

Influence of Anionic Form on Thermooxidation of TMAHP-Cellulose

IVAN ŠIMKOVIC* and MIROSLAV ANTAL, *Institute of Chemistry, Slovak Academy of Sciences, 842 38 Bratislava, Czechoslovakia*, KAROL BALOG and ŠTEFAN KOŠÍK, *Fire Research Laboratory, 82104 Bratislava, Czechoslovakia*, and JAN PLÁČEK, *Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia*

Synopsis

With the help of DTA, DTG elementary analysis of carbonized residues and ESR spectroscopy the influence of anionic form on thermooxidation of trimethylammoniumhydroxypropyl (TMAHP)-cellulose was studied. At 300°C the percentage of carbon in carbonized residue thermolyzed in oxidative atmosphere is higher than for the sample degraded in inert atmosphere. The percentage of hydrogen decreases simultaneously. The concentration of free radicals in thermolyzed residue also increases due to the presence of oxygen. We propose that oxygen is abstracting the hydrogen atoms from polysaccharide and unpaired electrons on carbon atoms are produced. At 400°C the percentage of carbon in residues prepared at inert atmosphere is higher than for residue formed at oxidative atmosphere. Also the concentration of free radicals in thermolyzed residues obtained in inert atmosphere is greater than for those from oxidative ones. That is why suppose that at this temperature oxygen is bonded to polysaccharide residue and free radicals are terminated. From the semiquantitative DTA we can make the following sequence of samples according to their increasing thermooxidative effect: unmodified cellulose < A-HSO₄⁻ < A-Br⁻ < A-I⁻ < A-NO₃⁻ < A-H₂PO₄⁻ < A-CH₃COO⁻ < A-HCO₃⁻ < A-F⁻ < A-Cl⁻ < A-OH^{p-}.

INTRODUCTION

There are many factors which are influencing the thermal stability of modified polymer. Some of the methods of thermal analysis which could be used for the study of this subject are: qualitative and semiquantitative DTA, DTG, elementary analysis, and ESR spectroscopy of carbonized residues. We used all this methods for studying the influence of anionic form on thermooxidation of TMAHP-cellulose.

EXPERIMENTAL

The thermoanalytical measurements (TG, DTG, and DTA) were performed on device Mettler TA-1 in a dynamic atmosphere of nitrogen, air, and oxygen (3 dm³ h⁻¹). Platinum-rhodium and platinum (Pt Rh 10 %-Pt) thermocouples employing aluminium oxide as the reference were used for DTA. The platinum pan was used in the case of ~ 7 mg weights and the high ceramical pan for ~ 100 mg sample weights. The rate of heating was 10 K min⁻¹ and the sensibility of DTA was 100 mV. When the qualitative DTA was used, the voltage differences between observed and reference sample in μV were calculated to Kelvin scale using Le Chatelier tables. The semiquantitative DTA was done in oxygen atmosphere after calibration

*To whom correspondence should be addressed.

of the temperature and heat content using benzoic acid, NH_4NO_3 , LiNO_3 , Bi, KNO_3 , Pb, Zn, MnCl_2 , and Al. The heats of chemical reactions (ΔQ) were calculated from the DTA curve using the relation between the apparatus constant and temperature of furnace with the help of ML-09 program for programmable calculator TI-59 (Texas Instruments).

ESR spectra were measured on an X-band spectrometer (Varian E-4). The measurements were done in glass tubes with inner diameter of 2.5 mm. No ESR signal was determined in an empty glass tube in our measurement range. The values of g factor were determined using 2,2,6,6-tetramethylpiperidine-N-oxid. The concentration of spins was related to the concentration of standard (Strong Pitch).

Elementary analyses were done on a Perkin-Elmer Elementary Analyzer (Model 240).

