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Reaction Mechanisms in Cellulose Pyrolysis

A Literature Review

by
Peter M. Molton
T.F. Demmitt

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REACTION MECHANISMS IN CELLULOSE PYROLYSIS

A LITERATURE REVIEW

by
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REACTION MECHANISMS IN CELLULOSE PYROLYSIS: A LITERATURE REVIEW

I. INTRODUCTION

During some of the very earliest work in Organic Chemistry, performed during the latter half of the nineteenth century, the pyrolysis of cellulose and cellulosic materials was a prominent field of investigation. Methods were developed for the pyrolysis of wood in particular, to make methanol, acetic acid, charcoal, wood preservatives, and other materials. With the advent of the Fischer-Tropsch process on the one hand, and access to cheap petroleum on the other, these processes rapidly became obsolete.

Consequently, research to elucidate the reaction mechanisms and pathways in cellulose pyrolysis was largely abandoned, except in a purely academic sense, since there was no longer any incentive to, for instance, increase the yield of methanol obtained from wood. Although there was a brief revival of interest in nonpetroleum sources of fuel and chemicals during the Second World War, this was concentrated mainly on the development of producer gas-operated vehicles (in Germany), and subsequently on the manufacture of methanol by the Fischer-Tropsch process (in S. Africa).

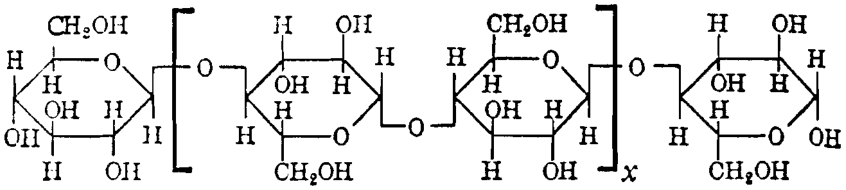
With the realization that petroleum supplies are running low and may be interrupted, and with the ever-increasing amounts of urban and agricultural waste being generated, there has recently been a resurgence of interest in the pyrolysis of cellulose-containing materials (e.g., wood, manure, and paper) as a source of both chemicals and fuel, and to reduce solid waste disposal problems. A number of processes for pyrolysis, notably the Garrett Process, are in various stages of commercialization. It seems almost inevitable that more importance will be attached to such processes in the future, since the problems which they are designed to alleviate will only become more acute with increasing industrial and urban development.

In parallel with the history of cellulose use as a fuel, the use of cellulose-derived fibers in textiles has been extended and many advances have been made in the knowledge of the structure, properties, and combustion characteristics of cellulose. In addition, mechanistic studies have been performed on the reactions of cellulose with water, alkali, and other substances.

Since the report of Hoppe-Seyler in 1871,(1) there has been much interest in the various decomposition reactions of cellulose, until at the present time there is a voluminous literature on the subject. Unfortunately, the review literature has not kept pace with the field; there are comprehensive and competent reviews in several restricted areas of cellulose properties, such as those of MacKay and David,(2) Shafizadeh,(3) and Broido and Kilzer,(4) dealing with various aspects of textile flameproofing, and that of Weiss(5) dealing with the conversion of cellulose to liquid fuels, but to our knowledge there has been only one attempt to review the reaction mechanisms involved in the decomposition of cellulose and related carbohydrates.(6) This is unfortunate, since more detailed understanding of these mechanisms could lead to considerable savings in research and development costs for the various industrial processes now being contemplated, point out new areas where basic research would be of use, and in addition be of considerable intrinsic scientific interest.

II. STRUCTURE OF CELLULOSE

The primary chemical structure of cellulose is that of a linear polymer of glucopyranose units, described more accurately as poly-(β-1,4-glucopyranose):



Other carbohydrates, and chain branching may occur to a very minor extent in natural cellulose. The degree of polymerization (DP)

varies widely according to the cellulose source and method of isolation. Hamilton and Mitchell(7) have summarized some of the available data on cellulose structure. These authors noted that natural (native) cellulose may have a DP between 3,500 and 10,000, while treated chemical cottons are significantly degraded (DP 200-2,100). Regenerated celluloses and cellulose derivatives such as nitrocellulose and cellulose acetate have DP values of between 175 and 550. Apart from the wide variation in the DP of various forms of cellulose, there are also major differences in the degree of crystallinity and crystal orientation in different samples. Basch and Lewin(8) have shown in a very thorough study that many of the reported literature differences in the behavior of cellulose on vacuum pyrolysis may be attributed to these differences in crystal structure and orientation as well as to variations in the DP.

As will be shown in the following pages, the purity and origin of the cellulose used in any reaction mechanism research is of critical importance, particularly since many of the materials commonly thought of as being relatively pure cellulose may contain significant amounts of lignin, hemicellulose, salts, and other materials which affect the pyrolysis mechanisms.

III. DIRECT DRY PYROLYSIS OF CELLULOSE AND RELATED COMPOUNDS

1. Initial Product Identification

It has been established by many authors (9-31) that the major product formed during cellulose pyrolysis is levoglucosan (β-1,6-(D)-anhydroglucopyranose), and that this product is obtained in yields varying between 3 and 63% by weight. Initially this appears somewhat surprising, since a direct dehydration of a glucose unit would have been expected, giving an unsaturated product. However, construction and examination of a molecular model of this compound shows an easy juxtaposition of the 1- and 6-hydroxyl groups, with the result that loss of water between these two groups is facile. Further examination of the glucose structure shows that all of the ring hydroxyl groups are in a

trans position relative to one another; only by inversion at a carbon atom can the required condition of the hydroxyl being trans to a hydrogen atom on the adjacent carbon atom be satisfied. Because of the relative difficulty of inversion within the ring, dehydration between the hydroxyls at positions 1- and 6- is favored, and levoglucosan is the product obtained.

2. Mechanism of Initial Formation of Levoglucosan from Cellulose

The dehydration of cellulose to levoglucosan may occur either after total depolymerization to glucose, in the undegraded cellulose itself, or at some intermediate stage during depolymerization. The question has been resolved by a number of determinations, including the effect of mild heating on the DP of cellulose, and the yields of levoglucosan obtained by pyrolysis of glucose, cellobiose, and cellulose.

It has been established that cellulose is very sensitive to mild heat and mechanical treatment (Table 1), and that the DP decreases via a second-order relationship with time of heating.(32) It was found that cellulose with an initial DP of 800, after heating at 202°C in the absence of air, degraded to a product with a constant DP of 300. This value was reached after 30 hr heating, and did not alter with another 25 hr of heating. The same cellulose, treated at 186°C required 100 hr of heating before approaching the 300 DP value asymptotically. The effect of temperature was shown further by a sample with an initial DP of 600, which in 10 hr at 230°C had reached a constant DP of 300. Continued heating for up to 50 hr did not alter this final DP value.

Thus, cellulose depolymerizes without loss in weight until a stable plateau is reached at a DP of about 300. Results obtained by other authors (Table 1) using a wide variety of cellulose samples agree with this conclusion in general, although final DP values between 100 and 700 were obtained. The fact that the

TABLE 1. Initial Depolymerization of Cellulose on Heating

MATERIAL	INITIAL DP	FINAL DP	TREATMENT CONDITIONS AND RESULT	REFERENCE
Cellulose	1450	300	Heating for 4 - 12 hr in an agate ball mill	34
Cellulose	1062	151	Heating for 2 hr at 250°C	35
Cellulose	1062	156	Heating for 4 hr at 250°C	35
Cellulose	1710	690	Ultraviolet Radiation	36
Wood cellulose	-	398	Mild oxidation	37
Cellulose	2200	150 to 200	Heating for 5 min at 76 - 20°C with $AlCl_3$ in CCl_4	38
Cotton	-	400	Heating at 150 - 250°C for 0.25 to 30 min	39
Dry cellulose	-	200	Heating at 300°C. A sharp increase in levoglucosan yield was observed at a DP of 200	29
Cellulose	-	300	The final DP was temperature independent	40
Cotton cellulose	1440	209 to 210	Heating in boiling 10% sulfuric acid	41
Cellulose	1440	200 to 205	Heating in kerosene at 200°C for 180 to 360 min	41

TABLE 1. (Continued)

MATERIAL	INITIAL DP	FINAL DP	TREATMENT CONDITIONS AND RESULT	REFERENCE
Mercerized cellulose	1537	100 to 130	Heating in kerosene at 200°C for 180 to 360 min	41
Cotton cellulose	1000	150	Acid hydrolysis; 50-63% of levoglucosan was obtained from the low DP material	15
Wood cellulose	800	300	Heating for 55 hr at 202°C	32
Wood cellulose	800	300	Heating for 100 hr at 186°C	32
Wood cellulose	600	300	Heating for 50 hr at 230°C	32
Cotton Linters	1842	145	Ethanolysis	42
Decrystallized cellulose	1230	700	Heating at 225°C	33
Cellulose	2650	455	Heating at 225°C	33
Deltapine cotton	3083	213	Heating at 251°C for 150 min	8
Pima cotton	3082	235	Heating at 251°C for 150 min	8
Mercerized Pima cotton	2870	185	Heating at 251°C for 150 min	8
Ramie	3300	565	Heating at 251°C for 150 min	8
Cellulose	150 - 1000		Gave a 54-60% yield of levoglucosan on heating	27
Cellobiose	2	2	Gave a maximum yield of 3 - 4% of levoglucosan on heating	27

depolymerization occurs without appreciable loss in weight (i.e., without simultaneous decomposition) was confirmed by Broido et al.,(33) who found a DP decrease from 2650 initially to 375 finally on heating cellulose, with a weight loss during this process of less than 1%. However, in further decreasing the DP from 375 to 350, a further 5.7% weight loss occurred, indicating the onset of decomposition.

The data in Table 1 show quite clearly that the initial reaction of cellulose on heating is one of chain cleavage to units of DP in the range 200 - 400 generally, with a subsequent formation of some levoglucosan on continued pyrolysis. Basch and Lewin(8) found that the reaction rate, as determined by weight loss, was inversely proportional to the square root of the DP, and that the initial and subsequent reaction rates were also proportional to the crystallinity of the sample. Much of the work on cellulose decomposition was performed using differential thermal analysis (DTA) and thermogravimetry (TGA). Since these methods do not provide chemical structures for the products, it can only be presumed that the depolymerization did not lead directly to levoglucosan formation by splitting out of a glucose unit from cellulose. If chain cleavage was followed by glucose formation and subsequent dehydration to levoglucosan, it would follow that the pyrolysis of glucose should give higher or equal yields of levoglucosan to those obtained from cellulose. There is ample evidence that this is not the case. For example, Gardiner(11) reported data on the pyrolysis of a wide range of carbohydrates, including cellulose, glucose, and cellobiose. Molar yields were reported for all products identified, and included yields of levoglucosan from cellulose, cellobiose and glucose of 38.5, 22.7, and 19.8%, respectively.

Thus it would appear that cellulose decomposes to levoglucosan *via* an initial partial depolymerization, with levoglucosan formation occurring directly from the shortened carbohydrate chain

and not primarily from either glucose or cellobiose. Gardiner(11) suggested that levoglucosan may be formed by a double internal nucleophilic attack by hydroxyl, with initial formation of a 1,2-epoxide and loss of one end of the cellulose chain followed by a cleavage of the epoxide with formation of the 1,6-anhydroglucose linkage. Subsequent hydrolysis or repetition of this on the adjacent glucose monomer unit would lead to free levoglucosan formation. This mechanism is thus a combination of internal chain cleavage with end-terminal cleavage of a single unit. Figure 1 depicts the reactions involved.

Although Gardiner's mechanism appears to be plausible, it has not been definitely proven, and mechanisms involving either carbonium ions or free radicals cannot be ruled out. Certainly, cellulose irradiated by ultraviolet light will decompose by a free radical mechanism, as demonstrated by Hon.(43,44) Hon found that light of wavelengths greater than 330-340 nm did not cause radical formation, while light of shorter wavelength resulted in free radical formation associated with hydrogen generation. The formation of radicals was very sensitive to the presence of water,(44) indicating that the decomposition of cellulose by this route could involve an interaction of the cellulose molecule with water. Thus, this mechanism would not necessarily apply to completely anhydrous cellulose. Bos(45) found that the hydroxyl groups which were responsible for hydrogen production on irradiation were those which were least hydrogen-bonded. Finally, it was found that formation of photo-induced radicals in cellulose also resulted in glycosidic bond cleavage.(46) This latter work would support the theory that cellulose may decompose a free-radical mechanism, although no special precautions to dry the samples were reported.

