

A Kinetic Study of the Thermal Degradation of Cellulose & Some Related Model Compounds

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Pyrolysis of cellulose and some related model compounds (cellobiose, levoglucosan, D-glucose and phenyl- β -D-glucopyranoside) has been investigated in nitrogen using dynamic TG, DTG and DTA techniques. The energies of activation for the dehydration of cellulose and the related model compounds are almost of the same order. The energies of activation for the decomposition of cellulose and cellobiose are much higher as compared to those for other model compounds. The free energies of activation for decomposition of cellulose and cellobiose are in the range 189-199 and for levoglucosan, D-glucose and phenyl- β -D-glucopyranoside in the range 165-174 kJ mol⁻¹. IR spectra of pyrolysis residues of these compounds give indication of dehydration and formation of a compound having carbonyl groups.

Although a lot of work has been reported on the analysis of pyrolyzed cellulose products¹⁻³, no systematic kinetic study has been made on the thermal degradation of cellulose and some related model compounds. In the present study, the pyrolysis of cellulose and some related model compounds, i.e., cellobiose, levoglucosan, D-glucose and phenyl- β -D-glucopyranoside⁴ has been investigated in nitrogen atmosphere from ambient temperature to 500°C using dynamic TG, DTG and DTA techniques. Different kinetic parameters have been determined by following the methods of Freeman and Carroll⁵, Broido⁶, and Dave and Chopra⁷.

Materials and Methods

Cellulose (from Dassel, West Germany) was dried to a constant weight *in vacuo* at 60°C. D-Cellobiose (from Koch-Light Laboratories Ltd., England) was purified by recrystallization from water-acetone. It was pulverized well and then dried at 60°C *in vacuo*. Levoglucosan was prepared by the method of Dimler⁸. D-Glucose was obtained from E. Merck, Bombay. The TG, DTG and DTA thermograms were obtained at a heating rate of 10°C/min using du Pont 950 TG and 900 DTA instruments attached to du Pont 990 thermal analyzer. The TG, DTG and DTA curves were run under a dynamic nitrogen (dried) atmosphere flowing at a rate of 60 ml/min; the scale sensitivities were 0.2 mg/cm, 0.08 (mg/min)/cm and 0.2 °C/cm respectively. Thermal analysis curve for phenyl- β -D-glucopyranoside was taken from the literature⁴ and was processed to obtain various kinetic parameters (Table 1). For IR studies (Beckman spectrophotometer IR-20, USA), 2% charred samples of model compounds and cellulose obtained after heating it to different temperatures (200-425°C) in nitrogen were prepared by the KBr technique.

Results and Discussion

The dynamic TG, DTG and DTA thermograms of cellulose (i), cellobiose (ii), levoglucosan (iii), and D-glucose (iv) recorded in the dynamic nitrogen atmosphere are shown in Figs 1-4.

The DTA curve for cellulose (Fig. 1) shows an endotherm loop due to evaporation of the moisture in the temperature range 70-80°C. A second very large endotherm begins at about 345°C, attaining the maximum at 372°C. This endotherm seems to be associated with the pyrolysis of cellulose into levoglucosan¹, water, carbon monoxide and dioxide⁹.

