unpeeling" of cellulose chains from crystallite surfaces. The effects of flame retardant on the kinetic parameters were explained in terms of this model. The depolymerization and generation of volatile pyrolysis products occur in a separate step subsequent to the rate-determining step, and are affected differently by the flame retardant.

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