

Influence of Anionic Form on Thermal Degradation of TMAHP-Cellulose

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Synopsis

Trimethylammoniumhydroxypropyl (TMAHP)-cellulose in 10 anionic forms (F^- , Cl^- , Br^- , I^- , HSO_4^- , NO_3^- , OH^- , HCO_3^- , $H_2PO_4^-$, CH_3COO^-) was prepared, and the influence of each anion on thermal degradation in inert atmosphere was studied. With the help of dynamic and isothermal thermogravimetry (TG) it was found that $H_2PO_4^-$ ions had the greatest retarding effect on TMAHP-cellulose degradation. From the values of rate constants it can be seen that all ionic forms of TMAHP-cellulose have the starting rate of thermal degradation greater than unmodified cellulose. The calculated values of activation energy of thermal degradation for different ionic forms are decreasing in following sequence: $H_2PO_4^- > F^- > NO_3^- > I^- > Br^- > HCO_3^- > Cl^- > HSO_4^- > OH^- > \text{unmodified cellulose} > CH_3COO^-$. From the results of pyrolyse measurements in combination with gas chromatography and mass spectrometry (Py-GC-MS) it follows that the products of the elimination of quarternary ammonium salts are trimethylamine, 3-hydroxy-2-propanone, and, in the case of OH^- form, water. In all other ionic forms the third product is the corresponding acid.

INTRODUCTION

The derivatives of cellulose with ion exchanging properties are good models for the study of thermal stability of polysaccharides because they make possible the modification of polysaccharidic material with different ions which have different effect during the thermolysis. The inorganic salts are in this case bonded by ionic bonds and not only mechanically added to the samples. TMAHP-cellulose is one of the examples of this group. We prepared 10 different anionic forms of TMAHP-cellulose and studied the effect of these anions during thermal degradation.

EXPERIMENTAL

Materials

The bleached cellulose (DP = 770) prepared from beech chips by the delignification with Kraft method was used as starting material for alkylation.

Sample A prepared from 2 g of cellulose was activated with 3 mL of 17.5% solution of NaOH for 0.5 h at 20°C. Then 5 mL of 50% water solution of 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) was added, and the mixture was reacted at 60°C for 2 h. After washing with water to pH = 8-10 the rest of the water was excluded with ethanol, and

the sample was then dried on air. The exchange capacity (Q) of the sample was 0.7 mmol g^{-1} .

The sample B was prepared from 2 g of TMAHP-cellulose (sample A) by activation with 9 mL of 17.5% solution of NaOH for 0.5 h, and subsequent alkylation with 9 mL of 50% water solution of CHMAC for 2 h at 60°C . The reaction was stopped by washing the sample with water, and then the sample was dried in the same way as sample A ($Q = 0.9 \text{ mmol g}^{-1}$). The obtained derivatives of cellulose in OH^- form were transformed to different forms using 1% water solutions of following salts: CH_3COONa , NaF, NaHSO_4 , NaI, NaBr, NaCl, NaNO_3 , NaH_2PO_4 , and NaHCO_3 . The samples were then washed with water and after washing with ethanol dried on air.

Methods

Thermogravimetric measurements were performed on device TGS-1 (Perkin-Elmer) in static nitrogen atmosphere using a heating rate 10 K min^{-1} . The sample weights were 1 mg (Al pan), and the temperature values were calibrated using ferromagnetic standards. In the case of isothermal measurements the used temperature was attained at a rate of 160 K min^{-1} . The rate constants were calculated from the time dependence $\ln m_0/m_t = f(t)$ using linear regression method, where m_0 is the weight of sample at the moment of reaching the desired temperature and m_t is the weight of sample after time t of isothermal heating. Only values which were measured during the first 10 min of thermolysis were used. The rate constants fitted first order rates and were considered as the starting rates of degradation. From the Arrhenius equation the activation energies of thermolysis were calculated. For all these calculations there were modified standard calculation programs in AOS^{1,2} and the programable calculators TI-58C and TI-59 (Texas Instruments) were used.

Mass spectra (23 eV, $300 \mu\text{A}$) were measured on device JMS-100 D using pyrolyzer PL-723 and gas chromatograph JGC-20K with column ($1 \text{ m} \times 3.1 \text{ mm}$) packet with Porapak P and using the temperature program ($60\text{--}250^\circ\text{C}$, 10 K min^{-1}). Helium was used as the inert gas. The temperature of injector was 150°C and for the separator 230°C . The sample was pyrolysed for 2 min and injected for 25 s. Prior to pyrolysis the sample was flushed with helium for 2.5 min and the pyrolysis was done at 350°C . The compounds were identified by comparison with standards.

