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COMMENTS AND DISCUSSIONS

A Critique of the Present State of Knowledge of The Mechanism of Cellulose Pyrolysis

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This critique reviews several divergent theories of cellulose pyrolysis, raises questions about experimental results obtained prior to the recent recognition of the importance of trace impurities, and indicates the need for sufficient detail in the reaction mechanism to permit a better prediction of the action of fire extinguishing and flame retarding chemicals.

The phrase "reaction mechanism" generally refers to a description of the stepwise processes by which one set of atoms or molecules changes into a different set. As this description becomes more detailed, it becomes of increasing value in predicting and directing the course of chemical reactions. Growing recognition of the unlimited potential of such detailed studies has led to an almost revolutionary expansion of the field of physical organic chemistry in the past generation. Such interest has led to the development of much new apparatus and techniques, which in turn have stimulated much more detailed investigations. As with other problems in this field, studies of the mechanism of the pyrolysis and combustion of cellulose are becoming increasingly refined. Thus, they can be expected to be increasingly useful in predicting and directing the course of the reactions involved.

Early studies of the pyrolysis of cellulose were confined to determination of such gross fractions as gas, tar, and char and to simple observation of how the combustibility of the sample varied with the relative proportions of these fractions. Such studies clearly established that the production of a large proportion of "tar" favors high flammability.[1,2]

As early as 1918, Pictet and Sarasin[3] isolated a crystalline substance from the tarry volatile products formed when they distilled cellulose in a vacuum. They named the substance "levoglucosan" in keeping with its formula ($C_6H_{10}O_5$), its negative optical rotation, and the fact that acid hydrolysis converted it to glucose. Josephson[4] determined that this substance was 1,6-anhydro-β-D-glycopyranose (see Fig. 1). These observations can be expressed crudely as

$$(C_6H_{10}O_5)_n \rightarrow mC_6H_{10}O_6 + \text{other products.}$$

Since this early report, investigators into the pyrolysis of cellulose have questioned: (1) the importance of levoglucosan in the combustion process; (2) the mode of levoglucosan formation; (3) the subsequent fate of the levoglucosan; (4) the nature of the "other products"; and (5) the mode of formation of these other products. The effect of inorganic salts and substituants on cellulose pyrolysis has also been recognized and investigated. Despite much excellent work, particularly since the early 1950's, the exact mechanism of the thermal decomposition of cellulose has remained highly controversial.

It has been well established[5] that levoglucosan constitutes a major component of

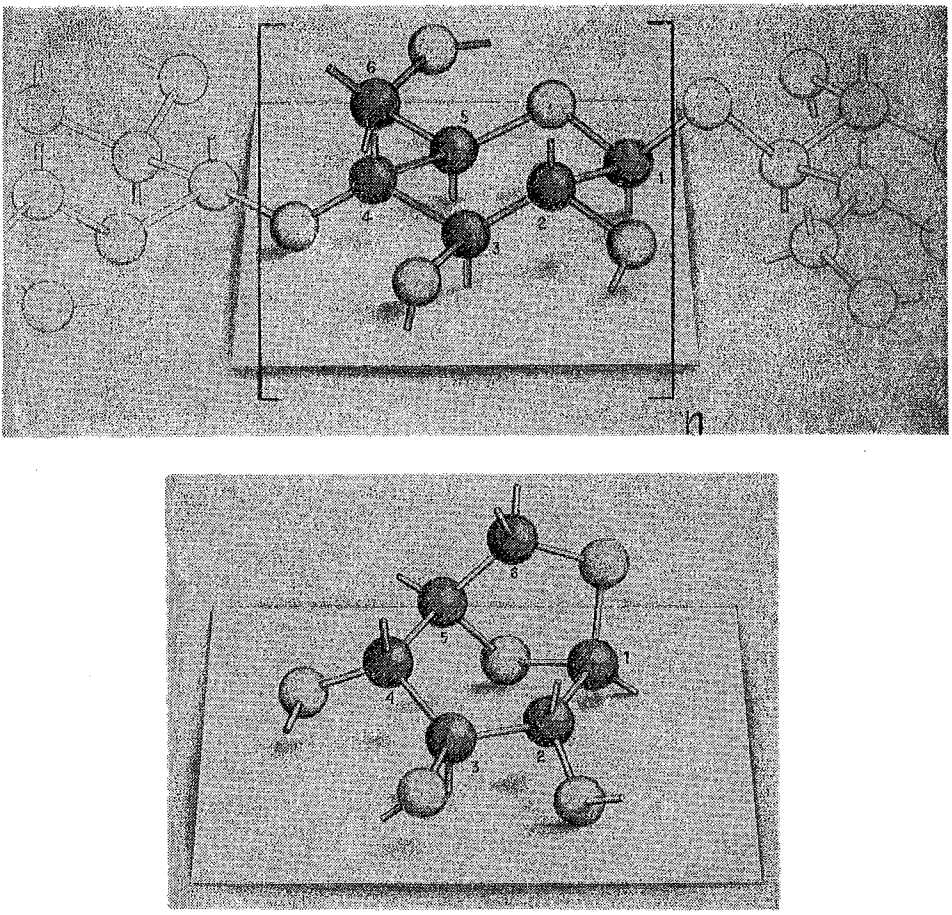

FIG. 1. Structure of cellulose (upper) and levoglucosan (lower).