The samples of TMAHP-cellulose marked in our previous work¹ as samples A were used. All other procedures and methods were mentioned also in our previous work.¹

RESULTS AND DISCUSSION

The course of reactions during thermal degradation of cellulose could be judged from DTA curves. In Table I the maxima of DTA and DTG curves of all samples are listed. The unmodified cellulose shows three maxima in

TABLE I
The Results of DTA and DTG Measurements for TMAHP-Cellulose in Different Forms in Inert and Oxidative Atmosphere

Sample	Atmosphere	DTA		DTG					
		°C	ΔTK	°C	max (mg min ⁻¹)				
Unmodified cellulose	Nitrogen	160	2.0	338	5.5				
		358	7.3						
		532	6.4						
	Air	165	1.5			334	6.1		
		349	8.0						
		510	7.3						
TMAHP-cellulose, OH-form	Nitrogen	167	1.6	210	0.2				
		354	8.4						
		520	5.3						
	Air	164	1.8			202	0.2		
		345	11.6						
		498	6.5						
TMAHP-cellulose, CH ₃ COO-form	Nitrogen	157	0.8	250	0.4				
		337	7.6						
		355	9.6						
	Air	507	5.2			330	2.2		
		165	1.6						
		334	14.4						
		487	6.2						
		167	1.8					275	0.8
		298	4.7						
337	6.9								
376	10.0								
498	6.2								
507	5.2								
TMAHP-cellulose, F-form	Nitrogen	167	1.8	275	0.8				
		298	4.7						
	337	6.9							
	376	10.0							
Air	159	1.1	278	0.8					
	285	3.6							

(Continued)

TABLE I (Continued)
The Results of DTA and DTG Measurements for TMAHP-Cellulose in Different Forms in Inert and Oxidative Atmosphere

Sample	Atmosphere	DTA		DTG		
		°C	ΔTK	°C	max (mg min ⁻¹)	
TMAHP-cellulose, HSO ₄ ⁻ form	Nitrogen	361	7.8			
		500	5.6			
		172	1.5	280	1	
		286	3.9	305	3	
		350	8.0			
	Air	510	6.0			
		169	1.6	284	1.1	
		284	4.4	303	3.7	
		345	10.0			
		498	7.0			
TMAHP-cellulose, I ⁻ form	Nitrogen	156	1.25	290	3.1	
		336	4.5			
		350	7.3			
		500	4.6			
		165	1.5	300	3.2	
	Air	305	4.4	322	0.7	
		358	6.7			
		510	4.9			
		163	1.4	295	3.6	
		313	4.9			
TMAHP-cellulose, Br ⁻ form	Nitrogen	355	6.9			
		503	5.0			
		168	1.3	293	4.1	
		330	8.9			
		491	6.2			
	TMAHP-cellulose, Cl ⁻ form	Nitrogen	114	1.8	295	1.2
			305	5.3	324	1.0
			353	7.8		
			525	7.2		
			118	1.5	287	1.5
Air		310	8.0	311	1.1	
		330	10.4			
		495	9.8			
		168	1.8	310	1.5	
		306	4.3	343	1.5	
TMAHP-cellulose, NO ₃ ⁻ form	Nitrogen	370	5.8			
		171	1.9	310	1.6	
		310	4.4	338	1.6	
		365	7.0			
		527	6.0			
	Air	182	1.6	298	4.2	
		304	3.4			
		366	3.3			
		158	1.3	299	4.7	
		303	3.6			
TMAHP-cellulose, H ₂ PO ₄ ⁻ form	Nitrogen	399	4.8			
		538	4.8			
		178	1.7	355	2.1	
		334	3.0			
		375	4.9			
	Air	165	1.8	343	2.3	
		368	7.0			
		543	5.3			

inert atmosphere. The area of all three exotherms is smaller in modified cellulose. We suppose that the first exotherm represents the thermal transition of cellulose.² The second exotherm is the sum of several reactions. The endothermic reaction is the homolytic cleavage of glycosidic linkages. The exothermic reactions are all reactions of free radicals within their surroundings (transglycosylation or other termination processes of unpaired electrons). The third exotherm in inert atmosphere is due to the formation of carbon-carbon bonds. It could be supposed that due to the smaller area under all DTA exotherms of modified samples the quantity of free radicals in gaseous phase decreases as compared to unmodified cellulose.

In oxidative atmosphere (Table I) the individual exotherms of DTA curves move to lower temperatures, and their area under curve increases. It is known that the thermooxidative effect starts to be evident below 300°C.³ On DTG curves the values of maxima slightly increase in comparison to inert atmosphere and also move to a lower temperature (Table I).

