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SPECULATIONS ON THE NATURE OF CELLULOSE PYROLYSIS†

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Abstract—Consideration of the available data on cellulose pyrolysis suggests that, with relative importance depending upon heating rate in the temperature range 200–400°C, very pure cellulose decomposes by two competitive endothermic processes. It is postulated that an unzipping reaction produces 1,4-anhydro-α-D-glucopyranose which rearranges to give levoglucosan. The other process, a dehydration, is considered to form the starting material for a subsequent exothermic process which results in CO_2, CO, further H_2O, and char. Although the known effects of some salts on cellulose pyrolysis can be explained by this mechanism, further experiments to more fully characterize the individual reactions, and isolate and determine the structure of unidentified intermediates, are clearly indicated.

INTRODUCTION

IN a recent critique[1] of the present state of knowledge of the mechanism of cellulose pyrolysis, we reviewed several divergent theories and indicated a need for greater detail in interpretation of the reaction mechanism as well as in the prerequisite experimental studies—certainly detail well beyond the early experiments which broke down the reaction products grossly into gaseous, tar, and char fractions. Much more information is needed to permit better prediction of the action of fire-extinguishing and flame-retarding chemicals. In particular, the critique called attention to the recent recognition of the importance of trace inorganic impurities in the cellulose[2,3] and to the question this recognition raises about earlier experimental results. The present paper considers briefly some of the more recent data and speculates about the nature of the pyrolysis reactions which could account for the observed results.

EXPERIMENTAL OBSERVATIONS

In addition to the early crude breakdowns of gross reaction products, currently available observations of cellulose pyrolysis include differential thermal analyses (DTA), thermogravimetric analyses (TGA), mass

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spectrometric thermal analyses (MTA), and gas and paper chromatographic separations of products. However, the cellulose samples used in these experiments have come from a variety of sources and undergone a number of diverse preparative treatments. The resulting variable ash content of the samples, in particular, markedly affects the pyrolysis behavior. For example, TGA curves[4] obtained with cellulose containing 0.1% ash (a concentration roughly that of ordinary filter paper) and with "ash free" cellulose (less than 0.01% ash) showed a difference of

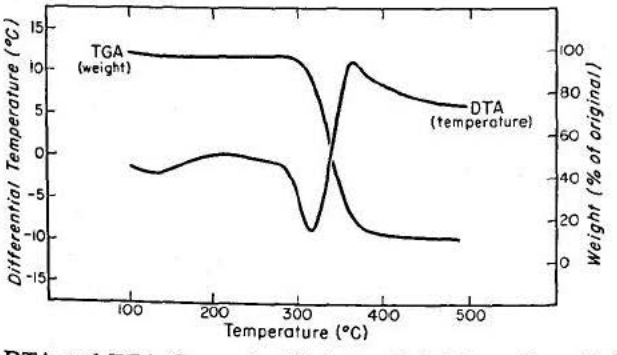


Figure 1.—DTA and TGA Curves for "Ash-Free" Cellulose (from Reference 4).

about 30°C in the temperature at which the first detectable weight change occurred when the samples were heated at a rate of 6°C per minute in a flowing nitrogen atmosphere. Thus, in interpreting the results of pyrolytic studies of cellulose, great care must be taken to insure that such interpretations are not grossly distorted by the effect of undefined impurities.

As may be seen from Figure 1, the TGA curve for "ash-free" cellulose, after an initial drop in weight attributable to evaporation of extra-cellulosic water, shows the first detectable weight loss at about 280°C, a rapid weight loss until about 360°C, and a tailing off of the weight curve towards a 10% residual "char" at higher temperatures. In the temperature region below 360°C, the corresponding DTA curve shows four distinct reaction zones: the initial endotherm attributable to extra-cellulosic water, a slight endotherm starting at about 220°C, a much sharper endotherm at about 280°C corresponding to the onset of the severe weight loss, and a sharp exothermic up-swing beginning at about 320°C.