3. Levoglucosan Formation from Related Compounds

Apart from its formation as a primary degradation product of cellulose, levoglucosan is formed by thermal decomposition

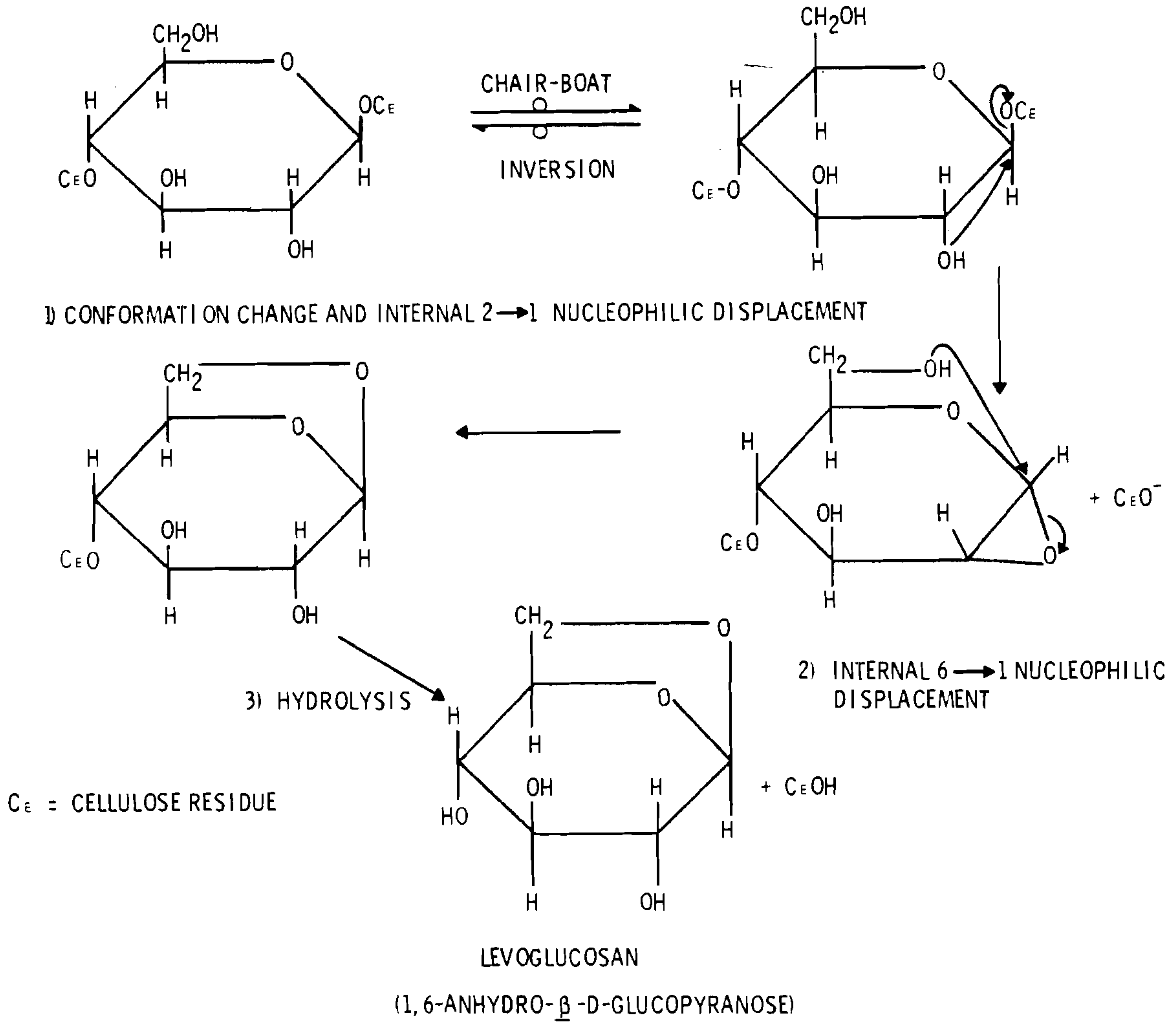


FIGURE 1. Internal Nucleophilic Attack Mechanism for the Conversion of Cellulose Directly to Levoglucosan(18)

of a variety of related compounds. These are listed in Table 2. The most comprehensive report of the formation of levoglucosan from carbohydrates related to cellulose is that of Houminer and Patai.(24) These authors hoped to gain insight into the decomposition mechanism of cellulose. They reported the somewhat surprising result that the yield of levoglucosan decreased with increased DP from 1 (glucose) through cellotetraose (DP=4) to cellulose. This may perhaps be explained on the basis of increased molecular stability to heat with increasing DP, since their operating temperature was 250° C, rather low for cellulose decompostion.

From the results shown in Table 2, it can be seen that the formation of anhydrosugars by pyrolysis is a common one; glycosides normally cleave to the aglycone in the process of generating levoglucosan or the equivalent anhydro-sugar. It is difficult, however, to discern any trends or mechanistic implications in these data.

The only available quantitative data on levoglucosan formation from various glycosides are reported in 2 articles.(11,24) The appropriate data are tabulated (Table 3). There is an apparent discrepancy in the yields of levoglucosan reported by heating various compounds <u>in vacuo</u> which may be attributed to the different temperatures (420°C in reference 11, and 250°c in reference 24) and times of heating. However, the formation of levoglucosan by pyrolysis of any compound containing glucose is established, although the available information does not appear to impart any significant insight into the decomposition mechanism involved.

4. Decomposition of Cellulose to Other Compounds

Although levoglucosan is a frequently observed product of cellulose decomposition, it is not the only one; indeed in some cases it is not even the primary or major product. The formation of levoglucosan from cellulose pyrolysis seems beyond doubt.

TABLE 2. Formation of Anhydrosugars by Pyrolysis

Compound Pyrolyzed	Product(s) Anhydrosugar/aglycone	Reference
Glucose	Levoglucosan	47
^{14}C-D-Glucose	Levoglucosan	48
Sucrose	Isosaccharosan, $C_{12}H_{20}O_{10}$; Caramelan, $C_{24}H_{36}O_{18}$; Caramelene, $C_{36}H_{50}O_{25}$	49
Sucrose (α-D-glucopyranosyl-β-D-fructofuranoside)	Levoglucosan	50
Maltose (4-0-α-D-glucopyranosyl-D-glucopyranose)	Maltosan, $C_{12}H_{20}O_{10}$	51
Lactose (4-0-β-D-galactopyranosyl-D-glucopyranose	Lactosan (β-galactosylgalactosan)	52
Rhamnose	Rhamnosan	53
Dulcitol	Dulcitan, $C_6H_8O(OH)_4$	54
Fructose	Levulosan	55
Levulose	Levulosan	10
Galactose	Galactosan	56
Mannitol	Isomannide, $C_6H_{10}O_4$	57
Mannitol	Mannitan, $C_6H_8O(OH)_4$	58
Salicin (2'-Hydroxymethylphenoxy-β-D-glucopyranoside	Levoglucosan + saliretin	59
Arbutin (p-Methoxyphenoxy-β-D-glucopyranoside)	Levoglucosan + hydroquinol	59
Phlorhizin (3',5'-dihydroxyphenoxy-β-D-glucopyranoside)	Levoglucosan + phloroglucinol + phloretic acid	59
Digitoxin ($C_{42}H_{66}O_{13}\cdot 0.5H_2O$)	Anhydrodigitoxose ($C_6H_{10}O_3$)	60,61
Lichenin	'Lichosan'	62
Lichenin acetate	'Lichosan acetate'	63
Inulin	Trifructosan, difructosan	64
Starch	Levoglucosan	65-67

TABLE 3. Yield of Levoglucosan from Pyrolysis of Carbohydrates

	Yield of levoglucosan	
Compound	from Gardiner (11)	from Houminer and Patai (24)
Amylose	28.8%	-*
Amylopectin	24.7	-
Cellulose	38.5	0
Cellotetraose	-	1.7
Cellotriose	-	3.2
Cellobiose	22.7	6.2
Glucose	19.8	-
Maltose	29.4	0
Trehalose	23.7	8.6
Lactose	27.2	0.6
Melibiose	22.3	0.8
Sucrose	18.2	2.8
Raffinose	17.0	-
3,6-Anhydroglucose	0	-
Galactose	0	-
Fructose	0	-
Mannose	0	-
Sophorose	-	2.6
Gentiobiose	-	3.3
α-D-methylglucoside	-	1.0 #
β-D-methylglucoside	-	trace$^{\#}$
β-D-phenylglucoside	-	5.4$^{\#}$
1,2-*O*-isopropylidene-*α*-D-glucofuranose	-	0.8$^{\#}$

Conditions: Gardiner - 420°C, 10-20 mm Hg, time not stated;
Houminer and Patai, 250°C, 30 min., 10^{-3} mm Hg

* - Not done. # - Heated for 20 min. only.

but this does not mean that cellulose cannot decompose by routes which do not involve levoglucosan. In fact it is possible, though unlikely, that levoglucosan is a major product simply because it is more stable than another product which degrades faster. The bulk of the available evidence supports the hypothesis that the primary route of cellulose decomposition takes place with levoglucosan as the first product, but other products have been observed. One of these is 1,6-anhydro-β-D-glucofuranose, which Gardiner(11) envisages as being formed through an energetically unfavored route involving an initial chair/boat conformation change, followed by a succession of three internal nucleophilic displacements, between hydroxyl groups at positions 4 ⟶ 1 (cleaving the glucose residue from the cellulose chain), 2 ⟶ 1, and 6 ⟶ 1, respectively. These changes are shown in Figure 2. Perhaps not surprisingly, 1,6-anhydro-β-D-glucofuranose is a minor product from cellulose pyrolysis, although its formation again seems to be beyond doubt. It has been isolated and identified by 1) gas chromatography, 2) as a chemical derivative, and 3) by mass spectrometry.(10-12,14,24,68,69) Other carbohydrate derivatives are formed from cellulose and have been identified by various means. They include both α- and β-D-glucose,(10,14) 1,6-anhydro-3,4-dideoxy-Δ^3-β-D-pyranosen-2-one (levoglucosenone),(70,71) 1,4:3,6-dianhydro-α-D-glucopyranose,(11,12) gluco-isosaccharinic acid,(39) 3-deoxy-D-erythrohexoseulose,(14,72) 3-deoxypentoseulose, and 3-deoxy-D-glyceropentoseulose.(72) Levoglucosenone was originally identified as cis-4,5-epoxy-2-pentenal(73) in cellulose pyrolysates. The yield was markedly increased after treatment of the cellulose by phosphoric acid. Lipska and McCasland(74) reassigned the identity of levoglucosenone as 1,5-anhydro-2,3-dideoxy-β-D-pent-2-enofuranose, but this was later changed again to 1,6-anhydro-3,4-dideoxy-Δ^3-β-D-pyranosen-2-one.(70) The latter result would appear to be the most reliable, since a thorough structural investigation was performed using a wide variety of techniques. The 3 structures are shown in Figure 3 for comparison.

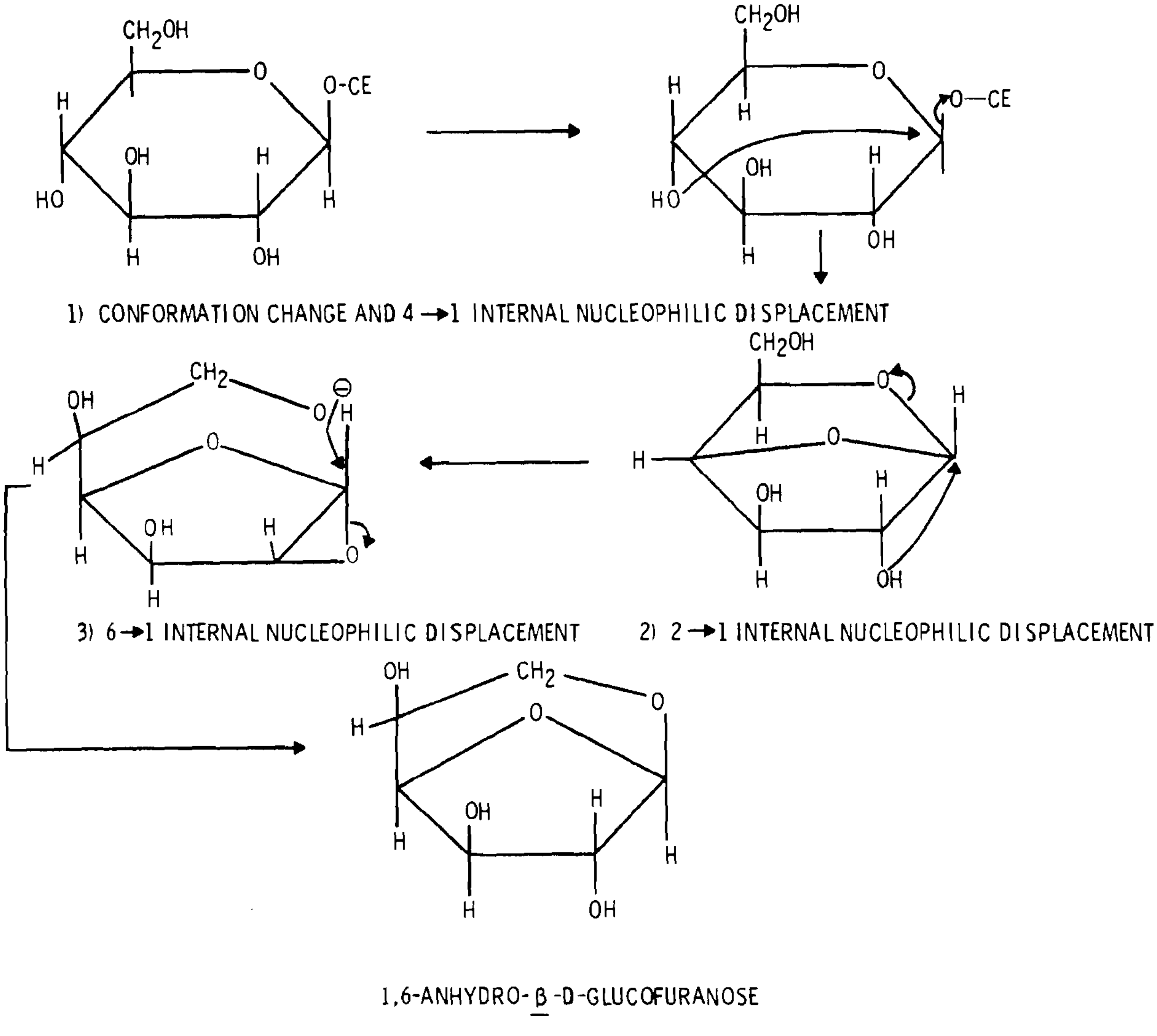
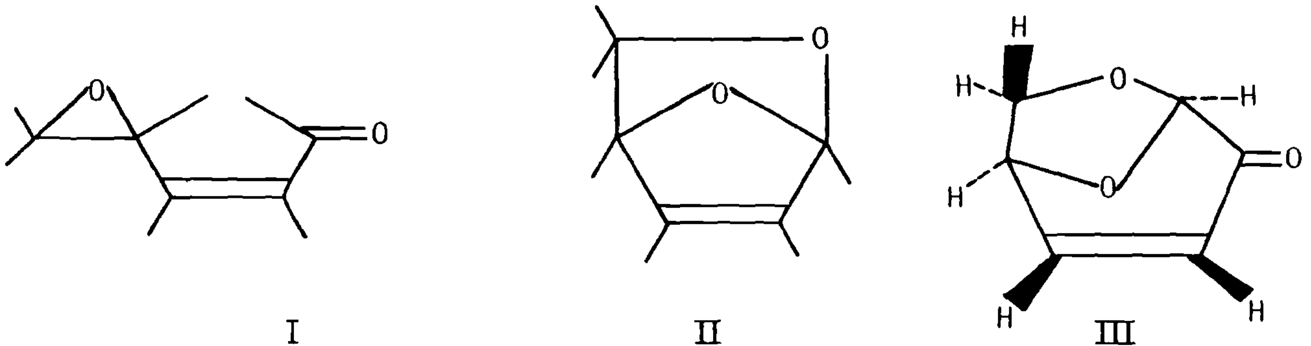


FIGURE 2. Mechanism of Formation of 1,6-Anhydro-β-D-Glucofuranose from the Nonreducing End Group of Cellulose



I

CIS- 4,5- EPOXY- 2- PENTENAL
(73)

II

1,5-ANHYDRO-2,3-DIDEOXY
-β-D-PENT-2-ENOFURANOSE
(74)

III

1,6-ANHYDRO-3,4-DIDEOXY
-Δ^3-β-D-PYRANOSE- 2- ONE
(69)

FIGURE 3. Structures Proposed for Levoglucosenone

Levoglucosenone is a logical product of the further decomposition of levoglucosan, but as levoglucosenone polymerizes rapidly at room temperature it cannot be considered as a precursor to the many other products of cellulose pyrolysis. The route from levoglucosan to levoglucosenone may involve a carbonium ion mechanism catalyzed by hydrogen ion, and involving charge rearrangement of the initially-formed carbonium ion from position #3 to 2, followed by dehydration.(70) Certainly some such rearrangement is necessary for this transformation, as otherwise the required geometry for E_1 elimination of water cannot be achieved. No work has yet been reported on the decomposition of the levoglucosenone polymer; thus any attempt to explain the mechanism would be pure speculation.

