Thermal Degradation of Cellulose and Its Esters in Air

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Received 9 May 1982; accepted 25 May 1982

The thermal degradation of cellulose and its esters (β-chloropropionate, acetate) in air has been studied by dynamic thermogravimetry and differential thermal analysis from ambient temperature to 600°C. The values of the energy of activation of thermal degradation, $E_a$, for cellulose and its esters lie in the range 155-225 kJ mol$^{-1}$. However, the values of free energy of activation for the degradation of cellulose and its esters are almost same and lie in the range 152-185 kJ mol$^{-1}$. This indicates that the basic step in the thermal degradation of cellulose and its derivatives is the same. IR spectra of the pyrolysis residues of cellulose β-chloropropionate gave indication of dehydration and formation of a compound having C=O groups.

Cellulose and its esters are used widely in the textile industry, and their thermal degradation enables us to understand the mechanism which renders them more resistant to heat and flame. The thermal degradation of cellulose itself has been investigated both in vacuo and in an inert atmosphere and a mechanism for decomposition of cellulose has been proposed.

The major weight loss in the pyrolysis of cellulose occurs below 400°C with the formation of water, carbon monoxide, carbon dioxide and levoglucosan. Esterification of cellulose with halogen-substituted acids provides an additional advantage, as it has been observed that certain elements like nitrogen and halogens when incorporated into the matrix of cellulose impart flame resistance to it. In the present study, cellulose samples treated with β-chloropropionic acid have been obtained and the kinetics of the thermal degradation of cellulose and its esters in air atmosphere from ambient temperature to 600°C has been studied using dynamic TG, DTG and DTA techniques. Different kinetic parameters have been obtained adopting the methods of Freeman and Carroll, Broido, Dave and Chopra and Kissinger.

Materials and Methods

Cellulose supplied by M/s Schleicher and Schüll, Dassel, West Germany and dried to constant weight in vacuo at 60°C was used. Xylene (BDH) was freed from thiophene, distilled and dried over sodium wire. β-Chloropropionic acid (Fluka, Switzerland) and perchloric acid (60%,) (Riedel-De-Haenag, Germany) were used as such.

The following samples of cellulose and its derivatives having different degrees of substitution were used: (i) cellulose; (ii) - (iv) cellulose β-chloropropionate samples obtained by treating cellulose (1.62 g) with β-chloropropionic acid (1.0853 g, 2.1706 g and 3.2559 g in 1:1, 1:2 and 1:3 molar ratio respectively) in xylene, mixed with perchloric acid (8% on the weight of cellulose) and refluxing the mixture under nitrogen atmosphere for 2 hr; the products were filtered through G-4 sintered glass funnel, washed thoroughly with water followed by ethanol and dried over P$_2$O$_5$ in vacuo; and (v) cellulose acetate (BDH Chemicals Ltd, Poole, England) extracted with ethanol in a soxhlet apparatus, dried in air, washed with hot distilled water, and again dried in air. The purified material was dried in vacuo at 60°C. The degrees of substitution of the different samples are given in Table 1.

Thermogravimetric analysis, derivative thermogravimetric analysis and differential thermal analysis—The TG and DTG thermograms were obtained using a Stanton Redcroft TG 750. The TG and DTG curves were run under a static air atmosphere and a scale sensitivity of 0.25 mg/cm and 0.1 (mg/min)/cm respectively. The TG measurements were made at a constant heating rate of 10°C/min.

The DTA-02-Universal model (M/s VEB Laborelektronik Halle, GDR) was used for recording the thermograms. The DTA curves were run under a static air atmosphere with the use of calcined alumina as a reference. The DTA measurements were made at a heating rate of 7.9°, 12.3°, 18.8° and 24.6°C/min respectively.

Infrared studies—For the IR studies (Beckman spectrophotometer IR-20, USA), 2% charred samples of cellulose β-chloropropionate (sample iii only) were prepared by heating it to different temperatures were prepared by the KBr technique. The charred samples obtained after heating it to different temperatures were prepared by heating them in a DTA cell in static air atmosphere. Heating was stopped at the desired...
temperature and the residues were allowed to cool and quickly transferred to a sealed sample container.