Cellulose $(C_6H_{10}O_5)_n$, is a nonbranching polymer, formed from glucose by splitting off one molecule of water between the C–1 position of one glucose and the C–4 position of the next. Levoglucosan $C_6H_{10}O_5$, is a bi-cyclic derivative of glucose, formed by splitting off one water molecule between the C–1 and C–6 positions of the same glucose molecule.

the "tar" fraction of cellulose pyrolysis and thus is a major factor in the combustion of cellulose. Other data contributing to the development of a satisfactory theory are coming from such general measurements as are made by gasometry and thermogravimetry[6] and from the determination of intermediate products of pyrolysis or combustion, using such analytical techniques as infrared spectroscopy,[7] paper chromatography,[8,9] and gas chromatography alone[10] or coupled with mass spectrometry.[11]

The extent of detail in the several theories which have been proposed is quite variable. Thus, Schuyten, Weaver, and Reid[12] in their review paper on the flameproofing of cellulose did not discuss the thermal decomposition of pure cellulose; they suggested that successful flameproofing agents are Lewis acids or bases which catalyze the dehydration of cellulose to a "high carbon content . . . difficulty com-

bustible" residue. Parks *et al.*[13] proposed that in the pyrolysis of cellulose a first order depolymerization to levoglucosan is the first and rate-determining step. On this basis, Schwenker and Pacsu[14] concluded that modifying cellulose at the C–6 position to minimize levoglucosan formation would markedly diminish flammability. The structures of cellulose and levoglucosan contravene the possibility that chain-breaking results from a direct displacement step initiated by the C–6 hydroxyl attacking the C–1 position of its own glucose ring. Instead, a prior elimination or displacement step is required.

Madorsky, Hart, and Straus[15] suggested a mechanism based upon two simultaneous random processes: dehydration (presumably similar to that suggested by Schuyten, Weaver, and Reid) and thermal scission of the C—O bonds anywhere in the polymer chain. They suggested that scission of the appropriate bond may result in the production of levoglucosan by the double displacement mechanism which McCloskey and Coleman[16] used to describe the base-catalyzed genesis of levoglucosan from β-D-glycosides. However, the fact that in Madorsky's experiments less levoglucosan was produced from cellulose in the presence of bases tends to discourage this analogy.

In 1956 Golova *et al.* began to publish results of their research into cellulose pyrolysis and oxidation. In their first paper[17] they concluded that hydrolysis, oxidation, and dehydration are all side reactions in the thermal destruction of cellulose. According to them, the main pyrolysis path involves a break at the C–1 position into fragments which isomerize into levoglucosan. Among other observations, they noted that adding glucose to cellulose reduced the yield of levoglucosan obtained on vacuum pyrolysis.

The following year, Golova and Krylova[18] reported the results of a more detailed study. In pyrolyzing cotton cellulose, they found that the original cellulose molecules first break down randomly into chains of about 200 anhydroglucose units. These chains then decompose by "unzipping" completely to produce levoglucosan. They did not speculate about the reason for the apparent stability of the cellulose molecule with degree of polymerization (DP) of 200, nor did their results establish whether the DP of 200 represented an average over a broad spectrum or was indeed a critical size for a cellulose molecule.

Additional papers by this research team presented their results on the yield of levoglucosan upon pyrolysis of such model compounds as β-D-glucose[19] and cellobiose,[20] described the isolation of such compounds as 1,6-anhydro-β-D-glucofuranose from cellulose pyrolysate[21] and of 2,3,6-trimethyl-1,4-anhydro-β-D-glucopyranose from trimethyl cellulose pyrolysate,[22] and showed that their samples of cotton cellulose and cellulose hydrate deocmposed by two different mechanisms.[23] However, more recent publications[24,25] describe drastic changes in results when the ash content of the materials are lowered from a little above to a little below 0.1 per cent. In fact, it appears that the only results they do not have to attribute, at least in part, to the effect of impurities in their samples, are those which led to their reported mechanism for the thermal decomposition of cotton cellulose.

Broido[26] also has observed that as little as 0.15 per cent "ash" markedly alters the pyrolysis and combustion behavior of cellulose papers.

These findings raise questions about all previous work in which the presence of such small amounts of ash was not considered. Where chemical modification of cellulose was accomplished by a process which may have altered the purity of the material (for example, in the work of Schwenker and Pacsu[14]), it becomes important

to separate the effect of the change in purity from the effect of the actual chemical modification of the cellulose.

None of the theories yet proposed has been sufficiently detailed to predict or even provide an explanation for the rather startling differences in the combustion behavior of a number of saccharides. For example, they do not explain why a chemical which extinguishes flaming in cellulose and starch also "catalyzes" the combustion of sucrose.[27]

Golova's results confirm that some initial reactions can produce shorter but still nonvolatile polymer chains. Pictet[28] and Wolfram *et al.*[29,30] have shown that some of the volatile products of primary reactions can recombine to form nonvolatile products. Thus, experiments that simply measure weight loss or gas evolution, while useful, cannot even give the true rate of reaction of the starting material. In order to permit better prediction of the course of the pyrolysis and combustion of cellulose and to better indicate useful methods of modifying this course, the mechanisms for these reactions must be described in much greater detail than they yet have been. As Hine put it in describing the recent growth of physical organic chemistry[31]:

> "In reactions where earlier investigators may have been satisfied to learn what intermediate was being formed in the rate-controlling step, many physical organic chemists are currently trying to learn much more: to determine the intermediates in all of the steps and the relative heights of the various energy barriers; to learn as nearly as possible the geometrical location of every atom throughout every stage of the reaction; and to learn how changes in reactant structure, solvent, and other reaction conditions affect the enregy barrier heights and molecular geometries."

By such criteria, the reaction mechanisms of carbohydrate pyrolysis are very poorly defined. Until these mechanisms are better understood, the gross effects of fire-extinguishing and flame retarding chemicals may be observed, but detailed prediction of their action will remain subject to considerable question.

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