By either TGA or DTA techniques, the detection of a reaction zone depends, of course, upon the sensitivity of the instrumentation. In particular, although DTA can be used to detect reactions involving no weight change, additional experiments can distinguish such cases from those resulting from differences in sensitivity. Thus, it can be simply demonstrated that the endothermic process starting at 220°C is concurrent with a slow weight loss, and is not merely a rearrangement without weight change. By heating a sample of the "ash free" cellulose at 230°C for a 24-hour period, a loss corresponding to about 10% of the starting weight is observed. The reality of a weight-loss reaction in this temperature region has been confirmed by Lincoln[5] using MTA, an analytical procedure many orders of magnitude more sensitive than the simple weight-loss determination. That this first slow weight loss represents a dehydration of the cellulose has also been confirmed by Lincoln who, on heating microcrystalline cellulose (0.04% ash) under vacuum in this temperature range, observed only water leaving the reaction chamber.

The deeper endotherm and more rapid weight loss evident from about 280°C in Figure 1 can be attributed to the tar formation resulting from the depolymerization of the cellulose molecule. The exotherm resulting in the remainder of the major weight loss corresponds to a char-forming reaction with the evolution of water and a large variety of small carbon-containing compounds.

A number of simple experiments indicate that the two endothermic reactions compete for the original cellulose molecules, and that the exothermic reaction involves the product from the first of these endothermic reactions. For example, a cellulose sample first held for a day at about 250°C forms about three times as much char at 400°C as does a similar sample heated directly to 400°C (about 30% instead of 10%). The thermograms obtained by Berkowitz,[6] and reproduced in Figure 2, provide perhaps the most striking confirmation of the interrelationship of these three reactions. In this figure, Curve A represents a thermogram of Whatman's cellulose heated in a stream of nitrogen at 6°C per minute. If the sample is first held at a temperature slightly below 200°C for twenty minutes, the exotherm occurring in this region increases as shown in Curve B. If a sample is first held around 250°C for one or two hours, the characteristic endotherms disappear completely, as shown by Curve C.

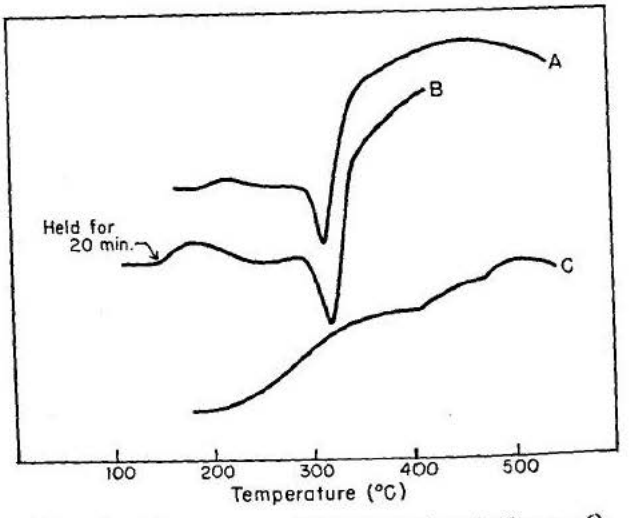


Figure 2.—Thermograms of Cellulose (from Reference 6).
A.—Whatman's Cellulose;
B.—Held for 20 Minutes near 150°C;
C.—Held for 2 Hours around 250°C.

The following set of reactions (summarized in Figure 3) correlates these experimental observations:

1. A dehydration, first observed at about 220°C; *i.e.*, pure cellulose reacts in a process involving the loss of water to yield a "dehydrocellulose."
2. A depolymerization, with volatilization of the product, first evident at about 280°C; *i.e.*, previously unreacted cellulose "volatilizes" via an endothermic process competitive with the dehydration.
3. A decomposition of the "dehydrocellose" formed in the first process—via one or more exothermic reactions—into a number of gaseous products and residual char. At lower temperatures the rate of decomposition is slower than the rate of formation, but the decomposition rate increases rapidly with temperature.