**Results and Discussion**

The DTA thermograms of pure cellulose (i), cellulose β-chloropropionate (ii-iv) (thermograms of only sample iii shown in the figures) and cellulose acetate (v) were recorded in air and are shown in Figs 1-3. The peak temperatures of the curves at different heating rates were measured and are presented in Table 1. The DTA curves for pure cellulose shows an endotherm loop in the temperature range 70°C-80°C. At about 250°C, the exothermic effect starts with peaking at 322°C, which may be due to auto-oxidation of carbonyl group and C-H bond. The endotherm at 336°C following the exotherm is presumably due to the oxygen in the sample atmosphere being exhausted before the combustion is complete, so that the remainder decomposes in an inert atmosphere. This endotherm seems to be associated with the pyrolysis of cellulose into water, carbon monoxide, carbon dioxide\(^2\) and levoglucosan\(^3\).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Compound</th>
<th>Degree of substitution</th>
<th>7.9°C min(^{-1})</th>
<th>12.3°C min(^{-1})</th>
<th>18.8°C min(^{-1})</th>
<th>24.6°C min(^{-1})</th>
<th>ΔH (J g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Cellulose</td>
<td></td>
<td>endo-therm</td>
<td>endo-therm</td>
<td>endo-therm</td>
<td>endo-therm</td>
<td>endo-therm</td>
</tr>
<tr>
<td>ii</td>
<td>Cellulose</td>
<td>0.054</td>
<td>316.0 329.0</td>
<td>322.0 336.0</td>
<td>327.0 342.0</td>
<td>330.0 346.0</td>
<td>407.9 309.6</td>
</tr>
<tr>
<td>iii</td>
<td>β-chloropropionate</td>
<td>0.079</td>
<td>261.0 269.0</td>
<td>267.0 275.5</td>
<td>272.0 281.5</td>
<td>276.0 286.0</td>
<td>170.4 468.5</td>
</tr>
<tr>
<td>iv</td>
<td>Cellulose</td>
<td></td>
<td>exo-therm</td>
<td>exo-therm</td>
<td>exo-therm</td>
<td>exo-therm</td>
<td>exo-therm</td>
</tr>
<tr>
<td>v</td>
<td>Cellulose acetate</td>
<td>2.309</td>
<td>323.9 336.0</td>
<td>329.0 343.0</td>
<td>334.5 350.0</td>
<td>339.5 354.5</td>
<td>131.0 1004.1</td>
</tr>
</tbody>
</table>

Table 1—Peak Temperatures in the DTA Thermograms and Heats of Pyrolysis (ΔH) for Cellulose and Its Derivatives in Air

Fig. 1—DTA, TG and DTG curves for untreated cellulose in air

Fig. 2—DTA, TG and DTG curves for cellulose β-chloropropionate (sample iii) in air
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... (I)

\[ \frac{dW}{dt} = z \frac{E_a}{R \cdot \text{RH} \cdot \exp \left( \frac{-E_a}{R \cdot \text{RH}} \right)} \cdot W^n \]  

where \( W \) is the weight fraction of the material undergoing degradation at time \( t \); \( \text{RH} \) is the rate of heating (°C/min); and \( Z \), the frequency factor.

From the slopes of the TG curves in Figs. 1-3, the values of \( \Delta \log R_t \) and \( \Delta \log W \) were calculated (Eq. 1) corresponding to an arbitrarily chosen \( \Delta \left( \frac{1}{T} \right) \) interval (in this case \( 0.2 \times 10^{-4} \)) and plots of \( \Delta \log R_t/\Delta \log W \) versus \( \Delta \left( \frac{1}{T} \right) \) were drawn (Fig. 4). The energy of activation, \( E_a \), was determined from the slope. The order of reaction, \( n \), was determined from the intercept.
and is found to be unity for all the cases. These parameters have been evaluated using the method of least squares for all the samples and for all the methods. Broido\(^5\) used Eq. (2) for determining kinetic parameters from TG curve:

\[
\ln \left( \frac{1}{y} \right) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln \left( \frac{R}{E_a} \cdot \frac{Z}{Z \cdot T_m^2} \right) \quad \ldots (2)
\]

where \(y\) is the fraction of the number of initial molecules not yet decomposed and \(T_m\) is the temperature at which the reaction velocity is maximum. From the slopes of TG curve in Figs. 1-3, a plot of \(\ln \left( \frac{1}{y} \right)\) versus \(\frac{1}{T}\) from Eq. (2) yielded a straight line (Fig. 5). The values of \(E_a\) and \(Z\) were obtained from the slopes and the intercepts of these plots respectively.

