

# Thermal Degradation of 6-Chlorocellulose and Cellulose-Zinc Chloride Mixture

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## Synopsis

Introduction of chlorine as a substituent or addition of zinc chloride lowers the decomposition temperature of cellulose and suppresses the flaming combustion by reducing the rate of production and the total amount of combustible volatiles. Samples of 6-chloro-6-deoxycellulose, with a low D.S., start to decompose with dehydrohalogenation. The resulting hydrogen chloride catalyzes the transglycosylation, dehydration, condensation and charring reactions as evidenced by production of large amounts of levoglucosenone, condensed tar, and char. A similar effect was produced by zinc chloride, except that it provided less levoglucosenone and more 3,6-anhydroglucose derivatives. Also, a larger amount of the additive was required to reach the optimal effect.

## INTRODUCTION

Thermal degradation of cellulosic materials and related model compounds<sup>1,2,3</sup> have been investigated in order to determine the sequence of reactions involved in the initiation, propagation, and termination of flaming combustion. In the previous article in this series,<sup>4</sup> it was shown that 6-chloro sugar derivatives are thermally less stable than the corresponding unsubstituted carbohydrates. When heated, they generate hydrogen chloride, which catalyzes a series of heterolytic reactions including transglycosylation, dehydration, inter- and intramolecular etherification, and condensation. The products of the latter reactions are ultimately carbonized through free-radical reactions producing large amounts of char.

A similar effect is produced on addition of zinc chloride, which as a Lewis acid catalyzes the sequence of dehydration and charring reactions.<sup>5</sup> These studies have been extended to the pyrolysis of cellulose after chlorination or addition of zinc chloride, in order to determine the role of chlorine derivatives in promoting the charring reactions at the expense of the combustible volatiles which fuel the flaming combustion.<sup>6</sup>

## EXPERIMENTAL

### Analytic Approach

Various methods of thermal analysis, including DTA (differential thermal analysis), TG (thermogravimetry), and DTG (derivative of thermogravimetry), were used to determine the temperature range of intensity of the concurrent and consecutive pyrolytic reactions.<sup>4</sup> The nature of these reactions was investigated by the analysis of the products formed under various conditions, including dynamic scanning and isothermal or flash pyrolysis.

### Preparation of Samples

Samples of 6-chloro-6-deoxycellulose were prepared by a modification of a method reported by Horton and co-workers.<sup>7</sup> Microcrystalline cellulose (Whatman CF-11) (100 g) was first activated by swelling in liquid ammonia (500 ml) for 2 hr. It was then mixed with DMF (dimethylformamide, 500 ml). The mixture was kept overnight and filtered. The wet cellulose was stirred twice with other batches of DMF (500 ml each) in a Waring blender for 3 min and filtered. The filtrate was finally heated in another batch of DMF on a steam bath overnight. A stirred suspension of the activated cellulose in DMF (200 ml) was treated with methanesulfonyl chloride (200 ml) by dropwise addition at 63°–64°C. Samples of 6-chloro-6-deoxycellulose with varying degrees of substitution were then obtained by periodic withdrawal of samples (5–10 ml) and pouring in ice water (300 ml) and filtering the precipitate. The products were purified by stirring in an aqueous solution (400 ml) of sodium carbonate, filtering, washing with water (5 × 500 ml), and finally drying in vacuo at 50°C.

The D.P. (degree of polymerization) of each sample was estimated indirectly through measurement of the intrinsic viscosity in Cadoxen,<sup>8</sup> and the D.S. (degree of substitution) was calculated from the chlorine content.

Properties of the products obtained are listed in Table I. Samples of the cellulose containing varying amounts of zinc chloride were obtained by adding the calculated amount of catalyst in methanol and evaporating the solvent under vacuum.

### Analytic Methods

Thermal, UV (ultraviolet), IR (infrared), and ESR (electron spin resonance) analyses were conducted by the methods and equipment described before.<sup>4,5</sup> Dynamic thermal analysis experiments were programmed at the rate of 15°C/min.