When the thermal degradation is judged with the help of semiquantitative DTA (Table II) in oxygen atmosphere, the quantity of heat released in this way could be determined. The heat of reactions determined using this method could be separated in three parts. The temperature intervals of this three parts are also in Table II. The greatest value of ΔQ_1 was found for TMAHP-cellulose in H_2PO_4^- form ($\text{A}-\text{H}_2\text{PO}_4^-$, 175.7 J g⁻¹). Approximately the same value was determined for $\text{A}-\text{OH}^-$ (170.4 J g⁻¹). Although all samples contain approximately equal quantities of physically bonded water¹, the value ΔQ_1 which is needed for their liberation is dependent upon the type of ionic bond which is formed between the anion and the functional group. During the evaporation of physically bonded water the unmodified cellulose exhibited the lowest value of ΔQ_1 (78.5 J g⁻¹). For ΔQ_2 there were samples with lower values than unmodified cellulose ($\text{A}-\text{Br}^-$, $\text{A}-\text{I}^-$). Also in this case the $\text{A}-\text{OH}^-$ sample had the highest value ($\Delta Q_2 = -4696.5$ J g⁻¹). These chemical reactions are exothermic, and it can be supposed that this sample eliminates the highest quantity of water among all studied samples.¹ That is why we propose the greatest contribution for influence on ΔQ_2 to be the termination of free radicals to water as the end product. The $\text{A}-\text{H}_2\text{PO}_4^-$ sample has the second highest value of ΔQ_2 . The H_3PO_4 formed probably also dehydrates at these conditions. It can be supposed that ΔQ_3 is the heat of oxidation of carbonized residue in the presence of inorganic acids or their dehydration products. The heat effect of this reaction is smaller than ΔQ_2 , and the resistant residue at 600°C represents mainly inorganic compounds. The unmodified cellulose is not containing inorganic compounds ($\Delta Q_3 = 0$ J g⁻¹). The sample with the greatest thermooxidation effect shows the highest value of $\Sigma\Delta Q_i$. Thus we can make the following sequence of samples according to their increasing thermooxidative effect: unmodified cellulose < $\text{A}-\text{HSO}_4^-$ < $\text{A}-\text{Br}^-$ < $\text{A}-\text{I}^-$ < $\text{A}-\text{NO}_3^-$ < $\text{A}-\text{H}_2\text{PO}_4^-$ < $\text{A}-\text{CH}_3\text{COO}^-$ < $\text{A}-\text{HCO}_3^-$ < $\text{A}-\text{F}^-$ < $\text{A}-\text{Cl}^-$ < $\text{A}-\text{OH}^-$. The heat values determined in this way cannot be compared to heats of combustion determined by bomb calorimeter measurements⁴, because they were measured at different conditions.

The elementar composition of thermolysed cellulose samples is given in Table III. For some of the anionic forms which were thermolyzed up to

TABLE II
Heat Contents (ΔQ_1 , ΔQ_2 , ΔQ_3 , and $\Sigma \Delta Q_i$) of Unmodified Cellulose and TMAHP-Cellulose in Different Anionic Forms

Material	Q_1		Q_2		Q_3		Q_i		R^{600} (mg)		
	m_0 (mg)	$^{\circ}\text{C}$	J/g^{-1}	m_1 (mg)	$^{\circ}\text{C}$	J/g^{-1}	m_2 (mg)	$^{\circ}\text{C}$		J/g^{-1}	
Unmodified cellulose	99.8	45-160	78.7	95.0	220-445	-3393.0	0	—	-3314.3	0	
A-F ⁻	99.4	65-190	134.7	93.5	190-405	-4248.1	8.0	405-535	-523.4	65-535	2.8
A-Cl ⁻	99.5	55-190	147.3	92.0	185-400	-3915.6	6.5	400-590	-974.4	55-590	0
A-Br ⁻	99.8	60-190	106.5	94.0	190-385	-2922.4	6.8	385-595	-891.0	60-595	1.5
A-I ⁻	99.7	60-175	98.7	94.0	190-385	-2986.7	8.8	385-575	-1077.5	60-575	0.5
A-OH ⁻	99.7	60-180	170.4	90.5	180-435	-4696.5	6.0	435-535	-508.8	60-535	0
A-HSO ₄ ⁻	99.2	70-175	100.3	92.0	195-430	-3416.8	6.5	430-540	-389.5	70-540	1.0
A-NO ₃ ⁻	99.3	60-185	117.5	93.5	185-390	-3523.5	9.0	390-560	-990.5	60-560	0.5
A-H ₂ PO ₄ ⁻	99.3	60-185	175.7	90.5	190-405	-4190.5	11.0	405-560	-398.6	60-560	4.5
A-HCO ₃ ⁻	99.4	60-170	132.3	91.5	165-390	-3936.1	8.9	390-570	-644.9	60-570	3.5
A-CH ₃ COO ⁻	99.0	55-185	148.4	92.0	190-375	-355.5	3.0	375-555	-1040.0	55-555	3.0

