Thermochimica Acta, 117 (1987) 187–199
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL AND SPECTROSCOPIC STUDIES ON C-2, C-3 AND C-6 SUBSTITUTED CELLULOSE WITH DIFFERENT GROUPS

RAJESH K. JAIN, KRISHAN LAL and HARI L. BHATNAGAR

Department of Chemistry, Kurukshetra University, Kurukshetra 132 119 (India)

(Received 6 January 1987)

ABSTRACT

The thermal behaviour of cellulose and its C-2, C-3 and C-6 derivatives substituted by acetyl, benzoyl and trityl groups has been studied in a static air medium by differential scanning calorimetry and thermogravimetry from ambient temperature to 450 °C. Various reactions involved viz. dehydration, deacetylation, debenzoylation, detritylation, oxidative decomposition and oxidation of charred residues are discussed. Thermodynamic functions for different stages of thermal degradation are obtained from TG curves using the method of Broido. The activation energies for cellulose and its C-2, C-3 and C-6 substituted derivatives are found to be in the range 136 to 253 kJ mol^{-1}. The IR spectra of these derivatives indicate formation of a compound containing C=C and C=O groups in the final residual char. The EPR signals indicate the formation of trapped and stable free radicals in the degradation of the compounds. Cellulose benzoate and its subsequent substituted derivatives show generation of a large amount of trapped free radicals during the decomposition. The mechanism of acid-catalysed thermal degradation of cellulose esters is proposed.

INTRODUCTION

The substitution of different groups at the C-2, C-3 and C-6 hydroxyl groups in cellulose chains alters the mechanism of thermal degradation and hence flame-retardant characteristics of cellulose. Some work on obtaining an understanding of the thermal behaviour of cellulose acetate [1,2] and cellulose benzoate [3] has been reported. However, scanty information is available on the mode of action of thermal degradation involving esterification of cellulose with different substituents at primary (C-6) and secondary (C-2 and C-3) hydroxyl groups. In this study, cellulose acetate and cellulose benzoate have been prepared and the products have been further substituted by different aliphatic or aromatic substituents at the remaining unreacted hydroxyl groups. The various aliphatic and aromatic esters of cellulose thus obtained have been subjected to thermal degradation from ambient temperature to 450 °C using thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) techniques. Kinetic parameters for the thermal degradation of cellulose and its various derivatives have been obtained by adopting the method of Broido [4]. Thermal degradation and flame-retardant properties of cellulose acetate and cellulose benzoate were compared with that of the doubly substituted esters of cellulose. Further, the thermally degraded charred products obtained at different temperatures have been analysed by IR and EPR spectra and the results obtained are discussed.

EXPERIMENTAL

The following samples of cellulose and its derivatives with different substituents were selected for this work. Sample (i): cellulose powder (from Schleicher and Schüll, Dassel, F.R.G.), dried to a constant weight in vacuo at 60 ° C; sample (ii): cellulose acetate was obtained by treating cellulose with acetic anhydride and anhydrous sodium acetate in pyridine at 60 ° C for 24 h, precipitated by pouring into water and ethanol mixture (1 : 2 v/v), purified by Soxhlet extractor in methanol and dried in vacuo over P_2O_5; sample (iii): cellulose benzoate was prepared by treating cellulose with benzoyl chloride in pyridine at 60 ° C for 16 h, precipitated and purified by the method for sample (ii); sample (iv): the benzoate of cellulose acetate was obtained by treating cellulose acetate with benzoyl chloride at 60 ° C for 16 h and purified by the procedure for sample (ii); sample (v): tritylate of cellulose acetate was prepared by treating cellulose acetate with triphenylchloromethane (trityl chloride) in pyridine at 100 ° C for 15 h, purified by Soxhlet extraction in methanol, followed by ether, and dried in vacuo over P_2O_5; sample (vi): the acetate of cellulose benzoate was obtained by treating cellulose benzoate with acetic anhydride and anhydrous sodium acetate in pyridine at 60 ° C for 24 h and purification by the procedure for sample (ii); sample (vii); the tritylate of cellulose benzoate was prepared by treating cellulose benzoate with trityl chloride at 100 ° C for 15 h and purified by the method for sample (v).

The acetyl and benzoyl content were determined by the ASTM method [5] and the trityl content was determined by converting the sample (v and vii) into trityl carbinol with concentrated sulphuric acid [6]. The degree of substitution (DS) of the various samples, determined from the acetyl, benzoyl and trityl contents, are given in Table 1.