Melting points were determined with a Fischer-Johns apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on silica gel IB-F (Baker-flex) irrigated with benzene-tetrahydrofuran (95:5). The spots were detected by spraying with ethanolamine. Gas-liquid chromatography (GLC) was performed with a Varian 1800 instrument equipped with thermal conductivity and hydrogen flame detectors. The volatile pyrolysis products were analyzed using a 10 ft × 0.125 in. stainless column packed with 80/100 mesh

TABLE I  
Preparation of 6-Chloro-6-deoxycellulose

Sample	Reaction conditions		Product			
	Temperature, °C	Time, hr	Color	Chlorine, %	D.S.	D.P.
A	63	1.5	white	0.40	0.018	222
B	63	2.5	white	0.50	0.023	226
C	63	3.7	white	1.16	0.053	228
D	63	7.1	white	1.96	0.091	211
E	63	19.6	tan	4.12	0.192	200 <sup>a</sup>
F	63	48.6	tan	5.72	0.270	189 <sup>a</sup>

<sup>a</sup> Product was partially soluble in Cadoxen.

Chromosorb W-DMCS as the support and 20% Carbowax 20M-TPA as the stationary phase. Composition of the tar fraction was determined by hydrolysis with boiling 1*M* hydrochloric acid for 4 hr and analysis of the sugar derivatives before and after the acid hydrolysis. The monomeric components of these mixtures were trimethylsilylated and analyzed by GLC, using a 8 ft × 0.125 in. stainless steel column packed with acid-washed, 100/120 mesh Chromosorb W-DMCS as the support and 3% OV-17 as the stationary phase. Water was analyzed with the same column as the volatile pyrolysis products. Quantitative GLC data were obtained by using a digital integrator calibrated with standard samples. Mass spectroscopy was performed on a Varian-Mat III GLC mass spectrometer at 80 eV after the compounds were resolved with an 8 ft × 0.125 in. stainless steel column packed with 80/100 Gas Chrom Q as the support and 10% Silar-5CP as the stationary phase. The microanalyses were performed by a commercial laboratory.

### Pyrolysis Products

The hydrogen chloride formed on programmed heating of chlorinated cellulose samples was recovered as silver chloride and analyzed as before.<sup>4</sup>

Water, carbon dioxide, and some of the low molecular weight organic compounds evolved on programmed heating of sample F (D.S. 0.270) were monitored by GLC mass spectrometry as reported previously.<sup>9</sup>

For flash pyrolysis small samples (1.5 mg) were heated to 500°C in less than 2 sec in a small furnace directly attached to the GLC instrument. Isothermal pyrolysis was carried out by heating larger samples (100 mg) in a current of nitrogen for 8 min in a modified Sargent microcombustion unit and the products were separated and analyzed as before.<sup>4,5,10-13</sup> The total amount of acids calculated as hydrogen chloride was determined by titrating the volatiles with 0.1*N* solution of sodium hydroxide. For direct analysis of the volatiles and water, small samples (5 mg) were pyrolyzed at 500°C or lower temperatures in a modified Perkin-Elmer pyrolysis unit directly connected to the GLC instrument.

## RESULTS

### 6-Chloro-6-deoxycellulose

A comparison between the dynamic thermal analysis data for pure cellulose and partially substituted 6-chloro-6-deoxycellulose (sample B, D.S. 0.023), shown in Figures 1(a) and 1(b), indicates major differences in the pyrolytic properties of the two compounds. Pure cellulose rapidly depolymerizes within the temperature range of 325°–375°C. The depolymerization involves substitution of the 1 → 4β-glycosidic linkage in cellulose by 1 → 6β- and other glycosidic linkages which provide a tarry mixture containing levoglucosan, other anhydrosugars, and some randomly linked low molecular weight sugar derivatives. Evaporation of the tar resulting from the transglycosylation reactions<sup>12</sup> gives a major endotherm and a rapid rate of weight loss (up to 40% per min) at 325°–375° and leaves only a small amount of carbonaceous char (6.5%) at 400°C. For the

