Initial Pyrolysis Reactions in Unmodified and Flame-Retardant Cotton

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ABSTRACT

Thermogravimetric data were used to make Arrhenius plots for the vacuum pyrolyses of unmodified cotton and of cotton finished with various add-ons of THPOH-NH$_3$ and THPS-urea-Na$_2$HPO$_4$ flame retardants. These plots show that all pyrolyses occurred in consecutive stages: The first and second initial stages, associated with the less ordered regions of the cotton fibers, and the main cellulose pyrolysis reaction, associated with cellulose crystallites. Cotton decrystallized by ball milling showed only the two initial pyrolysis stages. The second stage followed first-order kinetics. The first pyrolysis stage in unmodified cotton was characterized by a moderately low activation energy and by a large negative entropy of activation; the second stage showed a larger activation energy and a less negative entropy of activation. Mechanisms involving cellulose chain scission and chain unzipping are proposed for the first and second stages, respectively. Add-on of the two flame retardants had contrasting effects on the two initial pyrolysis stages. These effects are explained in terms of the way in which the flame retardants are deposited in the less ordered regions of cotton fibers.

INTRODUCTION

Studies of cellulose pyrolysis have produced varied and often con-
flicting information on mechanisms of the reaction [1, 2]. An under-
standing of the mechanisms of cellulose pyrolysis and the effects of
reagents on the pyrolysis is necessary to understand how flame
retardants act on cellulose to reduce the fractions of fuels in the
volatile pyrolysis products. Kinetic parameters of the pyrolysis
should provide information on the transition state and therefore on
the mechanism of the reaction. However, reported activation ener-
gies for cellulose pyrolyses [2] range from 22 to 150 kcal/mol.

The fraction of nonfuels in the volatile pyrolysis products in-
creases continuously with add-on of THPOH-NH$_3$ flame retardant on
cotton fabrics [3]. Pyrolysis of cotton fabrics finished with THPOH-
NH$_3$ occurs in a sequence of stages consisting of initial stages pre-
ceding the main cellulose pyrolysis stage and a char pyrolysis at
higher temperatures [4]. The energy of activation (E_a) and entropy
of activation ($\Delta S^{\ddagger}$) of the main cellulose pyrolysis stage were in-
creased by the flame retardant up to an add-on of 6%. These param-
eters remained almost constant at higher add-ons. The kinetic
parameters for the main cellulose pyrolysis stage of cotton finished
with THPS-urea-Na$_2$HPO$_4$ responded similarly to add-on [5].

These results were used to propose a model for the main cellu-
lose pyrolysis stage. The rate-determining step in the model is the
unpeeling of cellulose chains from crystallite surfaces. The com-
position of the volatile pyrolysis products (and thus the flammability
of the fabric) is determined by the thickness of the layer of flame
retardant through which the cellulose anhydroglucose units pass
before they are freed as the primary volatile products. This report
describes the initial stages of pyrolysis in unmodified and flame-
retardant cottons. Effects of add-on of the two flame retardants on
the initial states of cellulose pyrolysis are compared.

EXPERIMENTAL

The preparation of the fabrics and the procedure of the thermo-
gravimetric analyses have been previously described [4, 5]. All
thermogravimetric analyses were performed at a heating rate of
5°C/min in a vacuum of 1 torr or less. Kinetic analysis of the
thermogravimetric data was done by the method described previously
[4].

RESULTS AND DISCUSSION

In the kinetic analyses of pyrolyses of unmodified cotton and
cottons finished with THPOH-NH$_3$ [4] and THPS-urea-Na$_2$HPO$_4$ [5]

flame retardants, the low-temperature end of the Arrhenius plots (ln k vs 1/T) departed from the linear segments representing the main cellulose pyrolysis stage. The initial stages always represented a loss of 5-10% of the original weight. Such weight losses correspond fairly well with the estimates of the fraction of cotton cellulose in the less ordered regions (the "amorphous regions"). This correspondence was cited as supporting evidence in the model proposed [4, 5] for the main cellulose pyrolysis stage, which is associated with cellulose crystallites. The model implies that the cellulose in the less ordered regions must be removed in an initial step or steps before the main cellulose pyrolysis stage can occur. The nature of the initial stages of cellulose pyrolysis was not further discussed except for the statements that the flame retardants were deposited primarily in the less ordered regions and that phosphorus-containing species remained in the fibers during the initial pyrolysis steps.

The Arrhenius plots in Figs. 1 and 2 are typical of those for the fabrics in this study. All these plots consisted of three consecutive straight lines with or without transition areas between the lines. These plots indicate that cellulose pyrolysis occurs in three consecutive stages, or separate reactions, each with its own mechanism and transition state. These stages can be denoted (from right to left in the figures) as the first initial stage, the second initial stage, and the main cellulose pyrolysis stage. The plot for unmodified cotton (Fig. 1) could be interpreted as indicating competitive reactions that become dominant in different temperature ranges. However, such an interpretation is not feasible for some of the flame-retardant cottons, such as that in Fig. 2. The high negative slope of the second initial stage indicates that this reaction would mask the main pyrolysis reaction if it continued at higher temperatures. Thus, the second initial stage in this pyrolysis consumes a limited amount of substrate. In the model for the main reaction, less ordered regions of cotton fibers are consumed by the initial stages. Because of the basic similarity of the Arrhenius plots for all the fabrics in this study, it is assumed that the pyrolysis of all these fabrics occurs in three consecutive, not competitive, stages.

Because the model for the main cellulose pyrolysis stage assigns that process only to the cellulose crystallites, it was of interest to study the pyrolysis of a less crystalline cellulose, ball-milled cotton. The sample had no crystallinity detectable by x-ray diffraction. The Arrhenius plot for the ball-milled cotton (Fig. 3) has only two linear segments. The initial (low temperature) segment is close in temperature range, slope, and intercept to the first initial stage in the pyrolysis of unmodified cotton, but it covers a 9.2% weight loss instead of the 1.7% loss for unmodified cotton. The second stage for ball-milled cotton is close in initial temperature, slope, and intercept to the second initial stage in the pyrolysis of unmodified cotton, but it extends to the upper temperature limit of the cellulose pyrolysis range and covers an 80.8% weight loss instead of the 5.3%

FIG. 1. Arrhenius plot for pyrolysis of unmodified cotton in vacuum. Heating rate, 5°C/min. The points are experimental and the lines are the least squares fits for the pyrolysis stages.

loss for unmodified cotton. The data from the pyrolysis of ball-milled cotton thus support the model for the main cellulose pyrolysis reaction. The decrystallized cotton shows the two initial stages associated with less ordered regions, but does not show the main pyrolysis reaction associated with cellulose crystallites.