^a Resistant residue at 600°C.

TABLE III
Carbon, Hydrogen, and Nitrogen Content of TMAHP-Cellulose in Different Forms before
and after Thermal Degradation in Inert and Oxidative Atmosphere

Sample	Atmosphere	Final temperature of degradation (°C)	C (%)	H (%)	N (%)
Unmodified cellulose	—	—	44.3	6.3	0
	Nitrogen	300	45.8	5.7	0
	Air	300	48.2	5.4	0
	Oxygen	300	55.9	4.0	0
	Nitrogen	400	71.3	3.0	0
TMAHP- cellulose, OH ⁻ form	Air	400	65.3	1.8	0
	—	—	41.3	6.4	1.1
	Nitrogen	300	47.7	6.3	0.3
	Air	300	54.1	5.0	0.3
	Oxygen	300	67.6	1.4	2.2
TMAHP- cellulose, CH ₃ COO ⁻	Nitrogen	400	76.1	4.2	0.6
	Air	400	63.8	1.6	1.8
	—	—	42.7	6.7	0.9
	Nitrogen	300	47.3	6.5	0.3
	Air	300	53.3	5.1	0.2
TMAHP- cellulose, F ⁻ form	Oxygen	300	70.3	1.8	2.2
	Nitrogen	400	76.0	4.1	0.8
	Air	400	65.3	1.8	1.2
	—	—	42.2	6.8	0.9
	Nitrogen	300	49.9	5.9	0.5
TMAHP - cellulose, HSO ₄ ⁻ form	Air	300	55.8	4.4	0.8
	Oxygen	300	64.8	2.0	2.9
	Nitrogen	400	72.3	4.1	0.7
	Air	400	65.0	2.0	1.2
	—	—	41.4	6.7	1
TMAHP- cellulose, I ⁻ form	Nitrogen	300	58.8	5.4	1.3
	Air	300	63.2	4.0	1.5
	Oxygen	300	71.9	1.2	1.6
	Nitrogen	400	74.4	3.8	1.2
	Air	400	66.5	1.9	2.8
TMAHP- cellulose, Br ⁻ form	—	—	39.7	6.3	0.92
	Nitrogen	300	57.6	5.2	1.2
	Air	300	62.8	3.9	1.6
	Oxygen	300	68.8	1.6	3.1
	Nitrogen	400	74.6	4.1	1.7
TMAHP- cellulose, Cl ⁻ form	Air	400	64.8	1.7	2.2
	—	—	41.1	6.5	0.9
	Nitrogen	300	64.0	4.5	1.3
	Air	300	65.7	3.7	1.4
	Oxygen	300	67.1	1.3	3.4
TMAHP- cellulose, NO ₃ ⁻ form	Nitrogen	400	74.6	4.1	1.7
	Air	400	66.3	1.9	1.8
	—	—	42.2	6.8	1
	Nitrogen	300	58.8	5.0	0.9
	Air	300	59.5	4.8	1.1
TMAHP- cellulose, NO ₃ ⁻ form	Oxygen	300	69.8	1.4	3.8
	Nitrogen	400	75.4	4.2	1.3
	Air	400	66.7	2.0	1.4
	—	—	41.3	6.4	2.1
TMAHP- cellulose, NO ₃ ⁻ form	Nitrogen	300	48.6	6.1	1.0
	Air	300	56.5	4.9	1.5
	Oxygen	300	64.9	1.8	3.6

(Continued)