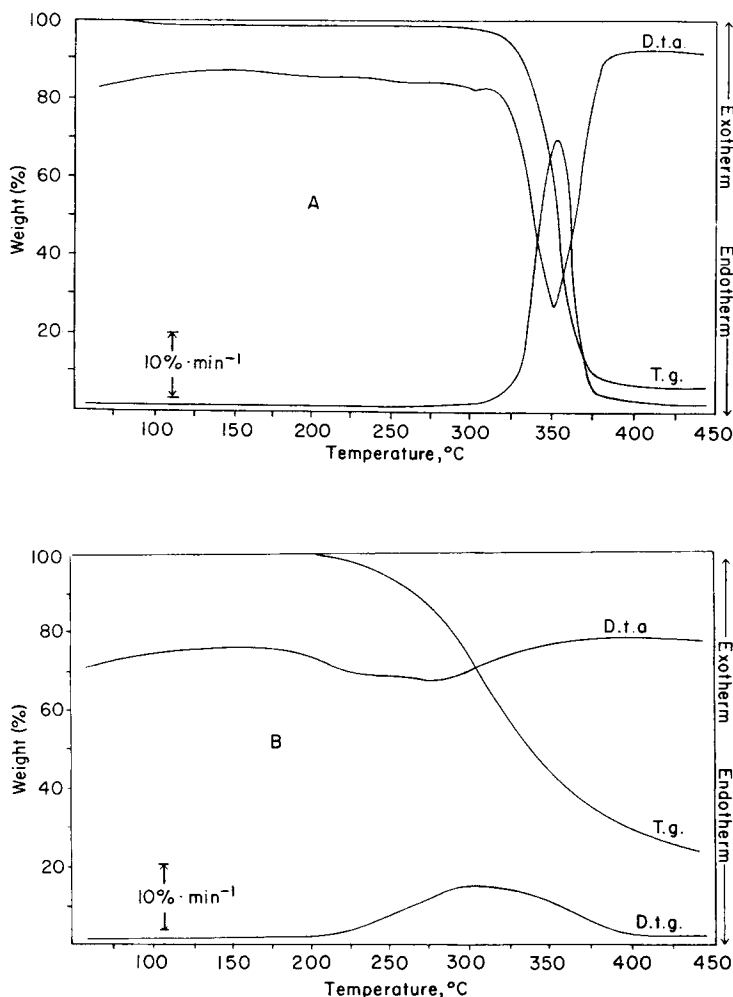


Fig. 1. Thermal analysis curves of: (a) microcrystalline cellulose, (b) 6-deoxy-6-chlorocellulose, D.S. 0.023, (c) 6-deoxy-6-chlorocellulose, D.S. 0.27, and (d) cellulose containing 5% zinc chloride.

chlorinated cellulose, the thermal decomposition starts at  $\sim 200^\circ\text{C}$ , with a very slight endotherm and gradual weight loss that leaves about 30% carbonaceous char at  $400^\circ\text{C}$ . The initial endotherm and the shift toward decomposition at lower temperatures were more pronounced for samples with higher chlorine content, as shown in Figure 1(c) for sample F with a D.S. of 0.27. The thermal analysis features of the above compounds and other samples of 6-chloro-6-deoxycellulose with varying degrees of substitution are summarized in Table II.

The nature of chemical reactions occurring at various temperatures was investigated by monitoring the volatile products and analysis of the residues. On heating sample B (D.S. 0.023), hydrogen chloride started to evolve at  $\sim 200^\circ\text{C}$ , indicating that the first thermal event involves dehydrohalogenation of the molecule. More than 80% of the combined chlorine disappeared on heating the sample to  $250^\circ\text{C}$  at a rate of  $15^\circ\text{C}/\text{min}$ .