Reaction Order

The extension of the second initial stage in the pyrolysis of ball-milled cotton to the end of the cellulose pyrolysis range made it possible to determine the reaction order of this stage. The method involves Arrhenius plots in which rate constants are calculated for various orders and is not applicable to initial stages of other cellulose pyrolyses in which the initial stages cover 10% or less weight

FIG. 2. Arrhenius plot for pyrolysis of cotton finished with 1.0% THPS-urea-Na_2HPO_4 in vacuum. Heating rate, 5°C/min. The points are experimental and the lines are the least squares fits for the pyrolysis stages.

loss at the beginning of the pyrolysis. Figure 4 is an Arrhenius plot for the second initial pyrolysis stage of ball-milled cotton calculated for reaction orders n = 0, 1, and 2. Only the first-order plot is linear. Thus the second initial stage in ball-milled cotton follows first-order kinetics. Because of the similarity between ball-milled and unmodified cotton in the second initial pyrolysis stages, it can be concluded that the latter also follows first-order kinetics. It is expected that the corresponding stages in pyrolyses of the flame retardant cottons also follow first-order kinetics.

The first initial pyrolysis stage of ball-milled cotton causes a weight loss of only 9%, and the corresponding stage in unmodified and flame retardant cottons causes much smaller weight losses (0.3-3.1%). Therefore, any attempt to determine the kinetic order of this reaction by the above method would be useless, as would be
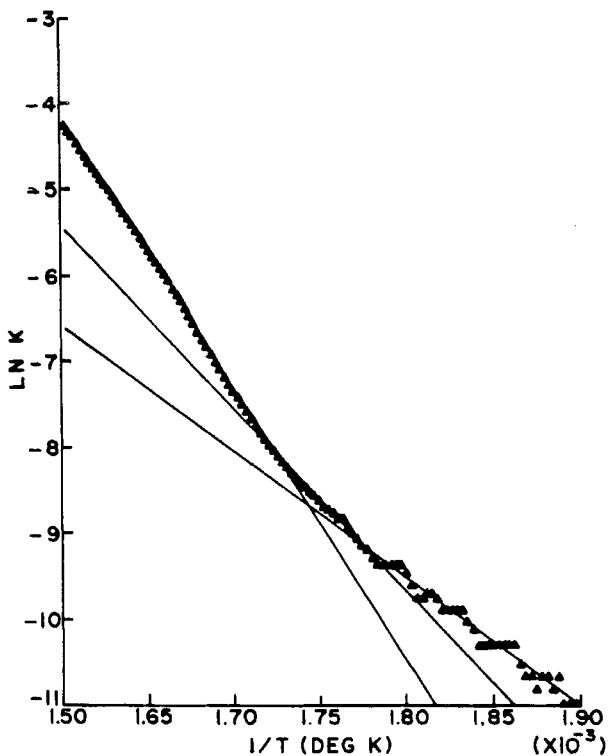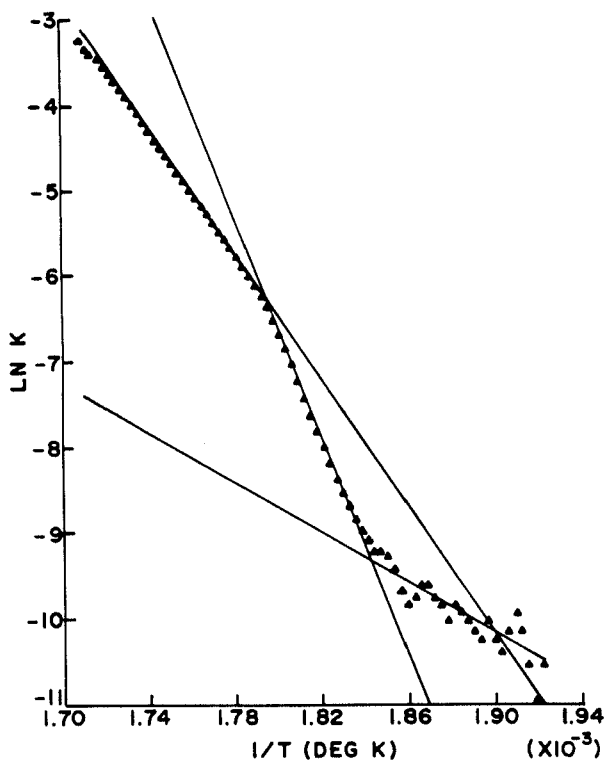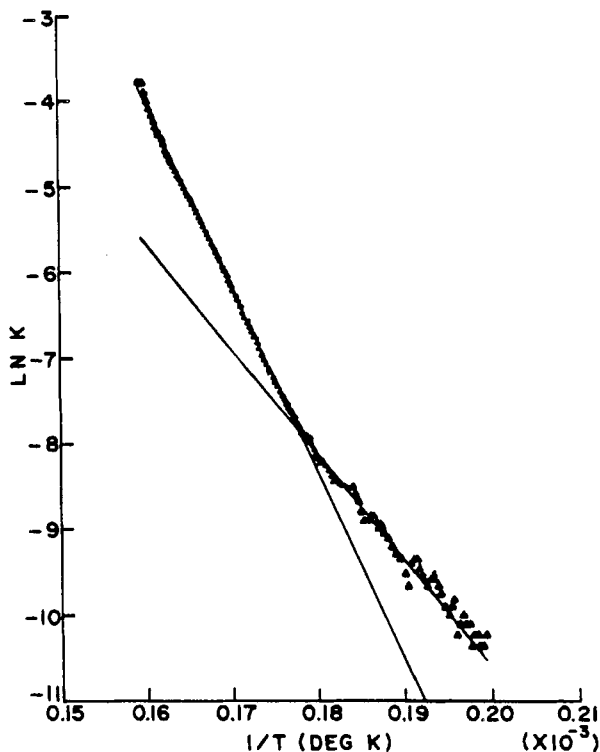
FIG. 3. Arrhenius plot for pyrolysis of ball-milled cotton in vacuum. Heating rate, 5°C/min. The points are experimental and the lines are the least squares fits for the pyrolysis stages.