If one assumes that the effect of inorganic impurities is to catalyze the dehydration and char-forming reactions at the expense of the depolymerization reaction, many of the observations found with impure cellulose may also be explained. Thus, the assumptions provide an obvious explanation of the large increase in char and decrease in

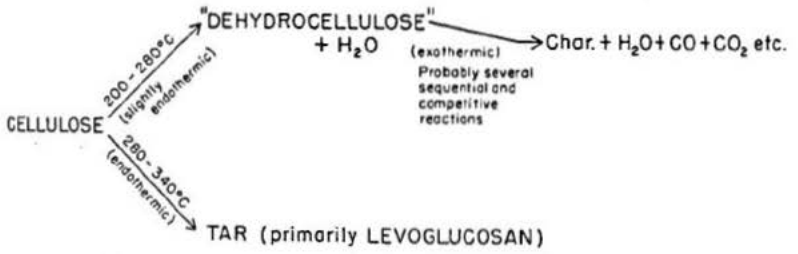


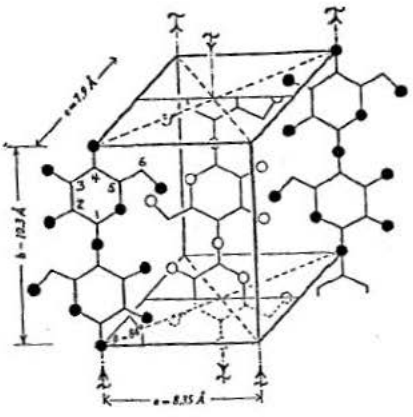
Figure 3.—General Scheme for the Pyrolysis of Cellulose.

tar observed with impure cellulose or with cellulose treated with a variety of fire-retarding agents. They can also reconcile apparently conflicting DTA results, *e.g.*, the range of temperatures at which various experimenters first observe the major endotherm. In fact, they can even alter interpretations of the number of reactions occurring, *e.g.*, the twin exotherms observed with impure cellulose can be interpreted as a single exotherm whose slope is interrupted by the endothermic volatilization.

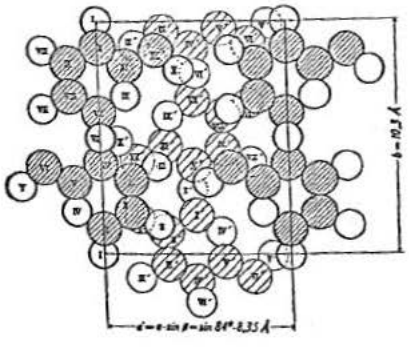
POSSIBLE MECHANISMS

Structure of cellulose. Currently held theories of the structure of native cellulose[7,8] describe cellulose as an array of chains of glucopyranose units linked together at the 1 and 4 positions by the elimination of water. Figure 4 illustrates the relationship between individual units of each chain, and between neighboring chains in the crystalline regions.[9] The detailed conformation of the individual units relative to the chain axis is not certain,[7] but Figure 4b illustrates one possible conformation. It also depicts the probable relationship along the *c* axis between the individual units of cellulose chains in neighboring *a*-*b* planes. As may be seen, the neighboring chains are held sufficiently close together in the crystalline region that steric considerations do not necessarily rule out the possibility that inter-molecular pyrolytic reactions (between two or more chains) can occur as readily as intramolecular reactions (*i.e.*, within a single chain).

Dehydration. Water can arise from dry cellulose by several dehydration reactions, which may be classified as (1) intra-ring, (2) inter-ring intra-molecular, and (3) inter-molecular. An intra-ring dehydration would arise through an elimination, resulting in a double



(a)



(b)

Figure 4.—The Crystalline Structure of Cellulose (from Reference 9).
A.—The Unit Cell;
B.—Projection of the *a*–*b* Planes along the *c* Axis of the Unit Cell.

bond, or through a displacement, resulting in an internal ether (or oxide). Inter-ring and inter-molecular dehydrations must ultimately produce new ether linkages, or new carbon–carbon single bonds.

Until a detailed analysis of the structure of "dehydrocellulose" is obtained, the exact nature of the water-forming process can only be inferred from restrictions such as the following: (1) Since the loss of water proceeds by a slightly endothermic process, whereas the

vaporization of water† requires about 9 kcal per mole, the process reactions must be exothermic by somewhat less than 9 kcal per mole. (2) The accompanying rearrangement of the native cellulose structure interferes with the subsequent depolymerization–volatilization process at higher temperatures.