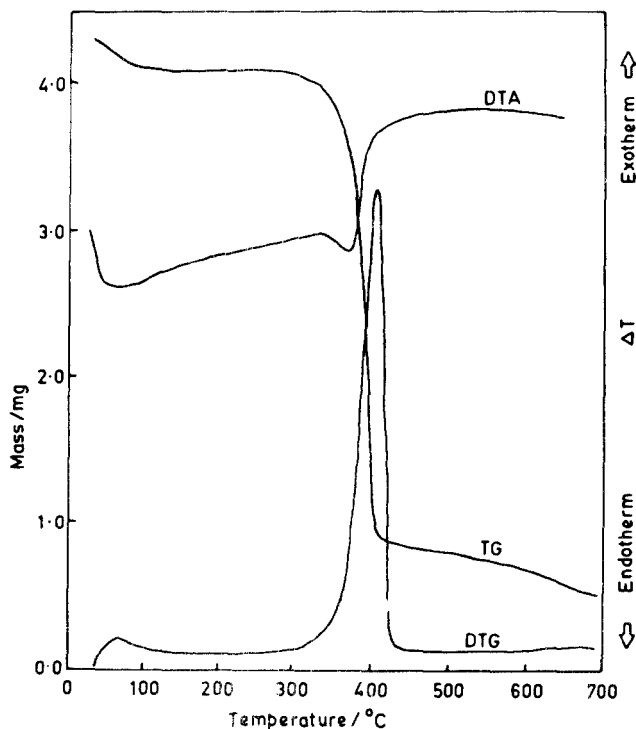


Fig. 1—Thermal analysis of cellulose in nitrogen.

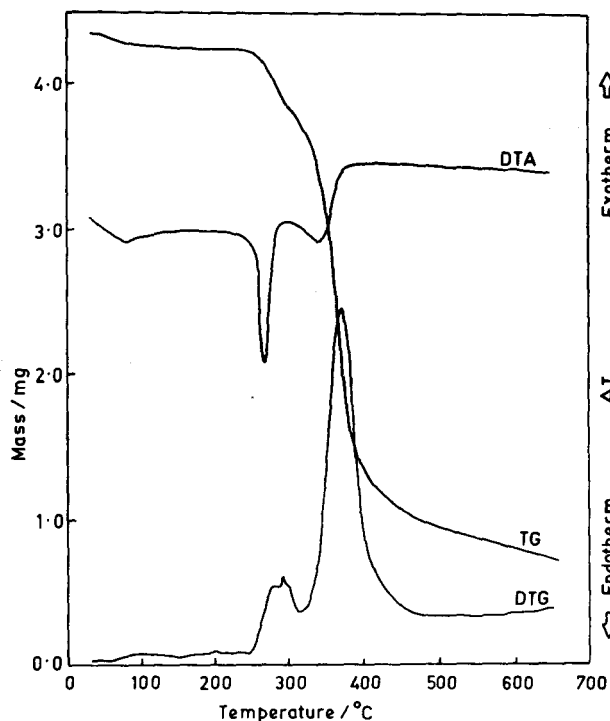


Fig. 2—Thermal analysis of cellobiose in nitrogen.

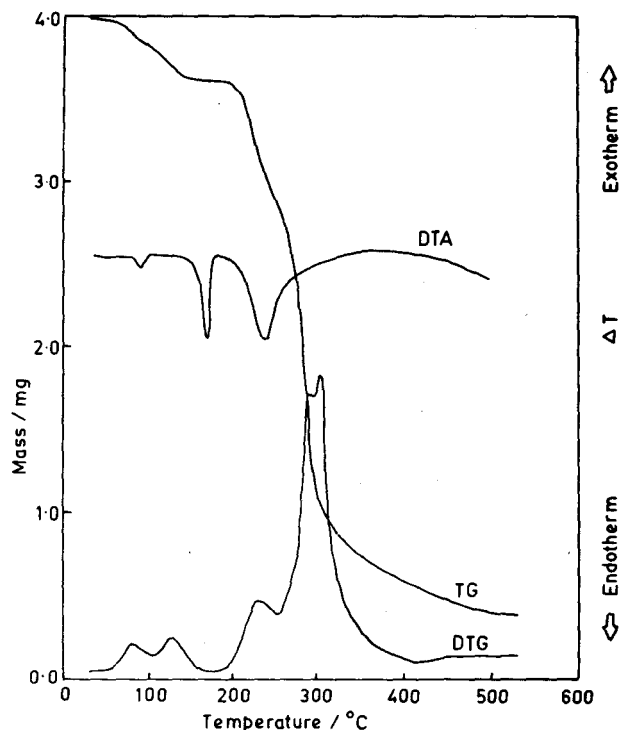


Fig. 4—Thermal analysis of D-glucose in nitrogen.

