Pyrolysis of Cellulose

Part II. Thermogravimetric Analyses and Determination of Carbonyl and Carboxyl Groups in Pyrocellulose

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A study was made of thermogravimetric analyses of microcrystalline cellulose, (Avicell), over a temperature range from 240°C to 300°C under air and nitrogen by means of a thermal balance. For comparative purpose, cellobiose and glucose were also used. The volatilization rate of cellulose was related to the amount of pyrolytic residue and accelerated owing to the oxidation in the presence of atmospheric oxygen. The apparent activation energies of pyrolysis were obtained from weight loss data.

Quantities of carbonyl and carboxyl groups in pyrocellulose increased linearly against degradation stages of cellulose irrespective of pyrolytic temperatures and times.

INTRODUCTION

In the course of pyrolysis of cellulose, the various chemical reactions occur simultaneously. The vacuum distillation of cellulose gives rise to levoglucosan \(^{1-3}\) by scission of glucosidic linkages. Other chemical changes of cellulose such as formation of oxycellulose \(^4\) and aromatic substances \(^5,6,7\) are also known. Change in cellulose structure as characterized by hydrolyzability greatly affects the nature and yields of pyrolytic degradation products. \(^8\)

In a previous paper, \(^9\) the pyrolytic degradation products of cellulose were reported. This report is concerned with a thermogravimetric analysis and determination of the modified groups in pyrocellulose (pyrolytic residues of cellulose) in order to follow the chemical changes of cellulose during pyrolysis.

EXPERIMENTAL

Samples. Microcrystalline cellulose (Avicell), used in this experiment was supplied by courtesy of Asahi Chemical Ind. Co., Ltd. Its average polymerization degree was 200. \(^9\) Glucose and cellobiose were obtained commercially.

Pyrocellulose for the determination of the modified groups was prepared as follows: cellulose (400 mg) was pyrolyzed at a definite temperature over a range from 200°C to 270°C under air and nitrogen. The weight loss during pyrolysis was recorded by means of a Shimazu thermal balance. The residue was washed with hot water, then with ethanol and acetone. Pyrocellulose was dried in vacuum at 50°C over 12 hrs.

Apparatus and methods. Thermogravimetric analyses of the samples were conducted by means of a Shimazu thermal balance. The sample (200 mg) in a platinum crucible was heated in the electric...
furnace previously maintained at the definite temperature with deviation ±3°C under air and nitrogen (nitrogen flow rate, 30 ml/min.) respectively, and the weight was recorded as a function of time.

Infrared absorption spectra of pyrocellulose were obtained by means of a Japan Spectroscopic model IR-S spectrometer equipped with NaCl prism by KBr method.

Determination of carbonyl and carboxyl groups in pyrocellulose.

The carbonyl groups in pyrocellulose were quantitatively analyzed by hydroxylamine hydrochloride method.\(^{10}\)

The carboxyl groups in pyrocellulose were determined by the method of calcium acetate based upon the cation exchange capacity of the cellulose.\(^{11}\)

RESULTS AND DISCUSSION

I. Analyses of weight loss data of the samples 1-1. Cellulose. On the basis of the results described earlier, the pyrolytic changes of cellulose can be arranged tentatively as follows:

A. Cellulose $\rightarrow$ B. Intermediates $\rightarrow$

C. Condensates $\rightarrow$

D. Volatiles $\rightarrow$

E. Secondary condensates $\rightarrow$ G. Char $\rightarrow$

F. Volatiles $\rightarrow$

The typical curves of weight loss obtained by this experiment under air and nitrogen are shown in Fig. 1. The weight loss is not uniform with time, but appears to proceed through three distinct phases, namely an induction period, an interval of rapid degradation, and a phase of slow degradation. These phases can be empirically related to the stages of the above pyrolysis scheme; an induction period in which the reaction A $\rightarrow$ B is dominant, an interval of rapid degradation B $\rightarrow$ C+D, and a slow degradation phase C $\rightarrow$ E $\rightarrow$ G. The pyrolytic changes of cellulose, however, are not so simple and the reactions are superimposed each other.

It has been known that dehydration is occurred in the initial 10% degradation stage of cellulose.\(^{12}\) As seen in Fig. 1, slight loss in weight in an induction period should be mainly ascribed to the loss of water.

From the curves shown in Fig. 1, the approximate straight portion is recognized. The volatilization rate \(k\) was obtained from the slope, here the rate \(k\) are represented by percent weight of the volatiles a minute. A time \(t_h\) from zero to 50% of weight loss, an induction period \(t_i\) (min.), and pyrolytic residues \(R\) (\% at 15 min.) were also obtained from the curve as indicators of pyrolysis. In Table I are summarized the results over a temperature range from 240°C to 300°C.

As shown in Table I, \(k\) generally is higher in the case of pyrolysis under air than nitrogen, and \(t_i\), \(t_h\) and \(R\) decrease with the increasing of \(k\).

