Thermal Degradation of Cellulose Model Compounds in Inert Atmosphere

IVAN ŠIMKOVIC, MÁRIA ĎURINDOVÁ, VINCENT MIHÁLOV, and JOZEF KÖNIGSTEIN, *Institute of Chemistry, Slovak Academy of Sciences, 842 38 Bratislava, Czechoslovakia,* and PETER AMBROVIČ, *Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia*

Synopsis

Thermal degradation of cellulose model compounds was studied using thermogravimetry (TG), electric spin resonance (ESR) spectroscopy, and gas chromatography–mass spectrometry (GS–MS). The molecular weight of samples did not influence the activation energy of gasification. In the case of catalytic influence of NaOH on cellulose thermolysis formation of gaseous products in the temperature range 250–350°C increased and a greater amount of residue was formed at 350–400°C compared to noncatalytic thermolysis. Residues of compounds with hemiacetal groups showed higher concentration of unpaired electrons than residues obtained from models with the blocked hemiacetal group.

INTRODUCTION

In the process of cellulose thermolysis, before there is any decrease of sample weight observed by TG a decrease of molecular weight can be noticed resulting from cleavage of glycosidic bonds.[1] When the decrease of sample weight begins to be evident, gaseous products are formed diffusing from the heating zone. Part of the products formed after cleavage of glycosidic bonds is reacting inter- and intramoleculary with the environment, forming a macromolecular product partially hydrolysable to monosaccharides.[1] It is not clear how bonds cleave occurs: heterolytically or homolytically. Other important reactions of thermolysis are the dehydratation and carbonization. The carbonization is beginning with C—C bonds splitting and the formed products undergo condensation and aromatic structures containing unpaired electrons are formed.[1]

The purpose of this work is to find new facts about reactions of cellulose thermolysis (cleavage of glycosidic bonds, transglycosylation, dehydration, gasification, and carbonization) using TG, ESR spectroscopy, and GC–MS of methylated thermolysis residues. The following substrates were used: D-glucose (1), 1,6-anhydro-β-D-glucopyranose (2), methyl β-D-glucopyranoside (3), D-cellobiose (4), methyl β-D-cellobioside (5), D-cellotriose (6), methyl β-D-cellotrioside (7), microcrystalline cellulose (8), reduced sample 8 (9), and sample 8 in the presence of NaOH (10). To prevent thermooxidation, the degradation was done in inert atmosphere.

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EXPERIMENTAL

Chemicals. The samples 1,2 (Lachema) and 8 (Avicel) were used. The compounds from 3 to 7 were prepared by known methods.[2] The substrate 9 was prepared from 1 g of 8 (PPS $\sim$ 140) by reduction with $NaBH_4$ (Fluka AG; 125 mg) in water (100 mL) at room temperature for several days. The sample was then dialyzed and lyophylized. Substrate 10 was prepared by adding 100 mg of 8 to 5 mL of methanolic solution containing sodium hydroxide (1 mg/mL), mixing, and removing the solvent under vacuum at room temperature to produce a solid residue.

Methods. TG measurments, ESR spectroscopy, and the calculations of rate constants and activation energies were described previously.[3,4] The samples of thermolyzed residues were heated by bringing the sample (5–10 mg) at a constant rate (10 K min^{-1}) to the desired temperature. GC–MS analyses were performed on JGC-20 K and JMS-100 D instruments. The mass spectra (E = 22 eV) were recorded at an electron emission of 300 μA in inert atmosphere of helium. The gas-chromatographic separations were carried out using stainless steel column (2 m $\times$ 2 mm) packed with SE-30 (w = 3%) on chromosorb WAW DMSCS (0.177/0.149 mm), and, after initial isothermic separation (4 min), linear temperature increase from 150 to 240°C with a heating rate of 4 K min^{-1} was programmed.

The degradation products were methylated according to Kuhn. To 4 mg of sample 0.1 mL of *N*,*N*-dimethylformamide was added together with 0.1 g of Ag_2O and 30 μL of CH_3I. The samples were methylated overnight at room temperature, without light and under stirring. The mixture was then diluted with $CHCl_3$ and filtered. The filter cake was washed several times with $CHCl_3$. To the filtrate xylene was added, vacuum-evaporated to dryness, and, after solubilization in CH_3OH, analyzed.

