

THERMAL STUDIES ON C-6 SUBSTITUTED CELLULOSE AND ITS SUBSEQUENT PHOSPHORYLATED PRODUCTS IN AIR

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ABSTRACT

The thermal behaviour of cellulose and its primary and, subsequently, secondary substituted derivatives, namely, cellulose tosylate, cellulose tritylate and phosphate, of these compounds in air was studied by differential thermal analysis and dynamic thermogravimetry from ambient temperature to 800°C. The various reactions involved, namely, dehydration, detosylation, detritylation, dephosphorylation, dehydrohalogenation, oxidative decomposition and oxidation of charred residue, have been discussed. The data obtained from TG were utilized to obtain various thermodynamic parameters of different stages of thermal degradation using the method of Broido. The values of activation energies for the oxidative decomposition of cellulose, cellulose tosylate, tritylate, phosphate, phosphate of cellulose tosylate and phosphate of cellulose tritylate were determined and are 238, 177, 109, 103, 204 and 134 kJ mol⁻¹, respectively. A new band at 900 cm⁻¹ in the IR spectra of secondary substituted phosphoryl derivatives indicates the formation of a polypyrophosphate compound which forms a glassy surface over burning cellulose, thus hindering the diffusion of volatile products. As a result, the large char yields obtained in the case of secondary substituted phosphoryl derivatives show that these compounds are effective flame retardants.

INTRODUCTION

The reaction of cellulose with various reagents is influenced by the size of the molecular chain and also by the difference in the reactivities and the availability of various hydroxyl groups at C-2, C-3 and C-6 of each repeating unit of cellulose. A few of the reagents, namely, tosyl chloride and trityl chloride, are known to react preferentially with primary hydroxyl group of cellulose [1–4]. It has been demonstrated that the phosphorylation of cellulose generally takes place at the primary hydroxyl group [5]. In a previous communication [6], it was shown that the phosphorus esters of cellulose had good flame retardant properties and that phosphorus oxychloride was a good phosphorylating agent, since the product formed reduces the amount of flammable volatile products produced on thermal degradation accompanied by an increased char yield. Although a lot of work has been reported in the literature towards obtaining an understanding of the thermal behaviour of

the primary substituted phosphorylated celluloses [5,7], little attention has been paid to their mode of action involving phosphorylation of cellulose at secondary (C-2 and C-3) hydroxyl groups. In the present study, reagents like tosyl chloride and trityl chloride, for the selective blocking of the primary hydroxyl group of cellulose, have been used to prepare primary substituted cellulose products. These products have subsequently been treated with phosphorus oxychloride to obtain secondary substituted phosphorylated products. The various primary and secondary substituted products of cellulose have been subjected to thermal degradation from ambient temperature to 800°C using DTA, TG and DTG techniques. Kinetic parameters for the thermal degradation of primary and secondary substituted cellulose derivatives have been obtained by adopting the method of Broido [8]. The composition of the charred products has been studied by IR spectra of chars obtained at different temperatures.

EXPERIMENTAL

The following samples of cellulose, cellulose tosylate, cellulose tritylate and its phosphorylated products were selected for the present work: sample (i), cellulose (from Schleicher and Scüll, Dassel, W. Germany), dried to a constant weight in vacuo at 60°C; sample (ii), cellulose tosylate was obtained by treating cellulose with *p*-toluene sulphonyl chloride (tosyl chloride) in pyridine at 25°C for 192 h, precipitating and purifying by the method of Heuser et al. [9]; sample (iii), cellulose tritylate was obtained [10] by treating cellulose with triphenylchloromethane (trityl chloride) in pyridine at 95°C for 16 h, purifying by Soxhlet extractor in methanol followed by ether and drying in vacuo over P₂O₅; sample (iv), cellulose phosphate was obtained [11] by treating cellulose with phosphorus oxychloride in pyridine at 60°C for 6 h and drying over P₂O₅ in vacuo at 60°C; sample (v), the phosphate of cellulose tosylate was obtained by treating cellulose tosylate with phosphorus oxychloride in pyridine at 30°C for 24 h and purifying by the method adopted for sample (iv); and sample (vi), the phosphate of cellulose tritylate was obtained by treating cellulose tritylate with phosphorus oxychloride in pyridine at 60°C for 6 h and purifying by the procedure used for sample (iv). The trityl content and the degree of substitution (DS) were determined by converting samples (iii) and (vi) into trityl carbinol with concentrated sulphuric acid [12]. The DS of both cellulose tritylate and phosphate of cellulose tritylate are 1.01. The percentages of P, S and Cl for different samples were determined [13,14] and are as follows: cellulose tosylate: S, 10.43% (DS 1.06); cellulose phosphate: P, 8.03; Cl, 2.42%; phosphate of cellulose tosylate: S, 8.34; P, 6.58; Cl, 3.20%; and phosphate of cellulose tritylate; P, 3.81; Cl, 1.19%.