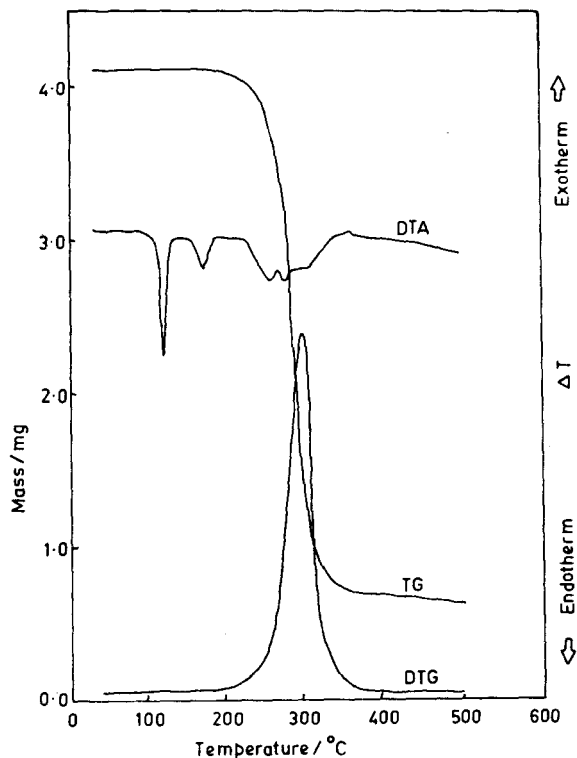
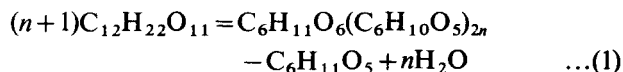


Fig. 3—Thermal analysis of levoglucosan in nitrogen.

Dynamic TG and DTG curves for cellulose show a single mass loss with the maximum at 407°C. The char yield obtained in this case is 20.4% at 750 K. The per cent char residue was obtained from the TG curve by dividing the mass of the sample after the loss of

physically bound water. The latter readings were taken off the curve at roughly 100–120°C before the gradient of the curve begins to change noticeably. The char yields of cellulose and its related model compounds are given in Table 2.

Chü¹⁰ selected cellobiose (4-O-β-D-glucopyranosyl-D-glucopyranose) as a basic unit of the cellulosic structure for understanding the reaction process. Dynamic TG curve (Fig. 2) for cellobiose in flowing nitrogen indicates practically negligible mass loss up to 250°C followed by a rapid mass loss beginning at 250°C. The mass losses are 5.2 and 11.8% at 288 and 315°C. The major mass loss begins at 315°C and increases rapidly to 79.7% at 750 K. The first derivative plot (DTG) also indicates that maximum rate of cellobiose pyrolysis occurs at 280, 292 and 373°C. These data suggest that three major reactions might be taking place during the pyrolysis of cellobiose. The DTA curve for cellobiose indicates two endotherms at 270 and 345°C, first endotherm representing the melting and dehydration of cellobiose. According to Bains¹¹, the dehydration of cellobiose gives long chains, such as cellulose, as represented by Eq. 1,



This is an exothermic reaction to the extent of 105 kJ per D-glucose residue formed. The second endotherm at higher temperature may be due to depolymerization of cellulose followed by decomposition to char and

Table 1—Energies of Activation, Frequency Factors and Reaction Order for Pyrolysis of Cellulose and Some Related Model Compounds