The DSC, TG and DTG thermograms were obtained using a Du Pont 910 DSC and 951 TG apparatus attached to a Du Pont 1090 thermal analyser, respectively. These curves were run under a static air atmosphere and at a heating rate of 10 ° C min^{-1}.

For the IR studies (using a Beckman spectrophotometer IR-20, U.S.A.), the charred samples of cellulose and its derivatives were prepared by the KBr technique using 2% char. The charred samples were prepared by heating them in a DTA cell under a static air atmosphere. Heating was

TABLE 1

Peak temperatures in the DSC thermograms for cellulose and its C-2, C-3 and C-6 substituted derivatives in air

Sample No.	Compound	Degree of substitution	Peak temp. of the DSC curve (°C)	Nature of the DSC curve	Char yield at 720 K in mass%
(i)	Cellulose	–	288	Endo (large)	
			318	Exo (small)	9.3
			374	Exo (large)	
(ii)	Cellulose acetate		233	Endo (large)	
		acetyl 1.72	286	Endo (large)	13.0
			344	Exo (large)	
(iii)	Cellulose benzoate	benzoyl 1.88	315	Endo (small)	12.6
			357	Exo (large)	
(iv)	Benzoate of	acetyl 1.72	194	Endo (small)	
	cellulose acetate	benzoyl 0.68	304	Endo (small)	15.1
			362	Exo (large)	
(v)	Tritylate of	acetyl 1.71	221	Endo (small)	
	cellulose acetate	trityl 0.54	300	Endo (small)	14.0
			358	Exo (large)	
(vi)	Acetate of	benzoyl 1.88	196	Endo (small)	
	cellulose benzoate	acetyl 0.46	301	Endo (small)	14.6
			344	Exo (large)	
(vii)	Tritylate of	benzoyl 1.88	238	Endo (small)	
	cellulose benzoate	trityl 0.30	283	Exo (large)	13.2
			378	Exo (large)	

stopped at the desired temperature and the residues were allowed to cool and quickly transferred to a stoppered sample container.

EPR spectra of charred samples of cellulose and its derivatives were recorded on a Varian E-112 EPR spectrometer operating at 9.45 GHz with a field modulation of 100 kHz. 100 mg of charred sample was taken in the quartz sample tube for each measurement. The 1,1-diphenyl-2-picryl hydrazyl (DPPH) signal was used as a standard for *g* values.

RESULTS AND DISCUSSION

The DSC, TG and DTG thermograms of (i) cellulose, (ii) cellulose acetate, (iii) cellulose benzoate, (iv) benzoate of cellulose acetate, (v) tritylate of cellulose acetate, (vi) acetate of cellulose benzoate and (vii) tritylate of cellulose benzoate were obtained in a static air atmosphere from ambient temperature to 450 °C and are shown in Figs. 1–7. The peak temperatures for the various endotherms and the exotherms of the DSC curves were measured and are given in Table 1. An endotherm observed below 100 °C is

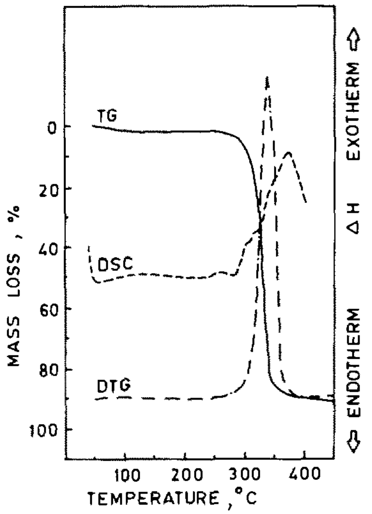

Fig. 1. Thermal analysis of cellulose in air.

due to the evaporation of moisture. The DSC thermogram of cellulose shows an endothermic peak at 288° C, corresponding to the dehydration and depolymerization of the sample. The exotherms at 318 and 374° C are due to oxidative decomposition of the residual products. The last two exotherms are accompanied by a sharp mass loss, shown by TG curve, leaving 9.3% of carbonaceous residue at 450° C.