Dave and Chopra\(^6\) made use of Eq. (3) for determining the energy of activation and the frequency factor from the DTG curve.

\[
k_1 = \left( \frac{A}{M_o} \right)^{n-1} \cdot \left( -\frac{dX}{dt} \right) \quad \ldots (3)
\]

where \(A\) is the total area (mg) under the DTG curve; \(a\), the area (mg) for the reaction up to time \(t\); \(\frac{dX}{dt}\), the height of the curve (mg/min) at time \(t\); \(M_o\), the initial mole fraction of the reactant; and \(n\), the order of reaction. The values of \(k_1\) obtained from Eq. (3) were plotted against \(\frac{1}{T}\) (Fig. 6), yielding the values of \(E_a\) and \(Z\).

Kissinger\(^7\) derived the following equations for determining the kinetic parameters from DTA curve regardless of the reaction order:

\[
\frac{d}{d \left( \frac{1}{T_m} \right)} \left( \ln \frac{R}{T_m} \right) = -\frac{E_a}{R} \quad \ldots (4)
\]
and

\[ \frac{E_a \cdot RH}{R \cdot T_m^2} = Zn(1-x)^{n-1} \exp \left( \frac{-E_a}{R \cdot T_m} \right) \]  

... (4a)

where \( RH \) is the heating rate (°C/min); \( T_m \), the peak temperature (°C); \( x \), the fraction reacted at time \( t \); and \( n \), the reaction order. Plots of \( \ln \frac{RH}{T_m^2} \) versus \( \frac{1}{T_m} \) yielded straight lines (Fig. 7) and the values of the energy of activation were obtained from the slopes of the curves. Eq. (4a) was used for determining the frequency factor.

The energy of activation, \( E_a \), and the frequency factor, \( Z \), for cellulose, cellulose \( \beta \)-chloropropionate samples (ii-iv) and cellulose acetate determined using Eqs. (1)-(4) are presented in Table 2. It is seen that the values of the energy of activation for the pyrolytic degradation of cellulose and treated cellulose samples obtained using different methods are not in close agreement. Further, the value of energy of activation for treated cellulose samples is less than that for pure cellulose. This means that the charring temperature for cellulose \( \beta \)-chloropropionate samples is lower than that for cellulose. The char yield obtained from treated cellulose samples is higher (Table 3), indicating that the treated cellulose samples are better flame retardants.

Assuming \( E_a = \Delta H^* + RT \) for a solid system \(^{12,13}\), the values of \( \Delta S^* \) and hence \( \Delta G^* \) were obtained at the average peak temperature of DTG (600°C) using the following equations \(^{12 - 14}\):

\[ k_1 = Z \exp \left( -\frac{E_a}{RT} \right) \]  

... (5)

\[ Z = \frac{ckT}{h} \exp \left( \frac{\Delta S^*}{R} \right) \]  

... (6)

\[ \Delta G^* = \Delta H^* - T \Delta S^* \]  

... (7)

The values of \( \Delta S^* \) and \( \Delta G^* \) for the pyrolysis of cellulose and cellulose derivatives are given in Table 3. The entropy of activation for thermal degradation is positive for pure cellulose sample and is lower for treated cellulose samples. This is due to the fact that with increasing degrees of substitution of chloropropionyl or acetyl group in cellulose, the magnitude of the degrees of freedom accompanying the formation of the activated complex goes on decreasing, thus making a more tightly bound matrix. The values of free energy of activation for the process at 600°C are found to be almost same, suggesting that the mechanism of thermal decomposition of all the chloropropionylated samples is basically the same.