The exchange capacities were determined as it was described previously.³

RESULTS AND DISCUSSION

From the dynamic TG curves it can be seen that all 10 anionic forms of TMAHP-cellulose are starting to degradate at lower temperatures as the unmodified cellulose (Table I). But at temperatures around 375°C all the modified derivatives have greater carbonized residue as the unmodified cellulose. At this temperature (Table I) we can make the following temperature dependent sequence of decreasing thermal stability: $\text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{OH}^- > \text{Br}^- > \text{HSO}_4^- > \text{I}^- > \text{HCO}_3^- > \text{CH}_3\text{COO}^- > \text{NO}_3^-$.

TABLE I
The Results of Dynamical TG Measurements (wt %) of TMAHP-Cellulose Depending upon Anionic Form in Inert Atmosphere

Sample	Temperature (°C)							
	105	250	275	300	325	350	375	400
A-H ₂ PO ₄ ⁻	95.0	90.5	85.9	64.3	45.7	41.4	38.5	35.3
A-F ⁻	97.3	92.0	84.5	75.0	62.2	40.3	32.0	29.6
A-Cl ⁻	97.3	94.8	91.5	77.3	56.6	37.6	31.9	28.4
A-OH ⁻	95.7	88.0	81.7	73.3	60.8	39.6	31.4	27.5
A-Br ⁻	97.4	95.0	92.2	61.5	41.2	35.2	31.2	28.3
A-HSO ₄ ⁻	95.9	94.7	89.8	73.5	43.1	34.4	30.1	27.1
A-I ⁻	97.7	96.1	93.3	63.7	42.0	33.0	29.3	26.8
A-HCO ₃ ⁻	95.2	84.5	79.0	70.2	53.8	33.5	26.9	23.7
A-CH ₃ COO ⁻	96.9	87.4	79.8	70.9	56.3	32.5	26.2	23.1
A-NO ₃ ⁻	97.5	95.6	92.3	78.0	50.5	29.4	23.2	19.7
Unmodified cellulose	98.7	97.6	97.3	96.6	93.0	80.5	18.7	14.4
B-Cl ⁻	97.0	93.7	80.4	57.1	43.2	34.2	30.4	27.5
B-OH ⁻	95.8	88.1	85.1	78.6	66.6	46.0	27.0	23.1
B-H ₂ PO ₄ ⁻	97.0	93.9	92.1	83.2	46.1	45.4	43.4	41.9

The results of isothermal TG measurements (Table II) are showing the same trend. The rates of degradation of all modified samples are greater than for unmodified cellulose. With increasing of the exchange capacity the rate constants of thermolysis are increasing too (samples B). The activation energies of thermolysis calculated from rate constants within the temperature interval of 300–340°C show that most of the modified samples have greater activation energy than an unmodified cellulose. The activation ener-

TABLE II
The Results of Isothermal TG Measurements of TMAHP-Cellulose Depending upon Anionic Form in Inert Atmosphere at Temperature Interval 300–340°C

Sample	Rate constants (min ⁻¹)					Arrhenius parameters	
	<i>k</i> ₃₀₀	<i>k</i> ₃₁₀	<i>k</i> ₃₂₀	<i>k</i> ₃₃₀	<i>k</i> ₃₄₀	<i>E</i> (kJ mol ⁻¹)	log <i>A</i>
A-H ₂ PO ₄ ⁻	0.0828	0.1060	0.2210	0.3000	0.6600	253.1	14.951
A-F ⁻	0.0106	0.0256	0.0435	0.1715	0.2217	233.9	11.572
A-NO ₃ ⁻	0.0589	0.1103	0.2151	0.4234	0.8840	197.9	10.810
A-I ⁻	0.1545	0.3083	0.6040	1.1335	2.2050	193.8	11.489
A-Br ⁻	0.1204	0.3450	0.8086	1.1169	1.7071	190.5	11.012
A-HCO ₃ ⁻	0.0108	0.0214	0.0383	0.0908	0.1340	190.0	8.566
A-Cl ⁻	0.0940	0.2069	0.3380	0.5851	0.9760	167.7	9.193
A-HSO ₄ ⁻	0.1205	0.2035	0.3690	0.5601	0.8720	145.7	7.925
A-OH ⁻	0.0201	0.0267	0.0421	0.0711	0.1112	128.7	4.963
Unmodified cellulose	0.0029	0.0092	0.0162	0.0254	0.0326	126.3	2.861
A-CH ₃ COO ⁻	0.0159	0.0236	0.0352	0.0591	0.0848	125.1	4.480
B-Cl ⁻	0.1378	0.2793	0.4873	0.7861	1.4139	166.7	9.507
B-OH ⁻	0.0492	0.0996	0.1354	0.1872	0.3326	130.5	5.982
B-H ₂ PO ₄ ⁻	0.0917	0.2144	0.3158	0.5091	0.9066	159.7	8.617