The DSC curve of cellulose acetate shows a major endothermic peak at 233° C associated with the melting point of the sample. The endotherm is

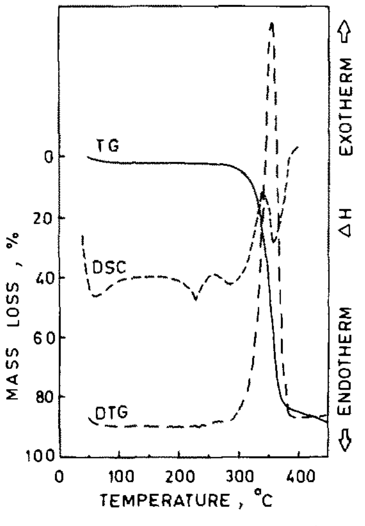

Fig. 2. Thermal analysis of cellulose acetate in air.

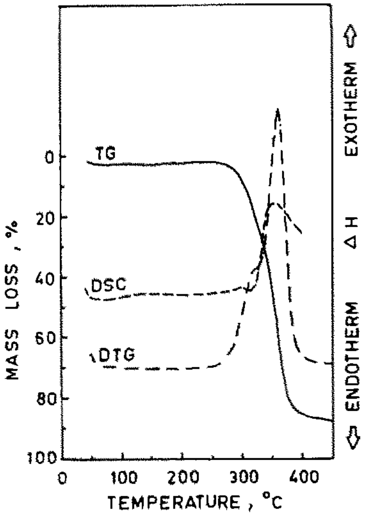

Fig. 3. Thermal analysis of cellulose benzoate in air.

followed by another endotherm at 286 °C which is attributed to the deacetylation reaction. The large peak at 344 °C is due to oxidative decomposition of the products catalyzed by the released acid. For cellulose benzoate, the DSC curve shows an endotherm at 315 °C due to debenzoylation process and the exotherm at 357 °C corresponds to the oxidative decomposition of the residual products.

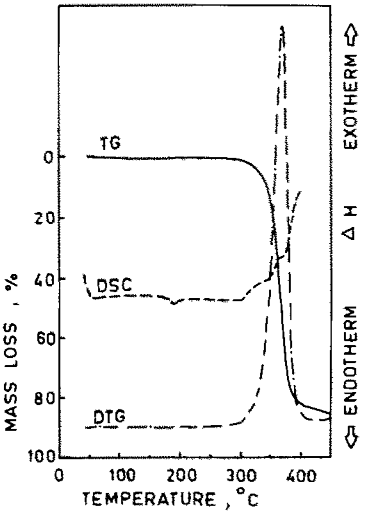

Fig. 4. Thermal analysis of benzoate of cellulose acetate in air.

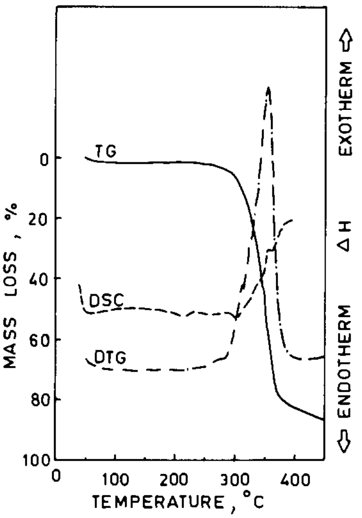

Fig. 5. Thermal analysis of tritylate of cellulose acetate in air.

In the case of benzoate of cellulose acetate and tritylate of cellulose acetate, the endotherms peaking at 194 and 221° C, respectively, are due to melting of the samples. The next endotherms for these compounds with peaking at 304 and 300° C are associated with deacetylation and debenzoylation, and deacetylation and detritylation reactions, respectively. The exotherms for the benzoate and the tritylate of cellulose acetate with maxima at 362 and 358° C, respectively, are attributed to oxidative decomposition of the products.

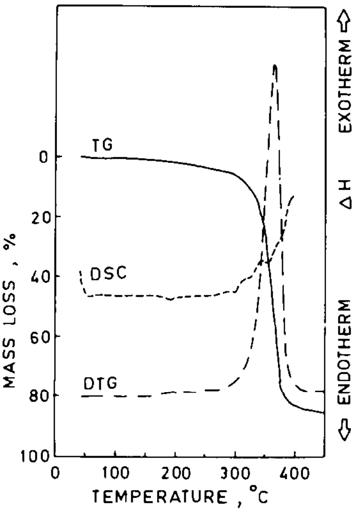

Fig. 6. Thermal analysis of acetate of cellulose benzoate in air.