Compound	Pyrolysis stage	Temperature range (°C)	E_a (kJ mol ⁻¹)			Frequency factor, Z (s ⁻¹)			Reaction order, n
			Freeman and Carroll method	Broido method	Dave and Chopra method	Freeman and Carroll method	Broido method	Dave and Chopra method	
Cellulose	Dehydration	290-350	—	124.6	127.9	—	1.19×10^7	1.57×10^7	—
	Decomposition	350-410	214.1	263.2	255.4	1.86×10^{15}	5.18×10^{18}	4.99×10^{17}	1.001
Cellobiose	Dehydration ^a	255-288	—	213.1	223.4	—	1.36×10^{18}	3.20×10^{19}	—
	Dehydration ^b	288-310	—	143.9	—	—	2.27×10^{11}	—	—
Levoglucosan	Decomposition	325-375	179.4	227.9	225.9	1.25×10^{13}	3.35×10^{16}	2.03×10^{16}	1.045
	Dehydration	210-250	—	95.5	93.1	—	1.60×10^6	7.24×10^5	—
D-glucose	Decomposition	250-300	140.4	155.8	162.2	6.34×10^{10}	2.08×10^{12}	6.46×10^{12}	0.984
	Dehydration	210-250	—	132.1	144.7	—	8.75×10^{10}	9.94×10^{12}	—
Phenyl- β -D-glucopyranoside	Decomposition	250-300	131.2	121.6	—	7.39×10^9	1.43×10^9	—	0.925
	Dehydration	250-290	—	140.4	—	—	1.35×10^{10}	—	—
	Decomposition	290-350	103.5	122.1	—	7.23×10^6	3.60×10^8	—	0.948

^aFirst stage of dehydration; ^bsecond stage of dehydration.

other volatile products. The two maxima in the DTG curve representing dehydration at 280 and 292°C of two molecules of water in cellobiose have probably merged into one peak in DTA curve.

Since pyrolysis of cellulose gives levoglucosan (1,6-anhydro- β -D-glucopyranose) as a major volatile product in addition to a variety of other glucose derivatives, TG, DTG and DTA curves for levoglucosan were also analyzed with a view to understanding the mechanism of degradation of cellulose. TG curve for levoglucosan (Fig. 3) shows negligible mass loss up to 200°C followed by a rapid mass loss at 250°C. The TG and DTG curves show a single mass loss step with the maximum at 302°C leading to 15.4% char yield at 750 K. The DTA thermogram indicates a solid transition near 120°C, melting near 180°C and decomposition above 230°C.

Tsuchiya and Sumi¹² pyrolyzed cellulose in vacuum at 370°C, trimethylsilylated the products containing —OH groups and showed the presence of α - and β -D-glucose in addition to levoglucosan. The TG and DTG curves for D-glucose (Fig. 4) show two minor mass losses with maxima at 80 and 120°C which may be attributed to the loss of water of hydration of D-glucose monohydrate and free water respectively. The second mass loss begins at about 200°C with a maximum at 230°C. This may be due to dehydration reaction of D-glucose. The next major mass loss occurs at an average maximum temperature of 298°C, giving char formation of 10.3% at 750 K. The DTA thermogram of D-glucose shows an endotherm at 82°C due to the melting of D-glucose monohydrate. A second endotherm occurs at 156°C due to the melting

of D-glucose. The next endotherm occurring at 240°C is due to the decomposition of the substrate.

Kinetic parameters for the decomposition of cellulose and related model compounds were determined using the procedure described by Freeman and Carroll⁵, Broido⁶, and Dave and Chopra⁷. The equations and corresponding plots (Figs 5-7) involved in these methods are discussed elsewhere¹³.

The energies of activation, E_a , the frequency factors, Z , and the order of reaction, n , determined for cellulose and the related model compounds (ii-v) in the nitrogen medium are presented in Table 1. Entropies (ΔS^*) and free energies of activation (ΔG^*) were determined as described elsewhere¹³ and are presented in Table 2.

The various processes i.e., dehydration, decomposition, etc. occurring during the pyrolysis of cellulose compete with one another, and the thermochemical data derived from the DTA results represent the net effect from such reactions. The amount contributed by each process to the net effect depends on the conditions under which pyrolysis occurs. Out of these processes, dehydration seems to be the important process leading to char formation as suggested by many workers^{14,15}. It is obvious from the discussion of the thermal curves for cellulose, cellobiose, levoglucosan, D-glucose and phenyl- β -D-glucopyranoside that water is evolved during initial stages of pyrolysis at low temperatures followed by other steps of pyrolysis.