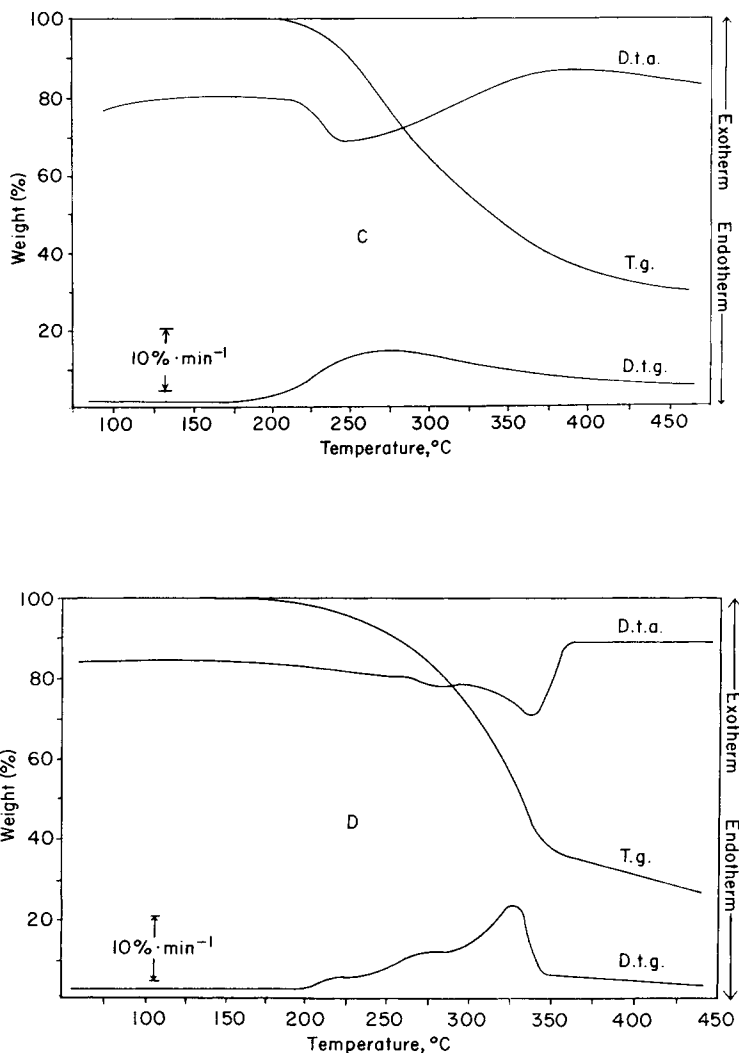


Fig. 1. (Continued from the previous page.)

The results obtained from scanning mass spectrometry of the volatiles formed on heating a sample of chlorinated cellulose (sample F, D.S. 0.27) within the temperature range of 100°–400°C are summarized in Figure 2. These data show the evolution of water ( $m/e$  17), carbon dioxide ( $m/e$  44), 2-furaldehyde ( $m/e$  95 and 96), 5-methyl-2-furaldehyde ( $m/e$  109 and 110),  $\beta$ -angelicalactone (4-hydroxy-2-pentenoic acid) ( $m/e$  98), and levoglucosone (1,6-anhydro-3,4-dideoxy- $\beta$ -D-glycero-hex-3-enopyranos-2-ulose) ( $m/e$  98 and 126) in the early stages of heating. Formation of the above products was confirmed by further isothermal and flash pyrolysis of various samples of chlorinated cellulose.