These two restrictions eliminate all intra-ring dehydration mechanisms, since these would involve a negative or zero energy change and would produce modified units which could still take part in a concerted volatilization. The restrictions also serve to make unlikely the only plausible inter-ring intra-molecular dehydration, *i.e.*, the formation of an ether link between the C-6 position of one ring and C-2 position of the succeeding ring (see Figure 4). Such a reaction would involve a slightly negative energy change, if any. On passing through such modified rings, a concerted depolymerization reaction would produce a dimer which would not be volatile. However, the rate and extent of volatilization of the residue would be affected only if a large percentage of the rings were so modified.

Similar considerations serve to eliminate an inter-molecular dehydration between chains in the same *a–b* plane (Figure 4). However, they do not eliminate the one remaining type, namely the reaction between molecules in adjoining *a–b* planes.

Reactions between superimposed cellulose chains most likely will involve hydroxyls on C-6 or C-2 since these groups lie directly above (or below) reactive points of adjacent molecules (see Figure 4). A simple etherification involving the hydroxyl groups at C-2 positions of adjoining rings would not meet the energy requirements of the observed reaction. However, an etherification which links the C-6 and the C-4 positions of adjoining rings could be followed by a rearrangement of the acetal form of a carbonyl group to the free aldehyde, as depicted in Figure 5. Such a sequence should be exothermic by about 9 kcal per mole. The resulting modification of the original cellulose molecule

† It is assumed that the heat of reaction with all materials in the condensed phase is equal to the heat of the same reaction if all materials were in the vapor phase. This assumption is equivalent to the assumption that, in reactions such as

$$ROH + HOR' \rightarrow ROR' + HOH,$$

the sums of the inter-molecular forces on either side of the arrow are the same. In turn, this requires that the total heats of vaporization for reactants equal those of products. Although useful data are nearly non-existent, the limited values which have been found (*e.g.*, etherification of amyl alcohol) indicate that the assumption is reasonable.

would stop the passage of the chain-reaction depolymerization. Also, the new ether link would prevent either of the linked rings from volatilizing. The subsequent collapse of the intermediate (Figure 5b) produces water and a tetrahydro-5-hydroxymethylfurfural system. Decomposition of the latter could yield the 5-hydroxymethylfurfural observed[10] in tar obtained from cellulose pyrolyses.

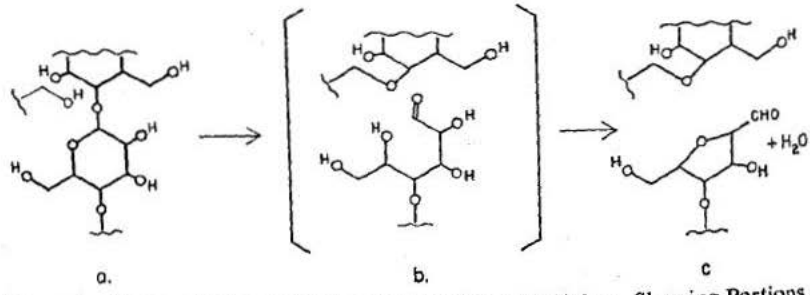


Figure 5.—Proposed Process for the Dehydration of Cellulose, Showing Portions of
A.—Unmodified Cellulose;
B.—Reaction Intermediate;
C.—"Dehydrocellulose".

Depolymerization. Levoglucosan (Figure 6c), the major constituent of pyrolytic tars, is an isomer of the cellulose monomer, with identical configurations at each of the five respective asymmetric centers. It may be obtained in high yield (much greater than 50%) from the pyrolysis of cellulose.[11] Thus we would expect its formation to occur by a simple process.

For each molecule of levoglucosan produced from cellulose, two bonds must be broken and one formed. The simplest mechanism would involve only the atoms united by these bonds, and may be described in terms of two interactions (Figure 6). The first interaction involves the displacement of the oxygen atom attached at C-1 of a glucosyl unit of cellulose by the rearward attack of the oxygen attached at C-4 of the same unit (an S_N2 type of reaction[12a]). Initially, the attacking species could be the C-4 hydroxyl group occurring free at the end of a chain or arising from a random scission of the cellulose chain. Subsequently it could be the anionic oxygen freed by removal of the first ring in a chain process continuing down the length of the molecule. The product of this displacement would be a monomeric anhydro-sugar, 1,4-anhydro-α-D-glucopyranose (Figure 6b).