In the initial stages of degradation (dehydration stage), the Freeman and Carroll method could not be applied to calculate kinetic parameters as this gave greater scattering in the points leading to uncertainty

in the value of E_a . Dave and Chopra method could not be applied to D-glucose and phenyl- β -D-glucopyranoside due to two overlapping maxima in the DTG curves. The energies of activation calculated by Broido, and Dave and Chopra methods for dehydration of cellulose, levoglucosan, D-glucose, phenyl- β -D-glucopyranoside and second stage for cellobiose are almost of the same order (95-140 kJ mol⁻¹). Difference in these values may be due to different temperature ranges. In case of cellobiose, the energy of activation for denaturation is very high,

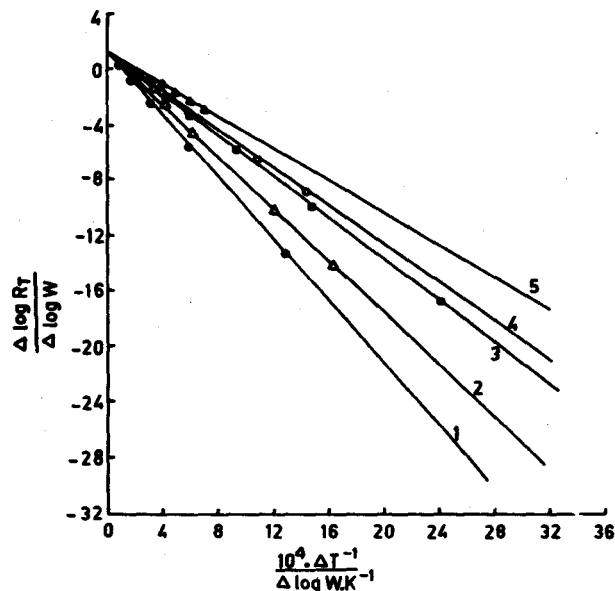


Fig. 5—Plots of $(\Delta \log R_T / \Delta \log W)$ vs $(10^4 \cdot \Delta T^{-1} / \Delta \log W) / K^{-1}$ using Freeman and Carroll equation for pyrolysis of cellulose (1), cellobiose (2), levoglucosan (3), D-glucose (4), and phenyl β -D-glucopyranoside (5) for decomposition stage in nitrogen.