RESULTS AND DISCUSSION

In Table I there are the results of dynamic TG measurements of 10 model compounds of cellulose. These models were chosen to simulate the reactions of different parts of cellulose macromolecule. The saccharides which contain hemiacetal hydroxyl groups mainly undergo gasification and carbonization.[5,6] The methylglycosides are gasified without degradation and undergo transglycosylation.[6,7] In the case of reduced microcrystalline cellulose, we consider the cleavage of glycosidic bonds to be the rate-determining step. An increased quantity of gaseous products is formed due to the catalytic effect of NaOH.[8] The supramolecular structure of macromolecules 8, 9, and 10 is different. This fact has also an influence on the thermolytical process.[9]

The saccarides containing reducible groups are gasifying under used conditions at 250°C (Table I). At this temperature D-cellotriose (6) has lost up to 50% from the substrate weight, D-glucose (1) about 20%, and D-cellobiose (4) only about 10%. It is known that at this temperature gaseous products are formed from all three substrates, and in models 4 and 6 also the glycosidic bonds are broken.[5,6] All three models give great amounts of residues at 400°C due to carbonization.

The product of cellulose degradation, 1,6-anhydro-β-D-glucopyranose (2), is quantitatively gasified at the applied heating rate, and at 350°C the

TABLE I
Results of Dynamic TG Measurements (wt %) of Models Related to Cellulose in Inert Atmosphere

Model	Temperature (°C)							
	105	250	275	300	325	350	375	400
D-Glucose (1)	99.5	79.8	71.1	51.3	33.5	26.0	22.5	20.5
1,6-Anhydro-β-D-glucopyranose (2)	99.4	41.7	20.3	14.1	3.1	0	—	—
Methyl β-D-glucopyranoside (3)	96.7	72.4	56.8	34.3	17.1	10.9	—	—
D-Cellobiose (4)	99.7	89.0	69.8	54.8	32.7	26.4	23.0	20.8
Methyl β-D-cellobioside (5)	97.5	97.0	95.0	81.7	38.3	15.7	—	—
D-Cellotriose (6)	98.3	53.0	48.0	44.6	40.6	36.6	33.2	30.7
Methyl β-D-cellotrioside (7)	97.0	96.1	95.8	92.1	50.7	13.0	—	—
Microcrystalline cellulose (8)	99.7	99.3	99.0	98.4	85.6	25.6	13.6	12.2
Reduced cellulose (9)	98.7	98.3	98.1	97.4	95.3	88.2	24.6	15.4
Cellulose/NaOH (10)	98.0	87.7	82.0	71.5	55.4	41.6	35.6	32.8

substrate has evaporated completely. The polymerization and carbonization depend largely on the working conditions.[10]

The methylglycosides which are more thermally stable than saccharides with hemiacetal hydroxyl groups (Table I) undergo at 250°C beside gasification also transglycosilation.[6] The amount of obtained residue at 325°C was found to depend on the molecular weight of the substrate. The analogous course for models 1, 4, and 6 could not be found at any temperature because the saccharides with hemiacetal hydroxyl group are able to undergo fragmentation and carbonization at temperatures as low as 250°C.[5,11]

The microcrystalline cellulose (8) which is prepared from cellulose by destroying the amorphous regions, gives a smaller quantity of residue after thermolysis at 350°C than model 6. The cellulose (d.p. $\sim$ 770)[3] prepared by Kraft method from wood, with lower degree of crystallinity and higher content of amorphous regions, shows the same shape of TG curve as sample 8 till 300°C while the amount of residue after thermolysis was greater at higher temperatures. As is known, the amorphous regions undergo carbonization easier than the microcrystalline ones.[9] The reduced cellulose (9) (without hemiacetal hydroxyl groups) is more stable during thermolysis than the modified one (8). The catalytic effect of NaOH is accompanied by an increased residue after thermolysis (Table I). Sample 10 gives the greatest amount of residue out of all studied models at 375°C.

