Pyrolysis of levoglucosan

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PYROLYSIS OF LEVOGLUCOSAN

by

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Chairman, Board of Examiners

Dean, Graduate School

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I. INTRODUCTION

In this work levoglucosan (1,6-anhydro-β-D-gluco-pyranose) has been used as a model compound for elucidating the complex reactions involved in pyrolysis of cellulose. Considerable work has been done on pyrolysis of cellulose, mostly in connection with the flame-proofing of cellulosic materials. Consequently, some basic features of the pyrolytic reactions have been established. However, postulation of a generally acceptable chemical mechanism has not been achieved because of insufficient experimental data.

Pyrolysis of cellulose has been found to proceed thorough two main pathways (I and II) shown below:

\[
\begin{align*}
\text{Cellulose} & \quad \xrightarrow{\text{I}} \quad \text{CO, CO}_2, \text{H}_2\text{O}, \text{C} & \rightarrow \text{Glowing Ignition} \\
& \quad \xrightarrow{\text{II}} \quad \text{Combustible Volatiles} & \rightarrow \text{Flaming Combustion}
\end{align*}
\]

High temperatures favor the pathway II and thermal degradation reactions 2, 3, 4, 5, 6 and 7.

It has been shown that levoglucosan is a major intermediate product in decomposition of cellulose that...
can be isolated in good yield from vacuum pyrolysis\textsuperscript{2-7} and further decomposed to a large number of secondary products. Thus, investigation of the pyrolytic behavior of levoglucosan provides a basis for understanding of the thermal decomposition of cellulose.

Glassner and Pierce\textsuperscript{8} studied isothermal pyrolysis of cellulose and levoglucosan in an inert gas atmosphere and found that the products are essentially identical over the range of temperature from 242 to 360°. This seems to support the contention that levoglucosan is a principal intermediate compound in thermal decomposition of cellulose.

However, Heyns and Klier\textsuperscript{9} contradict this contention. These authors found that a large number of mono- and disaccharides, amylopectin and cellulose, on pyrolysis at 300 to 500° for a short period of time, gave the same volatile degradation products. This led them to the conclusion that degradation, dehydration and condensation reactions of all these compounds involve similar polymeric intermediates that undergo secondary thermal degradation. A different distribution of pyrolysis products was found with DL-glyceraldehyde, hexitols, pentitols and 1,6-anhydrohexoses including levoglucosan. On the basis of these data they expressed the general opinion that anhydro sugars are not of any central significance in the thermal decomposition of carbohydrates to volatile products or black polymeric materials.
Several mechanisms have been proposed to explain the formation of levoglucosan from pyrolysis of cellulose. A Russian group\textsuperscript{10} has proposed that levoglucosan is formed mainly from the crystalline areas of cellulose through a peeling or unzipping reaction which proceeds through free radical intermediates (A). The proposed free radical peeling reaction involves initial cleavage of the oxygen bond at position 4, migration of the hydrogen from the C6 hydroxyl group to this position and the formation of an oxygen bridge between C6 and Cl. Addition of D-glucose lowers the yield of levoglucosan by blocking of the free radical centers and hindering the above reactions.\textsuperscript{11} Vacuum pyrolysis of trimethylcellulose is shown to provide 1,4-anhydro-tri-O-methyl-\(\alpha\)-D-glucopyranose and 2,3,6-tri-O-methyl-\(\alpha\)-D-glucose,\textsuperscript{12} indicating that when the C6 hydroxyl group is blocked the free radicals derived from the cleavage of the glucosidic bond could be stabilized by formation of a 1,4-anhydro ring.

Besides the free radical mechanism, several other intermediate compounds and rearrangements have been suggested to account for the transformation of cellulose to levoglucosan.

In the earlier literature,\textsuperscript{13,14} \(\beta\)-D-glucose had been considered as an intermediate compound (B), which on subsequent dehydration, provides levoglucosan. Experimental evidence against this theory has been produced by Golova...
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and associates\textsuperscript{15-17} who obtained small yields of levoglucosan from $\beta$-D-glucose and cellobiose respectively as compared to a 54-60% yield from cellulose.