most other methods based on weight loss. By analogy with the main cellulose pyrolysis stage and the second initial stage, and with pyrolyses of most other polymers, it can be assumed that the first initial stage follows first-order kinetics. This assumption simplifies the computations and does not affect variations in kinetic parameters caused by add-on of flame retardants. Only the absolute values of the parameters are affected, and those to a relatively minor extent.

There has been considerable discussion on the kinetic order of initial cellulose pyrolysis reactions [2]. There are several reports of first-order kinetics in the temperature range covered by the initial stages of cellulose pyrolysis [6, 7]. Other reports of zero-order kinetics for initial stages of cellulose pyrolysis may be interpreted as indicating first order in cases in which sufficient data are given. For example, data for pyrolysis of cellulose in nitrogen at 288°C
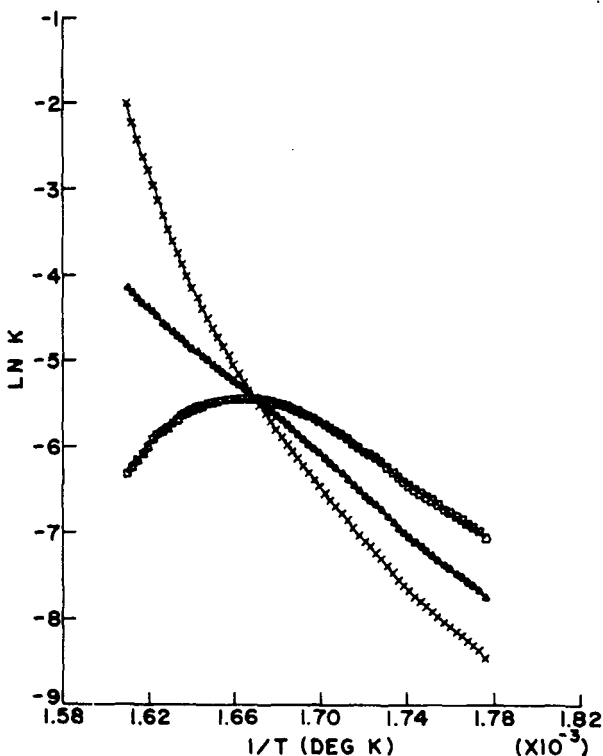
FIG. 4. Arrhenius plots for the second pyrolysis stage of ball-milled cotton. Calculated for reaction orders: 0 (□), 1 (△), and 2 (×).

were interpreted as indicating zero-order kinetics [8]. These data can be used in a first-order rate plot of $\ln (W - W_f)$ against time to give a linear relationship over the first 3 h of the pyrolysis. This plot gives a value for $\ln k$ (k in s^{-1}) of -9.6 as compared to a value of -9.2 at the same temperature from the kinetic parameters obtained in the present study for the second initial pyrolysis stage of unmodified cotton.

Unmodified Cotton

The kinetic parameters for the pyrolysis of unmodified cotton are given in Tables 1 and 2, which also include the kinetic parameters for

TABLE 1. First Initial Pyrolysis Stage

Add-on (%)	Temperature range (°C)	Weight loss (%)	E_a (kcal/mol)	ln A (A in s^{-1})	$\Delta S^{\ddagger}$ (cal/deg·mol)	$\Delta G^{\ddagger}$ (kcal/mol)
0.0	251–287	1.71	27.2	15.2	-32.7	45.5
0.0[a]	254–289	9.17	24.4	14.0	-34.1	43.7
		THPS-Urea-Na$_2$HPO$_4$ Cotton				
1.0	249–269	1.17	28.7	17.3	-27.5	43.3
3.5	239–266	1.90	19.6	9.2	-43.6	43.2
6.2	216–259	2.22	22.6	12.2	-37.6	42.7
10.2	229–254	2.09	20.8	10.9	-40.2	42.2
15.3	217–251	2.09	18.4	8.9	-44.2	42.0
17.9	213–255	2.97	18.4	9.1	-43.6	41.7

22.8	210-249	2.17	18.4	9.2	-43.5	41.8
29.3	214-250	2.17	18.9	9.8	-42.4	41.6
32.6	211-252	3.08	16.2	7.3	-47.2	41.6
			THPOH-NH$_3$ Cotton			
3.0	246-257	0.30	56.2	43.6	24.8	41.0
6.1	244-255	0.46	47.7	36.1	10.0	40.9
8.9	242-254	0.67	41.7	30.9	-0.4	40.8
11.2	230-252	0.83	39.7	29.2	-3.8	40.7
15.6	240-258	0.89	45.8	35.0	7.8	40.4
18.3	235-255	0.51	51.9	40.6	18.9	40.2
21.3	240-253	0.81	42.1	31.6	1.0	40.4
24.8	222-242	0.77	49.2	38.4	14.6	40.1

[a]Ball-milled cotton.