The rate constants and activation energies of thermal degradation of all studied models are summarized in Table II. These constants describe the first-order reactions [regression coefficients of functions $\ln m_0/m_t = f(t)$ were $R = 0.95-0.99$][3] and represent the starting rate values of gaseous products formation. These constants for carbohydrates with hemiacetal hydroxyl group (models 1, 4, and 6) increase with increasing molecular weight. The values of activation energy for the mentioned models increase according to the sequence: monosaccharide, trisaccharide, and disaccharide. These models are not so volatile as methylglycosides,[5,6] and so we attribute the increased activation energy value of D-cellobiose (4) to the presence of glycosidic bond. The value for disaccharide is higher as for trisaccharide. This seems to be due to lower stability of D-cellotriose (6) glycosidic bonds in thermolytic process in comparison to model 4. The rate constants and activation energies of models 2,3,5, and 7 represent mainly gasification of the substrate.[6,7] The rates of gasification for methylglycosides decrease with increasing molecular weight. The activation energies increase in the sequence: monomer, dimer, and trimer. The rate of microcrystalline cellulose (8) degradation is much lower than the values for models from 1 to 7. With decreased crystallinity of cellulose also the activation energies decrease. The cellulose prepared by the Kraft method[3] with different supramolecular structure in comparison to microcrystalline cellulose (8) gives higher values of rate constants and lower value of activation energy. The reduced microcrystalline cellulose (9) shows the lowest values of rate constants from all studied models, but the activation energy is lower than for unmodified cellulose (8). The sample 8 in presence of NaOH (10) undergoes gasification with the highest rate from all studied cellulose samples. The lower value of activation energy in comparison to 8 is due to the catalytic effect of NaOH in gasification process. Comparing activation energies of polysac-

TABLE II
Values of Rate Constants (min^{-1}) and Activation Energies ($kJ\ mol^{-1}$) of Thermolysis of Models Related to Cellulose in Inert Atmosphere

Model	Temperature (°C)							Activation energy
	240	270	280	290	300	310	320	
D-Glucose (1)	0.127	0.209	0.259	0.319	0.390	0.473	0.839	54.0
1,6-Anhydro-β-D-glucopyranose (2)	0.405	0.532	1.080	1.123	1.392	1.631	1.960	52.9
Methyl β-D-glucopyranoside (3)	0.021	0.323	0.430	0.669	0.813	1.159	1.900	113.4
D-Cellobiose (4)	0.068	0.213	0.303	0.368	0.433	0.971	1.129	88.4
Methyl β-D-cellobioside (5)	—	0.031	0.041	0.091	0.149	0.234	0.358	137.5
D-Cellotriose (6)	0.434	1.007	1.302	1.784	2.002	2.670	3.338	64.3
Methyl β-D-cellotrioside (7)	—	0.027	0.035	0.089	0.116	0.197	0.312	140.6
Microcrystalline cellulose (8)	—	0.001	0.002	0.003	0.005	0.007	0.018	134.6
Reduced cellulose (9)	—	0.001	0.001	0.002	0.003	0.004	0.005	86.8
Cellulose/NaOH (10)	—	0.023	0.045	0.074	0.102	0.131	0.182	106.2

charides with values for 1,4, and 6, we can conclude that they are similar, although the differences in molecular weight are evident. So the molecular weight has no influence on the value of gasification activation energy.

To gain some information about the reactions in solid phase, we also studied the residues of thermolysed samples obtained by TG. In Table III are the values of spin concentration in residues after thermolysis of some selected models. The cellulose 8 gives higher concentration of spins in thermolysed residues in comparison to sample 9. As is known,[4] the concentration of radicals in residues increases with the increasing content of carbon. Thus it could be concluded that the free hemiacetal hydroxyl group contributes to the increased carbonization and formation of unpaired electrons in residues in comparison to models with the blocked hemiacetal hydroxyl group. The samples of saccharides have a higher spin content in comparison to polysaccharides at 350°C, while at 400°C the opposite is true. This might be due to the different supramolecular structure of models 3,5, and 7 in comparison to 8 and 9.