Another proposed mechanism involves direct conversion of cellulose to levoglucosan by concerted displacements (C).\textsuperscript{18}

Presence of various simple inorganic compounds causes a decrease in the amount of tar (composed mainly of levoglucosan) in the pyrolyzate of cellulose.\textsuperscript{2-7} Complementary kinetic data obtained by TGA, show a lowering of the activation energy for the volatilization process and the catalytic effect of the inorganic compounds.\textsuperscript{19}

Heyns and Klier\textsuperscript{9} found that on pyrolysis of a large number of mono-, oligo- and polysaccharides at 300-500\degree C for a short period of time, addition of acid salts has a small effect on the composition of the pyrolysis products. The change consisted mainly in the enhanced formation of furan derivatives and reduction in formation of carbonyl compounds. Neutral salts were found to have no effect. Addition of basic salts suppresses the formation of furan derivatives and facilitates the formation of carbonyl compounds.

A variety of methods has been used for analysis of pyrolyzates from cellulose and related compounds (levoglucosan, starch, various monosaccharides).

In a study of isothermal pyrolysis of cellulose,
Schwenker and Pascu\textsuperscript{20} used classical organic methods and paper chromatography and identified several compounds.

Application of temperature programmed gas-liquid chromatography (GLC) enabled Schwenker and Beck\textsuperscript{21} to notice the presence of 34 compounds in pyrolyzate of cellulose. Some of the compounds were identified by comparison of retention times on three GLC columns of different polarity.

Glassner and Pierce\textsuperscript{8} constructed a pyrolysis chamber in which the samples of levoglucosan and cellulose were pyrolyzed in the stream of the GLC carrier gas, and subsequently analyzed by comparison of retention times, qualitative tests for functional groups and odor of the effluent gases.

In a study on pyrolysis of D-glucose, Heyns, Stute, and Paulsen\textsuperscript{22} used preparative GLC to obtain several fractions that were further analyzed by GLC capillary columns of high resolution power, connected to a mass spectrometer. Furthermore, a number of functional groups were tested by the "syringe reactions" method described by Hoff and Feit.\textsuperscript{23} This method involves elimination of some of the components by specific reactions in a syringe and analysis of the remaining material.

Martin and Ramstad\textsuperscript{24} devised a special two-stage gas chromatograph for analysis of flash pyrolysis products. With this system the pyrolysis was carried out directly in the carrier gas and the resulting products were analyzed.
by two different columns, one for separation of gases and the other for resolving the volatile products.
II. EXPERIMENTAL

1. Pyrolysis

Pyrolysis of the samples was performed in the Perkin Elmer pyrolysis accessory connected to an F & M gas liquid chromatograph, series 5750. Several fractions of the pyrolyzate were collected as they emerged from the column, and further analyzed for positive identification.

1. 1. Description of the Apparatus

The pyrolysis accessory is shown in Figure 1.

The pyrolysis chamber in this instrument is made from Pyrex glass with the exception of the part directly exposed to high temperatures in the furnace. This part is made of quartz and connected to the rest of the chamber by means of the graded seal. The maximum operating pressure is 30 PSIG and the temperature range of the furnace is up to 1000°. The samples are pyrolyzed in porcelain boats that can be moved in the pyrolysis chamber with a boat pusher or metal cylinders inside the chamber and a magnet outside. Porcelain boats were sometimes replaced with aluminum boats for convenience. All the quantitative work was done with porcelain boats.

1. 2. Operation

The pyrolysis experiments were performed at 600° to ensure rapid pyrolysis. The employed conditions allowed
Figure 1. Perkin Elmer pyrolysis accessory.
pyrolysis of relatively large samples and collection of the pyrolyzate fractions for further analysis.

The amount of the samples used was limited by condensation of excessive pyrolyzate in the colder regions of the pyrolysis chamber, rather than overloading of the GLC column. To minimize this condensation, pyrolysis was performed under the highest possible gas flow. The optimum amount of sample was found to be 40-50 mg.