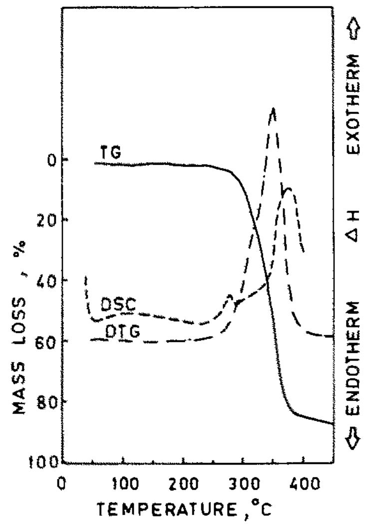

Fig. 7. Thermal analysis of tritylate of cellulose benzoate in air.

The DSC thermogram of acetate of cellulose benzoate shows an endotherm with a peak at 196 °C (melting of the sample). The endotherms at 301 and 238 °C for acetate of cellulose benzoate and tritylate of cellulose benzoate, respectively, are associated with the deacetylation and debenzoylation, and debenzoylation and detritylation reactions respectively. The endotherm is followed by the exotherm at 344 °C for acetate of cellulose benzoate and 283 and 378 °C for tritylate of cellulose benzoate which are due to the oxidative decomposition of the products.

The mass vs. temperature curves for cellulose and its derivatives are shown in Figs. 1–7. In some cases the initial but small mass loss due to adsorbed moisture was neglected. The kinetic parameters for the various stages of thermal degradation were determined using the method described by Broido [4]. The equation involved can be written as

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

where y is the fraction of the number of initial molecules not yet decomposed, T_m is the temperature of maximum reaction velocity and RH is the rate of heating.

Using the Broido method, plots of $\ln[\ln(1/y)]$ vs. $1/T$ for the various stages of thermal degradation are given in Figs. 8–10. The values of activation energies, E_a, and the frequency factors, Z, determined from the slopes and intercepts of these plots are given in Tables 2–4. These parameters have been evaluated using the method of least squares.

Tables 2–4 present activation energies and the frequency factors for various stages of thermal degradation for cellulose and its C-2, C-3 and C-6

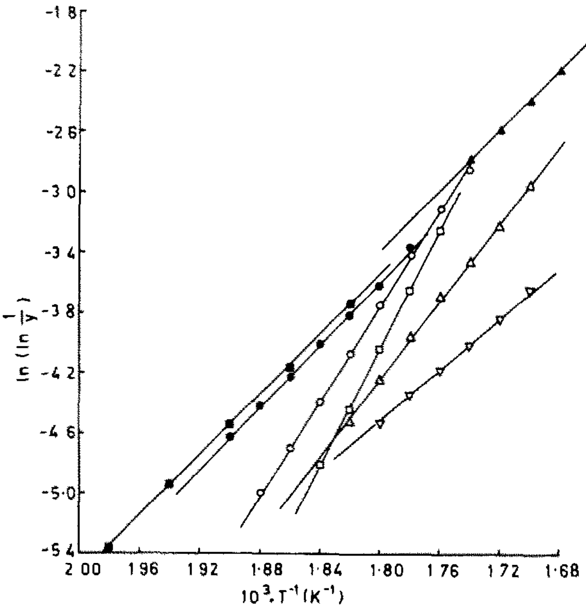

Fig. 8. Plots of $\ln[\ln(1/y)]$ vs. $10^3 \times T^{-1}$ (K^{-1}) using the Broido equation for cellulose (○), cellulose acetate (△), cellulose benzoate (□), benzoate of cellulose acetate (▽), tritylate of cellulose acetate (●), acetate of cellulose benzoate (▲) and tritylate of cellulose benzoate (■) in air for the first stage of thermal degradation.