Thermal analysis

The differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) thermograms were obtained using a MOM derivatograph (Paulik–Paulik–Erdey, Budapest). The DTA and TG curves were run under a dynamic air (dried) atmosphere flowing at 100 ml min⁻¹ and at a scanning rate of 10°C min⁻¹. The DTA measurements were related to calcined alumina.

Infrared spectroscopy

For the IR studies (Beckman spectrophotometer IR-20), the charred samples of cellulose and its primary and secondary substituted derivatives were prepared by the KBr technique using 2% char. The charred samples were prepared by heating them in the DTA cell in an air (dried) atmosphere. Heating was stopped at the desired temperature and the residues were allowed to cool and quickly transferred to a stoppered sample container.

RESULTS AND DISCUSSION

At the very outset, it may be mentioned that for cellulose tosylate (DS 1.06) and cellulose tritylate (DS 1.01), the tosyl and trityl groups show a preference for primary hydroxyls; these reactions have been shown to be 10–14 times as fast with primary as compared with the average of secondary hydroxyl groups of cellulose [2,3].

The associated DTA, TG and DTG curves of (i) cellulose, (ii) cellulose tosylate, (iii) cellulose tritylate, (iv) cellulose phosphate, (v) phosphate of cellulose tosylate and (vi) phosphate of cellulose tritylate were carried out in air atmosphere from ambient temperature to 800°C and are shown in Figs. 1–6, respectively. The peak temperatures for various endotherms and exotherms were measured and are given in Table 1. An endotherm below 100°C in all compounds is due to the evaporation of moisture. The DTA thermogram of cellulose tosylate shows a large exotherm, with a peak at 175°C, in the range 130–210°C. This may be due to the oxidative decomposition of cellulose tosylate accompanied by the scission of the tosyl group. The scission of the tosyl group from cellulose tosylate should give an endotherm; but this probably merges with the large exotherm due to the simultaneous decomposition of the compound. This indicates that in this temperature range detosylation and simultaneous decomposition, due to the catalytic effect of the released acid, take place. This is supported by a large mass loss of about 19% as shown by the TG curve (Fig. 2). The next exotherm at 285°C for this compound (DS 1.06) is due to oxidative decomposition of the residual unsubstituted anhydroglucose unit of cellulose. The

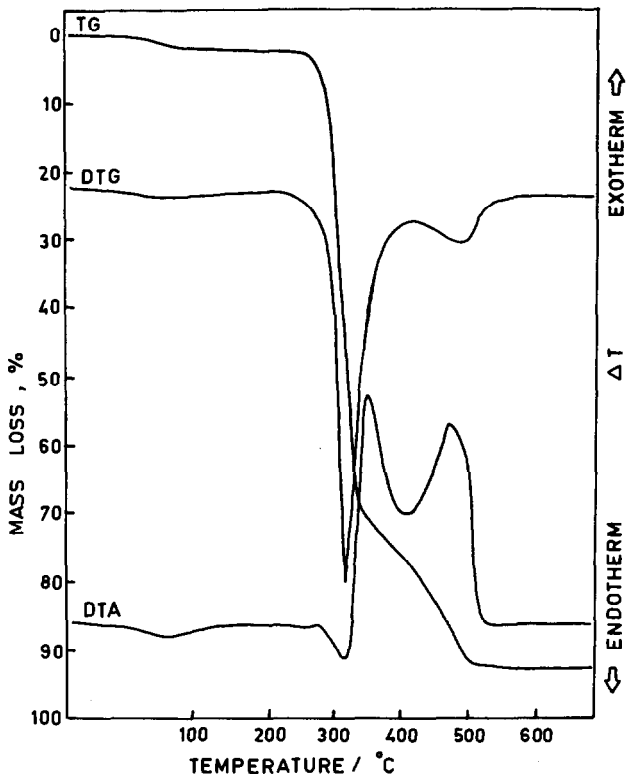


Fig. 1. Thermal analysis of cellulose in air.

last large exotherm at 526°C is due to the oxidation of the charred residue.