TABLE 2. Second Initial Pyrolysis Stage

Add-on (%)	Temperature range (°C)	Weight loss (%)	E_a (kcal/mol)	ln A (A in s^{-1})	$\Delta S^{\ddagger}$ (cal/deg·mol)	$\Delta G^{\ddagger}$ (kcal/mol)
0.0	287-309	5.3	39.5	26.3	-9.7	44.3
0.0[a]	290-354	80.8	43.2	30.9	-0.6	42.4
THPS-Urea-Na$_2$HPO$_4$ Cotton						
1.0	272-283	5.9	127.1	108.6	154.0	38.0
3.5	270-281	7.4	118.2	101.2	139.3	38.1
6.2	270-279	5.7	103.7	88.2	113.5	38.4
10.2	265-273	5.7	86.8	73.4	84.0	38.6
15.3	255-263	3.0	50.2	39.5	16.6	39.7
17.9	257-263	3.2	36.2	26.4	-9.3	40.3

22.8	251-267	3.3	37.4	27.5	-7.2	40.4
29.3	253-264	3.0	36.0	26.3	-9.6	40.3
32.6	254-266	4.1	41.0	31.2	0.2	39.8
			THPOH-NH$_3$ Cotton			
3.0	259-275	6.7	122.3	105.6	148.0	37.2
6.1	260-269	7.5	127.1	111.4	159.6	36.5
8.9	261-268	7.8	114.7	100.2	137.2	36.9
11.2	260-267	10.0	95.5	82.6	102.4	37.4
15.6	259-270	6.7	109.1	94.8	126.7	37.3
18.3	259-268	5.8	110.4	96.2	129.3	37.2
21.3	256-264	4.1	96.1	83.1	103.3	37.7
24.8	250-264	5.8	77.5	65.9	69.2	37.9

[a] Ball-milled cotton.

the pyrolysis of ball-milled cotton and the flame-retardant cottons. There is good agreement in kinetic parameters between unmodified and ball-milled cotton for both of the initial stages. The variation in kinetic parameters between ball-milled and unmodified cotton is similar to variations for replicate runs of unmodified cotton (for example, ± 3-4 kcal/mol for E_a). The variation in measured kinetic parameters for the initial pyrolysis stages is higher than that for the main cellulose pyrolysis stage because of the small weight losses in both initial stages, the low rates in the first stage, and the limited temperature range of the second stage.

The E_a for the second initial pyrolysis stage of unmodified cotton agrees with a number of reported values from cellulose pyrolysis. Most values for E_a reported for the initial stages of cellulose pyrolyses or for pyrolyses at or below $300°C$ range from 35 to 42 kcal/mol [6-12]. One report [6] gives values for E_a and $\Delta S^{\ddagger}$ of 39.4 kcal/mol and -8 cal/deg·mol, which are close to those found in the present study.

There have been scattered reports of much lower values for E_a for initial stages of cellulose pyrolysis [13, 14]. For example, Shafizadeh and Bradbury [14] report an E_a of 26 kcal/mol and a ln A of 12 (A in s^{-1}, calculated from their data) for the depolymerization of cotton cellulose in nitrogen in the temperature range 150-190°C. These values correspond well with the values reported here (27.2 kcal/mol and 15.2) for the first initial pyrolysis stage of unmodified cotton in vacuum measured from weight loss.

The kinetic parameters for the two initial stages are different from each other, and both sets are different from those for the main cellulose pyrolysis reaction of unmodified cotton (E_a = 62.2 kcal/mol, $\Delta S^{\ddagger}$ = 29.4 cal/deg·mol). These differences indicate that there are different transition states and therefore different mechanisms for each of the three pyrolysis stages. The negative values of $\Delta S^{\ddagger}$ for the two initial stages indicate that the transition states for these stages cannot involve a disordering of crystalline or semicrystalline regions of cellulose fibers, even though the less ordered regions, where these initial stages occur, are not truly amorphous and are expected to have a fairly high degree of order.

First Stage in Unmodified Cotton

The kinetic parameters of the initial cellulose pyrolysis stages may be used to provide clues and constraints for proposed mechanisms for these processes. A plausible first step in cellulose pyrolysis could involve chain scission. This proposal, of course, is not novel, and there have been a number of reports of kinetics of thermal

decompositions of cellulose as measured by decrease in degree of polymerization [7, 14-16]. The values of E_a reported in three of these studies [14-16] are close to the value found in the present study for the first initial stage in the pyrolysis of unmodified cotton. The relatively low E_a for this stage makes it unlikely that the rate-determining step is a homolytic bond scission, as has been proposed several times. The high negative value of $\Delta S^{\ddagger}$ indicates that the transition state is highly constrained, possibly in a quasicyclic form.

A possible rate-determining step could involve selected sites in the less ordered regions in which cellulose chains have a relatively large degree of freedom of movement. The rate-determining step would be preceded by a conformational change of an anhydroglucose unit from the C1 to the 1C conformation. The 1C conformation is highly unfavored and would account for the high value of the free energy of activation $(\Delta G^{\ddagger})$ of this pyrolysis step. The conformational change would be possible only in the less ordered regions, and the transition state would be highly constrained both in the reacting anhydroglucose unit and in the neighboring units. This high degree of restraint is reflected in the high negative value for $\Delta S^{\ddagger}$. In the 1C conformation, the hydroxyl group on C-6 can approach C-1 in a nucleophilic displacement reaction, possibly by way of a 1,2-anhydride.
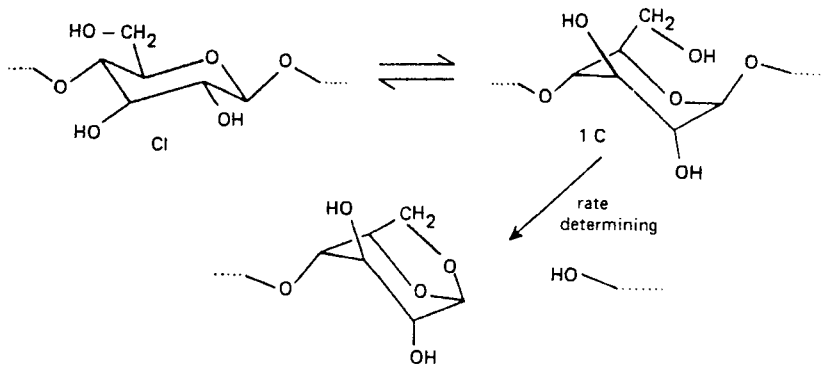
Although such a displacement reaction would be unfavored, it might be facilitated by strain on the C-1 to O-1 bond caused by its attachment to the cellulose chain. In the 1C conformation the O-1 to O-4 distance is approximately 1 A less than it is in the C1 conformation. The low value of E_a makes a heterolytic scission of the C-1—O-1 bond unlikely without solvation, and so an SN_1 mechanism is unlikely here. A similar mechanism involving the 3B instead of the 1C conformation could also be proposed, but the 1C conformation is preferred because levoglucosan exists in that conformation [17].