The second interaction involves the attack within this anhydride by its C-6 hydroxyl group on its C-1 carbon atom. Displacement of the 1-4 oxygen bridge produces levoglucosan. Displacement of the 1–5 oxygen bridge yields 1,6-anhydro-β-D-glucofuranose (Figure 6d), a minor product of cellulose pyrolysis.[13]

This mechanism accounts for a number of facts about cellulose pyrolysis. The "unzipping" it depicts would result in the large yields of levoglucosan and the large loss of weight from the cellulose observed

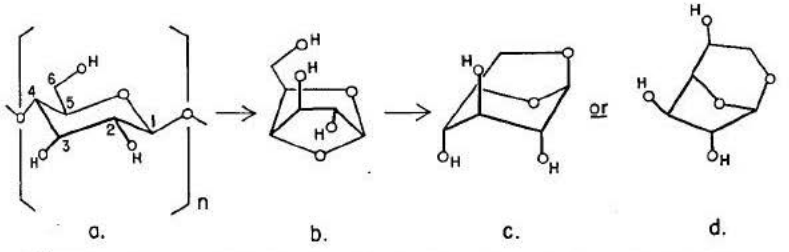


Figure 6.—Proposed Mechanism for the Depolymerization of Cellulose.
A.—The Glucopyranosic Monomer;
B.—1,4-Anhydro-α-D-Glucopyranose;
C.—1,6-Anhydro-β-D-Glucopyranose (Levoglucosan);
D.—1,6-Anhydro-β-D-Glucofuranose.

under certain conditions. The endothermic chair-to-boat conformational exchange in the first step would contribute to the DTA endotherm observed around 280°C as the monomer is evaporated on forming. Since the 1,4-anhydride should be volatile under pyrolytic conditions, the exothermic boat-to-chair conversion of the substance to levoglucosan could occur in the gas phase and so not affect the thermogram of the solid residue.

The C-6 hydroxyl and the C-1 oxygen bridge to the next unit of the polymer extend from the same side of any glucopyranose ring. They cannot interact by a concerted displacement mechanism. However, the C-4 oxygen bridge is opposite both of these groups. The proposed sequence of displacements is sterically plausible, and would produce the configurations of hydroxyl groups and oxygen bridges which are observed in levoglucosan.

Although 1,4-anhydro-α-D-glucopyranose, the proposed intermediate, has not been described in the chemical literature, a derivative, 2,3,6-trimethyl-1,4-anhydro-α-D-glucopyranose, has been obtained in 42% yield from the pyrolysis of trimethylcellulose.[14] At least one

other compound, 1,4-anhydro-α-D-ribopyranose,[15] is known to have the bicyclic system proposed for the intermediate. However, the instability of the intermediate relative to levoglucosan could complicate any attempt to observe or isolate it. Proof of its existence might depend upon its synthesis under mild conditions, followed by studies of its reactions when heated.

Decomposition. Several plausible mechanisms describing the decomposition of the "dehydrocellulose" residue are depicted in Figure 7. These include the reversal of typical condensation reactions between

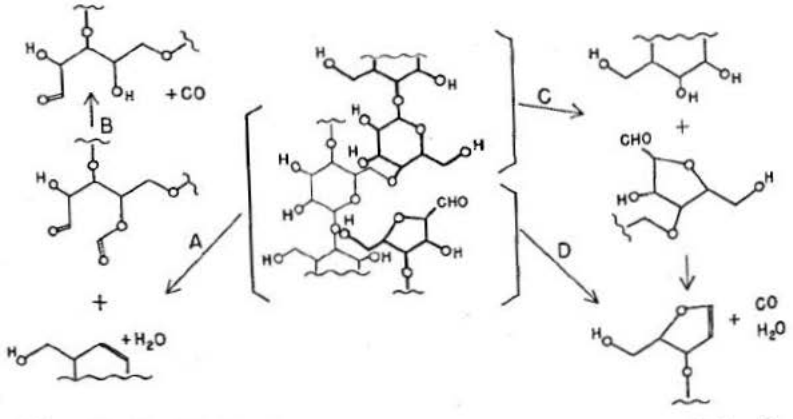


Figure 7.—Possible Reactions in the Decomposition of "Dehydrocellulose."