Among the other degradation products of cellulose are a number of furan derivatives and simple aliphatic aldehydes and ketones. For convenience, these are tabulated (Table 4). The amounts of these materials formed from cellulose are minor; thus it is not possible based on present evidence to decide whether they are genuine cellulose primary degradation products, or whether they arise from other intermediates (levoglucosan or levoglucosenone) in the cellulose degradation pathway. They may even result from some completely independent degradation route. One suggested route for the formation of carbonyl compounds involves their direct formation from cellulose by cleavage of a glucose ring(12,47) (Figure 4).

Some insight into this problem has been provided by Shafizadeh,(6) who reported experiments on the pyrolysis of phenyl β-D-glucopyranoside, cellulose, levoglucosan, 3-deoxy-D-erythro-hexosulose, and other compounds. The initial depolymerization reaction of cellulose was found to be the result of transglycosylation reactions, giving mixtures of anhydro-sugars (e.g., levoglucosan from cellulose), and randomly linked

TABLE 4. Non-Carbohydrate Materials Formed in the Pyrolysis of Cellulose

Product Identified	Reference	Product Identified	Reference
Furan	10,74-77	Cyclooctatetraene	74,77
2-Methylfuran	10,75,76	Pentene	74,77
2,5-Dimethylfuran	74,77	'Hydrocarbons'	10
2-Furaldehyde (Furfural)	9,10,74, 76-79, 81-86	Formaldehyde	7,9,11,79, 84,89
		Acetaldehyde	9,11,12, 74-78,84,85
Acetylfuroyl	87*		
5-Hydroxymethyl-2-furaldehyde	9-12,74,77	Glyoxal	9,11,12, 79,88,89
2-Furyl Hydroxymethyl ketone	11,12	Propanal (Propionaldehyde)	9,74,75,77, 79,84,85
5-Methyl-2-acetylfuran	87*		
3-Hydroxymethylfuran	78	Butanal (*n*-Butyraldehyde)	9,11,12,74 77,79,84,85
Methylfuroic acid	87*		
5-Methyl-2-furaldehyde	10,74,76, 77,82	2-Methylpropanal (*i*-Butyraldehyde)	84
2-Hydroxymethylfuran (Furfuryl alcohol)	74,76,77	Pentanal (*n*-Valeraldehyde)	84
3-Methylcyclopentane-1,2-dione	87*	3-Methylbutanal (*i*-Valeraldehyde)	84
2-Hydroxy-3-methyl-3-cyclopentene-1-one	74,77	2-Butenal (Crotonaldehyde)	74,77
Cyclopentanone	74,77	2-Methyl-2-butenal (Tiglaldehyde)	76
Cyclohexanone	76	*cis*-4,5-Epoxy-2-pentenal	73
Butyrolactone	74,76,77	Glyceraldehyde	11,12
4-Hydroxy-2-pentenoic acid δ-lactone	87*	2-Ketopropandial (Mesoxaldehyde)	11,12

TABLE 4. (Continued)

Product Identified	Reference	Product Identified	Reference
2-Ketopropanal (Pyruvaldehyde)	11,12, 74,77	Methanol	9,75,79
		Methyl formate	76
Hydroxyethanal (Glycolaldehyde)	11,12	Hydroxypropanone (Acetol)	74,76,77
Propenal (Acrolein)	9,11,12, 74,75,77, 79,84	Formic acid	9,74,77,85, 89
		Acetic acid	9,74,77,79, 80,82,85,89, 91
Acetone	9,11,12,25, 74-76,79, 84	Propanoic acid	76,85
2-Butanone (Ethyl methyl ketone)	9,11,12,74, 77,84	Butanoic acid	85
2-Pentanone (Diethyl ketone)	12,84	i-Butyric acid	85
		Glycolic acid	89
3-Methyl-2-butanone (i-Propyl methyl ketone)	84	Lactic acid	9,89
Butenone (Methyl vinyl ketone)	74,77	Pyruvic acid	11,12
		Dilactic acid	89
2,3-Butandione (Diacetyl)	74,76,77	4-Ketopentanoic acid (Levulinic acid)	11,12
Dihydroxyacetone	11,12	3-Hydroxy-2-ketopropanal (Hydroxypyruvaldehyde)	11

*From Glucose pyrolysis

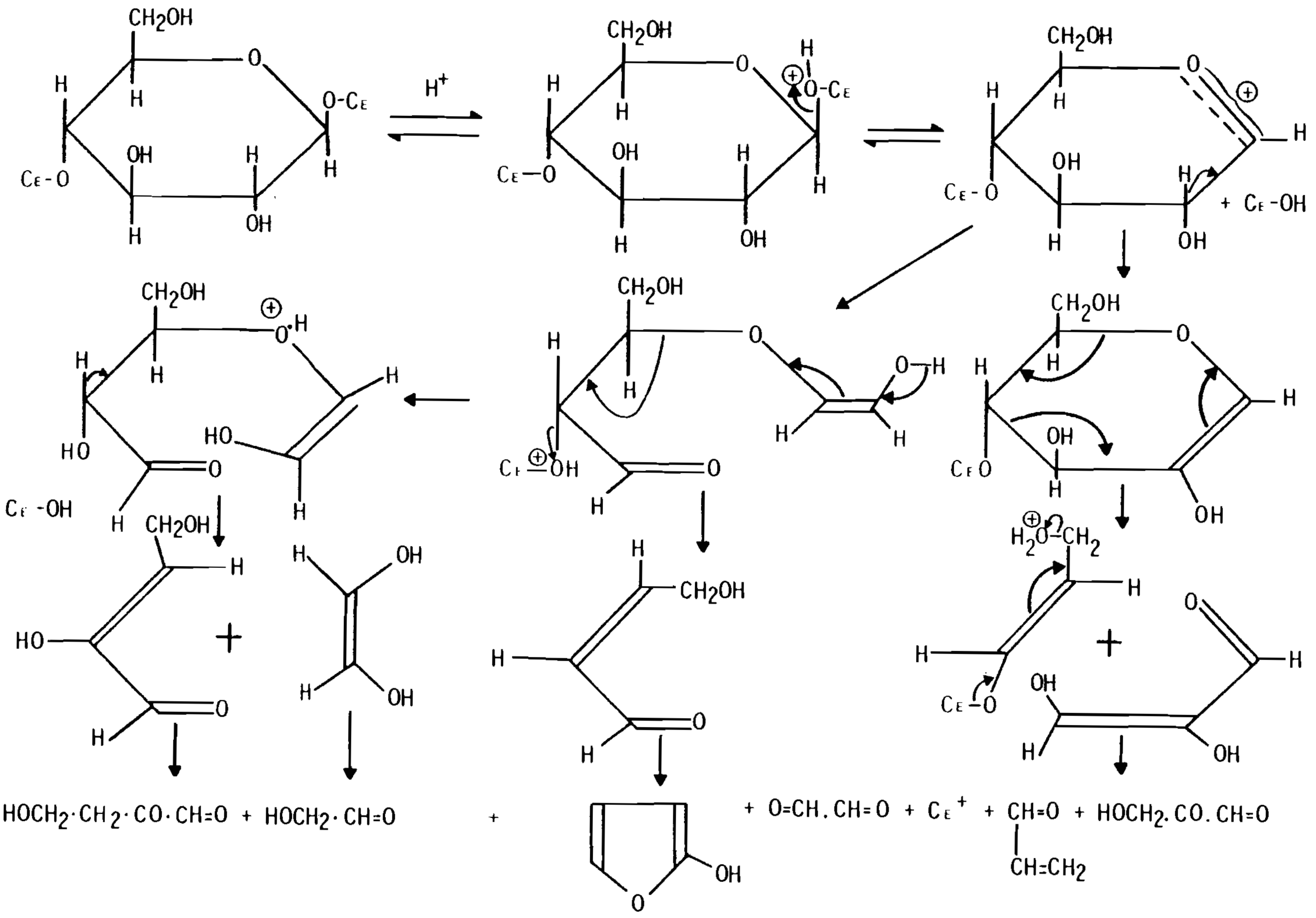


FIGURE 4. Mechanism of Formation of Carbonyl Compounds from Cellulose.(107)

oligosaccharides. Shafizadeh also found that cellulose pyrolysis led to a mixture of levoglucosan, 1,6-anhydro-β-D-glucofuranose, traces of α- and β-D-glucose, 3-deoxy-D-erythro-hexosulose, and other products, in broad agreement with other authors. Further, pyrolysis of levoglucosan labeled with ^{14}C at the 1-, 2-, or 6-positions permitted assignment of the portion of the glucose molecule from which the degradation products were derived. The major degradation products from levoglucosan pyrolysis were identified as 2-furaldehyde, 2,3-butanedione (diacetyl), pyruvaldehyde, acetaldehyde, and glyoxal. 3-Deoxy-D-erythro-hexosulose was also indicated as being a major intermediate in the pyrolytic decomposition of cellulose to furan derivatives, leading to the formation of char (38%), water (18.5%), carbon dioxide (12.5%), carbon monoxide (4%), and tar and volatile organic materials on pyrolysis at 550°C. The volatile organic materials were very similar to those obtained by cellulose pyrolysis, and consisted partly of 2-furaldehyde (furfural), 2-methylfuran, 5-methyl-2-furaldehyde, 2-furfuryl alcohol, and furan.

5. Formation of Aromatic Structures on Cellulose Pyrolysis

It is well known that any organic material, heated sufficiently strongly, will form a char. This char is often and inaccurately considered to be fairly pure carbon. Most of the earliest work on cellulose pyrolysis was concerned with the composition of the char or "artificial coal," since it was thought that coal itself was formed by the action of heat and pressure on cellulose (the lignin component of plant material was ignored initially). The conversion of cellulose to condensed aromatic structures and ultimately to char was described as 'coalification.' Very little work of any impact has been done on the chemical mechanisms involved in this transformation - even the mechanism of, for instance, levoglucosan conversion to phenols

has not been studied. Yokokawa et al.,(91) and Tsukashima(92) dealt with the aromatic carboxylic acids which were produced after pyrolysis and oxidation of cellulose and lignin, but apart from a comment that rather larger amounts of phthalic acid were produced from cellulose than lignin, this work(92) confirmed the fact that the 'char' contains aromatic structures. Smith and Howard(94) showed that the charring of cotton at temperatures of between 190-400° C led to a progressive increase in the carbon content of the char, from 45 to 86%. Benzene and diphenyl were obtained from the char after it was oxidized and decarboxylated.

An infrared examination of the progressive thermal decomposition of cellulose and lignin has been reported.(95) Aromatic C-H out-of-plane deformation absorption bands appeared at temperatures above 425°C; at lower temperatures, there were changes associated with loss of water, formation of aromatic carbonyl groups, and the disappearance of C-OH groups. This would indicate that the mechanism of aromatization occurs via intermediate aromatic ketones, although the exact mechanism of formation of these is still unclear.

A different approach to the problem was taken by Bergius,(96) who analyzed the gases produced from cellulose maintained at 250°C for several hours. There was an initial change in elemental composition corresponding to:

$$4(C_6H_{10}O_5)_x \xrightarrow{250°C} 2(C_{12}H_{10}O_5)_x + 10x\ H_2O$$

This change raised the carbon content of the residue from 44.5 to 62.5%. Carbon dioxide and water were obtained on further heating, the change corresponding to:

$$4(C_6H_{10}O_5)_x \xrightarrow{250°C} C_{20}H_{16}O_2 + 10\ H_2O + 4CO_2 + 2H_2$$

TABLE 5. Aromatic Hydrocarbons from Cellulose Pyrolysis[a]

Hydrocarbon	Derived from Pyrolysis of: Cellulose	Starch	Glucose	Oxalic Acid
Anthracene	337[b]	104	36	30
Fluorene	584	32	7	3
Pyrene	219	35	66	2
3-Methylpyrene	131	11	1	1
Acenaphthylene	160	56	27	15
Fluoranthrene	164	94	45	0
1:2-Benzanthracene	186	116	43	0
1:2-Benzpyrene	65	4	11	0
3:4-Benzpyrene[c]	78	17	29	1
Anthanthrene	10	1	5	0.2
Coronene	44	3	1	2

(a) After Gilbert and Lindsay.(97)
(b) In micrograms/100 grams at 650°C.
(c) 3:4-Benzpyrene has also been observed by others.(103,104) Benzene, toluene, and other aromatic compounds have been identified also.(74,77,105)

This second product contained 50% of carbonyl oxygen, which is in agreement with the results of Hofman et al.(94)

Prolonged heating of almost any organic substance will eventually yield small amounts of aromatic compounds, as demonstrated by Gilbert and Lindsay.(97) Some of their results are shown in Table 5. These authors showed the formation from cellulose of a variety of carcinogenic aromatic compounds, including 3,4-benzpyrene and fluorene. They also demonstrated the generation of the same compounds from oxalic acid, a relatively simple organic compound.

A number of other aromatic substances have been identified in cellulose pyrolysates (Table 6), though work on the mechanisms for their formation is almost completely lacking.