### Table 2—Energy of Activation, Frequency Factor and Reaction Order for Pyrolysis of Cellulose and Its Derivatives in Air

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>Frequency factor ( Z/s^{-1} )</th>
<th>Reaction order, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freeman and Carroll method</td>
<td>Broido and Chopra method</td>
<td>Kissinger method</td>
</tr>
<tr>
<td>i</td>
<td>178.9</td>
<td>198.2</td>
<td>184.7</td>
</tr>
<tr>
<td>ii</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>iii</td>
<td>172.3</td>
<td>181.9</td>
<td>169.7</td>
</tr>
<tr>
<td>iv</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>v</td>
<td>163.0</td>
<td>183.4</td>
<td>166.7</td>
</tr>
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</table>

*Compounds referred to as Samples No. i to v are the same as in Table 1.*
Table 3—DTG Maxima, Entropy and Free Energy of Activation and Char Yields for Pyrolysis of Cellulose and Its Derivatives in Air

<table>
<thead>
<tr>
<th>Sample No.*</th>
<th>DTG maxima/°C</th>
<th>$\Delta S^*$(J deg$^{-1}$ mol$^{-1}$) at 600 K</th>
<th>$\Delta G^*$ (kJ mol$^{-1}$) at 600 K</th>
<th>Char yield at 700 K %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freeman and Brodio method</td>
<td>Dave and Kissinger method</td>
<td>Freeman and Carroll method</td>
<td>Brodio method</td>
</tr>
<tr>
<td>i</td>
<td>344.0</td>
<td>6.2</td>
<td>27.7</td>
<td>4.9</td>
</tr>
<tr>
<td>ii</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>iii</td>
<td>301.0</td>
<td>12.8</td>
<td>18.6</td>
<td>—</td>
</tr>
<tr>
<td>iv</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>v</td>
<td>362.0</td>
<td>—</td>
<td>33.0</td>
<td>—</td>
</tr>
</tbody>
</table>

*Compounds referred to as Samples No. i to v are the same as in Table 1.

Fig. 8—IR spectra of (a) cellulose $\beta$-chloropropionate sample (iii) and (b-e) chars of cellulose $\beta$-chloropropionate sample (iii) at different temperatures (b) 260°C, (c) 290°C, (d) 320°C, and (e) 350°C.

Infrared examination of chars—An inspection of the IR spectra of the chars (Fig. 8) obtained at different temperatures from the pyrolytic degradation of cellulose $\beta$-chloropropionate (sample iii) confirms the above observations. The spectrum for the char obtained at 200°C showed no change in the absorption bands compared to that of the initial sample (curve a), while at 260°C (curve b), the spectrum showed evidence of dehydration. There is a decrease in the intensity of the hydroxyl stretching vibration bands (3405, 3350, 3305 cm$^{-1}$). Also, at this temperature, the bands due to cellulose $\beta$-chloropropionate at 2900 (C-H str), 1720 (C=O str), 1430 (CH$_2$ sym bending), 1370 (C-H bending), 1335 (O-H inplane bending), 1315 (CH$_2$ wagging), 1280 (C-H bending), 1160 (antisym bridge C-O-C str), 1125, and both 1060 and 1035 cm$^{-1}$ (skeletal vibrations involving C=O str), etc. showed slight decrease, indicating minor degradation of cellulose $\beta$-chloropropionate along with dehydration. At 290°C, all the above-mentioned bands due to cellulose $\beta$-chloropropionate almost disappeared and the absorption due to C=O stretching (1720 cm$^{-1}$) became intense, indicating that the skeletal rearrangement and the evolution of volatile products commence only at higher temperatures. At 350°C, the conjugated C=C band at 1640 shifted to 1600 cm$^{-1}$, suggesting the extension of conjugation of the C=C bonds in the residue from cellulose $\beta$-chloropropionate.

Pyrolytic mechanism—Recently, Scotney$^{15}$ proposed a mechanism for the thermal degradation of cellulose triacetate in vacuo, suggesting deacetylation in the polymer chain and chain scission at the 1,4-glycosidic linkages between the pyranose rings. The former process results in the formation of acetic acid and the latter in the formation of the tarry material. During pyrolysis of the samples of cellulose $\beta$-chloropropionate, most of the chloropropionic acid, if not all, is probably formed by cis-elimination involving a $\beta$-hydrogen atom, as suggested by Scotney$^{15}$. A detailed mechanism for the thermal degradation of cellulose derivative has been proposed elsewhere.$^{14}$

Acknowledgement
One of the authors (R.K.J.) is thankful to authorities of Kurukshetra University, Kurukshetra for providing a research fellowship.

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