TABLE III (Continued)
Carbon, Hydrogen, and Nitrogen Content of TMAHP-Cellulose in Different Forms before and after Thermal Degradation in Inert and Oxidative Atmosphere

Sample	Atmosphere	Final temperature of degradation (°C)	C (%)	H (%)	N (%)
TMAHP-cellulose, H ₂ PO ₄ ⁻ form	Nitrogen	400	73.4	3.7	1.8
	Air	400	63.6	1.7	3.1
	—	—	40.7	6.7	0.8
	Nitrogen	300	63.9	4.5	0.4
	Air	300	61.6	3.2	1.5
	Oxygen	300	60.9	2.2	2.0
TMAHP-cellulose, HCO ₃ ⁻ form	Nitrogen	400	70.0	3.4	1.4
	Air	400	62.6	1.8	1.6
	—	—	41.9	6.6	1.0
	Nitrogen	300	47.0	6.2	0.2
	Air	300	53.7	5.3	0.3
	Oxygen	300	69.4	1.6	2.1
	Nitrogen	400	75.8	4.2	0.2
	Air	400	62.6	1.8	1.6

300°C in inert atmosphere a much greater content of carbon was found as compared to unmodified cellulose (A-HSO₄⁻, A-I⁻, A-Br⁻, A-Cl⁻, A-H₂PO₄⁻). This means that these five samples carbonize much quicker due to the presence of these anions. The percentage of carbon is increased by the presence of oxygen during thermolysis. The content of hydrogen in residues decreases simultaneously. These facts support the supposed homolytic hydrogen cleavage of polysaccharide by the reaction with oxygen.³ The A-H₂PO₄⁻ sample showed the smallest difference in carbon concentration. When the thermal degradation was stopped at 400°C, the differences of carbon content between unmodified and modified cellulose are smaller. The samples thermolyzed to 400°C contain a lower percentage of carbon as samples subjected to an inert atmosphere. This shows that the oxygen from air is incorporated into the carbonized residue. It is known that the oxygen is consumed during thermooxidation.⁵ From Table III it can be also seen that nitrogen originating from the TMAHP functional group remains also in the residue during thermal degradation or thermooxidation.

The concentration of free radicals in carbonized residue is given in Table IV. The samples A-I⁻, A-H₂PO₄⁻, and A-Br⁻ exhibited several times higher concentrations of unpaired electrons than unmodified cellulose when the thermolyses were carried out in inert atmosphere and stopped at 300°C. Quantity of unpaired electrons in carbonized residues is increasing when several elements with flame-retardant properties are used.⁶ The quantity of free radicals in gaseous phase is decreasing simultaneously.⁷ As a consequence, the flammability of this gases decreases due to the lower exothermic effect of free radicals termination reactions. The concentration of free radicals increases in the presence of oxidative atmosphere, and the differences between samples are smaller. But the unmodified cellulose shows the lowest concentration of free radicals in the presence of oxygen. That is in agreement with of results of Košík et al.⁵ who found higher consumption of oxygen during the thermooxidation of modified samples in

TABLE IV
The Concentration of Free Radicals in Residues after Thermolysis in Inert and Oxidative Atmosphere to Temperature 300 or 400°C