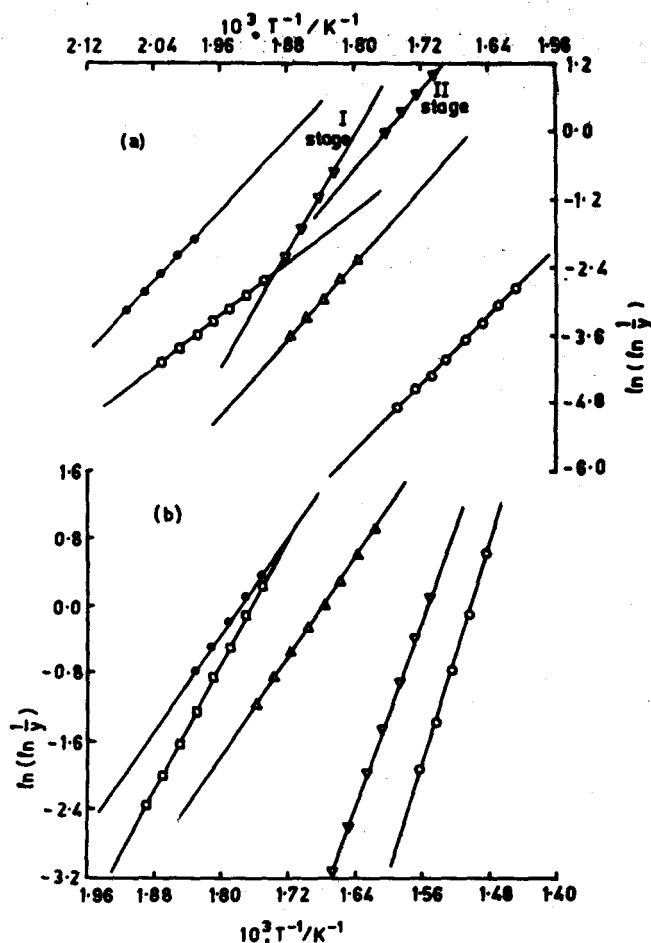


Fig. 6—Plots of $\ln \left(\frac{1}{y} \right)$ vs $10^3 \cdot T^{-1} / K^{-1}$ using Broido equation for pyrolysis of cellulose (O), cellobiose (V), levoglucosan (□), D-glucose (●) and phenyl- β -D-glucopyranoside (Δ) for (a) dehydration stage and (b) decomposition stage in nitrogen.

Table 2—DTG Maxima, Entropies, Free Energies of Activation and Per Cent Char Yields for Pyrolysis of Cellulose and Some Related Model Compounds

Compound	Pyrolysis stage	DTG maxima (°C)	ΔS^* (J deg ⁻¹ mol ⁻¹) at 600 K			ΔG^* (kJ mol ⁻¹) at 600 K			Per cent char yield at 750 K
			Freeman and Carroll method	Broido method	Dave and Chopra method	Freeman and Carroll method	Broido method	Dave and Chopra method	
Cellulose	Dehydration	—	—	-123.5	-121.3	—	193.8	195.7	20.41
	Decomposition	407.0	33.3	99.2	79.8	189.1	198.7	202.6	
Cellobiose	Dehydration ^a	280.0	—	88.1	114.3	—	155.2	149.8	20.32
	Dehydration ^b	292.0	—	-41.7	—	—	163.4	—	
	Decomposition	373.0	-8.3	57.3	53.1	182.1	188.5	189.1	
Levoglucosan	Dehydration	—	—	-140.2	-146.8	—	174.6	176.2	15.39
	Decomposition	302.0	-52.2	-23.2	-13.8	166.8	164.7	165.4	
D-Glucose	Dehydration	230.0	—	-49.6	-10.2	—	156.9	145.9	10.26
	Decomposition	290.0,	—	—	—	—	—	—	
		302.0	-70.1	-83.7	—	168.3	166.8	—	
Phenyl- β -D-glucopyranoside	Dehydration	304.0,	—	-65.1	—	—	174.5	—	10.55 (at 700 K)
		332.0	—	—	—	—	—	—	
	Decomposition	—	-127.7	-95.2	—	175.1	174.2	—	

^aFirst stage of dehydration; ^bsecond stage of dehydration.