6. Pyrolysis of Levoglucosan

In the study of cellulose decomposition mechanisms, there are two other general approaches besides the study of cellulose decomposition *per se*. One of these is the study of the decomposition of compounds related to cellulose (e.g., cellulose acetates), and the other is the study of decomposition in supposed decomposition products of cellulose, such as levoglucosan. The latter work is based on the assumption that an intermediate in the pyrolysis pathway will itself yield qualitatively identical products to the parent material. Levoglucosan and its derivative, levoglucosenone, are not the only likely immediate products of cellulose decomposition that have been identified with any degree of certainty to date. For instance, Shafizadeh(6) has reported results of the pyrolysis of 3-deoxy-D-erythro-hexosulose which strongly supports the idea that this compound is a major intermediate in the decomposition of cellulose (see p.16). A number of authors have examined the products of thermal decomposition of levoglucosan(77,79,89,96,98-102) and are in general agreement

TABLE 6. Phenols Obtained from Cellulose Pyrolysates

Compound Identified	Identification Method	Reference
Phenol	GC, MS	77,87
	GC only	74
	Paper chromatography, GC	85
o-Cresol, m-Cresol, and p-Cresol	GC, MS	77
	GC only	74,85(a)
2,5-Dimethylphenol	GC, MS	77
	GC only	74
3,4-Dimethylphenol	GC, MS	77
	GC only	84

(a) p-Cresol was not identified in this work.

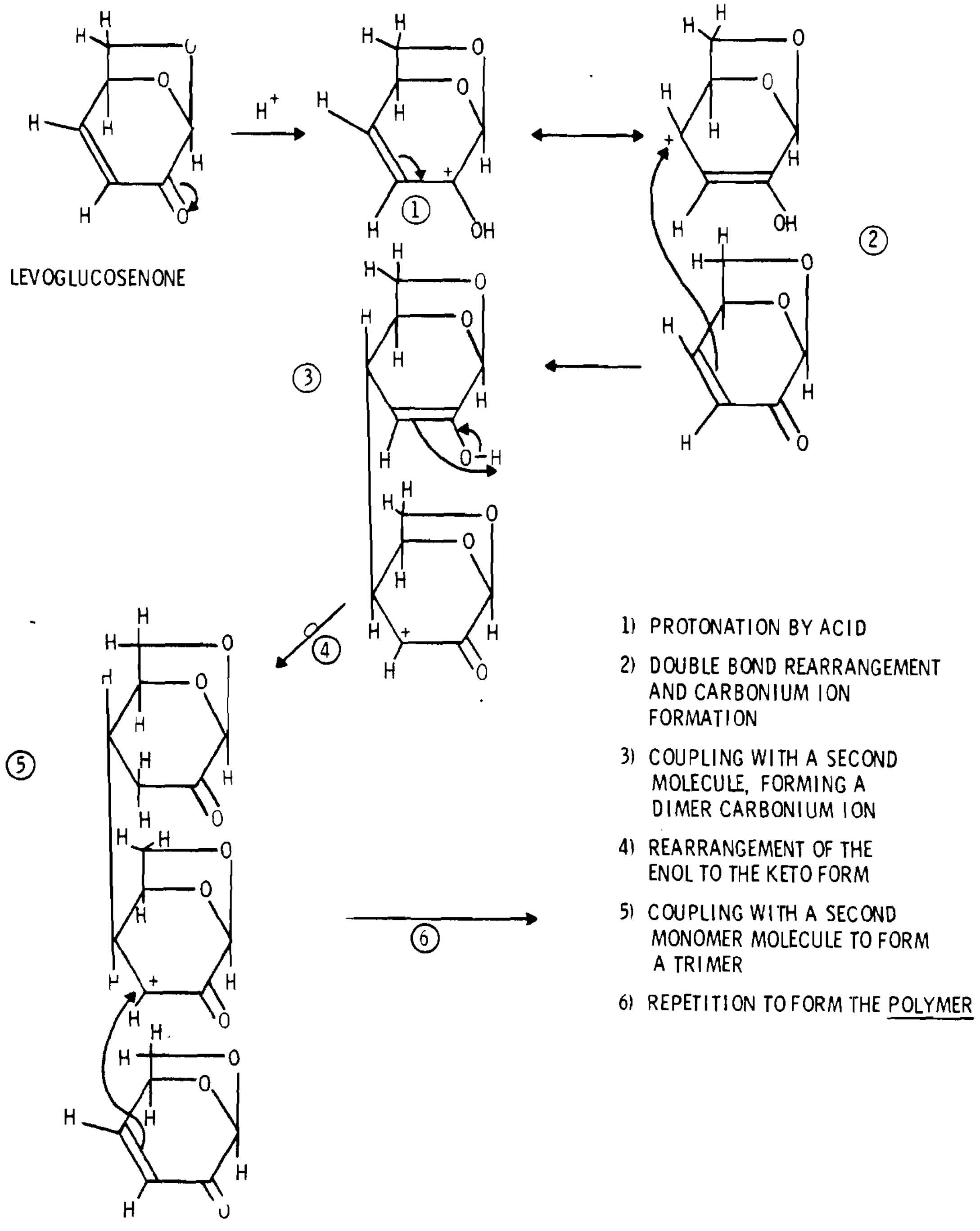
that these products are the same as those from cellulose pyrolysis. Wodley(77) added the comment that the difference between levoglucosan and cellulose pyrolysis consisted of the absence from levoglucosan pyrolysates of 2-hydroxymethylfuran, butyrolactone, phenol, cresols, 2,5-dimethylphenol, and one unknown compound (present in cellulose pyrolysates), and increased amounts of 2 other unknowns.

Arseneau(98) visualized the decomposition of cellulose as occurring through 2 competing reactions; (1) Dehydration commencing at 210°C and leading ultimately to the production of char, and (2) A competitive reaction leading to depolymerization and levoglucosan formation starting to become significant at about 270°C and increasing rapidly in rate with increased temperature. The levoglucosan formed would then lead to the observed decomposition products. The only difference between this and other models is that the formation of char and levoglucosan would be independent.

The difficulty with Arseneau's rather simplified mechanism is that the next decomposition product of levoglucosan may be levoglucosenone, as described earlier (p. 16). Levoglucosenone seems to be the primary product of levoglucosan decomposition, itself the primary product from cellulose. Unfortunately, levoglucosenone polymerizes rapidly even at room temperature, with no change in elemental analysis.(70) This raises the complication of divergent pathways leading to the ultimate cellulose decomposition products - the one pathway through levoglucosenone, which then decomposes directly, and the other by the decomposition of the levoglucosenone polymer, assuming that this latter decomposition is not simply the inverse of the formation reaction. A carbonium ion mechanism has been proposed(70) for the formation of levoglucosenone from levoglucosan; applying the same carbonium ion type of mechanism to the polymerization reaction in the

classical manner leads to the complex polymer shown in Figure 5, although it should be noted that a free-radical polymerization cannot be ruled out and may even be the more probable route to this same polymer. There are obviously many ways in which such a complex material as levoglucosenone may polymerize, and the structure in Figure 5 should only be considered as one possibility. However, it would seem logical that levoglucosenone polymerization would be in competition with its further degradation to simpler substances. The use of radioactive tracers would shed some light on the mechanisms of levoglucosenone reactions as Shafizadeh has already reported for levoglucosan pyrolysis,(6) and could also permit some kinetic data to be obtained which might help to establish the relative importance of the various possible reaction pathways.

Among the other degradation products common to both cellulose and levoglucosan are a number of furan derivatives and simple aliphatic aldehydes and ketones (Table 4, p.17). The amounts produced are very minor. Because of this fact, it is not possible to decide whether they arise from cellulose directly, as has been suggested,12) from levoglucosan or its polymeric derivatives, from some other minor product of cellulose pyrolysis such as <u>1,6-anhydro-β</u>-D-glucofuranose, or even from an initially formed furan by further decomposition.(47) However they are formed, furan derivatives and aldehydes are chemically reactive and can undergo very rapid reactions with other substances, including cellulose and even themselves. Hence the low yield of furans should be no cause for surprise. However, it would be overly simplistic to assume their formation by a direct pathway from cellulose without further careful experimentation.



1) PROTONATION BY ACID
2) DOUBLE BOND REARRANGEMENT AND CARBONIUM ION FORMATION
3) COUPLING WITH A SECOND MOLECULE, FORMING A DIMER CARBONIUM ION
4) REARRANGEMENT OF THE ENOL TO THE KETO FORM
5) COUPLING WITH A SECOND MONOMER MOLECULE TO FORM A TRIMER
6) REPETITION TO FORM THE POLYMER

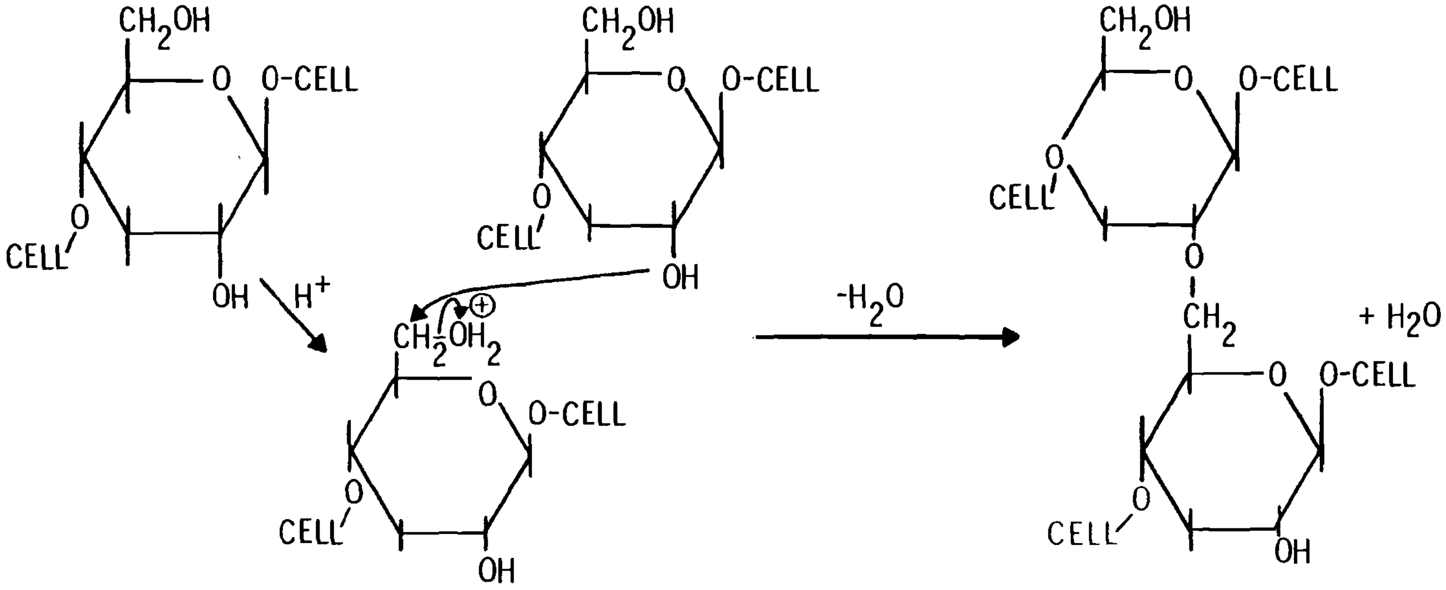
FIGURE 5. Tentative Pathway for the Polymerization of Levoglucosenone by a Carbonium Ion Mechanism

7. Crosslinking of Cellulose during Heating

While dealing with the subject of the possible formation of other polymers from levoglucosenone during the pyrolysis of cellulose, it is pertinent to note that cellulose itself is a polyfunctional molecule and is also capable of reacting in such a manner as to generate species of higher, rather than lower molecular weights. This is particularly true if the reactions between cellulose and some of its degradation products are included.

Although cellulose crosslinking is a commonly used way of stabilizing cellulose derivatives, the mechanism of the crosslinking reactions have received very little attention. The available data have been reviewed.(106) Crosslinking appears to occur by various mechanisms, including carbonium ion and free radical, depending on the reactant added (if any) and the reaction conditions employed. Simple heating of cellulose at 170-200°C for up to 40 hr in air or nitrogen led to some depolymerization by cleavage of the glycoside linkages, and to crosslinking by ester and ether bridge formation between chains.(107) The mechanism was probably ionic, involving a simple dehydration reaction between hydroxyl groups on adjacent chains to form ethers (Figure 6). The formation of esters requires the presence of a carboxyl group, which is absent in unoxidized cellulose. If some oxidation is present, then a carboxyl group on cellulose may esterify with an hydroxyl group on an adjacent molecule (Figure 7); alternatively, an acidic degradation product of cellulose may link two chains. This is shown in Figure 8, using oxalic acid as the example of the derived acid.

Rodrig _et_. _al_.(108) examined the effect of formaldehyde (a known cellulose decomposition product) on crosslinking and subsequent pyrolysis of cellulose. The stability of cellulose was increased by interchain crosslinking, but there were opposing effects due to the resultant reduction in the DP and hydrogen



SUMMARY:

PROTONATION OF A HYDROXYL GROUP ON ONE CELLULOSE CHAIN FOLLOWED BY BIMOLECULAR NUCLEOPHILIC DISPLACEMENT AND LOSS OF WATER, USING A SECOND CELLULOSE CHAIN AS THE NUCLEOPHILE.

(ONLY THE RELEVANT GROUPS IN CELLULOSE ARE SHOWN, FOR SIMPLICITY).