This proposed mechanism fits the kinetic parameters and the association of this pyrolysis stage with a decrease in degree of polymerization, but it does not account for the weight loss associated with the reaction in the present work. A reexamination of the pyrolysis-mass spectrometric data [3] indicates that the primary volatile products in this range consist of carbon dioxide, water, and carbon monoxide. These products could be formed in secondary steps that occur rapidly after the rate-determining step, which results in chain scission. Relaxation of the broken cellulose chains could permit decarboxylation, dehydration, and decarbonylation reactions to evolve the observed products from cellulose molecules that have been oxidized or otherwise damaged in processing and purification of the cotton fabric.

This proposed mechanism for the first initial stage of cellulose pyrolysis does not involve the atmosphere. The correspondence in kinetics between the present study done in vacuum and previous studies done in nitrogen [14-16] indicates that the reaction is unaffected by the presence or absence of an atmosphere. However, this reaction is not observed in pyrolyses conducted in air because of thermal autooxidation reactions [14] that compete successfully in this temperature range with the nonoxidative process.

Second Stage in Unmodified Cotton

The second initial cellulose pyrolysis reaction is responsible for removal of the cellulose anhydroglucose units in the less ordered regions and depolymerization of cellulose down to the leveling-off degree of polymerization representing cellulose crystallites. The kinetic parameters for this process show significant differences from those for the first stage: E_a is higher, $\Delta S^{\ddagger}$ is less negative, and $\Delta G^{\ddagger}$ is slightly lower. Thus there is a larger energy barrier for this stage, the transition state is constrained (but less so than that for the first stage), and the transition state is not as highly unfavored. A reexamination of pyrolysis-mass spectrometric data [3] for the temperature range covered by this stage showed that the primary pyrolysis products included levoglucosan and 1,4:3,6-dianhydro-α-D-glucopyranose in addition to water, carbon dioxide, and carbon monoxide. The products included none of the furan derivatives or levoglucosenone, which are major primary products from the main pyrolysis stage.

Two possible mechanisms for this stage can be proposed to account for the anhydroglucoses observed as primary products, the kinetic parameters, and the depolymerization aspect of this stage. It is presumed that this stage is an unzipping process rather than a random chain-scission process.

One possible mechanism, which leads to levoglucosan, is similar to that proposed for the first initial pyrolysis stage. In this mechanism

there is a C1 to 1C conformational change in the anhydroglucose unit next to the terminal unit containing the 1,6 anhydride bond. The rate-determining step in this mechanism is the displacement of 0-1 to 0-6 in the penultimate anhydroglucose unit to yield free levoglucosan and a new terminal unit having a 1,6 anhydride bond. This process is in effect an unzipping reaction from a cellulose chain end in which C-1 is not attached to another anhydroglucose unit. The transition state for this mechanism is constrained in the 1C conformation and involves a transannular displacement of 0-1 by 0-6, but the constraint is not as great because the reaction occurs near a chain end. Therefore, the accommodation of a shorter 0-1–0-4 length does not have to be spread through the cellulose chain but can be achieved by displacing only the terminal anhydroglucose unit, resulting in a less negative $\Delta S^{\ddagger}$. This same consideration would account for a higher E_a because the accommodation of the conformational shift by the terminal anhydroglucose unit would result in less strain on the C-1–0-1 bond of the reacting unit.

A second possible mechanism for this stage is an unzipping reaction resulting in 1,4:3,6-dianhydro-α-D-glucopyranose from cellulose chain ends with free 4-OH groups. In this process, the terminal anhydroglucose unit shifts to the 1B conformation. Two nucleophilic displacements leading to anhydride bridges can occur in this conformation: attack by 0-3 on C-6, leading to the 3,6 anhydride bridge and elimination of water, and attack by 0-4 on C-1, leading to the 1, 4-anhydride bridge and freeing the anhydroglucose unit from the chain. It is assumed that the 3,6 bridge is formed first, because 1,4-anhydroglucose has not been reported as a pyrolysis product of cellulose, and 1,4:3,6-dianhydro-α-D-glucopyranose is a
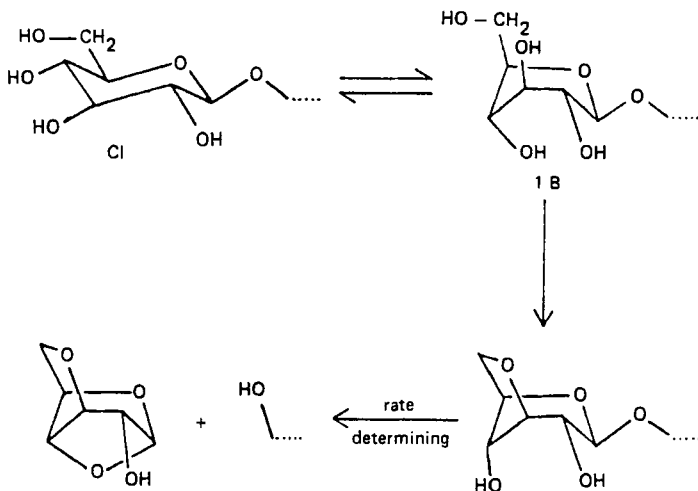
major primary pyrolysis product of cellulose [18]. The rate-determining step could be either displacement because the kinetic parameters are compatible with transition states for both displacements: both transition states are constrained in a single anhydroglucose unit, accounting for the moderately negative $\Delta S^{\ddagger}$, and both involve backside attack on unstrained (and unsolvated) C—O bonds, accounting for the moderately high E_a.

Both of the proposed mechanisms for the second pyrolysis stage are compatible with the kinetic parameters for the stage and cannot be distinguished on this basis alone. Pyrolysis-mass spectrometric data indicate that the products from both mechanisms are formed in this stage and that levoglucosan is formed in greater amounts. Therefore, both processes occur simultaneously in this stage, and the observed kinetic parameters are combinations of those from both mechanisms. The linearity of the Arrhenius plots, particularly that for ball-milled cotton, over a wide temperature range (Fig. 3) indicates that the activation energies are similar.