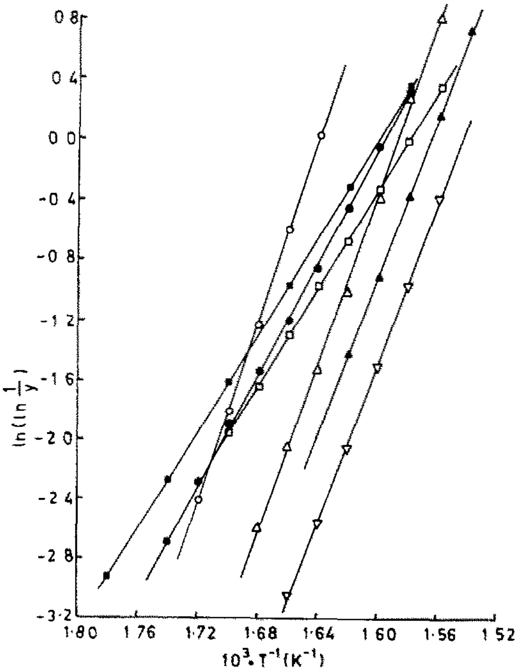

Fig. 9. Plots of $\ln[\ln(1/y)]$ vs. $10^3 \times T^{-1}$ (K^{-1}) using the Broido equation for cellulose (○), cellulose acetate (△) cellulose benzoate (□), benzoate of cellulose acetate (▽), tritylate of cellulose acetate (●), acetate of cellulose benzoate (▲) and tritylate of cellulose benzoate (■) in air for the second stage of thermal degradation.

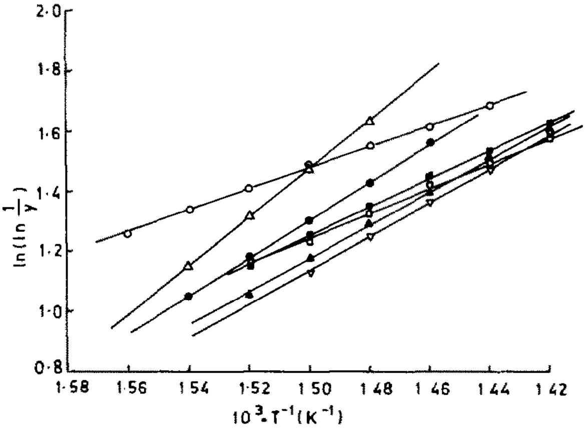

Fig. 10. Plots of $\ln[\ln(1/y)]$ vs. $10^3 \times T^{-1}$ (K^{-1}) using the Broido equation for cellulose (○), cellulose acetate (△), cellulose benzoate (□), benzoate of cellulose acetate (▽), tritylate of cellulose acetate (●), acetate of cellulose benzoate (▲) and tritylate of cellulose benzoate (■) in air for the third stage of thermal degradation.

substituted derivatives in static air. Table 2 shows that for the first stage of thermal degradation of cellulose, mainly due to dehydration, the activation energy is 131 kJ mol^{-1}. These values for cellulose acetate and cellulose benzoate are 108 and 163 kJ mol^{-1}, respectively, and are due mainly to deacetylation and debenzoylation. The activation energies for the benzoate and tritylate of cellulose acetate, and acetate and tritylate of cellulose benzoate fall to 73, 86, 86 and 84 kJ mol^{-1}, respectively, from the value of 131 kJ mol^{-1} for pure cellulose.

TABLE 2

Activation energies and frequency factors for the first stage of thermal degradation of cellulose and its C-2, C-3 and C-6 substituted derivatives in air (Broido method)

Sample No.	Compound	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})	Mass loss (%)
(i)	Cellulose	250–305	130.9	3.73×10^8	5.7
(ii)	Cellulose acetate	270–320	108.3	1.35×10^6	5.0
(iii)	Cellulose benzoate	260–305	163.3	3.90×10^{11}	6.8
(iv)	Benzoate of cellulose acetate	280–320	73.0	3.23×10^2	2.5
(v)	Tritylate of cellulose acetate	245–300	86.1	1.77×10^4	4.3
(vi)	Acetate of cellulose benzoate	280–330	86.2	1.99×10^4	6.9
(vii)	Tritylate of cellulose benzoate	230–280	83.5	1.10×10^4	3.2

TABLE 3

Activation energies and frequency factors for the second (decomposition) stage of thermal degradation of cellulose and its C-2, C-3 and C-6 substituted derivatives in air (Broido method)

Sample No.	Compound	DTG maxima (°C)	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})	Mass loss (%)
(i)	Cellulose	334	305–355	252.9	6.54×10^{19}	78.6
(ii)	Cellulose acetate	355	320–375	237.2	5.61×10^{17}	74.5
(iii)	Cellulose benzoate	360	305–385	136.1	1.18×10^{9}	74.1
(iv)	Benzoate of cellulose acetate	370	320–385	220.3	6.27×10^{15}	75.0
(v)	Tritylate of cellulose acetate	353	300–370	154.7	6.27×10^{10}	70.6
(vi)	Acetate of cellulose benzoate	364	330–385	224.8	2.79×10^{16}	66.5
(vii)	Tritylate of cellulose benzoate	349	280–370	135.5	1.52×10^{9}	75.4