FIGURE 6. Crosslinking in Cellulose through Ether Formation

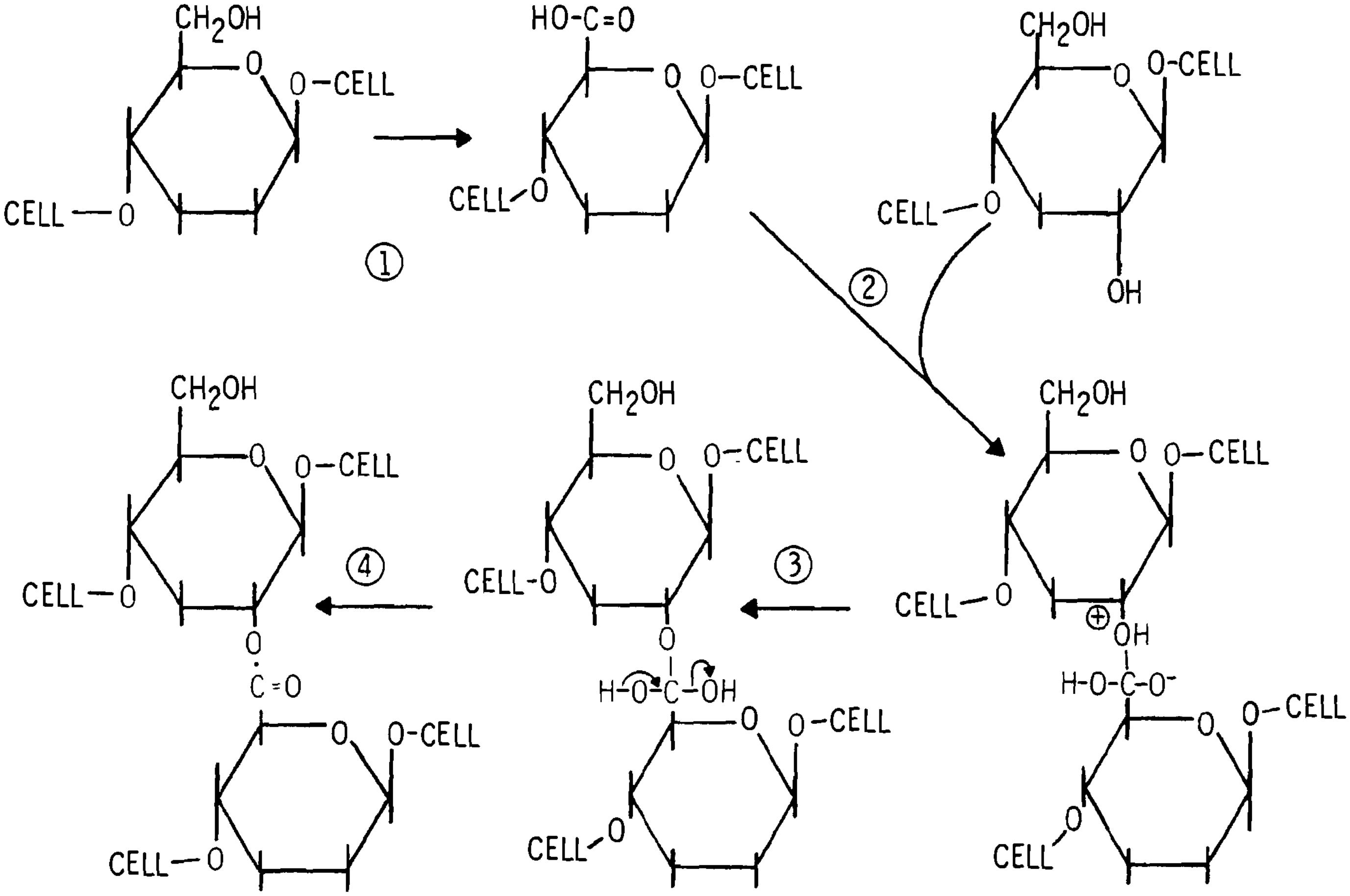
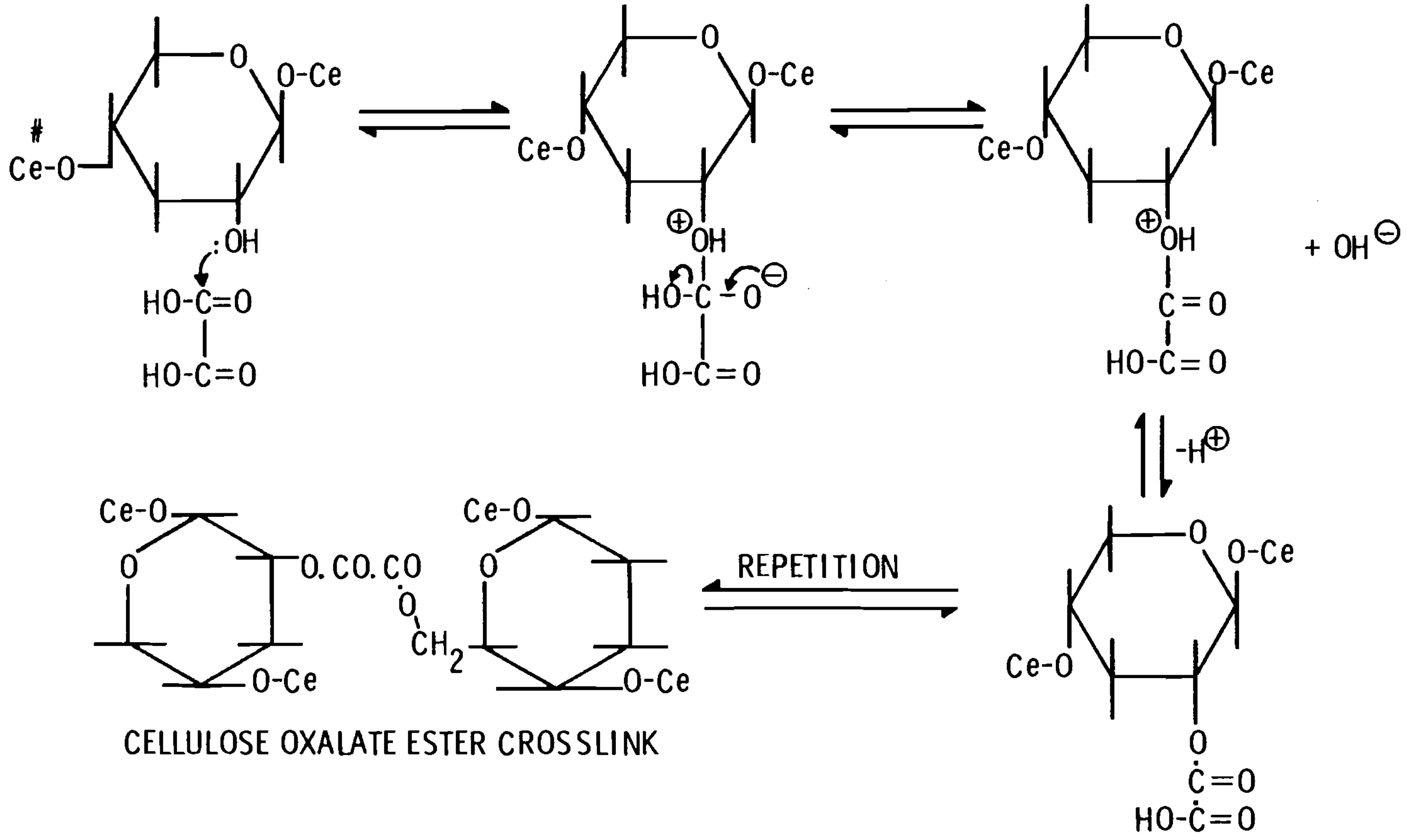


FIGURE 7. Crosslinking of Cellulose by Ester Formation between Chains



* ONLY REACTING GROUPS ARE SHOWN FOR SIMPLICITY

\# Ce = CELLULOSE CHAIN

FIGURE 8. Crosslinking of Cellulose through Ester Formation with a Pyrolysis Product

bonding. Additional stabilization of the product was attributed to changes in the crystallinity of the cellulose. The mechanism of formaldehyde crosslinking of cellulose was found to involve protonation of hydrated formaldehyde followed by dehydration to yield the active species, rather than protonation of a cellulosic -OH group and dehydration to a cellulose carbonium ion.(109) This ionic mechanism was temperature dependent.(116) The classical carbonium ion mechanism for cellulose crosslinking has also been discussed.(111)

The involvement of free radicals in cellulose crosslinking has been studied by a number of authors. Heating of cellulose acetate films in darkness in either oxygen or nitrogen at 50°C for 150 hr did not cause any discoloration,(112) although irradiation at this temperature with UV light (primarily 253.7 mm wavelength) caused rapid darkening. The data were interpreted to mean that oxidation and irradiation of cellulose generated free radicals by different mechanisms. Thus, caution should be exercised in comparing experiments where radical initiation in cellulose was caused by either irradiation or by chemical agents or heat. The action of heat on cellulose clearly produces free radicals, as demonstrated by the appearance of an intense paramagnetic resonance signal(113) after slow charring of cellulose below 600°C. The number of radicals generated was significant - one per 2000 carbon atoms, or approximately one free radical for each 330 glucose units. This would be quite sufficient to cause crosslinking of the cellulose chains, and in fact the observed rapid decline in the resonance absorption intensity at temperatures in excess of 600°C was attributed to aromatization through crosslinking, leading eventually to graphite. Free radicals have been shown to be formed by simple mechanical grinding of cellulose.(114) Grinding of cellulose with hexane

in a ball mill for 18-29 hr led to radical formation, as shown by electron paramagnetic resonance and chemical radical trapping mechniques. The activation energy for radical formation in cellulose was found by Arthur and Hinojosa(115) to be 33 Kcal/mole, with chain reaction initiation on heating to between 250-300°C. This is in agreement with results obtained by thermogravimetry, where dehydration of cellulose takes place by an ionic mechanism at lower temperatures, and is surpassed in rate at above 300°C by a different mechanism.(98) Irradiation of cellulose with gamma-radiation was also shown to result in free radical formation,(116) leading in this case to a linear decrease in the water absorption properties of the cellulose by about 10-15% to a total radiation dose of 10^7 rad, probably caused by cellulose chain crosslinking.

Initiation of chain reactions in cellulose at high temperatures is only to be expected, since carbon-carbon bonds characteristically break homolytically rather than heterolytically at high temperatures. The bulk of the available evidence supports the theory that an initial carbonium ion-mediated dehydration mechanism predominates at low temperatures (below 250°C), and that this yields to a free radial chain reaction at temperatures of 300°C and higher.(117) Both mechanisms may lead to some crosslinking reactions, by routes that have already been discussed. Thus, a description of the decomposition mechanisms of cellulose must not only deal with immediate degradation products, but also with secondary products arising from the decomposition of non-cellulosic high molecular weight materials (such as poly-levoglucosenone).

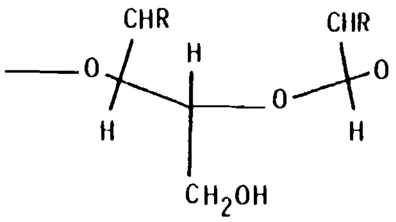
8. Pyrolytic Reactions of Cellulose Derivatives

It has already been commented that there are three ways of studying cellulose decomposition mechanisms: (1) by identifying the decomposition products from cellulose pyrolysis; (2) by

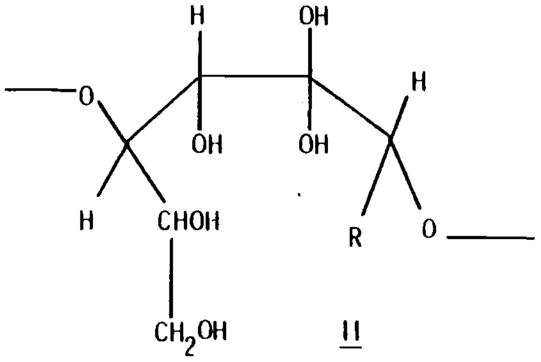
pyrolyzing known or suspected intermediates and correlating the product distribution with that obtained from cellulose; or (3) by pyrolyzing cellulose derivatives with known structural modifications such that some pathways for decomposition may be blocked or modified in known ways. The latter approach will now be discussed briefly, although a comprehensive review of cellulose derivative reactions would be out of place here. Instead, the pyrolytic reactions of cellulose derivatives will be discussed in the restricted sense of their being relevant to a determination of decomposition mechanisms in cellulose itself.

The relationship between the chemical structure of cellulose and the thermal stability of its derivatives was studied by Lyalyushkin et al.(118) Based on the additional stability conferred on cellulose by impregnation with phenylenediamines, it was concluded that thermal instability in cellulose arises when aldehyde or hydroxyl groups are formed (as in I and II, Figure 9). Marked increases in thermal resistance occurred when the 'R' group in formula I was replaced by the group $=NC_6H_4NH_2$, or when 'R' in II was replaced by $-NHC_6H_4NH_2$. Structure III may also have been formed. After phenylenediamine impregnation, cellulose could be heated at 180°C in the presence of 6% moisture for 6 hr without deterioration, while untreated cellulose was severely degraded under these conditions.

Another group of additive treatments to cellulose which probably act through chemical modification includes iodination and benzhydrylation. Iodination(74) resulted in the formation of a large amount of char for a given weight loss rate; benzhydrylation had a lesser but similar effect, while both treatments together resulted in a lower char yield compared to untreated cellulose. These somewhat puzzling results were attributed to an effect on the decomposition rate of levoglucosan.

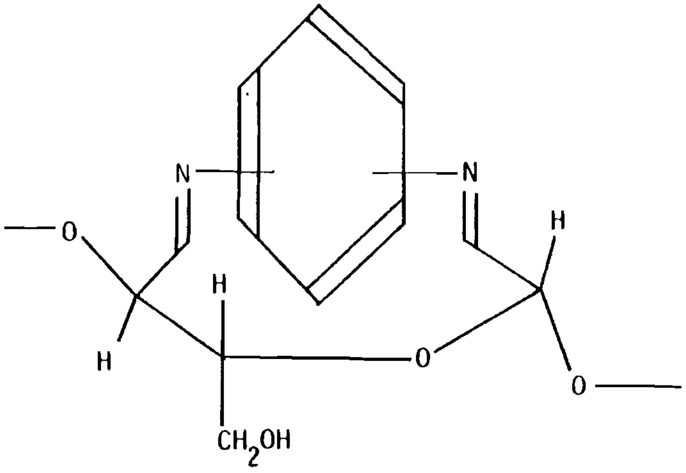


I R' = $=NC_6H_4NH_2$



II

R = $-NHC_6H_4NH_2$



III

FIGURE 9. Modifications to Cellulose Structure Which Confer Thermal Stability(118)

Any of the treatments (iodination alone, benzhydrylation alone, or both) reduced the number of low molecular weight degradation products observed, from 59 without treatment to 5 after treatment. The major products from chemical treatment followed by pyrolysis were water and levoglucosenone. More work needs to be done on this interesting effect before a specific mechanism can be proposed, but it would appear that the normal degradation mechanism for cellulose pyrolysis has been disrupted by substitution of hydroxyl functions by iodine or benzhydryl groups.