various double-bond, carbonyl, and hydroxyl functions. Thus Process A includes a concerted retro-benzoin-dehydration reaction. This is followed by a typical decomposition of a formate ester to give carbon monoxide and an alcohol (Process B). Process C, a rearrangement with opening of the pyranose ring, is followed by Process D, a concerted decarbonylation-dehydration reaction. Other analogous reactions could be portrayed. In each case the formation of the carbon–oxygen double bond or of carbon monoxide can provide energy which contributes to the exotherm of the DTA curve.

Carbon dioxide can arise from decarboxylation of the acids formed in Cannizzaro-type disproportionations. The fact that many acids decarboxylate readily, whereas the reduction products would be more stable to heat, would account for the excess of carbon dioxide over reduced products in the gaseous effluent.

The products of such decompositions, shorn of carbons and water, could undergo inter-molecular condensations of neighboring hydroxylic functions with some of the new double bonds. The result of such condensations and further dehydrations and other decompositions would be the complex material known as char.

The intermediates depicted above can undergo other reactions to produce such molecules as formaldehyde, acetaldehyde, and other small molecules which bear carbonyl, hydroxyl, and double-bond functional groups. Through hydride ion transfers, hydrogen, methane, and other molecules of low oxidation state can also arise. Both types of products have been observed to originate from the pyrolysis of cellulose.[2]

Effects of catalysts. The reactions proposed to account for the dehydration and decomposition of cellulose are known to be affected by Lewis acids or bases. For example, Hine has illustrated the basic catalysis of the S_N2 type of etherification,[12b] of the hemiacetal-hydroxy-aldehyde interconversion,[12c] of decarbonylation,[12d] of Cannizzaro-type disproportionations,[12e] and of β-eliminations (of water, in our case) to form double bonds.[12f] In contrast, however, the chain-reaction depolymerization involves a self-sustaining sequence of concerted displacements which should remain unaffected by added acids or bases.

Thus, the addition of salts such as $KHCO_3$ would be expected to catalyze the rate of formation of "dehydrocellulose." Since this reaction competes with the depolymerization for cellulose, less cellulose would remain to depolymerize as the sample temperature was increased. The added salt would also catalyze the decomposition of the "dehydrocellulose," thus leading to an increased rate of formation of CO_2, CO, and char.

Although the general effect of Lewis acids or bases can be predicted, the relative effectiveness of various such materials is quite a different matter. Also remaining to be explained is the effectiveness of materials which cannot qualify as Lewis acids or bases. In particular, the wide difference in effectiveness of apparently similar salts is yet unexplained. If flaming combustion is entirely attributable to the volatilization of a cellulosic monomer, its elimination is not restricted to treatments which enhance the dehydration reaction. Anything which would interfere with the depolymerization, or would lead to a non-volatile product of depolymerization, would also reduce the flaming process. Thus, the conclusions so far established, while encouraging in their

consistency, suggest the need for considerably more research before the quantitative effectiveness of specific retardants can be successfully predicted.

SUMMARY

The pyrolytic decomposition of cellulose involves at least three distinct processes, each including one or more reactions. The first, slightly endothermic, process is attributed to an inter-molecular reaction with loss of water to form a "dehydrocellulose." During the second endothermic process, which competes with the first process for native cellulose, levoglucosan, the major constituent of the tar, is postulated to arise from the rearrangement of 1,4-anhydro-α-D-glucopyranose formed in an unzipping reaction. Finally, the exothermic process is ascribed to reactions of the "dehydrocellulose," which experiences carbon–carbon and carbon–oxygen bond ruptures and hydride ion transfers to produce volatile carbon-containing compounds and hydrogen, and inter-molecular condensations to produce char.

The known effects of Lewis acids and bases in catalyzing reactions of this type explain the action of many inorganic impurities in enhancing the formation and decomposition of "dehydrocellulose" at the expense of the depolymerization reaction. However, further experiments which more fully characterize the individual reactions, and isolate and determine the structures of unidentified intermediates, are clearly indicated.

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