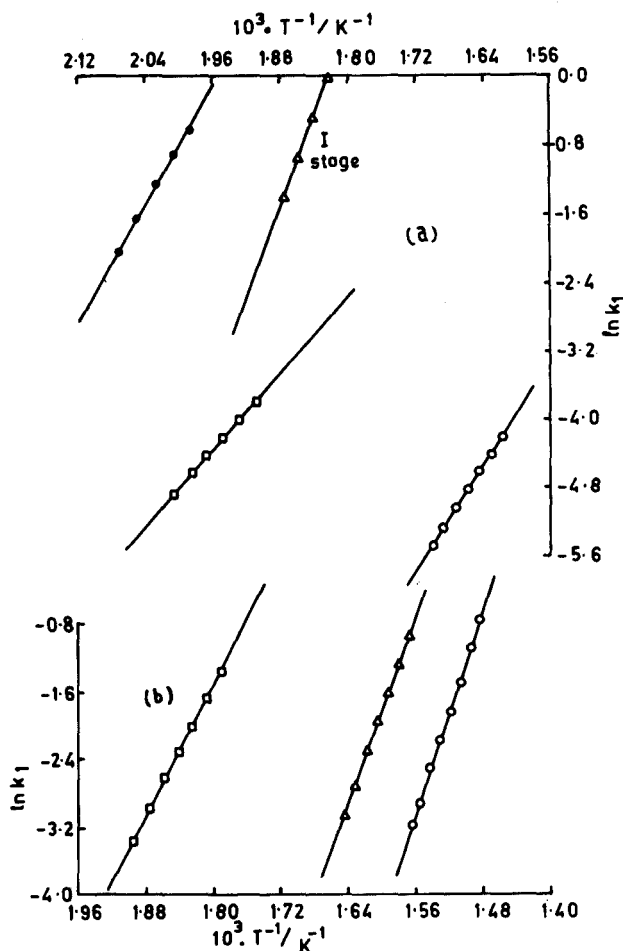


Fig. 7—Plots of $\ln k_1$ vs $10^3 \cdot T^{-1} / K^{-1}$ using Dave and Chopra equation for pyrolysis of cellulose (○), cellobiose (Δ), levoglucosan (□) and D-glucose (●) for (a) dehydration stage and (b) decomposition stage in nitrogen.

indicating a different mechanism for dehydration process.

The entropies and free energies of activation for the dehydration process of these compounds are also presented in Table 2. In most of these cases, the entropies of activation are negative indicating thereby the decrease in the degrees of freedom accompanying the formation of the activated complex. However, the free energies of activation for cellobiose and D-glucose and for levoglucosan and phenyl- β -D-glucopyranoside are almost the same.

At higher temperatures (after dehydration), cellulose and cellobiose (after conversion to long chain molecules) depolymerize and decompose leading to other degradation products. In case of cellulose and cellobiose, the energies of activation are much higher as compared to those of levoglucosan, D-glucose and phenyl- β -D-glucopyranoside. This may be due to the fact that depolymerization (leading to levoglucosan) and decomposition processes are occurring simultaneously in both these compounds and de-

polymerization may be the rate determining step. In the case of other compounds the depolymerization step is missing and the compounds directly decompose to give char products. Murphy¹⁶ also reported that the thermal decomposition followed two separate paths. The first path was described as a slow reaction corresponding to degradation of the main structure, and the second path was one in which some secondary structure was undergoing rapid decomposition. Glassner and Pierce¹⁷ also indicated that both cellulose and levoglucosan gave identical product distribution as determined by gas-liquid chromatography.

The entropies of activation for cellulose and cellobiose are positive while these are negative for other compounds. This indicates that considerable disorder is produced when cellulose and cellobiose are depolymerized and decomposed, respectively. In other compounds, due to absence of depolymerization step, the entropies of activation are negative showing the decrease in the degrees of freedom accompanying the process of activated complex. The free energies of activation obtained by Broido⁶ method for decomposition of cellulose and cellobiose are in the range 189–199 kJ mol⁻¹ whereas for levoglucosan, D-glucose and phenyl- β -D-glucopyranoside these are in the range 165–174 kJ mol⁻¹. This shows that cellulose and cellobiose form one type of similar intermediate while levoglucosan, D-glucose and phenyl- β -D-glucopyranoside form another type of similar intermediate.

With a view to knowing about the nature of the pyrolysis products of the model compounds and cellulose, these were subjected to pyrolysis from 200 to 425°C under nitrogen atmosphere and the IR spectra of the residual products were recorded. At lower temperatures (200–300°C), the spectra for the chars showed evidence of dehydration by decrease in absorption attributable to hydroxyl stretching (3405, 3350, 3305 cm⁻¹). At 400°C, all the normal bands of the unpyrolyzed model compounds and cellulose disappeared, the absorption due to C=O stretching (1720 cm⁻¹) became intense indicating thereby that the skeletal rearrangements and the evolution of volatile products commence at higher temperatures. At this temperature, the conjugated C=C band at 1640 shifted to 1600 cm⁻¹ suggesting the formation of more C=C bonds in the model compounds and cellulose.

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