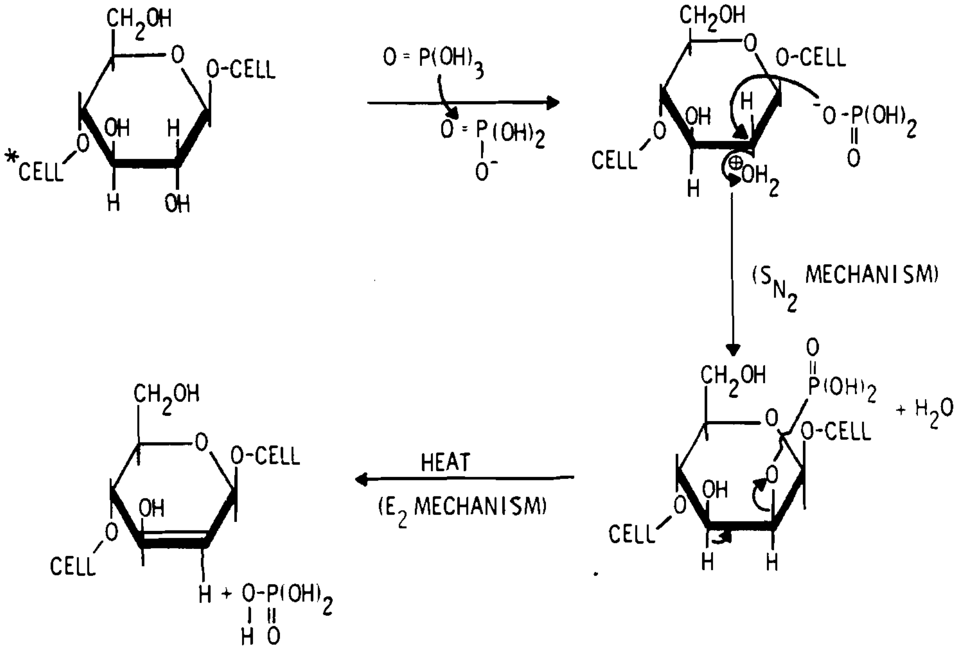
Much of the work reported on cellulose pyrolysis mechanisms involves the testing of various chemical flame retardants. Since the flaming reactions in cellulose are believed to be a function of the pyrolytic tar rather than the cellulose itself, the efficacy of an additive or chemical modification to cellulose is often measured in terms of decreased tar yields relative to char.(23) In fact, the yield of levoglucosan has often been confused with the yield of tar on the assumption that the two are virtually identical.

Generally, compounds containing phosphorus, halogens, and nitrogen are the most effective agents in decreasing tar yields from cellulose pyrolysis. Denson(119) found that ammonia formation was implicated in the action of nitrogen-containing additives, and suggested that the mode of action was the conversion of cellulosic carboxyl groups to the more stable amides and nitriles; phosphorus-containing compounds acted through the formation of phosphoramides.

The mechanism of action of phosphates on cellulose pyrolysis char yields was investigated by Hendrix,(120) using phenyl phosphates as additives. These organic phosphates formed phosphate esters with cellulosic hydroxyl groups; at 300°C the esters decomposed with the elimination of an organic phosphate, forming a dehydrated cellulose. The probable mechanism, involving

esterification, protonation of an hydroxyl group, and an S_{N_2} displacement, is shown in Figure 10. Nitrogenous bases had a synergistic effect with phosphates, due to their reaction with phenyl phosphates to form complex phosphoramides. These latter compounds reacted with cellulose to form esters at lower temperatures and in higher yields than did triphenyl phosphate alone. Interestingly, levoglucosan was not a major intermediate in the pyrolysis of cellulose treated with phenyl phosphates, phosphoramides, or other chemicals capable of forming phosphoramides. This would indicate that there are separate and distinct mechanisms for char and levoglucosan formation from cellulose itself. In the case of the phosphate-catalyzed reaction, the effect of the phosphate can easily be rationalized. By forming an ester, an inversion of configuration occurs at one hydroxyl group. This places the phosphate ester group in the *trans* configuration to a hydrogen atom on the adjacent carbon atom, required for E_2 elimination to become more favored. Without this inversion the preferred dehydration occurs between carbon atoms 1 and 6, leading to levoglucosan formation. The greater ease of phosphate cleavage relative to hydroxyl also aids in the elimination of water to form an unsaturated cellulose.

Direct phosphorylation of cellulose and heating of the product was also investigated by Inagaki *et al.*,(121) who concluded from their studies on the pyrolysis of cellulose methylphosphonate and cellulose phosphate ammonium salts that the initial decomposition occurred *via* a *cis-β*-elimination mechanism with formation of a double bond. Hence, the subject of the normal *trans* compared to the proposed *cis* elimination mechanism has yet to be resolved. Katsuura and Inagaki(122) also observed that the rate of double bond formation in pyrolyzed cellulose in the presence of phosphorus-containing flame retardants was directly proportional to the self-extinguishing character of the cellulose.



*CELL- = CELLULOSE CHAIN; $O=P(OH)_3$ = ORTHOPHOSPHORIC ACID; THE S_{N_2} MECHANISM IS SHOWN; THE S_{N_1} MECHANISM WOULD ALSO OCCUR. EITHER MECHANISM RESULTS IN INVERSION - TOTAL INVERSION BY S_{N_2} AND 50% INVERSION BY S_{N_1}. THE RESULT IS THE FORMATION OF A PHOSPHATE ESTER GROUP TRANS TO A HYDROGEN ATOM ON THE ADJACENT CARBON ATOM, SUCH THAT ELIMINATION CAN OCCUR TO FORM A DOUBLE BOND. TO SHOW THIS INVERSION, THE CELLULOSE MOLECULE IS PICTURED AS BEING IN A PLANE AT RIGHT ANGLES TO THE PAPER -- THE THICK BLACK BONDS BEING THE PORTION OF THE MOLECULE ABOVE THE PAPER PLANE.

FIGURE 10. Mechanism of Cellulose Double Bond Formation in the Presence of Phosphoric Acid Additive

The efficiency of various phosphorus-containing flame retardants was also proportional to the electron density in the phosphate group, and hence to the ease of elimination of this group.

Rafalsk'ii *et*. *al*.,(123) studied the effect of phosphorylation of cellulose and pyrolysis of the metal salts of the phosphorylated material. With no metal, decomposition was observed at 210°C, while the Mg, Be, Ni, Pb, and Ba salts did not start to decompose until between 280-330°C. In the absence of a metal ion, complete decomposition occurred by 250°C while temperatures in excess of 330°C were needed to complete the decomposition in the cases of the above metal salts. The copper salt, on the other hand, started to decompose at 230°C. Since copper salts are well known promoters of free radical reactions, these data indicate that there may be different decomposition mechanisms operating concurrently, although there is no direct evidence for this. There is one report(124) that inorganic salts promote C-C bond cleavage in cellulose rather than the normal C-O glycosidic bond cleavage.

Kislitsyn *et*. *al*.,(125) examined the applicability of free radical mechanisms to cellulose pyrolysis by the addition to cellulose of two stable radical generators: *di-β*-naphthylphenylenediamine, and 2,6-bis-(2-hydroxy-3-tert-butyl-5-methylbenzyl) 4-methylphenol. These compounds caused homolytic cleavage in cellulose, with intramolecular chain transfer. The overall activation energy was 30.5 Kcal/mole. The pyrolysis carried out at 335°C and 100 mm Hg yielded no detectable levoglucosan. This indicates that the normal mechanism for levoglucosan formation was suspended by the addition of free radical generators, and therefore that levoglucosan is formed through an ionic mechanism.

Wodley(77) studied the effects of flame retardants on cellulose and levoglucosan pyrolysis, and found that the formation of pyrolysis products from the untreated materials was essentially

independent of temperature in the range 330-440°C, and that the gas chromatograms of the products were consistent with a mechanism involving production of levoglucosan as the first step in the degradation of cellulose. The addition of ammonium dihydrogen phosphate or potassium bicarbonate (well-known flameproofing agents) did not alter the nature of the products from pyrolysis. It is thus evident that not all flameproofing agents containing phosphorus act in the same manner as triphenyl phosphate(120) or methyl phosphonate,(121) since these latter agents caused loss of water by elimination from within the glucose ring and suppressed the formation of levoglucosan.

Of the wide range of other cellulose derivatives which have been investigated for their behavior on pyrolysis, most were studied to determine their thermal stability for practical use rather than to determine their decomposition mechanisms. Although much useful information can be obtained from the published data on such compounds, it would not be pertinent to discuss it in detail here. Hence, the major articles and conclusions are summarized in Table 7. In place of a detailed description, examples illustrative of the different approaches and problems encountered will be given.

Unfortunately from the standpoint of determination of reaction mechanisms, much of the work on the pyrolysis of cellulose derivatives was carried out in the presence of air, which could have altered the mechanism. Oxygen is a diradical of rather weak activity, but is nonetheless capable of causing modifications in reaction modes. One example of how this occurs is in the formation of cellulosecarboxylic acids on heating. It is not unlikely that considerable esterification crosslinking could occur in such a case which would not occur if the pyrolysis were carried out under vacuum or in the presence of an inert gas. A more concrete

TABLE 7. Degradation of Cellulose Derivatives and Cellulose Additive Mixtures

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
Cellulose + organic phosphates	Supported ester/dehydration mechanism for additive effect. Ph.D. Thesis.	118
Cellulose + phenylenediamines	Structural support for stable group formation theory of additive action	118
2-*0*-methylcellulose	350°C/0.02 torr. 16% 1,6-anhydro-2-0-Me-β-D-glucopyranose identified as benzoate and by NMR. Obtained through a 1,4-anhydro-intermediate.	128
Cellulose triacetate	Heated at 900° yielded acetylated mono- and di-saccharides and oligomers, AcOH, ketene, and water.	129
Cellulose triacetate	Heated at <350° yielded a non-graphitizing char with complete loss of acetate.	130
Cellulose triacetate	Deacetylation and chain scission at the 1,4-glycosidic link, followed by condensation of C_5H_4O + C_5H_4 units.	131
Ethylcellulose Ethylcellulose Ca or Na salt	Increased heat stability was conferred by converting ethylcellulose into salts.	132
Ethylcellulose + 0.4% NaOH/1 hr/20°	1% oxalic acid at 60° for 2 hr or 98° for 1 hr degraded the Na salt less than untreated ethylcellulose.	133

TABLE 7. (Continued)

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
Trimethylcellulose	Heat produced 2,3,6-tri-0-methyl-1,4-anhydro-1,5-glucopyranose and 2,3,6-tri-0-methylglucose.	134
Methylcellulose	With 6.5-32.1% methoxyl, heat at 350-600° for 1 min. Methoxyl content of the cellulose was proportional to the methanol content of the pyrolyzate. The optimal temperature for maximum methanol production was inversely proportional to the methoxyl content of the cellulose.	135
Cellulose	REVIEW. $KHCO_3$ and other additives enhance formation and decomposition of hydrocellulose at the expense of depolymerization.	136
Cellulose diacetate-vinyl fluoride graft copolymer Cellulose diacetate	Decomposition started at >200°C; weight loss after 2 hr at 300° was 60-70%, and proportional to the $-CH_2-CH_2F$ content. The diacetate was 80% decomposed at 180°C.	137
Cellulose acetate, DP = 300-500 Cellulose acetopropionate, DP = 280-300 Cellulose acetobutyrate, DP = 280-300	At 150-200° the acetate of DP 300 was most resistant. Stabilizers (0.0015-0.002 mole/kg) were 4-methallyloxydiphenylamine, phenothiazine, and hydroquinone.	138

TABLE 7. (Continued)

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
Mesyl 6-bromocellulose Mesyl 6-fluorocellulose	Blockage of the 6-OH group decreased the flammability by preventing levoglucosan formation.	139
Cellulose *p*-Aminobenzylcellulose Acrylate-grafted cellulose	Heat stability was in the order cellulose>*p*-aminobenzylcellulose> acrylate-cellulose.	140
Cellulose acetate Cellulose propionate	Acid catalyst degradation mechanism by DP decrease with water, H_2SO_4, AcOH, EtCOOH, Ac_2O, $(EtCO)_2O$ at 25° and 35°.	141
Cellulose acetate propionate	Decomposition started at 220° by depolymerization. Volatile products obtained at 260-300°.	142
Cellulose diacetate	Stabilized by Ca^{2+} and Na^+.	143
Cellulose acetate Ethylcellulose	Increased heat resistance as Na, Ca, Mg salts. Degradation was homolytic without metal ions, by C-O cleavage. Ions inhibited free radicals.	143
Cellulosic materials	Oxidized with NO_2 to 6-carboxymethylcellulose; treated with $NaHSO_4$, Na_2SO_3, and $Al_2(SO_4)_3$, gave Al salt of 6-carboxymethylcellulose, which was heat-resistant.	144

TABLE 7. (Continued)

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
Monocarboxycellulose Monocarboxycellulose Pb salt	Lead salt was more stable. At $\leq 220°$ degraded by decarboxylation and depolymerization; dehydration at .245°; ring opening at >260°.	145
Cotton linters Rayon cord Viscose yarn	$NaIO_4/NaClO_2$ oxidation introduced carboxyl groups; decomposition rate at 140-200°C was directly proportional to carboxyl group concentration; DP decreased very rapidly.	146
Monocarboxycellulose	More stable than its salts; at >250°C the NH_4 salt was the most stable salt, becoming the least stable at <250°C. Li, Tl, K, NH_4, and Na salts tested.	147
Cellulose Monocarboxycellulose	At 490°C the reaction was heterogeneous and was autocatalyzed by low molecular weight products.	148
Cellulose dialdehyde Carboxymethylcellulose Tricarboxycellulose Monocarboxycellulose	Rate of degradation in vaccum was increased by the introduction of CH=O or CO.OH groups.	149
Cellulose Monocarboxycellulose Al and Cr salts	At <270°C cellulose was more heat resistant than its salts; decomposition activation energy for cellulose was 51.7 Kcal/mole; salts depolymerized to form levoglucosan.	150

TABLE 7. (Continued)

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
6-carboxycellulose NH_4^+ and anilinium salts	Complex decomposition with 6 DTA peaks.	151
Cotton cellulose Fortisan regenerated cellulose Arnel cellulose triacetate NO_2-oxidized cellulose	Vacuum pyrolysis gave tar yields decreasing in the order: cellulose>fortisan>arnel>oxidized cellulose.	152
Cotton cellulose	H_2SO_4/5 min/100°C pretreatment - I	153
Hydrated cellulose	From cuprammonium salt solution - II	153
Cotton cellulose	10% NaOH/1 hr/0°C - III	153
Cellulose hydrate fiber	- IV	153
Viscose silk	- V	153
	Hydrolyzability and levoglucosan yield were for I (5.21, 60-63%); II (10.76, 14-15%); III (9.55, 36-37%); IV (23.5, 4-4.5%); V (23.2, 4.8-5%). This was also the order of increase in crystallinity.	
Alkali cellulose + 0.15 g/l of $CoSO_4 \cdot 7H_2O$	At 55°C, decreased degradation time by 55 min.	154
Cotton cellulose + glucose	60% levoglucosan yield if water was present; 25-30% levoglucosan yield if glucose was present.	17

TABLE 7. (Continued)

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
Hydrated cellulose	5-14% levoglucosan yield. Hydrolysis, oxidation, dehydration were hence side reactions in levoglucosan formation.	17
Cellulose + 2-20% glucose	Decreased levoglucosan yield from 55-60% to 30%.	28
Cellulose + 20% glucose	Decreased levoglucosan yield compared to cellulose alone.	27
Cellulose + phosphate-containing flame retardants	Self-extinguishing propensity was proportional to the rate of double bond formation, which was proportional to the rate of ester elimination, proportional to the electron density in the phosphate group, and to the efficiency of the flame retardant.	122
$\left.\begin{array}{l}\text{Birch wood}\\\text{Sulfite pulp}\end{array}\right\}+$ Na_2CO_3; Zn, Cd, Al acetates	At 100 atm, 280-370°C, pyrolysis increased char yield to 42% compared to untreated material (33.6%).	155
Cellulose ammonium phenylphosphate Cellulose ammonium phenylphosphonate Cellulose	The order of initiation of weight loss with increasing temperature was: phosphate<phosphonate<cellulose.	156

TABLE 7. (Continued)

MATERIAL AND ADDITIVE	CONDITIONS AND RESULTS	REFERENCE
Phosphorylated cellulose	Decomposition started at 210°C, complete by 250°C.	123
Phosphorylated cellulose Cu salt	Decomposed at 230°C.	123
Phosphorylated cellulose Mg, Be, Ni, Pb, Ba salts	Lost water at 280-330°C; decomposed by >330°C.	123
Cellulose ammonium phosphate Cellulose + $NH_4H_2PO_4$	Different decomposition mechanisms.	157
Cellulose phosphonate	Initial decomposition temperature decreased with increased phosphorus content; 2-step decomposition with a rearrangement of phosphonate to phosphate.	158
Cellulose nitrate	Activation energy for decomposition was 37-39 Kcal/mole.	159

example of the effect of oxygen has been reported.(126) Cellulose ethers heated in the presence of oxygen underwent homolytic degradation mediated by oxygen insertion into labile C-H bonds, resulting in the formation of unstable hydroperoxides. The normal degradation mechanism in the absence of oxygen is heterolytic (i.e., ionic).