In the flash pyrolysis, small samples of chlorinated cellulose were heated to 500°C in less than 2 sec, and the volatile products were directly analyzed by GLC. The results, listed in Table III, showed a substantial proportion of levoglucosone (8%–13%) derived from a combination of transglycosylation and dehydration (see scheme 1) and smaller quantities of 2-furaldehyde, 5-methyl-2-

TABLE II  
Thermal Analysis Features of 6-Chloro-6-deoxycellulose and Cellulose Containing Zinc Chloride

Sample	Substrate		DTA peaks, °C		DTG peaks, °C Dec.	TG residue at 400 °C, %
	D.S.	Additive, %	Range	Peak		
<i>Microcrystalline Cellulose</i>						
			300-375	340	351	6.5
<i>6-Chloro-6-deoxycellulose</i>						
A	0.018		210-360	225, <sup>a</sup> 285	300, <sup>a</sup> 335 <sup>a</sup>	12.0
B	0.023		200-360	225, <sup>a</sup> 280 <sup>a</sup>	300, 325 <sup>a</sup>	30.0
C	0.053		200-350	225, 280	285	29.2
D	0.091		200-345	225, 280	230, <sup>a</sup> 280	32.0
E	0.192		205-340	225, 275	215, 260	31.5
F	0.270		190-340	220	240	31.5
<i>Cellulose Containing Zinc Chloride</i>						
		1	275-365	345	340	12.2
		3	200-360	333	275, <sup>a</sup> 327	30.5
		5	200-358	275, <sup>a</sup> 333	275, <sup>a</sup> 327	31.0
		7	175-340	225, <sup>a</sup> 310 <sup>a</sup>	265, 310	40.0
		10	175-330	210, <sup>a</sup> 260, <sup>a</sup> 305 <sup>a</sup>	265, 310	41.3

<sup>a</sup> A shoulder.

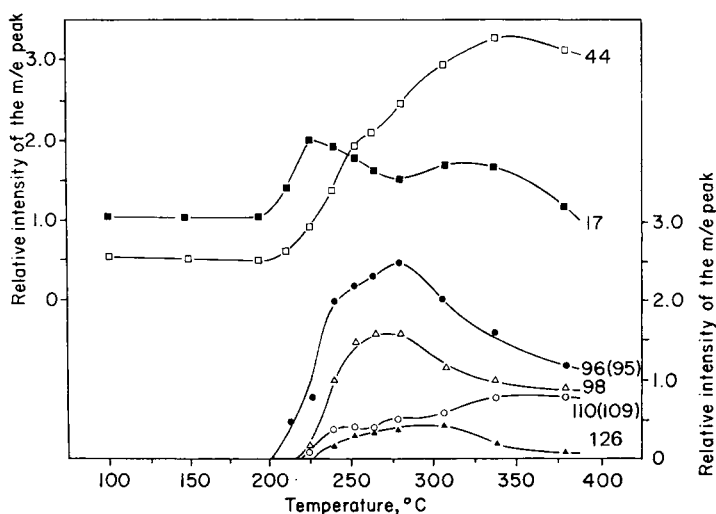


Fig. 2. Mass spectrometry of the pyrolysis products of 6-chloro-6-deoxycellulose (sample F, D.S. 0.270).

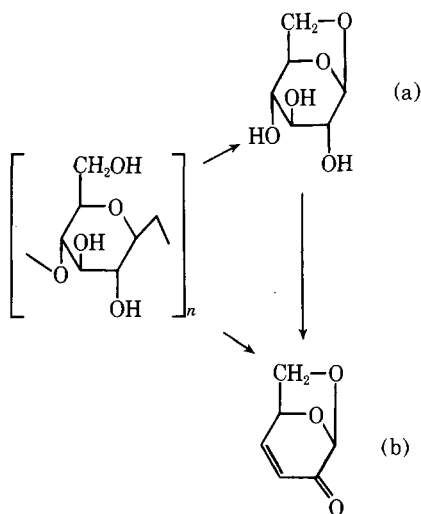
furaldehyde,  $\beta$ -angelicalactone, and levulinic acid, which are derived through acid-catalyzed dehydration reactions.