For cellulose tritylate, the small endotherm in the temperature range 148–190°C with a peak at 157°C is visualized as resulting from the scission of trityl C-O bearing the trityl ether moiety. The TG curve shows only a mass loss of 1.5% in this temperature range. The low degradation rate may be attributed, in part, to the presence of a tertiary carbon atom in the substituent group which results in the stability of the cellulose derivative. The large exotherm in the temperature range 210–292°C with a maximum at 274°C is due to the oxidative decomposition of the compound. The TG curve (Fig. 3) also shows that the rapid mass loss of this compound takes place in this temperature range and that ~41% mass disappears during this process. The next large exotherm, beginning at 292°C and terminating at 430°C, appears with a maximum at 334°C. This may be visualized as resulting from the decomposition of the residual unsubstituted portions of the cellulose and also due to loss of triphenylmethane. The last large exotherm at 542°C is associated with the oxidation of charred residue.

In the case of cellulose phosphate (containing P, 8.03; Cl, 2.42%), a small endotherm is observed at 160°C. It is suggested that for this compound the initial reactions are due to dephosphorylation and dehydrohalogenation and

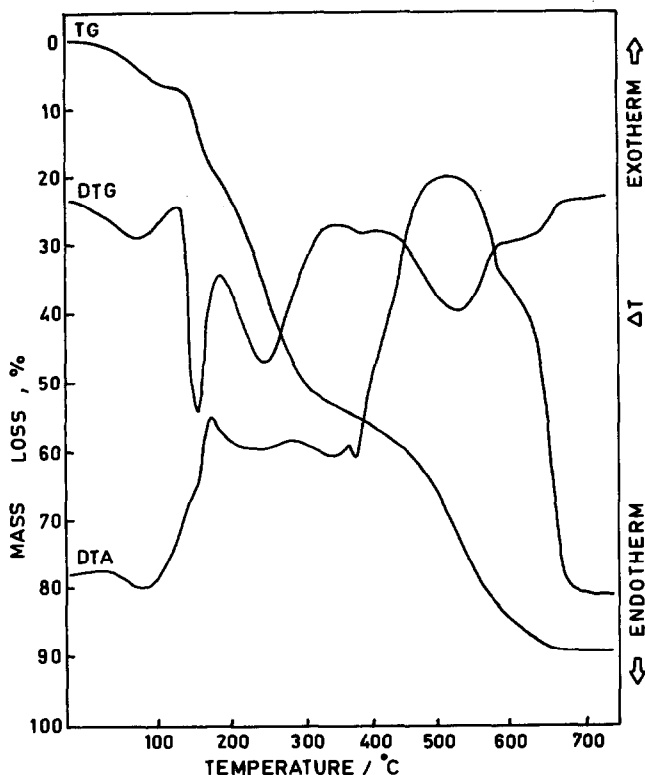


Fig. 2. Thermal analysis of cellulose tosylate in air.

that the acids released then catalyze the decomposition of the cellulose products. The TG curve shows a mass loss of $\sim 9\%$ in the temperature range $120\text{--}182^\circ\text{C}$. The next large exotherm at 290°C may be associated with the oxidative decomposition of the products. The large mass loss of 34% in TG supports this observation. The last exotherm in the temperature range $390\text{--}715^\circ\text{C}$, as usual, is due to the oxidation of the charred residue.

The DTA thermograms of cellulose phosphate, cellulose tosylate and phosphate of cellulose tosylate show an interesting behaviour. The exotherm at 290°C for cellulose phosphate is shifted to a lower temperature, i.e., 220°C for the secondary substituted phosphate of cellulose tosylate. This indicates that both the tosyl group in the primary position and the phosphoryl group in the secondary position of cellulose catalyze the decomposition of the cellulose products. The next two small exotherms in the temperature ranges $240\text{--}317$ and $317\text{--}360^\circ\text{C}$ may be explained as for cellulose tosylate.