gies values (E) decrease in the following sequence: $A-H_2PO_4^- > A-F^- > A-NO_3^- > A-I^- > A-Br^- > A-HCO_3^- > A-Cl^- > A-HSO_4^- > A-OH^- > \text{unmodified cellulose} > A-CH_3COO^-$. The increase of the exchange capacity from 0.7 to 0.9 mmol g^{-1} decreased the activation energy of thermal degradation in the case of $B-H_2PO_4^-$ while in the case of $B-OH^-$ and $B-Cl^-$ E values remained constant.

To explain these results, we analyzed the products of thermal degradation using the technique Py-GC-MS. The following products of thermal degradation were identified: carbon monoxide, carbon dioxide, hydrogen, methylchloride, water, acetaldehyde, nitrogen, trimethylamine, 3-hydroxy-2-propanon, 2-butenal, 2-methylfuran, furan, biacetyl, acetic acid, methylacetate, 2-furaldehyde, *N*-methylpyrrole, *N,N*-dimethylpyrrole, butane, 2-methyl-3-buten-4-olide, 5-methyl-2-furfuryl alcohol, 5-methyl-2-furaldehyde, syringol, pyrocatechol, and guayacol. The composition of gas products did not change with anionic form of TMAHP-cellulose. Only the relative ratio between the components varied. We suppose that the products of TMAHP-group elimination are trimethylamine and 3-hydroxy-2-propanon and the third component is water in the case of OH^- form or the corresponding acid for all other forms. We can explain the increasing rate of degradation as a result of formed acid action which remains in residue. The aminoderivatives and 3-hydroxy-2-propanon were not identified between gas products of unmodified cellulose thermolysis. The derivatives of pyrrole are probably condensation products of trimethylamine and compounds formed during the thermolysis of cellulose. The furane derivatives are the products of dehydration catalyzed with acids. These derivatives were identified also between degradation products of unmodified cellulose. Because the acetic acid is formed during the pyrolysis of unmodified cellulose, it is possible that the furane derivatives are formed in this case by the catalytic effect of this acid. Methylchloride was identified during thermal degradation of TMAHP-cellulose in all forms and also in the case of unmodified cellulose. This compound is the degradation product of wood components formed during bleaching of cellulose with chlorine compounds. Aromatic compounds are the degradation products of lignin macromolecule. These compounds could have been attached to cellulose and probably resisted delignification.

The values of activation energies illustrated the thermal stability of anions in the TMAHP group. The highest activation energy of thermolysis is of TMAHP-cellulose in the $H_2PO_4^-$ form (253.1 kJ mol^{-1}). This value is twice as large as the value of unmodified cellulose (126.3 kJ mol^{-1}). It can be supposed that it is the result of synergistic effect of the phosphorus-nitrogen^{4,5} system. These two elements condensate together with carbon during the process of carbonization and consequently greater after thermolysis residue is formed (Table I). In this way the quantity of gas fuel decreases, and so is the flammability of material modified in this way.

The relationship between activation energy values and logarithms of preexponential factors is linear ($R = 0.9244$). This compensation law shows that the mechanism of the rate-determining step of thermal degradation of cellulose derivatives, unmodified cellulose as well as cellulose samples with different exchange capacity, is similar. The Arrhenius parameters are

calculated from first-order rate constants with regression coefficients close to 1 ($R = 0.95-0.99$). The fact that also unmodified cellulose fits the linear dependence of activation energies upon the decadeous logarithm of preexponential factors can be explained with the theory that in this case the rate determining step, is also the cleavage of glycosidic bonds. The values of Arrhenius parameters depend strongly on conditions and method of determination.⁶⁻⁸ That is why those values are not absolute but relative, and comparable only with models analyzed the same way.

As a concluding remark it could be said that TMAHP-cellulose in $H_2PO_4^-$ and F^- forms are the most stable materials against thermal degradation in inert atmosphere among studied cellulose derivatives.

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