The products of thermolysis were also analyzed using GC–MS after methylation of residues. As can be seen (Fig. 1), methyl β-D-glucopyranoside (3) thermolysis stopped at 300°C formed two pairs of compounds. It was found that they are two 1,2-linked and two 1,6-linked disaccharides of hexoglycane type. The mass spectra of these compounds are known.[12] It can be seen (Fig. 1) that the substrate is practically not present in the mixture and the ratio of disaccharides in the pair is 1:1. The compounds were formed from 3 by transglycosylation, the individual compounds in the pair probably differing in the type of glycosidic bonds. Disaccharides are formed probably through a nucleophilic attack by a hydroxyl group of one glucoside molecule on C-1 of another.[6] It is not clear if the both anomers could be formed under these conditions in equal quantity. That is why we are not excluding the possibility of disaccharide formation by the homolytic cleavage of bonds.

When 1,6-anhydro-β-glucopyranose (2) was thermolyzed up to 250°C and the residue analyzed by GC–MS, a mixture of four compounds was obtained. The first of these compounds (Fig. 2, compound a) was the substrate itself. According to the literature,[13] we identified the second and the third compound as being two epimers of 1,6-anhydrofuranose (m/z 172, 145). On the basis of known laws of mass spectrometric fragmentation of per-*O*-methyl derivatives of saccharides,[14,15] we ascribe the structure of the fourth com-

TABLE III
Concentration on Unpaired Electrons (spin $mg^{-1} \times 10^{-16}$) in Thermolyzed Residues of Model Related to Cellulose in Inert Atmosphere

Model	Temperature (°C)		
	325	350	400
Methyl β-D-glucopyranoside (3)	0.31	4.02	17.13
Methyl β-D-cellobioside (5)	—	7.65	19.50
Methyl β-D-cellotrioside (7)	—	5.66	21.94
Microcrystalline cellulose (8)	—	1.12	29.70
Reduced cellulose (9)	—	0.65	24.42

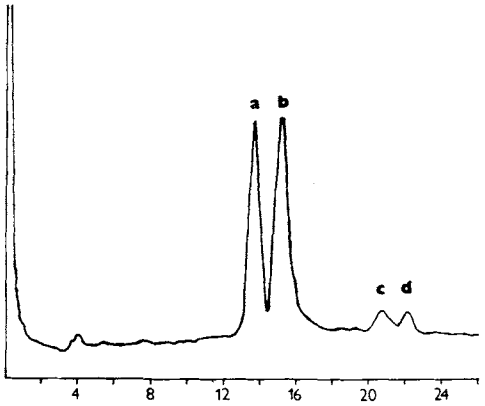

Fig. 1. Gas chromatogram of methylated residue after degradation of methyl β-D-glucopyranoside to 300°C. Per-*O*-methyl derivatives of: (a) 1,6-linked disaccharide of hexoglycane type; (b) 1,6-linked disaccharide of hexoglycane type; (c) 1,2-linked disaccharide of hexoglycane type; (d) 1,2-linked disaccharide of hexoglycane type.

pound to the per-*O*-methyl derivative of 1,6-anhydrodisaccharide of hexoglycane type linked by 1,4-glycosidic bond [*m/z* 233 (baJ), 219 (aA_1), 207, 187, 173, (baJ_1-60), 155, 127, 111, 101 88 (100%), 75, 73, 71].

When methyl β-D-cellobioside (5) was thermolyzed up to 300°C, the residue methylated and analyzed by GC–MS, a mixture of compounds was observed as shown in the gas chromatogram (Fig. 3). The mass spectra of the first five compounds (compounds a–c on Fig. 3) were identical to the spectra of per-*O*-methyl derivatives of methyl β-D-glucopyranoside, 1,6-anhydro-β-D-glucopyranose, methyl β-D-cellobioside, 1,6-anhydrodisaccharide of hexo-