For the secondary substituted phosphate of cellulose tritylate, cellulose phosphate and cellulose tritylate, an endotherm below 160°C is due to dephosphorylation, dehydrohalogenation and detriylation, while the subsequent exotherms observed at 243 ($180\text{--}262^\circ\text{C}$), 290 ($182\text{--}390^\circ\text{C}$) and 274°C ($210\text{--}292^\circ\text{C}$) for the three compounds, respectively, are due to oxidative

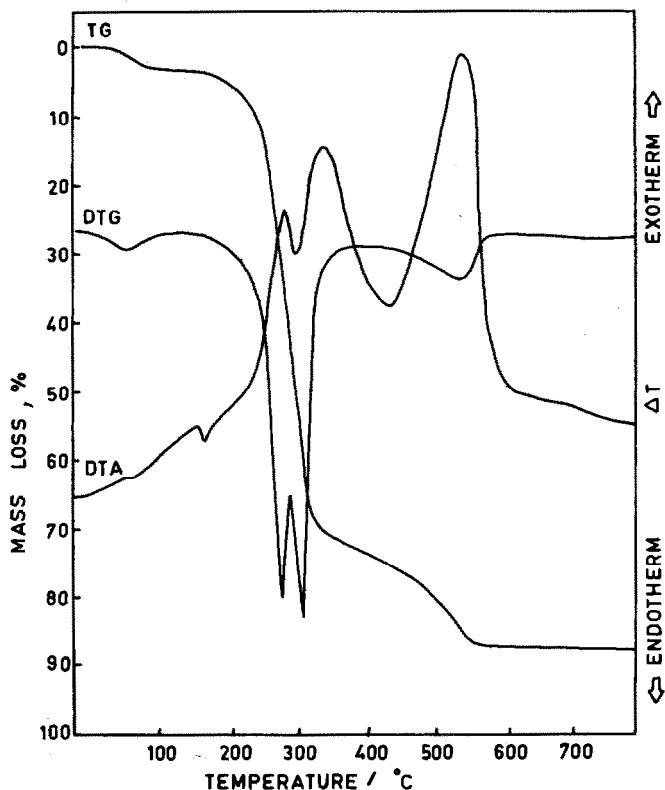


Fig. 3. Thermal analysis of cellulose tritylate in air.

decomposition of the products catalyzed by the acids released. It can be seen that phosphorylation in the secondary position of the cellulose enhances the thermal degradation and lowers the decomposition temperature as compared to the primary substituted phosphate of cellulose. The exotherm at 365°C for the phosphate of cellulose tritylate is due to the loss of the trityl group and decomposition of the residual products.

The mass versus temperature curves for cellulose and its primary and secondary substituted derivatives are shown in Figs. 1–6. In some cases, the initial but small mass loss due to adsorbed moisture was neglected. The kinetic parameters for various stages of thermal degradation were determined using the method described by Broido [8]. The equation involved in the Broido method can be written as

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

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

Using the Broido method, plots of $\ln[\ln(1/y)]$ versus $1/T$ for various stages of thermal degradation are given in Figs. 7–9. The values of the

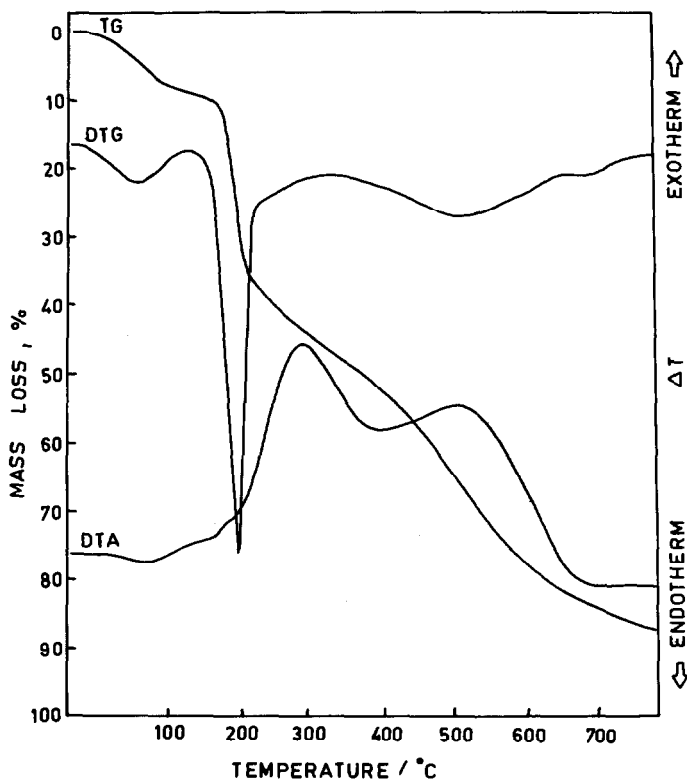


Fig. 4. Thermal analysis of cellulose phosphate in air.

activation energies, E_a , and the frequency factor, Z , determined from the slopes and intercepts of these plots, respectively, are given in Tables 2–4. These parameters have been evaluated using the method of least squares.