Some adjustments were made on the original instrument. Because of the large samples used and frequency of the experiments, accumulation of the tarry materials in the connections of the instrument created a problem. The valve allowing the carrier gas to bypass the pyrolysis chamber was especially sensitive in this respect. This valve was removed and the operation carried out with the pyrolysis chamber connected directly to the GLC. Because of the rapid pyrolysis condition there was no noticeable change in the chromatogram.

An auxiliary injection port, allowing the introduction of known compounds in the pyrolyzate stream, was installed in place of the aforementioned valve. The adjustment consisted of a Swagelock tee connector in which the middle branch was closed with a small size GLC injection port septum.

Finger tightening of the joints usually was sufficient to prevent leakage. However, it was noticed that a
relatively small leak can cause a serious pressure drop
and increase all the retention times. Otherwise the repro­ducibility of the chromatographic patterns was very good.

The pyrolyzate was chromatographed with both flame
ionization and thermal conductivity detectors.

The fact that the substances like $\text{H}_2\text{O}$, $\text{CO}_2$ and CO
are not ionizable in hydrogen flame (and therefore not
detectable by the flame ionization detector), provided
a unique condition for investigation of the pyrolyzate.
The large amount of water in the pyrolyzate was recorded
by the thermal conductivity detector as a peak superimposed
on other volatile fractions (that were detected by flame
ionization detector). However, because of a larger quantity
of water, there was little interference from the rest of
the volatiles in a quantitative measurement of the water
by the external standard method. For the purpose of trapping
various fractions, the effluent stream was divided by
means of splitters. These splitters divided the stream
through two stainless steel capillary tubes of different
lengths into a ratio inversely proportional to their
lengths (40:1). The splitting did not cause any measurable
delay in the movement of one stream with respect to the
other, thus the separated substances appeared at the collection
exit practically in the same time as recorded by either
flame ionization or thermal conductivity detector.
2. Qualitative Analysis of the Pyrolyzates

2.1. 2,4-Dinitrophenylhydrazone Derivatives

The preparation and investigation of 2,4-dinitrophenylhydrazone derivatives of the carbonyl compounds supplied infrared (IR) spectra, thin layer chromatography (TLC) and melting point data for positive identification of some fractions.

Preparation. The 2,4-dinitrophenylhydrazones were prepared by bubbling the effluent stream through about 0.5 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl. The reaction mixture remaining after a few hours was then centrifuged and decanted. The small precipitate was washed twice with small portions of methanol and dried in a vacuum drying apparatus at 60°.

Only one operation often yielded enough material for recrystallization from methanol or nitrobenzene. In the case of nitrobenzene solution, slow evaporation of the solvent at ambient conditions produced some crystals which were separated by centrifugation, washed with the solvent and dried in vacuum. Alternatively, the crude 2,4-dinitrophenylhydrazone was dissolved in hot methanol, a few drops of water were added to induce incipient turbidity, and the solution was cooled down slowly.

IR Spectra. Potassium bromide pellets containing the 2,4-dinitrophenylhydrazones were prepared for differentiation of structural isomers by IR spectroscopy. Although an IR
absorption spectrum is not generally too sensitive to impurities, it was found that the IR spectra of crude compounds provided unequivocal identification only in exceptional cases.

Thin Layer Chromatography (TLC). \(^{28,29}\) Thin layer chromatography of 2,4-dinitrophenylhydrazones was carried out with Eastman Sheets 6060 and 6062 and Gelman Chromatography Media plates in an Eastman-Kodak developing apparatus. Samples were applied from a solution in chloroform or tetrahydrofuran by thin capillary tubes. Standard samples of known compounds were prepared in the same way as the unknown and used for comparison. The developing reagent was ethanolamine \(^{28}\) which gives different colors with various types of 2,4-dinitrophenylhydrazones. The solvent systems consisted of: a. diethyl ether-ligroin (b.p. 60-90°) 60:40; b. benzene-ligroin (b.p. 60-90°) 70:30; c. benzene-tetrahydrofuran 93:7.