The activation energies for the second stage of thermal degradation of C-2, C-3 and C-6 substituted cellulose samples (ii) to (vii) are 237, 136, 220, 155, 225 and 136 kJ mol^{-1}, respectively. These activation energies are mainly due to oxidative decomposition of the compounds and are much lower than the value for cellulose (253 kJ mol^{-1}). On comparing the activation energies of benzoate and tritylate of cellulose acetate with the parent compound, cellulose acetate, it is observed that the value of the

TABLE 4

Activation energies and frequency factors for the third stage of thermal degradation of cellulose and its C-2, C-3 and C-6 substituted derivatives in air (Broido method)

Sample No.	Compound	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})	Mass loss (%)
(i)	Cellulose	355–430	30.8	1.75	4.3
(ii)	Cellulose acetate	375–415	66.8	2.39×10^{3}	4.0
(iii)	Cellulose benzoate	385–440	37.0	3.66×10^{1}	4.2
(iv)	Benzoate of cellulose acetate	385–440	46.0	2.67×10^{1}	6.2
(v)	Tritylate of cellulose acetate	370–415	53.1	1.36×10^{2}	7.3
(vi)	Acetate of cellulose benzoate	385–440	47.1	3.47×10^{1}	6.8
(vii)	Tritylate of cellulose benzoate	370–440	37.8	5.83	6.4

activation energy for benzoate of cellulose acetate falls to 220 kJ mol^{-1}, while for tritylate of cellulose acetate the value falls to 155 kJ mol^{-1} from 237 kJ mol^{-1} for cellulose acetate. It appears that the introduction of aromatic functional groups into cellulose acetate decreases the activation energy and the greater the substitution of phenyl groups in cellulose acetate matrix, the greater is the decrease in activation energy. On the other hand, if an acetyl group is introduced into cellulose benzoate (sample vi), the activation energy increases considerably to 225 kJ mol^{-1} from the value of 136 kJ mol^{-1} for cellulose benzoate. Also the decomposition temperature range (330–385 °C) for the former is higher than that of the latter (305–385 °C) showing that the acetyl group in cellulose benzoate decreases its flame retardancy. This is supported by the fact that mass loss for the second stage of thermal degradation in acetate of cellulose benzoate (66.5%) is much lower than that of cellulose benzoate (74.1%).

After the decomposition stage, the charred residues of cellulose and its C-2, C-3 and C-6 substituted derivatives are oxidized in air in the temperature range 355–440 °C. The activation energies and frequency factors for the third stage of thermal degradation are presented in Table 4. The activation energies and the mass losses are in the range 31–67 kJ mol^{-1} and 4.0–7.3%, respectively.

In order to study the nature of thermal degraded products of cellulose and its derivatives, these were heated in the temperature range 250–400 °C in air and the IR spectra [7] of the residual products obtained at different temperatures were recorded. The changes in the IR spectra of chars of untreated and treated cellulose are as follows. At low temperatures (250–325 °C), where an initial mass loss occurs in TG, the decrease of the intensity of the hydroxyl stretching vibration bands (3450, 3350 and 3305 cm^{-1}) and the bands at 3040 (=C–H str.), 2940 (–C–H str.), 1720 (C=O str.) and 1110 cm^{-1} (C–O–C str.) indicate that the dehydration, deacetylation, debenzoylation and detritylation processes take place during the initial stage of thermal degradation of cellulose and its C-2, C-3 and C-6 substituted derivatives. At elevated temperatures, the intensities of all the normal bands in the fingerprint region (1500–800 cm^{-1}) due to cellulose and modified celluloses decrease and the bands at 1720 (C=O) and 1630 cm^{-1} (C=C) become intense, indicating that skeletal rearrangement and the evolution of volatile products commence at elevated temperatures. At still higher temperature (400 °C), the bands due to cellulose and treated cellulose almost disappear and the absorption bands at 1720 (C=O) and near 1000 cm^{-1} (C=C) become intense and the absorption band at 1630 cm^{-1} shifts to 1600 cm^{-1} (due to conjugated C=C) suggesting the extension of conjugation of the C=C bonds in the residues from cellulose and its substituted derivatives, and the formation of compounds containing C=O groups.