From Table 2 it is observed that for the first stage of thermal degradation of cellulose, mainly due to dehydration, the activation energy is 172 kJ mol^{-1} ; which for cellulose tritylate, cellulose phosphate and phosphate of cellulose tritylate reduce to 61, 61 and 32 kJ mol^{-1} , respectively. This is mainly due to detritylation, dephosphorylation and dehydrohalogenation of these compounds. In the case of cellulose tosylate and phosphate of cellulose tosylate, the lowering of the decomposition temperature is so great that the detosylation and decomposition of the cellulose derivatives occur simultaneously. This may be due to the release of *p*-toluene sulphonic acid, a strong dehydrating agent, which catalyzes the decomposition of these compounds. The activation energies, mainly due to the oxidative decomposition (second stage) of cellulose tosylate and phosphate of cellulose tosylate, reduce to 177 and 204 kJ mol^{-1} , respectively, compared to 238 kJ mol^{-1} for cellulose (Table 3). The higher activation energy for the secondary substituted phosphate of cellulose tosylate may be due to its higher temperature range of decomposition as compared to cellulose tosylate. The activation energy for

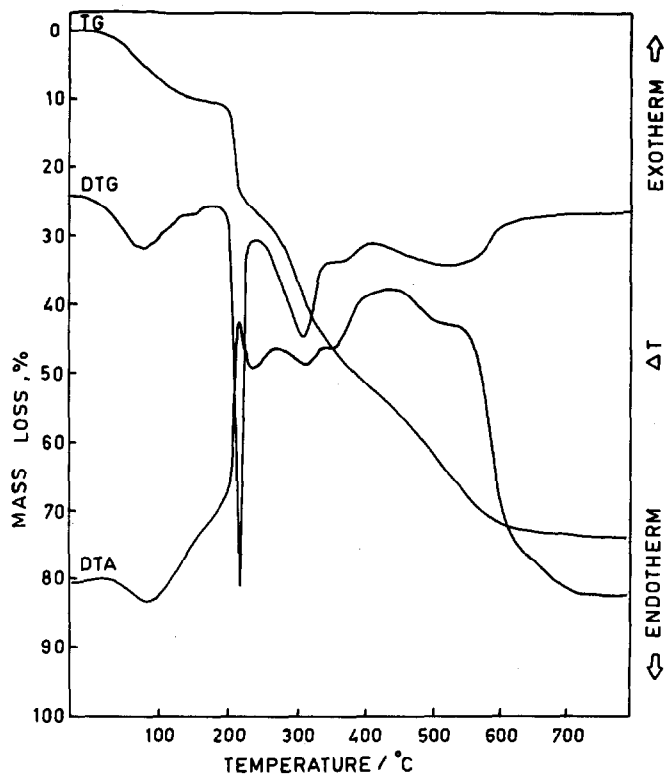


Fig. 5. Thermal analysis of phosphate of cellulose tosylate in air.

decomposition of preferentially primary substituted phosphate of cellulose (sample iv) is 103 kJ mol^{-1} . The considerable decrease in the activation energy of cellulose phosphate as compared to cellulose shows that the primary substituted phosphoryl group changes the mechanism of thermal degradation in such a way as to reduce the decomposition temperature of cellulose, thus diminishing the formation of levoglucosan due to blocking of primary hydroxyl group by the phosphoryl group.

For cellulose phosphate, cellulose tritylate and phosphate of cellulose tritylate, the activation energies for the decomposition stage are 103, 109 and 134 kJ mol^{-1} , respectively. These values are considerably lower than those of cellulose. However, the activation energy for the phosphate of cellulose tritylate has increased to 134 from 109 kJ mol^{-1} for cellulose tritylate, which may be due to the introduction of a phosphoryl group on the secondary position of cellulose tritylate. After decomposition, the residual material of cellulose derivatives is found to degrade further in air; their activation energies (Table 3) are comparatively low ($22\text{--}97 \text{ kJ mol}^{-1}$).