2. Schiff's Reaction.

To distinguish between an aldehyde or a keto compound, the fractions showing positive 2,4-dinitrophenylhydrazone reactions were bubbled through 0.5 ml of a freshly prepared Schiff's reagent in 10 x 75 mm test tube. The test for an aldehyde group was considered positive if a violet color appeared immediately. A negative reaction was not considered to show the absence of an aldehyde group (e.g., furfural failed to give the reaction even when present in a fairly large amount).
2.3. Ultraviolet Spectra

A bent capillary tube cooled in liquid nitrogen was used to collect a fraction for subsequent UV spectroscopy as shown in Figure 2. The tube was rinsed with 95% ethanol and the sample kept in the refrigerator. The UV spectrum of the sample was determined with the Hitachi EPS-3, Coleman Recording Spectrophotometer. Because of the small amount of sample, molar absorptivity was not determined.

2.4. pH Test for Carboxylic Compounds

Samples for the pH test were collected in thin capillary tubing cooled in liquid nitrogen as before. A cylindrical droplet formed immediately after the trap was taken out of the liquid nitrogen. The capillary tube was then broken at a place close to the droplet and the sample was transferred to a piece of universal indicator paper by squeezing the rubber connector as shown in Figure 3. Both formic and acetic acid present in the pyrolyzate showed a pH of 1 to 2.

3. Quantitative Analysis

About 40-mg samples of finely powdered levoglucosan were weighed in porcelain boats. Different amounts of 0.0963 M ZnCl₂ solution in 95% ethanol were then added through a microsyringe. After evaporation of the major part of the ethanol at room temperature, samples were vacuum dried overnight at 60°C.

This method was adopted because direct weighing of
Figure 2. Preparation of samples for UV spectroscopy.

Figure 3. pH Test for carboxylic compounds.
ZnCl$_2$ is very difficult due to its hygroscopicity. External standards were used for gas chromatographic determination of water and furfural. Char was determined by weighing the residue left in the boat.
III. RESULTS

1. **Analysis of Pyrolyzates**

The gas chromatograms of levoglucosan pyrolyzates were obtained under the following experimental conditions:

- **Pyrolysis temperature**: 600°
- **Carrier gas (He) flow rate**: 100 ml/min
- **GLC injection port temperature**: 200°
- **Oven temperature programmed**: 8°/min from 50 up to 182°
- **Temperature of the thermal conductivity detector**: 250°
- **Temperature of the flame ionization detector**: 350°
- **Bridge current**: 165 mA
- **GLC column**: 12 feet, 1/4" stainless steel tubing packed with 10% Carbowax 20 M on Holoport F

The chromatogram in Figure 4, obtained with thermal conductivity detector under a big attenuation, shows the amounts of the major components of pyrolyzate, fixed gases (a) and water (b), relative to the rest of the volatiles.

A more detailed chromatogram (Figure 5), obtained with flame ionization detector under the low attenuation, served as the basis for qualitative analysis of the organic volatiles. The chromatogram shows the following features:

- **Peak 1** corresponds to at least four organic fixed gases: Carbon dioxide, carbon monoxide and hydrogen,
Figure 4. Gas chromatogram of pyrolyzate from levo-glucosan (with thermal conductivity detector).
Figure 5. Gas chromatograms of pyrolyzates from untreated levoglucosan (I) and levoglucosan treated with 10% zinc chloride (II) (with flame ionization detector).
which have been reported earlier as components of the fixed gases fraction,\textsuperscript{24} are not shown on the chromatogram, because they are not detectable by flame ionization detector.

Peak 2 corresponds to acetaldehyde. This is shown by the IR spectrum of the 2,4-dinitrophenylhydrazone derivative, the Rf value for the same derivative obtained by TLC, and a positive Schiff's reaction.

Peaks 3, 4 and 5 provide a combined effluent which shows only the end absorption in the UV spectrum and a negative Schiff's reaction. They give a fairly weak 2,4-dinitrophenylhydrazone reaction and form a derivative which on examination by TLC method gives the same Rf value and develops the same color with ethanolamine as acrolein. GLC retention time of acrolein coincides with that of peak 4.