Other samples of the chlorinated cellulose derivative with a D.S. of 0.023 were preheated at different temperatures ranging from 200° to 300°C, which resulted in a weight loss of 2.1%–29.5% accompanied by dehydrohalogenation. Flash pyrolysis of the preheated substrates showed a sharp decrease in the production of the dehydration products. The yield of levoglucosenone was reduced from 12.5% to 3.3%–0.6%, indicating that the hydrogen chloride released at the initial

TABLE III  
Volatile Products Formed on Flash Pyrolysis of 6-Chloro-6-deoxycellulose Samples Before and After Preheating

D.S.	Substrate		Products formed at 500°C, %				
	Preheating, °C	Weight loss, %	2-Furaldehyde	5-Methyl-2-furaldehyde	$\beta$ -Angelicalactone	Levoglucosone	Levulinic acid
0.000	—	—	1.2	0.5	0.2	1.4	T
0.018	—	—	1.8	0.7	0.4	12.8	T
0.023	—	—	1.0	0.8	0.7	12.5	T
	200	2.1	0.2			3.3	
	220	2.8	0.3			3.0	
	240	5.1	0.3			3.1	
	250	7.1	0.4			3.2	
	260	10.2	0.3			1.3	
	280	17.8	0.3			1.3	
	300	29.5	0.3			0.6	
0.053	—	—	1.0	0.9	0.6	13.4	T
0.091	—	—	1.1	0.6	0.4	10.6	0.2
0.192	—	—	1.3	0.6	0.4	11.4	1.2
0.270	—	—	1.1	0.6	0.4	8.3	1.2

stage of pyrolysis catalyzes the subsequent transglycosylation and dehydration of the unchlorinated sugar units within the molecule.



Scheme 1. Production of levoglucosan (a) and levoglucosenone (b) from cellulose.

The nature of the secondary reactions was investigated by isothermal pyrolysis at 500°C, which provided a cross section of the pyrolytic products. These products, listed in Table IV, consisted of a variety of volatile organic compounds, hydrogen chloride, carbon dioxide, water, carbonaceous char, and a tar fraction.

GLC analysis of the volatile fraction gave the same type of compounds that was obtained by flash pyrolysis at 500°C. However, the yield of levoglucosenone was much lower because of the instability and further decomposition of this product under the pyrolytic condition as described in a previous publication in

TABLE IV  
Pyrolysis Products of 6-Chloro-6-deoxycellulose and Cellulose Containing Zinc Chloride at 500°C

Product	Yield, %											
	6-Chloro-6-deoxycellulose						Cellulose + zinc chloride					
	A	B	C	D	E	F	Neat	1%	3%	5%	7%	10%
Acetic acid	T <sup>a</sup>	T	T	T	T	T	T	T	T	T	T	T
$\alpha$ -Angicalactone	T	T	T	T	T	T	T	T	T	T	T	T
2-Furaldehyde	0.7	0.6	0.6	0.7	1.0	1.0	0.4	1.4	1.7	1.9	2.0	2.0
5-Methyl-2-furaldehyde	0.4	0.5	0.3	0.6	1.0	1.0	T	0.4	0.5	0.3	0.2	0.2
2-Furfuryl alcohol	T	T	T	0.1	0.3	0.3	T	T	T	T	T	T
$\beta$ -Angicalactone	T	T	T	T	T	T	T	T	T	T	T	T
Levogluconone	0.3	0.4	0.9	0.6	0.3	0.3	0.3	0.3	0.2	0.1	<0.1	<1.0
Total acid (HCl, carboxylic acids)	3.4	3.4	3.6	4.6	6.8	9.7	2.5	2.7	2.8	3.0	3.3	3.9
Carbon dioxide	3.1	2.7	3.0	2.9	3.3	3.5	6.0	19.6	20.4	23.1	27.2	29.0
Water	26.5	28.4	27.6	26.3	26.9	24.0	12.0	19.6	29.1	30.8	35.4	42.4
Char	21.0	22.7	26.4	28.4	28.5	29.2	8.0	19.6	36.8	30.5	24.7	14.7
Tar	35.6	31.2	26.7	25.6	24.8	22.6	65.8	48.6	48.6	30.5	24.7	14.7
Before acid hydrolysis												
3,6-anhydro-D-glucose	(2.8) <sup>b</sup>	(0.5)	(0.3)	(0.4)	(0.6)	(1.4)	T	(3.3)	(4.8)	(5.9)	(6.9)	(6.7)
1,6-anhydro- $\beta$ -D-glucopyranose	(10.0)	(5.2)	(4.5)	(4.0)	(3.2)	(1.5)	(46.2)	(16.8)	(8.1)	(9.1)	(6.0)	(4.2)
1,6-anhydro- $\beta$ -D-glucofuranose	(2.0)	(0.4)	(0.3)	(0.4)	(0.3)	(0.1)	(3.6)	(1.2)	(0.3)	(0.3)	(0.2)	T
After acid hydrolysis												
3,6-anhydro-D-glucose	(8.0)	(8.6)	(7.7)	(8.2)	(12.1)	(17.6)	(1.5)	(14.4)	(21.0)	(23.3)	(25.3)	(37.9)
D-glucose	(20.0)	(8.9)	(12.8)	(8.0)	(6.8)	(2.1)	(77.3)	(30.0)	(21.4)	(18.2)	(11.2)	(10.1)