The proposed mechanisms for this stage are independent of the atmosphere. This feature of the mechanism is supported by the similarity in kinetic parameters for the second stage from this study of pyrolyses in vacuum and other studies of pyrolyses in nitrogen [8, 10, 14]. Competing autooxidation processes partially mask this second stage in pyrolyses conducted in air, but the difference in activation energies makes the unzipping processes predominant over autooxidation processes at the high end of the temperature range for this stage [14] and particularly in experiments conducted at fast heating rates (such as flaming combustion).

Effects of Flame Retardants on First Pyrolysis Stage

The data in Table 1 can be used to measure the effects of add-on of the flame retardants on the initial pyrolysis stages and to compare the effects of the two flame retardants. The two flame retardants have different effects on the first stage. THPS-urea-Na_2HPO_4 at 1% add-on has little effect on the kinetic parameters of the first stage. Above 1% add-on, E_a is slightly decreased and $\Delta S^{\ddagger}$ is more negative than for unmodified cotton. These kinetic parameters are almost constant on 3.5% or higher add-ons. The differences at higher add-ons, with the possible exception of the highest add-on, are probably not significant. A possible variation in the E_a values of 2-3 kcal/mol is to be expected on the basis of replicate experiments and from the nature of the data for the first stage, in which rates are close to zero and weight differences between measurements are close to the limits of accuracy of the TGA equipment. This variation can be seen in Figs. 1 and 2 in which the noise in the region of the first stage is amplified by calculating logarithms of rates close to zero.

The effects of THPS-urea-Na_2HPO_4 on the kinetic parameters (particularly $\Delta S^{\ddagger}$) of the first pyrolysis stage show that there is a larger difference in degree of restraint between the initial state and the transition state in the flame-retardant cotton than in the unmodified cotton. This difference could result from either a less restrained initial state or a more restrained transition state in the flame-retardant cotton. Partial or complete polymerization of the finish as the fabric is heated during the drying step could leave the fibers in a partially swollen state after drying. Thus unfilled voids in parts of the less ordered cellulose regions could provide increased mobility for some of the cellulose chains in the less ordered regions. This increased mobility would result in a lower degree of restraint in the initial state of the anhydroglucose units undergoing conformational changes on the way to the transition state, resulting in a more negative $\Delta S^{\ddagger}$. The same effect might cause more strain on the C-1–0-1 bond being displaced in the transition state, resulting in a lower value for E_a.

The effects of THPOH-NH_3 are less clear and more difficult to explain. The general pattern seems to be an increase of E_a and $\Delta S^{\ddagger}$ by a small add-on of THPOH-NH_3, followed by a possible gradual decrease in the values of these parameters with increasing add-on. A large random variation is apparently superimposed on this trend. It is assumed that this random variation is caused by the very small weight losses over the temperature range of this stage (10-40 μg).

The effect of THPOH-NH_3 on the first pyrolysis stage contrasts strongly with that of THPS-urea-Na_2HPO_4. The change in kinetic parameters caused by the lowest add-on of THPOH-NH_3 is large enough to indicate that the mechanism has been changed significantly from that of unmodified cotton. The mechanistic change in the first stage may be a result of the THPOH monomer being deposited in the less ordered cellulose regions. On drying, the fibers could collapse more completely around the small and mobile monomer molecules, and, after curing, any voids in the less ordered regions would be filled with THPOH-NH_3 polymer. Thus the THPOH-NH_3 finish would immobilize cellulose chains in the less ordered regions so that they cannot move readily enough to permit the conformational changes postulated for this step in unmodified cotton. The rate-determining step would then be a process in which the immobilization is broken, perhaps by breaking bonds in the flame-retardant polymer. This suggestion is supported by the identification of ammonia as a pyrolysis product from initial pyrolysis stages of flame-retardant cotton fabrics [19].

Effects of Flame Retardants on Second Pyrolysis Stage

Small add-ons of both flame retardants have a major effect on the kinetic parameters of the second initial pyrolysis stage (Table 2).

Small add-ons increase E_a and $\Delta S^{\ddagger}$ to values significantly higher than those for the main cellulose pyrolysis stage [5]. This major effect by a small amount of added substance and the existence of discrete cellulose pyrolysis stages may account for the wide range of values reported [2] for "the E_a" of cellulose pyrolysis.

The radical change in kinetic parameters indicates that the rate-determining step of this stage is changed drastically by small amount of the flame retardants. This kinetic effect may result from an immobilization by the flame retardant of a large fraction of the cellulose chains in the less ordered regions beyond isolated points at which chain scission occurs in the first stage. This immobiliza-tion may be caused by partial filling of voids in the less ordered regions by small amounts of flame retardants, resulting in decreased mobility of cellulose chains adjacent to the voids. The rate-deter-mining step would then be the mobilization of cellulose chains in the less ordered regions by breaking bonds in the flame retardant. The identification of ammonia as a volatile product during the initial (but not the main) pyrolysis stages of flame-retardant cottons [19] sup-ports the assumption that the flame retardant is involved in this stage. The high values for E_a would then result from the breaking of enough bonds to mobilize the cellulose chains, and the large positive values of $\Delta S^{\ddagger}$ would result from the lessening of restraint on these cellulose chains. The relaxed chains would then be subject to unzipping proc-esses similar to those in unmodified cotton. However, the rate-determining step would be the chain-freeing process rather than the unzipping process with the resultant change in kinetic parameters from those for unmodified cotton.

The two flame retardants contrast sharply in their effects on the kinetic parameters of the second stage at higher add-ons. This difference may be graphically illustrated in Figs. 5 and 6 which show the effects of add-on of the flame retardant on the E_a for all three cellulose pyrolysis stages.