Peak 5 is tentatively identified as methanol on the basis of its retention time.

Peaks 6 and 7 give a strong 2,4-dinitrophenylhydrazone reaction, negative Schiff's test and only the end absorption in the UV spectrum. The 2,4-dinitrophenylhydrazone (recrystallized from nitrobenzene) had a melting point of 310-315° (m.p. which corresponds to the 2,4-dinitrophenylhydrazone derivative of 2,3-butanedione [biacetyl]: 314-315°).\textsuperscript{30} Thus, peak 7 was identified as 2,3-butanedione which has the same
retention time. This was further supported by TLC which also showed the presence of another carbonyl compound in this group.

Peak 8 gives a strong 2,4-dinitrophenylhydrazone reaction, positive Schiff's test and has a peak in UV spectrum at 218 m\(\mu\), which corresponds to properties of crotonaldehyde (2-butenal).

Peaks 9 and 10 give positive Schiff's test and a 2,4-dinitrophenylhydrazone with melting point 300-303\(^\circ\) recrystallized from nitrobenzene (m.p. of 2-oxopropanal [pyruvaldehyde] bis 2,4-dinitrophenylhydrazone: 299-300\(^\circ\)). The TLC of this compound gives an Rf value corresponding to 2-oxopropanal, which according to Byrne, falls between the glyoxal (ethanedial) and 2,3-butanedione 2,4-dinitrophenylhydrazone derivatives.

Peaks 13, 14 and 15 give a 2,4-dinitrophenylhydrazone with melting point of 324-328\(^\circ\) recrystallized from nitrobenzene (m.p. of glyoxal 2,4-dinitrophenylhydrazone: 328\(^\circ\)). The TLC of this compound gives an Rf value corresponding to glyoxal. Furthermore, the GLC retention time for glyoxal corresponds to peak 14. Peak 15 is identified as acetic acid on the basis of the pH test and GLC retention time.

Peak (shoulder) 16 corresponds to formic acid as indicated by the pH and the retention time.

Peak 17 corresponds to furfural. Furfural was first
found in the pyrolyzate of levoglucosan treated with zinc chloride, where it occurred in a relatively large quantity. The 2,4-dinitrophenylhydrazone derivative, when recrystallized from methanol, had a melting point of 226-229.5° alone or in a mixture with an authentic sample. In addition, it was identified by GLC retention time, TLC of the 2,4-dinitrophenylhydrazone and UV spectrum in the ethanolic solution ($\lambda_{max_2}: 273 \text{ m}$; $\lambda_{max_2}: 226 \text{ m}$; corresponding wavelengths for authentic compound: $\lambda_{max_1}: 273 \text{ m}$; $\lambda_{max_2}: 228 \text{ m}$; molar absorptivities were in qualitative agreement). TLC of the 2,4-dinitrophenylhydrazone derivative of the corresponding fraction in pyrolyzate of the untreated levoglucosan shows the presence of furfural together with another carbonyl compound which remains unidentified.

In contrast with the previous work, this study showed that among the carbonyl compounds, acetaldehyde has the shortest retention time on Carbowax 20 M and that formaldehyde is retained much longer. Also, no acetone or propionaldehyde could be detected in a sufficient amount to allow their assignment to one of the GLC peaks.

2. The Effect of ZnCl$_2$ Treatment

The difference in chromatograms in Figure 6 shows the effect of ZnCl$_2$ treatment on the volatile pyrolysis products of levoglucosan. Corresponding peaks were recorded under the same attenuation.
Figure 6. Gas chromatograms of pyrolyzates from untreated levoglucosan (I) and levoglucosan treated with 0.50% zinc chloride (II) (with thermal conductivity detector).
The major difference between the chromatograms for treated and untreated levoglucosan appears in peaks a, b and c, which correspond to fixed gases, water and furfural respectively. Corresponding peaks were recorded under the same attenuation.

The external standard technique was used in quantitative measurement of water and furfural, but this method could not be applied to fixed gases. Therefore, only the change in the peak area was measured.