The effect of traces of acids on pyrolysis degradation mechanisms is illustrated by the work of Rosenthal.(127) Although this work was performed with the cellulose derivatives in solution in the respective acid anhydrides, the degradation was acid-catalyzed and would thus be expected to follow the same mechanism even in the presence of only traces of acids (such as could be formed by reaction of traces of oxygen with cellulose). The crux of the work was the discovery that cellulose acetate and cellulose propionate degraded at different rates - the acetate degraded 4x slower than the propionate. The explanation which was offered to account for this relied heavily on small steric differences between the acetate and the propionate. Whether or not this is the correct explanation, it serves to illustrate the problems associated with the determination of specific and unequivocal reaction mechanisms in cellulose pyrolysis.

9. The Effects of Inorganic Salts on Cellulose Pyrolysis Mechanisms

Another aspect of the overall problem which has received considerable attention is the effect of flame retardants on cellulose. Many inorganic salts are active in this regard. Quite apart from their commercial value, flame retardants are of importance for their use in elucidating reaction mechanisms because in many cases they have a specific action (such as depressing the yield of tar in cellulose pyrolysis), or because they react with cellulose in a specific way and allow some particular part

of the degradation reaction sequence to be enhanced or another to be depressed. Having stated this, it should also be borne in mind that in some cases the use of flame-retardants to elucidate mechanisms may lead to additional complications rather than simplifications because of the addition of yet one more variable in the reaction sequence.

There are in general three types of additives to cellulose which are active flame-retardants. These are 1) inorganic salts added in small quantities and which probably act primarily by physical means (e.g., borax), 2) inorganic and organic additives, present in small quantities, and which probably act as catalysts by direct chemical reaction with the cellulose to promote char formation (e.g., H_3PO_4), and 3) chemically modified celluloses (e.g., cellulose xanthate). The latter compounds have already been discussed.

The promotion of char formation at the expense of tar formation is generally believed to be responsible for chemical flame retardant action,(23) the flaming action being assumed to be due to the levoglucosan. This statement is supported by the work of Holmes and Shaw,(23) who found that purified cotton cellulose yielded mainly a combustible tar and water when pyrolyzed at 418°C in either vacuum or dry air. Addition of a flame retardant (in this case, tetrakishydroxymethylphosphonium chloride/urea/methylolmelamine, 1:1 borax/boric acid, or sodium metavanadate) resulted in increased yields of gas and char and decreased yields of tar, including levoglucosan. The tar was identified as a major factor in the flammability of cotton, the amount of tar and the flammability being directly related. These results were based on earlier results obtained by Madorsky et. al.,(22) from a study of pyrolyzed cotton, cotton hydrocellulose, and viscose rayon

impregnated with sodium carbonate and chloride. Both groups of authors were in agreement concerning the relative importance of the tar ('levoglucosan') in the flaming reaction.

Tang(160) determined thermochemical and kinetic factors during cellulose pyrolysis in the presence of additives, and concluded that inorganic salts decreased the pyrolysis activation energy and favored dehydration of cellulose to char over conversion to tar and levoglucosan, in essential agreement with Holmes and Shaw(23) and Madorsky et. al.(22) However, this work also showed differences between various additives. Ammonium phosphate and sulfate were the most effective agents, supporting the hypothesis of Denson(119) that these act through amide and nitrile formation mechanisms. Sodium tetraborate (borax) was able to catalyze the decomposition of levoglucosan to char before it was consumed in flaming reactions, a finding which is worthy of further investigation since it indicates a direct link between levoglucosan formation and char formation, which some authors have considered as being formed independently (e.g., (120)). Boric acid and ammonium pentaborate did not prevent flame formation but did reduce the char glowing reaction with air; sodium chloride decreased flaming and increased char glow. Potassium bicarbonate and disodium phosphate had moderate effects on tar formation and flaming. Although these effects were all observed during oxidation processes, and therefore highly suspect from the point of view of chemical reaction mechanisms taking place in the absence of air (such as pyrolysis), they do nonetheless indicate considerable differences in reaction mechanisms between various inorganic additives. Furthermore, even phosphorus and nitrogen-containing additives (ammonium salts and phosphates) which could theoretically act by forming amides, nitriles, or phosphate esters as has been suggested as one possible mechanism of action, do not always

act in the same manner. Thus there is room for further work in this area. In particular, the causal relationship between levoglucosan, tar and char formation, and flaming needs to be studied more carefully. The assumption that tar equals levoglucosan equals high flaming intensity is commonly made in the literature, and may be without foundation. For instance, some evidence has been obtained that levoglucosan yield and flame retardant action may not be directly related.(161) It was also found that both acidic and basic retardants accelerated the early stages in cellulose decomposition.

A group of inorganic flame retardants which has been extensively studied is the alkali metal bicarbonates, carbonates, and hydroxides. These probably all act by the same mechanism, since on heating the bicarbonates decompose at low temperatures to the carbonates, which react with acidic groups in the cellulose before further decomposition to the hydroxides. Broido(162) found that as little as 0.15% of $KHCO_3$ added to cellulose significantly altered the pyrolysis reactions. Up to 1.5% of potassium bicarbonate lowered the initiation temperature for decomposition by 80°, and eliminated flame-producing reactions in air in favor of reactions leading to glowing combustion. Similarly, $KHCO_3$ treatment of cellulose reduced the tendency to ignition on exposure to intense thermal radiation; however, the additive greatly increased the tendency to glowing ignition by increasing the rate and degree of pyrolysis. Production of hydrogen, methane, ethane and ethene were enhanced by the additive at the expense of tar formation.(163)

The effect of sodium bicarbonate and hydroxide and potassium hydroxide, either impregnated on cellulose or added as powders, has been determined by Dolan.(164) Generally, Dolan's results

support Broido's conclusions, although Dolan added much larger amounts of the alkalies so that physical impediment to the combustion process could have occurred.

An extensive study of the effect of various additives on cellulose pyrolysis has been published by Halpern and Patai.(26) These authors also classified the additives according to the probable reaction mechanism of their effect on pyrolysis. Concentrations of the additives as low as 10^{-4} moles/g of cellulose had significant effects both on the velocity of the cellulose decomposition process and the nature of the products formed. The conclusions reached from these experiments are as follows:

Basic additives such as sodium carbonate, acetate, and oxalate accelerated the rates of formation of water, acids, and CO_2. Tar formation was also accelerated, but there was no detectable anhydrosugar formation (i.e., levoglucosan) at 250°, and only small amounts at 275°. The number of double bonds in the residue was also much greater than in pure cellulose, indicating catalysis of dehydration between adjacent carbon atoms within a ring, (forming a double bond) rather than between two hydroxyl groups (forming an ether). Neutral salts such as sodium and lithium chlorides and sodium sulfate tended to act as weak bases. Hydrogen chloride was lost from the system NaCl-cellulose on heating, but not from sodium chloride alone, indicating a direct reaction with cellulose and NaCl before hydrogen chloride was produced.

Acidic additives such as sodium dihydrogen phosphate, sodium hydrogen sulfate, and trimesic acid (1,3,5-benzenetricarboxylic acid), acted in a different fashion. There was no appreciable effect on the rate of anhydroglucose formation, but two different major effects were noted on the char. The bulk of the weight loss from cellulose treated with $NaHSO_4$ was made up from water and levoglucosan, leaving a char consisting of 67% anhydroglucose

units. Sodium oxalate addition resulted in a weight loss entirely due to water, with 52% of anhydroglucose units in the char and presumably a much greater proportion of char derived from ring degradation products.

In another article in this series, Patai and Halpern(35) found that sodium bisulfate was a relatively poor agent for catalysis of carboxylic acid formation from cellulose, in comparison with trisodium phosphate, which was a good catalyst. Also, the best catalyst for levoglucosan formation was the worst for acid formation, again suggesting that cellulose pyrolysis occurs through competing reactions leading to char and water (dehydration) on the one hand, and to tar formation on the other. In a related context, Broido et. al.,(71) found that cellulose pyrolysis (without additives) led to levoglucosenone formation as well as to levoglucosan formation; pyrolysis of levoglucosan did not yield levoglucosenone. Total degradation occurred when levoglucosan was mixed with an equal weight of sodium bisulfate, and pyrolyzed. With cellulose and $NaHSO_4$, pyrolysis halved both the tar and levoglucosan yields.

The complexity of results and the differences between results obtained by many different workers only services to underline the fact that cellulose pyrolysis occurs through several competing reactions.

Borax (sodium tetraborate decahydrate) has been known as an effective flameproofing agent since early times. The literature on the discovery of this flameproofing agent and similar agents has been reviewed by Shafizadeh.(3) Since the first discoveries were the result of empirical searches rather than programmed experimentation based on a probable mechanism of action, this early work will not be further reviewed here. Evidence has been presented to suggest that the mechanism of action of borax and to

some extent of boric acid also, is one involving the solid state.(12) Arseneau found that although the action of borax was one of heat transfer hindrance through foam formation(165) there was also a reduction in the activation energy of the endothermic discoloration reaction from 27.8 to 25.1 Kcal/mole, and an <u>increase</u> in the activation energy of the major exothermic reaction in cellulose decomposition from 34.5 to 40.3 Kcal/mole! To further add confusion to this already complex mechanism of cellulose decomposition ammonium chloride caused an increase in the activation energy of the endothermic discoloration reaction from 27.4 to 31.8 Kcal/mole.

Physical effects in cellulose pyrolysis mechanisms were further implicated by Bains,(166) who suggested that fire retardants catalyze the loss of water from cellulose in the early stages of pyrolysis, causing the formation of a layer of insulating char over the compact crystalline portions of the cellulose.

Finally, to further complicate the issue, the degradation product of cellulose - glucose - has been found to exert an autocatalytic effect on the pyrolysis system. Golova <u>et</u>. <u>al</u>.,(27) observed that cellulose can yield 73-75% of a distillate solid at room temperature and containing 54-60% of levoglucosan, while glucose yielded 39-42% of solid distillate and only 5-6% levoglucosan. The addition of 2-20% of glucose to cellulose resulted in a reduction of the levoglucosan yield from cellulose by up to 30%. <u>Glucose</u> therefore acted as an inhibitor of levoglucosan formation in cellulose pyrolysis. Cellulose hydrate was observed to yield 5-14% of levoglucosan on pyrolysis.(17) Hence, hydrolysis, oxidation, and dehydration were considered to be side reactions in cellulose pyrolysis; the major reaction was suggested as cleavage at the glycosidic linkage of cellulose to yield fragments which either isomerize into levoglucosan or react differently to produce tar.

As will be apparent from the preceding discussion, the mechanism of additive catalysis of cellulose pyrolysis is most complex and in all probability involves several different mechanisms. Shafizadeh(3) listed these various mechanisms in 4 categories, although this is probably an oversimplification. The categories of additive catalysis were:

1. Coating of the cellulose fibers by the melted or foamed retardant and restriction of the escape of volatile pyrolysis products.
2. Thermal or heat sink effects, where the additive effectively reduces the temperature of the cellulose by absorbing the heat of combustion for its own decomposition.
3. Gas composition variation in the pyrolysis products by catalyzing the formation of non-flammable gases such as CO_2, or free radical traps which prevent flame propagation.
4. Chemical effects, such as the esterification and β-elimination mechanism proposed for phosphate-based fire retardants. This is the most authentic chemical mechanism and the one which has received the most attention in this current review. In terms of assisting the conversion of cellulose to tar at the expense of gases, water, and char, this category is by far the most important.

The foregoing brief summary cannot be considered as exhausting the literature work which has been done on the effect of additives on cellulose pyrolysis. However, since much of this work was not done with the intent of elucidating reaction mechanisms, a thorough review of the topic would be out of place here. Some further information is listed in Table 8.