<sup>a</sup> Trace amount.

<sup>b</sup> Figures in parentheses are percentages of the tar fraction.



this series.<sup>13</sup> The instability of levoglucosenone was further demonstrated by isothermal heating of various samples at temperatures ranging from 300° to 450°C. The resulting data (see Table V) show that more levoglucosenone is obtained on pyrolysis at low temperatures. On pyrolysis at 300°C, chlorinated cellulose samples gave 8% to 9% levoglucosenone, which compares favorably with the 9% to 12% yield obtained from cellulose on addition of an Arrhenius acid<sup>13,14</sup> under similar conditions.

The tar formed on pyrolysis of pure cellulose contained mainly levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) (46.2%), its furanose isomer (3.6%), and polymeric transglycosylation products,<sup>12</sup> which on hydrolysis provided large quantities of D-glucose (77.3%) and very little 3,6-anhydro-D-glucose. The tar fractions formed from the pyrolytic reactions of the chlorinated cellulose samples contained comparatively little levoglucosan and other anhydro sugars and on hydrolysis gave small amounts of D-glucose (2%–20%) but relatively larger quantities of 3,6-anhydro-D-glucose (8.0%–17.6%).

These data indicate the production of nonglycosidic condensation products which, on further heating, could char through the homolytic cleavage of the substituents on the carbon chain.<sup>4,5,13</sup> The progress of the latter reactions was investigated by ESR spectrometry. ESR scanning of the pyrolysis residues of 6-chloro-6-deoxycellulose (sample F) within the temperature range of 150°–300°C showed that development of carbonaceous char at temperatures above 230°C is accompanied by increasing production of stable free radicals.

### Cellulose–Zinc Chloride Mixture

Thermal analysis curves of a sample of cellulose containing 5% ZnCl<sub>2</sub> [Fig. 1(d)] show a broad decomposition endotherm in the range of 200°–358°C which peaks at 333°C. The decomposition endotherm is accompanied by ~64% weight loss, leaving 34% charred residue at 400°C. The thermal analysis features of other samples of cellulose containing varying amounts of zinc chloride are summarized in Table II. These data show that higher proportions of catalyst lower the decomposition temperature even further and result in a very broad endotherm with no distinct peaks, apparently due to the overlapping of a variety of concurrent and consecutive reactions.