Add-on of THPOH-NH$_3$ above 3% has little effect on the kinetic parameters of the second stage other than a gradual decrease in E_a and $\Delta S^{\ddagger}$ at the highest add-ons. Thus the effect of add-on of THPOH-NH$_3$ on the kinetic parameters of the second stage is qualitatively similar to its effect on the kinetic parameters of the main cellulose pyrolysis stage except at the lowest add-on. The lower values for the fabric with 11.2% add-on are real, because pyrolysis in vacuum and nitrogen gave very similar values for the kinetic parameters for this stage. The variation from the trend by this fabric is there-fore ascribed to a variation in finishing or processing the fabric.

Larger add-ons of THPS-urea-Na$_2$HPO$_4$ affect the kinetic param-eters of the second stage differently than larger add-ons of THPOH-NH$_3$. The largest effect of THPS-urea-Na$_2$HPO$_4$ is at the lowest add-on. Increasing add-on decreases the values of E_a and $\Delta S^{\ddagger}$
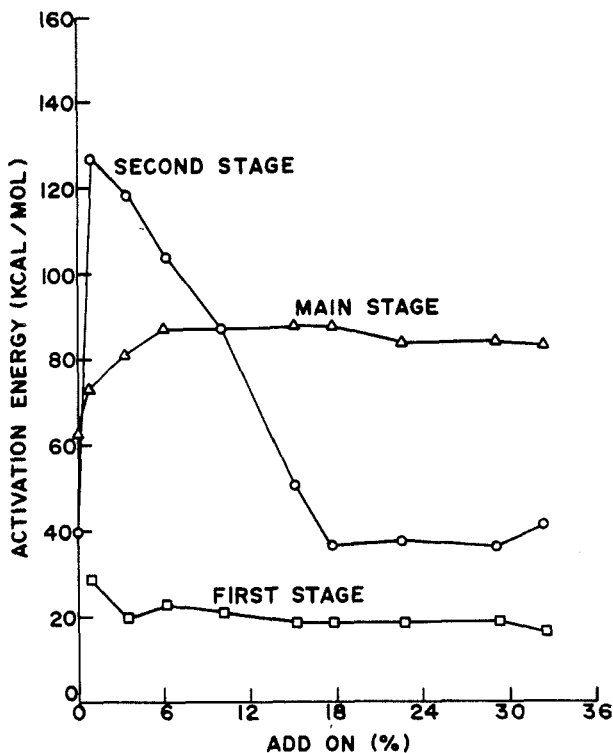
FIG. 5. Plots of E_a against add-on of THPS-urea-Na$_2$HPO$_4$ on cotton. First initial stage ($\square$), second initial stage ($\circ$), main pyrolysis stage ($\triangle$).

continuously until they reach values equivalent for those for unmodi-
fied cotton at an add-on of 17.9%. Increasing add-on above this value
has little further effect on the values of the kinetic parameters for
this stage. Thus a large add-on of THPS-urea-Na$_2$HPO$_4$, but not of
THPOH-NH$_3$, reverses the immobilization of the cellulose chains in
the less ordered regions. A possible explanation for this effect would
be the deposition of THPS-urea-Na$_2$HPO$_4$ polymer in the less ordered
regions in such a manner that some of the voids of the swollen state
of the fibers are retained as they were when they were wet with the
padding solution, but not in such a manner that the voids are filled.
Such an effect would leave the cellulose chains in the less ordered
regions with enough freedom from restraint to allow the second
stage in fabrics with high add-ons of THPS-urea-Na$_2$HPO$_4$ to proceed
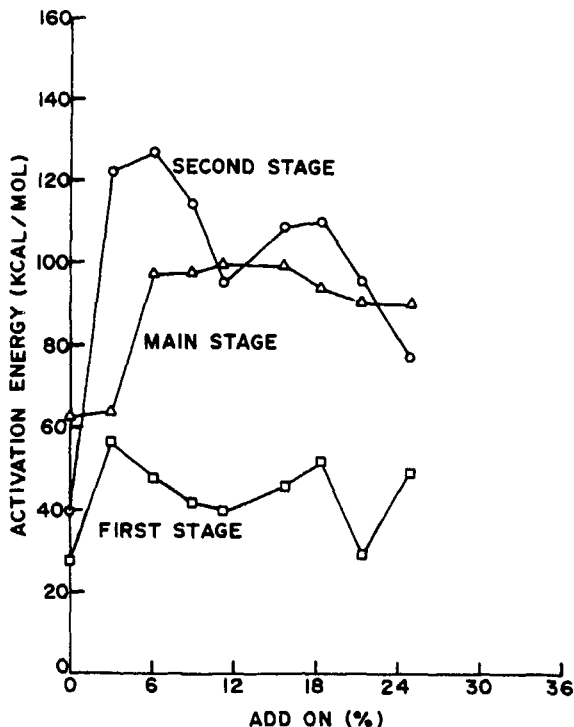in the same way as in unmodified cotton.

FIG. 6. Plots of E_a against add-on of THPOH-NH₃ on cotton.
First initial state (□), second initial stage (○), main pyrolysis
stage (△).

This explanation is reasonable because the THPOH-NH₃ finish is
applied differently from the THPS-urea-Na₂HPO₄ finish. THPOH is
applied to the fabric, which is then dried, allowing the fibers to
collapse around the monomeric reagent. The fabric is then cured in
an almost dry state with gaseous ammonia. Thus the voids in the
less ordered regions are filled with THPOH-NH₃ polymer, and mobil-
ity of the cellulose chains in these regions is restricted, with the
observed results on the kinetic parameters of the second stage. The
THPS-urea-Na₂HPO₄ padding solution contains all the components
of the final polymer. Thus, if some polymerization of the finish
begins as a result of heating during the drying step, sufficient poly-
mer would be built up in the voids in the less ordered regions to keep
open some of the voids as the fabric dries, leaving voids in the less
ordered regions in the dried and cured fabric. If sufficient polymer
is formed in the voids of the wet fabrics with high add-ons of

THPS-urea-Na_2HPO_4 during the drying step, the unfilled voids leave the cellulose chains free enough from restraint to give the observed effects on the kinetic parameters of the second stage. This same effect may be seen in the response of the kinetic parameters of the first stage to higher add-ons of THPS-urea-Na_2HPO_4.