Plots of \(\log k\) versus reciprocal of absolute temperature are shown in Fig. 2. The acti-

Pyrolysis of Cellulose. Part II

TABLE I. THE INDICATORS OF PYROLYSIS OF CELLULOSE

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k$ (%/min.)</th>
<th>$t_i$ (min.)</th>
<th>$t_h$ (min.)</th>
<th>$R$ (%)</th>
<th>$E$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>50.0</td>
<td>1.4</td>
<td>2.1</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>29.5</td>
<td>2.3</td>
<td>3.4</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>260</td>
<td>15.0</td>
<td>3.3</td>
<td>5.4</td>
<td>31</td>
<td>22.0</td>
</tr>
<tr>
<td>240</td>
<td>5.0</td>
<td>4.0</td>
<td>12.8</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k$ (%/min.)</th>
<th>$t_i$ (min.)</th>
<th>$t_h$ (min.)</th>
<th>$R$ (%)</th>
<th>$E$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.0</td>
<td>1.3</td>
<td>1.9</td>
<td>23</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>1.8</td>
<td>2.8</td>
<td>20</td>
<td></td>
<td>20.0</td>
</tr>
<tr>
<td>20.0</td>
<td>2.6</td>
<td>3.9</td>
<td>23</td>
<td></td>
<td>27.0</td>
</tr>
<tr>
<td>10.0</td>
<td>5.4</td>
<td>7.7</td>
<td>27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Plots of log $k$ versus Reciprocal of the Absolute Temperature.
1: pyrolysis under air, 2: pyrolysis under nitrogen.

The activation energy $E$ of the pyrolysis of cellulose was calculated by Arrhenius equation and found to be 16.9 kcal under air and 22.0 kcal under nitrogen.

The activation energy of "Avicell" under nitrogen was higher than that of cotton and Rayon with 14 and 17 kcal respectively reported by Suga.

I-2. Glucose and Cellobiose. Glucose and cellobiose were used as models of cellulose. It has been known that glucose is produced by pyrolysis of cellulose and the pyrolytic degradation products of glucose are reasonably identical with those of cellulose.

Typical curves of weight loss of glucose and cellobiose obtained by the experiments under air are shown in Fig. 3. The indicators and the activation energies of pyrolysis of the samples were obtained same as in the case of cellulose.

In Table II are summarized the results.

I-3. Relation between $k$ and $t_h$. From the experimental data presented in Tables I and II, plots of $k$ versus reciprocal of $t_h$ are shown in Fig. 4.

As shown in Fig. 4, the approximate linear relationship between $k$ and reciprocal of $t_h$ is observed.

I-4. Relation between $R$ and $k$. The yields

13) S. Suga, Nenryo Kyokaishi, 44, 228 (1965).
TABLE II. THE INDICATORS OF PYROLYSIS OF GLUCOSE AND CELLOBIOSE

<table>
<thead>
<tr>
<th>Glucose</th>
<th>Under nitrogen atmosphere</th>
<th>Under air atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$k$ (%/min.)  $t_t$ (min.)</td>
<td>$t_h$ (min.) $R$ (%)</td>
</tr>
<tr>
<td>(°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>290</td>
<td>86.0</td>
<td>1.1</td>
</tr>
<tr>
<td>270</td>
<td>47.0</td>
<td>1.3</td>
</tr>
<tr>
<td>250</td>
<td>25.0</td>
<td>1.6</td>
</tr>
<tr>
<td>230</td>
<td>8.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Under nitrogen atmosphere</td>
<td>Under air atmosphere</td>
</tr>
<tr>
<td>Temperature</td>
<td>$k$ (%/min.)  $t_t$ (min.)</td>
<td>$t_h$ (min.) $R$ (%)</td>
</tr>
<tr>
<td>(°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>290</td>
<td>80.0</td>
<td>1.2</td>
</tr>
<tr>
<td>270</td>
<td>45.0</td>
<td>1.6</td>
</tr>
<tr>
<td>250</td>
<td>32.0</td>
<td>2.0</td>
</tr>
<tr>
<td>230</td>
<td>12.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Fig. 4. Relation between $k$ and $t_h$.
- cellulose, × glucose, ▲ cellobiose

Fig. 5. Relation between $R$ and $k$.
- cellulose: ○ under air
- cellobiose: △ under nitrogen
- glucose: ▲ under air
- cellobiose: ● under nitrogen

of pyrolytic residues $R$ are considered to vary by the relative ratio of the volatilization rate to the condensation (or polymerization) rate of the sample. Fig. 5 represents the relation between $R$ and $k$.

Fig. 5 shows that for cellulose, $R$ against $k$ under nitrogen is higher than under air. On the contrary, in the case of glucose almost reverse relation is recognized.