The resulting quantitative data are summarized in Table I.

Comparison of gas chromatograms in Figure 5 also reveals other minor consequences of ZnCl₂ treatment. A disappearance of peaks 14 (glyoxal), 13, 15 (acetic acid), 9 (2-oxopropanal) and 10, was accompanied with a change in configuration of peaks 2, 3 and 4. There was little change in the rest of the peaks. The unchanged fractions from pyrolyzate of treated and untreated levoglucosan were compared by TLC of 2,4-dinitrophenylhydrazone derivatives (Figure 7), UV spectra and pH determination, and were found to be essentially identical.

The effect of ZnCl₂ treatment on the composition of pyrolyzate can be summarized as follows:

1. The amount of water was increased 4.6 times (from 5.5% to 25.3%).

   aAll the percentages are given with respect to the amount of levoglucosan.
Table I. Analysis of Pyrolyzate from Levoglucosan and Levoglucosan Treated with Zinc Chloride

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Levoglucosan (mg)</th>
<th>ZnCl₂ (%)</th>
<th>H₂O (mg)</th>
<th>H₂O (%)</th>
<th>Fixed gases (^b) (mm²)</th>
<th>Fur-fural (mg)</th>
<th>Fur-fural (%)</th>
<th>Residue (mg)</th>
<th>Residue (%)</th>
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<tr>
<td>1</td>
<td>37.9</td>
<td>0</td>
<td>1.7</td>
<td>4.5</td>
<td>c</td>
<td>c</td>
<td>0.6</td>
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<tr>
<td>2</td>
<td>41.3</td>
<td>0</td>
<td>2.1</td>
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<td>c</td>
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<td>0</td>
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<td>c</td>
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<td>2.2</td>
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<tr>
<td>4</td>
<td>40.1</td>
<td>1.0</td>
<td>10.7</td>
<td>26.6</td>
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<td>21.8</td>
<td>6.7</td>
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\(^a\) Percent based on levoglucosan

\(^b\) GLC peak areas from pyrolysis of 1 mg of levoglucosan which provides comparative values

\(^c\) Trace amounts
Figure 7. TLC separation of 2,4-dinitrophenylhydrazones of the carbonyl compounds on silica gel. Solvent benzene-ligroin (b.p. 60-90°) 70:30.

A, C, E, G, I, K, derivatives from pyrolyzate of levoglucosan corresponding to GLC peaks (Figure 5, I) 2; 3, 4, 5; 6, 7; 8; 17; 13, 14, 15; respectively.

B, D, F, H, J, derivatives from pyrolyzate of levoglucosan treated with zinc chloride corresponding to GLC peaks (Figure 5, II) 2; 3; 6, 7; 8; 17; respectively.

Colors developed with ethanolamine: b = brown, r = red, bl = blue.
2. The total amount of fixed gases was increased 3.7 times.

3. The charred residue showed an increase of 6.6 times (from 3.2% to 21%).

4. The total amount of furfural was increased to 0.6% from a practically unmeasurable small quantity.

5. The amount of glyoxal, 2-oxopropanal and acetic acid was drastically reduced.

6. The same effects were produced by 5%, 1% or 0.5% ZnCl₂.

7. The amount of gases detectable by flame ionization detector was increased two times.

3. Pyrolysis of Cellulose

Figure 8 compares the gas chromatograms of cellulose and levoglucosan, which are quite similar except for a larger amount of glyoxal in the pyrolyzate of cellulose.