Sample	Atmosphere	Final temperature of degradation (°C)	Calculation of free radicals $\times 10^{-18}(\text{spin}/\text{mg}^{-1})$	g factor ^a
Unmodified cellulose	Nitrogen	300	2	2.0034
	Air	300	1	2.0035
	Oxygen	300	14	2.0032
	Nitrogen	400	78	2.0031
TMAHP-cellulose, OH ⁻ form	Air	400	46	2.0031
	Nitrogen	300	2	2.0034
	Air	300	5	2.0031
	Oxygen	300	89	2.0030
TMAHP-cellulose, CH ₃ COO ⁻ form	Nitrogen	400	81	2.0029
	Air	400	35	2.0032
	Nitrogen	300	1	2.0048
	Air	300	3	2.0035
TMAHP-cellulose, CH ₃ COO ⁻ form	Oxygen	300	80	2.0031
	Nitrogen	400	123	2.0029
	Air	400	60	2.0030
	Nitrogen	300	5	2.0032
TMAHP-cellulose, F ⁻ form	Air	300	2	2.0033
	Oxygen	300	96	2.0031
	Nitrogen	400	75	2.0032
	Air	400	53	2.0032
TMAHP-cellulose, HSO ₄ ⁻ form	Nitrogen	300	6	2.0033
	Air	300	12	2.0031
	Oxygen	300	22	2.0030
	Nitrogen	400	61	2.0032
TMAHP-cellulose, I ⁻ form	Air	400	43	2.0030
	Nitrogen	300	20	2.0032
	Air	300	13	2.0031
	Oxygen	300	109	2.0030
TMAHP-cellulose, Br ⁻ form	Nitrogen	400	95	2.0032
	Air	400	54	2.0032
	Nitrogen	300	13	2.0032
	Oxygen	300	16	2.0032
TMAHP-cellulose, Cl ⁻ form	Nitrogen	400	135	2.0032
	Air	300	99	2.0032
	Nitrogen	300	58	2.0032
	Air	400	8	2.0033
TMAHP-cellulose, NO ₃ ⁻ form	Nitrogen	300	9	2.0034
	Oxygen	300	103	2.0030
	Nitrogen	400	95	2.0032
	Air	400	69	2.0032
TMAHP-cellulose, H ₂ PO ₄ ⁻ form	Nitrogen	300	5	2.0034
	Air	300	12	2.0031
	Oxygen	300	111	2.0032
	Nitrogen	400	106	2.0030
TMAHP-cellulose, H ₂ PO ₄ ⁻ form	Air	400	62	2.0030
	Nitrogen	300	18	2.0030
	Air	300	21	2.0031
	Oxygen	300	97	2.0030
TMAHP-cellulose, H ₂ PO ₄ ⁻ form	Nitrogen	400	76	2.0031
	Air	400	98	2.0030

(Continued)

TABLE IV (Continued)
The Concentration of Free Radicals in Residues after Thermolysis in Inert and Oxidative Atmosphere to Temperature 300 or 400°C

TMAHP- cellulose, HCO ₃ ⁻ form	Nitrogen	300	1	2.0031
	Air	300	6	2.0030
	Oxygen	300	139	2.0031
	Nitrogen	400	121	2.0032
	Air	400	50	2.0030

comparison to unmodified ones. When thermolysis is stopped at 400°C the quantity of free radicals formed in inert atmosphere is higher than in oxidative atmosphere (the sample A-H₂PO₄⁻ is the exception). While at 300°C oxygen did support the homolytic cleavage of the C-H bond, at 400°C it bonds to the rest of the polysaccharide via carbon atoms with unpaired electrons; subsequently, the free radicals are terminated.³ The width of ESR spectra lines was from 0.45 to 0.75 mT. Although the values of *g* factors do not much differ from each other, it could be said that their values decrease with increasing temperature as known from the literature.⁸

So when we summarize the results of all thermoanalytical methods, the most suitable method for the study of thermooxidation is the semiquantitative DTA. The influence of some anions on the concentration of free radicals in carbonized residue is still unclear. It is connected with the influence of some inorganic compounds on radical reactions during thermooxidation.⁹

References

1. I. Šimkovic, M. Antal, V. Mihálov, J. Königstein, and M. M. Micko, *J Appl. Polym. Sci.*, **30**, 4707 (1985).
2. T. Nguyen, E. Zavarin, and E. M. Barral II, *Macromol. Sci. Rev. Macromol. Chem.*, **C20**, 1 (1981).
3. F. Shafizadeh and A. G. W. Bradbury, *J. Appl. Polym. Sci.*, **23**, 1431 (1979).
4. R. A. Susott, W. F. DeGroot, and F. Shafizadeh, *J. Fire Flammability*, **6**, 311 (1975).
5. M. Košík, V. Lužáková, V. Reiser, and A. Blažej, *Fire Mater.*, **1**, 19 (1976).
6. F. Shafizadeh and P. P. S. Chim, *Am. Chem. Soc. Symp. Ser.*, **43**, 57 (1977).
7. A. Tkáč and I. Špilda, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1495 (1981).
8. I. C. Lewis and L. S. Singer, *Chem. Phys. Carbon*, **17**, 1 (1981).
9. R. McCarter, *J. Consum. Prod. Flammability*, **4**, 346 (1977).

Received December 11, 1984

Accepted February 11, 1985