The similarity between the thermal decomposition of samples of chlorinated cellulose and cellulose containing various amounts of zinc chloride was further demonstrated by isothermal pyrolysis at 300°, 400°, and 500°C. As shown in Tables IV and V, both treatments were qualitatively the same but quantitatively different. Samples containing zinc chloride provide more char and 2-furaldehyde

TABLE V  
Major Volatile Pyrolysis Products of 6-Chloro-6-deoxycellulose and Cellulose–Zinc Chloride Mixture Formed at 300° and 400°C

Product	Temp., °C	Yield, %											
		6-Chloro-6-deoxycellulose						Cellulose with zinc chloride					
		A	B	C	D	E	F	Neat	1%	3%	5%	7%	10%
2-Furaldehyde	400	0.9	0.8	0.6	0.5	0.4	0.4	0.4	1.6	2.1	1.8	2.0	2.1
	300	0.3	0.3	0.4	0.4	0.4	0.5	0.4	0.7	1.9	0.8	1.4	1.3
Levoglucosenone	400	7.9	5.3	5.1	4.7	4.8	4.5	0.7	2.1	1.8	2.1	2.2	1.4
	300	7.8	7.7	8.1	9.2	8.5	7.2		1.6	2.2	1.7	2.3	2.2

but less levoglucosenone. Also, their tar fractions after acid hydrolysis provide more 3,6-anhydro-D-glucose.

## CONCLUSIONS

This study shows that the presence of an acidic material, whether introduced as an additive or generated during the pyrolysis process, lowers the temperature of decomposition, suppresses the production of the combustible volatiles, and spreads the evolution of these materials over a wider range of temperature, resulting in a major reduction in the rate of release of the combustible gases which fuel the flaming combustion.<sup>6</sup> These effects are produced by catalyzing the transglycosylation, dehydration, and condensation reactions, which lead to charring as shown for model compounds.

For the partially substituted 6-chloro-6-deoxycellulose, the initial decomposition reactions begin with the dehydrohalogenation at  $\sim 200^\circ\text{C}$ , which is about  $100^\circ\text{C}$  lower than the initial decomposition temperature of pure cellulose. The released hydrogen chloride then catalyzes a series of heterolytic reactions including transglycosylation, dehydration, inter- and intramolecular etherification, and other condensation reactions, which provide levoglucosenone, other volatile compounds, and tarry condensation products. Finally, homolytic cleavage of the substituents on the carbon chain of the condensation products gives a carbonaceous char, still containing trapped and relatively stable free radicals. The involvement of acid-catalyzed dehydration reactions is clearly indicated by the production of relatively large quantities of levoglucosenone at lower temperatures or on flash pyrolysis when further decomposition of the product is hampered. The yield of this product dropped dramatically (from 12.5% to 0.6%) when the combined halogen was eliminated by preheating a sample to  $300^\circ\text{C}$ . Furthermore, both dynamic and isothermal experiments showed that the extent of charring reaches a plateau with about 2% substitution, indicating that only a small proportion of combined halogen is necessary to achieve the maximum catalytic effect. The increased charring results not only from acid-catalyzed dehydration reactions but also from the acid-catalyzed condensation of the intermediate products which can no longer escape from the heated zone by evaporation and remain to be roasted and charred.

Lewis acid, represented by zinc chloride, showed an effect similar to that of hydrogen chloride in catalyzing the dehydration, condensation, and charring reactions. However, the experimental results revealed some distinct differences between these two types of catalysts. Addition of zinc chloride produced more char and less levoglucosenone. These data are confirmed by the previous investigations of cellulose and related model compounds, which show that the pyrolysis products contain more levoglucosenone when Arrhenius acids are used as a catalyst,<sup>13,14</sup> because zinc chloride is a much more effective catalyst for the condensation and charring of the intermediate dehydration products, such as levoglucosenone, than the Arrhenius acids. Analysis of the tar fraction also shows that more 3,6-anhydro- $\beta$ -D-glucose is formed in the presence of zinc chloride.

In terms of catalytic efficiency, however, the combined halogen is more effective in smaller quantities because it could release hydrogen chloride at the right time, when the pyrolytic reactions are initiated. Furthermore, the released

hydrogen chloride could enter both the condensed and the gas phase reactions. The latter effect is particularly important because a synergistic result may be expected when the active component of a flame retardant such as antimony chloride<sup>6,15</sup> could promote the dehydration and charring in the condensed phase and suppress the combustion of the organic volatiles in the gas phase.

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