EPR spectra of chars of pure cellulose and C-2, C-3 and C-6 substituted cellulose samples (i) to (vii) were obtained in air medium at 300 °C and are

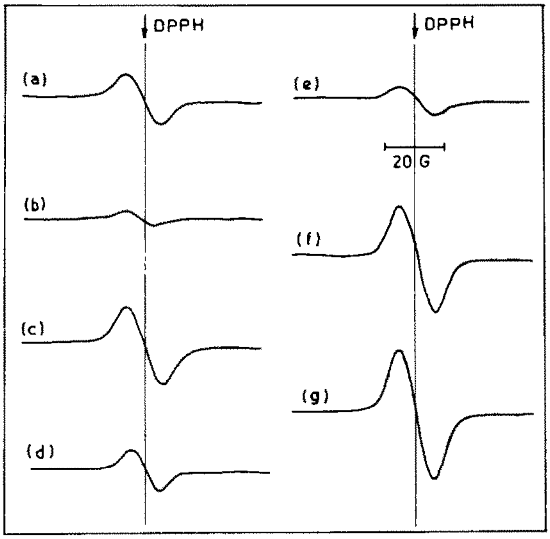

Fig. 11. EPR spectra of chars of (a) cellulose, (b) cellulose acetate, (c) cellulose benzoate, (d) benzoate of cellulose acetate, (e) tritylate of cellulose acetate, (f) acetate of cellulose benzoate and (g) tritylate of cellulose benzoate at 300 ° C.

shown in Fig. 11. The relative intensities of the EPR spectral lines were computed by measuring the peak-to-peak derivative amplitude and peak-to-peak width of the derivative spectral line using the method described by Wertz and Bolton [8]. The relative intensities thus calculated by this procedure and hence the relative concentrations of the free radicals [9] of the chars of cellulose, cellulose acetate, cellulose benzoate, benzoate of cellulose acetate, tritylate of cellulose acetate, acetate of cellulose benzoate and tritylate of cellulose benzoate are found to be in the ratio of 1.0 : 0.2 : 1.6 : 0.5 : 0.6 : 2.1 : 2.5, respectively. It is obvious that there is formation of trapped free radicals during the decomposition of cellulose and its derivatives. For cellulose benzoate and its subsequent substituted derivatives viz. acetate of cellulose benzoate and tritylate of cellulose benzoate, a higher concentration of free radicals in comparison to cellulose has been observed. This may be due to the presence of aromatic benzoyl group in cellulose benzoate and its subsequent derivatives. Further, the formation of free radicals is generally associated with char formation during decomposition of a compound. As the number of free radicals formed is small for cellulose acetate, benzoate of cellulose acetate and tritylate of cellulose acetate, little char production [10] for these compounds should be expected. However, contrary to our expectation, char yields for these compounds are higher than that of cellulose (Table 1). This shows that free radical mechanism is not dominant in the degradation of these compounds. These compounds decompose to acid fragments which catalyse oxidative decomposition to produce water and char. The detailed mechanism of acid-catalysed thermal degradation of cellulose esters has been discussed in detail elsewhere [3].

ACKNOWLEDGEMENT

This research has been financed in part by a grant made by the United States Department of Agriculture, authorized by Public Law 480.

REFERENCES

1 A. Scotney, Eur. Polym. J., 8 (1972) 163.
2 W.P. Brown and C.F.H. Tipper, J. Appl. Polym. Sci., 22 (1978) 1459.
3 R.K. Jain, K. Lal and H.L. Bhatnagar, J. Anal. Appl. Pyrol., 8 (1985) 359.
4 A. Broido, J. Polym. Sci., Part A-2, 7 (1969) 1761.
5 T. Murakami and E. Ishii, Bunseki Kagaku, 12 (1963) 657.
6 R.L. Whistler and M.L. Wolfrom (Eds.), Methods in Carbohydrate Chemistry, Vol. 1, Academic Press, New York, 1962, p. 472.
7 R.K. Jain, K. Lal and H.L. Bhatnagar, Makromol. Chem., 183 (1982) 3003.
8 J.E. Wertz and J.R. Bolton, Electron Spin Resonance, McGraw-Hill, New York, 1971, p. 32.
9 N.-S. Hon, J. Polym. Sci., Polym. Chem. Ed., 13 (1975) 1933.
10 R.K. Jain, K. Lal and H.L. Bhatnagar, J. Appl. Polym. Sci., 33 (1987) 247.