Figure 9 shows the chromatogram of cellulose treated with ZnCl₂ by mixing in a mortar. There is a striking qualitative and quantitative similarity between the pyrolyzates of levoglucosan and cellulose, both treated with ZnCl₂. The results obtained from quantitative analysis of the pyrolyzates from cellulose and levoglucosan treated with ZnCl₂ are presented in Table II and can be summarized as follows:

1. The amount of water was increased 3.5 times (from 12% to 42%).

2. The total amount of fixed gases was increased 1.9 times.

3. The charred residue showed an increase of 4.7 times (from 6.2% to 29%).

*All the percentages are given with respect to the amount of cellulose.
Figure 8. Comparison between the gas chromatograms of pyrolyzates from cellulose (I) and levo-glucosan (II) (with flame ionization detector).
Figure 9. Gas chromatograms of pyrolyzates from cellulose (I) and cellulose treated with 10% zinc chloride (II) (with flame ionization detector).
### Table II. Analysis of Pyrolyzates from Cellulose and Cellulose Treated with Zinc Chloride

<table>
<thead>
<tr>
<th>experiment</th>
<th>cellulose (mg)</th>
<th>ZnCl₂&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>H₂O (mg)</th>
<th>H₂O&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>fixed gases&lt;sup&gt;b&lt;/sup&gt; (peak areas mm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>residue (mg)</th>
<th>residue&lt;sup&gt;a&lt;/sup&gt; (%)</th>
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</table>

<sup>a</sup>Percent based on cellulose

<sup>b</sup>GLC peak areas from pyrolysis of 1 mg of cellulose which provides comparative values
IV. DISCUSSION

In this work levoglucosan was used as a model compound for the study of pyrolysis of cellulose. A number of different pathways for the pyrolysis of cellulose have been proposed ranging from a belief expressed by Parks\textsuperscript{18} that the decomposition of cellulose proceeds exclusively through formation of levoglucosan to a general exclusion of levoglucosan as a main intermediate product.\textsuperscript{3} Our analytical data which are, except for minor differences, in accord with the work of Glassner and Pierce,\textsuperscript{2} support the conclusion that the majority of volatile decomposition products could be formed through the decomposition of levoglucosan as a primary intermediate, but random cleavage of C-C bonds of anhydro D-glucose units, also results in a formation of some volatile products, notably glyoxal.

The TGA and DTA data\textsuperscript{31} indicate the complexity of the reactions involved in thermal decomposition of levoglucosan. The exotherm in the DTA curve for levoglucosan (Figure 10) starting at about 280° with a corresponding change in the rate of volatilization (as indicated by the corresponding TGA curve) could signify the polymerization of levoglucosan. The TGA data show a simultaneous decomposition of this product, thus indicating a more involved pathway for the formation of volatile products.

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Figure 10. Thermograms of untreated levoglucosan (I) and levoglucosan treated with 5% zinc chloride (II).
Among the different mechanisms suggested for thermal decomposition of cellulose, the formation of free radicals as proposed by Pakhomov seems to be the most plausible. Depending on experimental conditions, the free radicals formed by cleavage of glycosidic bonds could be stabilized by formation of levoglucosan or some polymerization products. They could also further decompose to a number of low molecular weight volatile products.

The presence of ZnCl₂ strongly promotes dehydration reactions in the case of both cellulose and levoglucosan, leading to a striking similarity in the composition of volatile products. The dehydration reaction is characterized by an increased formation of furan derivatives and reduced cleavage of C-C bonds. Formation of furan derivatives suggests a similarity with acid catalyzed decomposition of carbohydrates which provides 5-hydroxymethylfurfural and its decomposition products, notably levulinic acid.

DTA and TGA data also indicate an alteration in the course of the thermal degradation reactions. In the presence of ZnCl₂ the volatilization starts at a lower temperature and proceeds at a slower rate to leave a significantly increased amount of charred residue (Figures 10 and 11). Almost the same effects are observed by treatment with 0.5 to 5% ZnCl₂. Furthermore, DTA and TGA data indicate a lowering of activation energy for the process of
Figure 11. Thermograms of untreated cellulose (I) and cellulose treated with 5% zinc chloride (II).
volatilization as observed by Tang and Neill. These observations indicate the catalytic effect of $\text{ZnCl}_2$. However, whether $\text{ZnCl}_2$ remains chemically unchanged after the pyrolysis still remains to be determined.
V. REFERENCES

12. A. M. Pakhomov, O. P. Golova and I. I. Nikolaeva,
31. F. Shafizadeh, C. W. Philpot, N. Ostojic, unpublished work.