TABLE 8. Effect of Inorganic Salts on the Pyrolysis of Cellulose

MATERIAL	ADDITIVE	RESULTS	REFERENCE
Plant	Natural minerals	Maximum rate of weight loss at 175-300°, and decomposition temperature, both proportional to silica-free mineral conc.	167
Cellulose	H^+, Na^+, Ca^{2+}, Fe^{2+}	At 140-200°, additives increased the carboxyl and carbonyl content and resin content and decomposition rate. The initial decomposition rate was independent of the metal ion, but subsequently increased in the order Na<H<Fe.	168
Cotton cellulose	Natural ash	At 0.06-0.09% ash, $\leq$45% levoglucosan was formed; the formation was maximum when 20-30% cellulose had decomposed. At 0.02% ash, 4-10% of levoglucosan was formed; the formation was maximum when 15-20% decomposed.	169
Cellulose hydrate	Natural ash	Decomposed at lower temperature than cellulose in all cases.	169
Cellulose, lignin, wood	2% Borax, NaCl, $KHCO_3$, $AlCl_3 \cdot 6H_2O$, $NH_4H\ PO_4$	All except borax decreased the temperature initiation of rapid weight loss.	170
Cellulose	None	Completely decomposed at 360°, char 16%.	
Cellulose	$AlCl_3$ in CCl_4, EtOH, or $PhNO_2$	DP decreased to 150-200 within 5 min.	38
Filter paper Avicel	Phosphoric acid	Decreased activation energy; increased char yield.	171

TABLE 8. (Continued)

MATERIAL	ADDITIVE	RESULTS	REFERENCE
Douglas Fir wood	None. Heated at 250°, 350°, 550°, and examined by scanning electron microscopy.		172
Douglas Fir wood	$ZnCl_2 + Na_2Cr_2O_7$	No difference from untreated wood.	172
Douglas Fir wood	Urea + Ammonium phosphate + glucose	Cell walls became thermoplastic.	172
Wood, cellulose, lignin	2% and 8% by weight of borax, $KHCO_3$, NaCl $AlCl_3 \cdot 6H_2O$, $NH_4H_2PO_4$, H_3PO_4; 8% Na_2HPO_4, $(NH_4)_2SO_4$, $NH_4B_5O_8 \cdot 8H_2O$	Net heat of pyrolysis of lignin and wood initially endothermic, became exothermic; cellulose pyrolysis endothermic. All additives decreased levoglucosan yield.	173
Cellulose	Borax, $AlCl_3$, $NH_4H_2PO_4$	Caused increased thermal oxidation rate at below 200°C and decreased the flammability above 200°C.	171
Cellulose	None	1st Order depolymerization mechanism, with an activation energy of 40.5 Kcal/mole.	175
Cellulose	$KHCO_3$	Dehydration and depolymerization mechanism.	
Cellulose	H_3PO_4, KBr, K_2CO_3, borax, $NH_4H_2PO_4$	No correlation between the effect of flame retardants and the levoglucosan yield. Both basic and acidic retardants accelerated the early stages of pyrolysis.	161

TABLE 8. (Continued)

MATERIAL	ADDITIVE	RESULTS	REFERENCE
Cellulose	Borax, NaCl	Additive increased char yield on heating in vacuum.	176
Cellulose	NH_4Br, $(NH_4)_2HPO_4$, borax		177
Cellulose, sugar (ash-free)	40 different additives	Effect on char yield determined; importance of mineral content in cellulose.	178
Cotton cellulose	None	CO/CO_2 ratio = 0.112	179
Cotton cellulose	Phosphate salts	CO/CO_2 ratio = 4	179
Cotton cellulose	Vanadium halides	CO/CO_2 ratio increased	179
Cotton cellulose	47 other additives	CO/CO_2 ratio increased by a lesser amount than phosphates or V salts.	179
Cotton cellulose	Na_2CO_3, Li_2CO_3, LiCl, NaCl, K_2CO_3	All decreased the tar yield.	179
Cotton cellulose	Phosphates, borax, $Ce(SO_4)_2$, $CrCl_3$, $SbCl_3$, $ZnCl_2$	No afterflow.	179

TABLE 8. (Continued)

MATERIAL	ADDITIVE	RESULTS	REFERENCE
Cellulose	Ammonium salts	Increased oil yield by 17%.	180
Cellulose	Sulfates of Fe^{3+}, Na, Mg, Zn, Al	Decomposition rate increased in the temperature range 20-400°C.	181
Cellulose	10% $Fe_2(SO_4)_3$	80-150° for up to 100 hr. Activation energy 16 Kcal/mole for decomposition.	181
Cellulose	Cu_2Cl_2, $CuCl_2$, $ZnCl_2$	Bond cleavage caused by hydrolysis and <u>then</u> oxidation, not the reverse.	182
Cellulose	Na_2SiO_3, K_2CO_3, $KHCO_3$, KOPh, $(NaOOC)_2$	Tar yield decreased on pyrolysis.	183
Cellulose	$ZnCl_2$ in water		184
Wood	Borax, K_2CO_3	Lowered activation energy for pyrolysis	185
Cellulose	Inorganic salts	Promoted C-C bond cleavage rather than C-O (hydrolysis)	124
Cellulose	"Flame retardants"	Increased decomposition rate and char.	186
Cellulose	"Flame retardants"	GC/pyrolysis; comparison of levoglucosan formation with untreated cellulose. The additives decreased the decomposition temperature but not the GC trace appearance.	187

TABLE 8. (Continued)

MATERIAL	ADDITIVE	RESULTS	REFERENCE
Cellulose	Boric acid	Increase in start of the decomposition temperature.	188
Cellulose	$(NH_4)_2HPO_4$, NH_4Cl	Decrease in start of the decomposition temperature.	188
Cellulose	$AlCl_3$ in dry CCl_4	Depolymerization; decreased polymer mol. wt. range and degree of crosslinking.	189
Cellulose	H_2SO_4, HBr, HCl	150-190°/2-8%/1-3 hr. HCl gave a 45% yield of levulinic acid at 150°/1 hr.	190
Cellulose	"Flame retardants"	Number of compounds produced by pyrolysis at 330-400° was decreased by retardants.	82
Cellulose	Alkali metal base, Alkali metal base salts	Decreased the transition temperature, activation energy, tar, increased the residue, did not alter 1st order reaction kinetics.	191
Cellulose, etc.	Borax, NaCl, $KHCO_3$, $AlCl_3$, $NH_4H_2PO_4$, H_3BO_3, $(NH_4)_2B_{10}O_{16}$	Borax reduced flaming, as did 2% NaCl. 2% $KHCO_3$ was equivalent in effect to 8% NaCl.	192

TABLE 8. (Continued)

MATERIAL	ADDITIVE	RESULTS	REFERENCE
Cellulose	$KHCO_3$ (0.15, 1.5%)	Lowered by 80° the initiation temperature of decomposition; eliminated flaming reactions in favor of glowing combustion.	162
Cellulose	NH_4Cl	Increased endothermic discoloration reaction activation energy from 27.8 to 31.4 Kcal/mole.	165
Cellulose	Borax	Decreased this activation energy to 25.1 Kcal/mole.	165
Cellulose	2% $KHCO_3$	Time-of-flight MS study. $KHCO_3$ increased degradation rate 7-fold at 300°C; little difference in volatile compounds.	193
Cellulose	1.5% $KHCO_3$	Increased sensitivity to glowing ignition; enhances combustible gas production, decreases tar formation.	163
Cellulose	$(NH_4)_2HPO_4$	Acted as a proton source, catalyzed the dehydration reaction, decreased activation energy and tar formation, increased char.	194
Cellulose fabrics	"Flame retardants"	Computer simulation of pyrolysis. Ph.D. Thesis.	195

IV. SUMMARY

Cellulose pyrolysis is a complex process involving many competing reactions. The initial reaction of cellulose is one of a reduction in the DP to about 300, and subsequent formation of the anhydride 1,6-anhydro-β-D-glucopyranose (levoglucosan) and other products. Conversion to the monomer, glucose, does not occur to any significant extent, since it has been shown that levoglucosan is the major product of cellulose pyrolysis but a relatively minor product of cellobiose or glucose pyrolysis (Figure 11). The levoglucosan may be produced by a combined chain cleavage and rearrangement mechanism, which can take place at any point in the cellulose chain. An alternative minor product - 1,6-anhydro-β-D-glucofuranose - may only be formed at the non-reducing end of the chain. Levoglucosan is then believed to dehydrate to levoglucosenone. Further degradation products of the two anhydrosugars include furan derivatives, particularly 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde, although the detailed mechanisms for their formation are unknown. Large numbers of other simple molecules are also produced in trace amounts, with no proven causal relationship between any of the major products and any of the minor products.

Alternatively, the levoglucosan may polymerize to an uncharacterized polymer with a continuous carbon chain, which can conceivably either degrade to the observed minor products, or form the observed char product.

At some stage of the pyrolysis, at temperatures in excess of 300°C, cellulose itself undergoes a crosslinking reaction which may involve a free radical mechanism. The ultimate fate of the crosslinked product, or even its importance in the overall degradation network, are unknown.

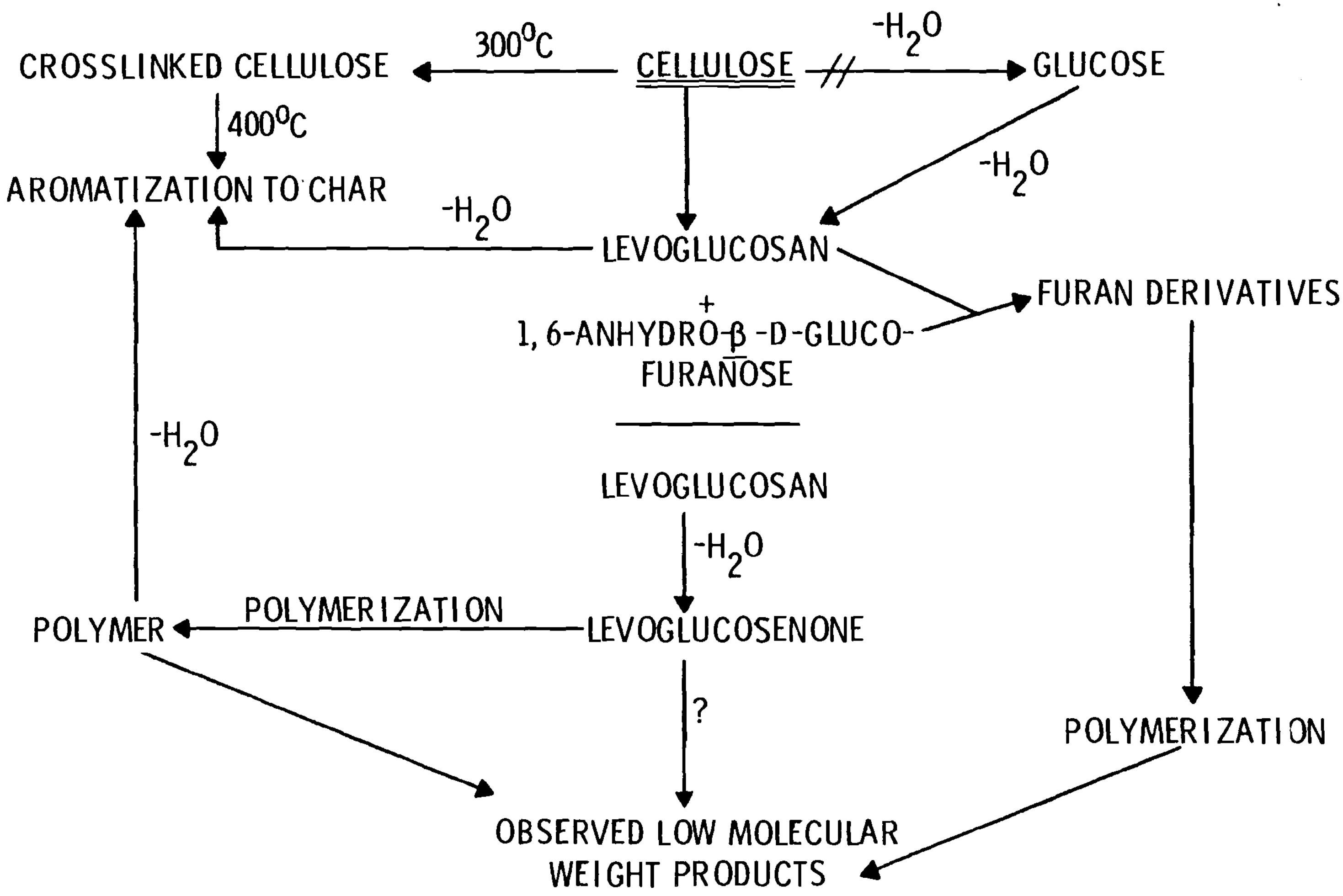


FIGURE 11. Summary of Probable Routes for Cellulose Pyrolysis

The addition to cellulose of various inorganic salts, or modification of the cellulose molecule by the addition of foreign groups, leads to considerable alteration in the nature and quantities of the products observed on pyrolysis. Phosphates and ammonium salts or amines appear to form cellulose derivatives on heating, such as the amides, nitriles, phosphoramides, or phosphonic acids. These degrade through a direct dehydration mechanism with the formation of double bonds within the glucose rings and do not appear to form levoglucosan, although there is some disagreement about this conclusion. The mode of action of the various other salts which are commonly used as flameproofing agents is obscure, since no work has been done on the pyrolysis of cellulose/salt mixtures in the absence of air. Thus, beyond a statement that these salts appear to depress the yield of volatile tar from cellulose, little is known regarding their mechanism of action. Physical effects as well as chemical have been suggested.

V. CONCLUSIONS

The history of research into the mechanisms of cellulose pyrolysis may be divided into three areas. Firstly, the early work beginning in the nineteenth century, where classical methods of analysis of the complex mixtures of products obtained yielded basic information - the formation of levoglucosan as a major product, for instance. Secondly, with the advent of sensitive instrumental analytical techniques such as thermogravimetric analysis, mass spectrometry, and gas chromatography, the identification of many minor components became possible. The third stage has only just begun, and involves the synthesis of all of the information into an overall scheme for cellulose pyrolysis, including detailed reaction kinetics and mechanisms for each stage of the process. Most probably, this will involve mainly

isotopic labeling with carbon and deuterium, coupled with analysis by radiochromatography and gas chromatography/mass spectrometry.

There are many problems which remain to be solved. To name but a few, the question of whether or not levoglucosan is a true intermediate in the cellulose degradation pathway; whether levoglucosenone polymerizes or degrades to furans; the origin of the char; the degradation pathway to furans; the relative importance of free radical and ionic mechanisms at various temperatures; the importance of crosslinking of cellulose in modifying the overall pathway by generating different polymers which can also degrade thermolytically.

Ultimately, the application of a systematic research program to elucidate the catalytic effects of various additives to cellulose may lead to new ways of degrading cellulose such that specific and desirable products may be obtained, or minimizing char yields where the production of liquid fuel is the object in view.

Despite the century and a half of research into the mechanisms of cellulose pyrolysis, and the voluminous literature on the subject, the bulk of the necessary work still has to be done before any sort of a consistent and rational degradation scheme can be proposed, or before any useful predictive work can be done on the effects of various additives.

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