SUMMARY AND CONCLUSIONS

Arrhenius plots were made from thermogravimetric data on vacuum pyrolyses of unmodified cotton and cotton finished with various add-ons of THPOH-NH_3 and THPS-urea-Na_2HPO_4 flame retardants. The plots showed that all pyrolyses occurred in three consecutive stages. The first and second initial stages were associated with the less ordered regions of the cotton fibers, and the main cellulose pyrolysis stage was associated with cellulose crystallites. Cotton cellulose that had been decrystallized by ball milling pyrolyzed in two stages which were identical to the two initial stages for unmodified cotton. The second stage for ball-milled cotton followed first-order kinetics.

The first initial pyrolysis stage in unmodified cotton is characterized by a low E_a and a high negative $\Delta S^{\ddagger}$. This pyrolysis stage has previously been associated primarily with a decreasing degree of polymerization during heating. In the proposed mechanism for this stage, chain scission occurs in selected areas of the less ordered regions by a C1 to 1C conformational change in a cellulose anhydroglucose unit, after which 0-6 displaces 0-1 to give cellulose chains terminated by a 1,6 anhydride bridge and a free 4-hydroxy group. This mechanism is consistent with the kinetic parameters and with product distributions in the temperature of this stage measured by pyrolysis-mass spectrometry.

The second initial pyrolysis stage in unmodified cotton is characterized by a moderately high E_a and a small negative value for $\Delta S^{\ddagger}$. Pyrolysis-mass spectrometric data show that levoglucosan and 1,4:3, 6-dianhydroglucopyranose but no furan derivatives or levoglucosenone are evolved in this stage. Two mechanisms involving cellulose chain unzipping reactions are proposed to account for the data. One mechanism leading to levoglucosan involves unzipping from a cellulose chain end having a 1,6 anhydride bridge by a process similar to that of the first pyrolysis stage, but involving the anhydroglucose unit second from the end of the chain. The other proposed mechanism is an unzipping of cellulose chains having a free 4-hydroxy group on the terminal anhydroglucose unit. This mechanism involves displacement of 0-6 by 0-3, preceded or followed by displacement of 0-1 by 0-4 to give 1,4:3,6-dianhydroglucopyranose and a new free 4-hydroxyl group. The kinetic parameters are consistent with both proposed mechanisms, and the product distribution indicates that both processes occur simultaneously.

Small add-ons of THPS-urea-Na_2HPO_4 flame retardant have little effect on the kinetic parameters of the first pyrolysis stage. Larger add-ons of the flame retardant decrease E_a and make $\Delta S^{\ddagger}$ more negative. This effect indicates that a lessening of restraint on cellulose chains occurs in the initial state of the pyrolysis. In contrast, small add-ons the $THPOH-NH_3$ flame retardant increase E_a and make $\Delta S^{\ddagger}$ positive, and larger add-ons slightly decrease these values. This effect is attributed to an immobilization of cellulose chains in the less ordered regions by the $THPOH-NH_3$ polymer so that bonds in the flame retardant must be broken before the cellulose chains can move to allow anhydroglucose units to assume the conformation leading to chain scission.

Small add-ons of both flame retardants cause large increases in the values of E_a and $\Delta S^{\ddagger}$ for the second initial pyrolysis stage. This effect occurs because the flame retardant fills voids in the less ordered regions. This filling reduces the mobility of the cellulose chains in the less ordered regions and retards the chain unzipping processes. Increasing the add-on of $THPOH-NH_3$ flame retardant has little further effect on the kinetic parameters for this stage. Increasing the add-on of THPS-urea-Na_2HPO_4 to 18% causes the E_a and $\Delta S^{\ddagger}$ for the second stage to decrease to values typical of unmodified cotton. This effect is attributed to partial polymerization of the flame retardant when the fabric is dried before curing. This polymerization keeps the less ordered regions in a partially swollen state as the fibers collapse when dried and leaves enough flexibility in the cellulose chains of the less ordered regions for the second stage to occur normally as in unmodified cotton. THPOH remains monomeric during drying and therefore allows the cotton fiber to collapse, resulting in the filling of voids with polymer when the THPOH is cured with ammonia vapor.

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REFERENCES

[1] F. Shafizadeh, Adv. Carbohydr. Chem., 23, 419 (1968).
[2] M. Lewin and A. Basch, in Flame-Retardant Polymeric Materials, Vol. 2 (M. Lewin, S. M. Atlas, and E. Pearce, eds.), Plenum, New York, 1978, pp. 1-41.

[3] W. E. Franklin and S. P. Rowland, Text. Res. J., 49, 170 (1979).

[4] W. E. Franklin, J. Macromol. Sci.-Chem., A19, 95 (1983).

[5] W. E. Franklin, J. Fire Retardant Chem., 9, 263 (1982).

[6] E. J. Murphy, J. Polym. Sci., 58, 649 (1962).

[7] D. P. C. Fung, Tappi, 52, 319 (1969).

[8] A. E. Lipska and W. J. Parker, J. Appl. Polym. Sci., 10, 1439 (1966).

[9] A. G. W. Bradbury, Y. Sakai, and F. Shafizadeh, Ibid., 23, 3271 (1979).

[10] C. Fairbridge, R. A. Ross, and S. Sood, Ibid., 22, 497, (1978).

[11] W. K. Tang and W. K. Neill, J. Polym. Sci., Part C, 6, 65 (1964).

[12] P. K. Chatterjee, J. Appl. Polym. Sci., 12, 1859 (1968).

[13] K. Kato and N. Takahashi, Agric. Biol. Chem., 31, 519 (1967).

[14] F. Shafizadeh and A. G. W. Bradbury, J. Appl. Polym. Sci., 23, 1431 (1979).

[15] A. Pacault and G. Sauret, C. R. Acad. Sci., 246, 608 (1958).

[16] M. A. Millet, L. J. Western, and J. J. Booth, Tappi, 50, 74A (1967).

[17] R. E. Reeves, J. Am. Chem. Soc., 71, 2116 (1949).

[18] F. Shafizadeh, R. H. Furneaux, T. T. Stevenson, and T. G. Cochran, Carbohydr. Res., 61, 519 (1978).

[19] W. E. Franklin, Anal. Chem., 51, 992 (1979).