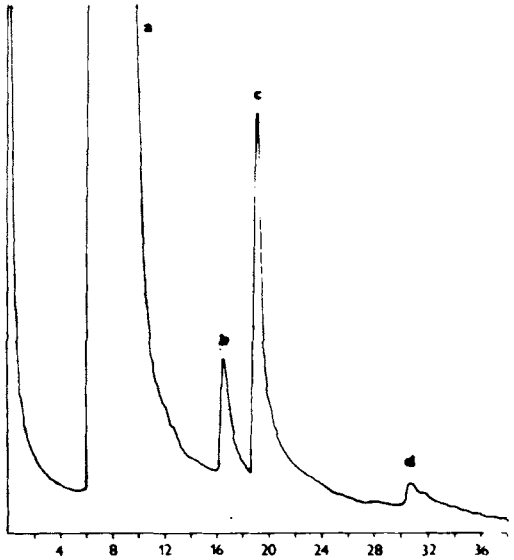

Fig. 2. Gas chromatogram of methylated residue after degradation of 1,6-anhydro-β-D-glucopyranose to 250°C. Per-*O*-methyl derivatives of: (a) 1,6-anhydro-β-D-glucopyranose; (b) 1,6-anhydrofuranose; (c) 1,6-anhydrofuranose; (d) 1,6-anhydrodisaccharide of hexoglycane type linked by 1,4-glycosidic bond.

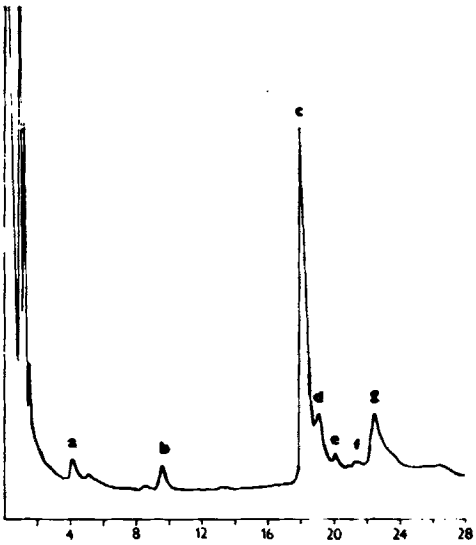

Fig. 3. Gas chromatogram of methylated residue after degradation of methyl β-D-cellobioside to 300°C. Per-*O*-methyl derivatives of: (a) methyl β-D-glucopyranoside; (b) 1,6-anhydro-β-D-glucopyranose; (c) methyl β-D-cellobioside; (d) 1,6-anhydrodisaccharide of hexoglycane type linked by 1,4-glycoside bond; (e) 1,1-linked disaccharide of hexoglycane type; (f) methyl β-D-cellotrioside; (g) 1,6-anhydrotrisaccharide of hexoglycane type linked by 1,4-glycosidic bonds.

glycane type linked by (1—4) glycosidic bond and (1—1) linked disaccharide of hexoglycane type.[12,14] The last two peaks (compounds f and g on Fig. 3) in gas chromatogram were ascribed[14,15] to per-*O*-methyl derivatives of methyl β-D-cellotrioside [*m/z* 483 (abcJ$_1$), 423 (abcJ$_1$-60), 391 (baA$_2$), 305 (baF$_1$), 279 (bcJ$_1$-60), 187 (aA$_2$)] and 1,6-anhydrotrisaccharide of hexoglycane type linked by (1—4) glycosidic bond [*M/z* 437 (abcJ$_1$), 423 (baA$_1$), 391 (baA$_2$), 377 (abcJ$_1$-60), 233 (bcJ$_1$), 219 (bcJ$_1$-60), 187 (aA$_2$), 173 (cA$_1$)]. The identified compounds are the products of glycosidic bonds cleavage, dehydration, and transglycosylation of the substrate 5. When the models 7 and 8 were thermolyzed to 350°C, the only compound present in the residue after methylation was the per-*O*-methyl derivative of model 2. No per-*O*-methyl derivatives were identified in thermolyzed residues of models 9 and 10 after methylation when the substrates were degraded up to 350°C. From these results it can be concluded that under these conditions all saccharides undergo transglycosylation to polymeric compounds, fragmentation to gaseous products or condensation to carbonized residue.

CONCLUSIONS

From the results of TG measurements we concluded that the molecular weight has no influence on the activation energies of carbohydrate gasification. The increased production of gaseous products during thermolyzation of cellulose catalyzed with NaOH is accompanied by increased formation of thermolysis residues. The free hemiacetal hydroxyl group contributes to the increased carbonization and formation of unpaired electrons in residues in comparison to models with blocked hemiacetal hydroxyl group. The iden-

tified products of thermolysis confirm dehydratation, transglykosylation, and cleavage of glycosidic bonds, respectively.

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