From these facts, it is most reasonable to consider that during pyrolysis of glucose atmospheric oxygen affects greatly the way of condensation of the sample at the lower temperature range. In a previous paper,\(^\text{16}\) it was reported that at the continuously rising temperature, weight loss of glucose was rather slow than that of cellulose and cellobiose over a range of temperature from 240° to 360°C. It has been also known that glucose is de-

hydrated to anhydromonosaccharides such as 1,2-anhydroglucose\(^{17}\) and levoglucosan, and to di- and triglucosaccharides\(^{18}\) during pyrolysis.

II. Infrared absorption spectra of pyrocelluloses

Infrared absorption spectra of pyrocelluloses prepared under air are shown in Fig. 6.

As shown in Fig. 6, there is little differences between spectra of pyrocellulose (b) prepared at 200°C and that of original cellulose (a) except for stretching vibration band of carbonyl at 1720 cm\(^{-1}\). The absorption intensity of this band was intensified by both elevating of temperature and prolonging of duration of pyrolysis. The bands at 1205 and 1335 cm\(^{-1}\) should be due to OH bending vibration, and the bands at 1285, 1318, 1374 and 1425 cm\(^{-1}\) due to CH and CH\(_2\) bending vibration\(^{19}\) All of them disappeared with the proceeding of pyrolysis. Three bands at 1015, 1030 and 1060 cm\(^{-1}\) based on C-O bond joining carbon and a hydroxyl group\(^{19}\) are also weakened.

A band at 1630 cm\(^{-1}\), shown in Fig. 6, is most likely due to absorbed water in cellulose.\(^{19}\) With regard to this assignment, it was reported by Ōtani\(^{15}\) that pyrocellulose prepared at 250°C under nitrogen showed an absorption band at 1630 cm\(^{-1}\) which should be due to non-conjugated C=C bond.

Infrared absorption spectra of pyrocellulose prepared under nitrogen were approximately identical with those of under air. The degree of changes of absorption bands, however, were lower than those of under air, being compared at the same weight loss percent.

On the basis of these results, it is most reasonable to consider that such chemical changes as dehydration, scission of pyranose ring and C—OH, C—H bonds of the sample are occurred in the course of pyrolysis of cellulose.

III. Quantities of carbonyl and carboxyl groups in pyrocellulose

The correlation between quantities of carbonyl and carboxyl groups in pyrocellulose and the weight loss percent of cellulose are shown in Figs. 7 and 8 respectively. Each straight line in the graphs has been fitted with those derived by the least squares method.

Regression coefficients of both lines in Fig. 7 are 1.41 under air and 0.87 under nitrogen respectively. The regression lines of Y upon X are represented as Y=1.41X+3.7 (under air) and Y=0.86X−2.6 (under nitrogen), where Y

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\(^{18}\) H. Sugisawa and E. Edo, Chem. and Ind., 1964, 892.

Fig. 8. Carboxyl Groups in Pyrocellulose.

Regression coefficients of both lines in Fig. 8 are 1.59 under air and 0.84 under nitrogen respectively. The regression lines of Y upon X are represented as $Y=1.59X-5.10$ (under air) and $Y=0.84X-3.7$ (under nitrogen), where Y is milliequivalent of carboxyl groups/100 g of pyrocellulose.

Figs. 7 and 8 show that quantities of carbonyl and carboxyl groups in pyrocellulose increase linearly against weight loss percent. On the basis of these results, it is most reasonable to consider that the chemical changes of cellulose in the earlier stage of pyrolysis are proceeded uniformly irrespective of the reaction temperatures and times.

As shown in Table I, Figs. 7 and 8, the volatilization rate and quantities of carbonyl groups in pyrocellulose were higher under air than under nitrogen. This is obviously due to the oxidation with atmospheric oxygen. Pyrolytic degradation of the sample, however, should be non-oxidative in character.

The oxidation of cellulose with atmospheric oxygen may be postulated according to the mechanism of the oxidation of alkali cellulose,\(^{20}\) that is, mono- or di-functional radicals are formed\(^{21}\) in the course of pyrolysis of cellulose, and the oxidation is initiated as follows:

\[
\begin{align*}
R_{\text{cell}}\text{CHO} + O_2 & \rightarrow R_{\text{cell}}\text{CO} + \text{HOOC} \\
R_{\text{cell}}\text{CO} - R_{\text{cell}}\text{H} & \rightarrow R_{\text{cell}}\text{CO} + R_{\text{cell}}\text{H} \\
R_{\text{cell}}\text{CO} + O_2 & \rightarrow R_{\text{cell}}\text{CO(OO)} \\
R_{\text{cell}}\text{CO(OO)} + R_{\text{cell}}\text{H} & \rightarrow R_{\text{cell}}\text{CO(OOH)} + R_{\text{cell}}
\end{align*}
\]

As described earlier in section II, with the proceeding of pyrolysis, the oxidation must be occurred nonspecifically in anhydroglucose unit of cellulose.

The fact that oxidized cellulose is formed even in the absence of air, may be explained by scission of glucosidic linkage and ether bond in pyranose ring according to the former study on carbonization of cellulose undertaken by Otani.\(^{5}\)