High temperature exotherms ($> 380^\circ\text{C}$) in an air atmosphere for cellulose and its primary and secondary substituted derivatives are due to the oxida-

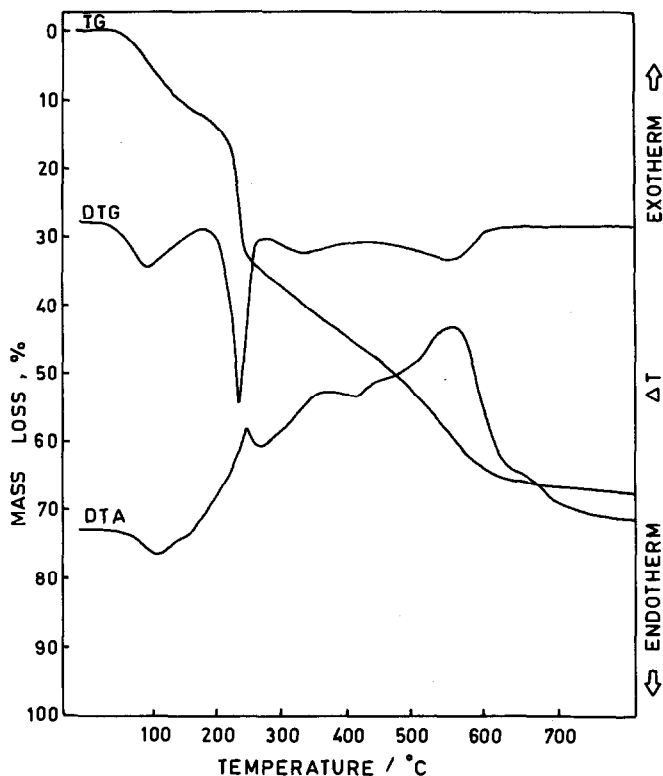


Fig. 6. Thermal analysis of the phosphate of cellulose tritylate in air.

tion of char residues. Activation energies and frequency factors for this stage are presented in Table 4.

The values of the activation entropies, ΔS^* , and the free energies of activation, ΔG^* , at 500 K for the oxidative decomposition of cellulose and its derivatives were also calculated as described elsewhere [15] and are given in Table 5. The activation entropy is positive for cellulose and it decreases for cellulose derivatives. A considerable lowering in activation entropy is found in the case of cellulose tritylate, cellulose phosphate and phosphate of cellulose tritylate. However, this decrease is somewhat compensated by the activation enthalpy. The free energies of activation for these compounds are in the range 144–157 kJ mol⁻¹. These values are quite different from the corresponding value for cellulose, thereby showing that a different mechanism of oxidative decomposition operates for cellulose derivatives.

It is generally observed that the amount of char formed during thermal degradation of cellulose treated with a particular flame retardant is related to the degree of flame resistance exhibited by the treated cellulose sample. In order to gain insight into the flame retardant properties of these compounds, the char yields (in mass%) were determined at 975 K from TG curves and are given in Table 5. It is evident from the char yields of cellulose tosylate,

TABLE 1

Peak temperatures in the DTA thermograms for cellulose and its primary and secondary substituted derivatives in air

Sample No.	Compound	DTA curve			Nature of the DTA peak
		Initiation temp. (°C)	Peak temp. (°C)	Termination temp. (°C)	
(i)	Cellulose	—	75	—	Endo (large)
		260	274	280	Exo (small)
		280	314	325	Endo (large)
		325	350	405	Exo (large)
		405	468	520	Exo (large)
(ii)	Cellulose tosylate	—	80	—	Endo (small)
		130	175	210	Exo (large)
		240	285	341	Exo (small)
		341	362	373	Exo (small)
		373	526	700	Exo (large)
(iii)	Cellulose tritylate	—	65	—	Endo (small)
		148	157	190	Endo (small)
		210	274	292	Exo (large)
		292	334	430	Exo (large)
		430	542	670	Exo (large)
(iv)	Cellulose phosphate	—	77	—	Endo (small)
		120	160	182	Endo (small)
		182	290	390	Exo (large)
		390	508	715	Exo (large)
(v)	Phosphate of cellulose tosylate	—	87	—	Endo (small)
		180	220	240	Exo (large)
		240	276	317	Exo (small)
		317	338	360	Exo (small)
		360	470	720	Exo (large)
(vi)	Phosphate of cellulose tritylate	—	98	—	Endo (small)
		138	155	170	Endo (small)
		180	243	262	Exo (large)
		262	365	415	Exo (large)
		440	560	645	Exo (large)

tritylate and phosphate that these compounds give higher char yields (12.4–16.3%) as compared to cellulose (7.8%), indicating their flame retarding properties. Further, cellulose tosylate and tritylate, when substituted in the secondary position by a phosphoryl group show much higher char yields (28.9–33.2%), thus diminishing the formation of flammable volatile products. Although the secondary substituted phosphate compounds show higher DTG maxima than the preferentially primary substituted phosphate of

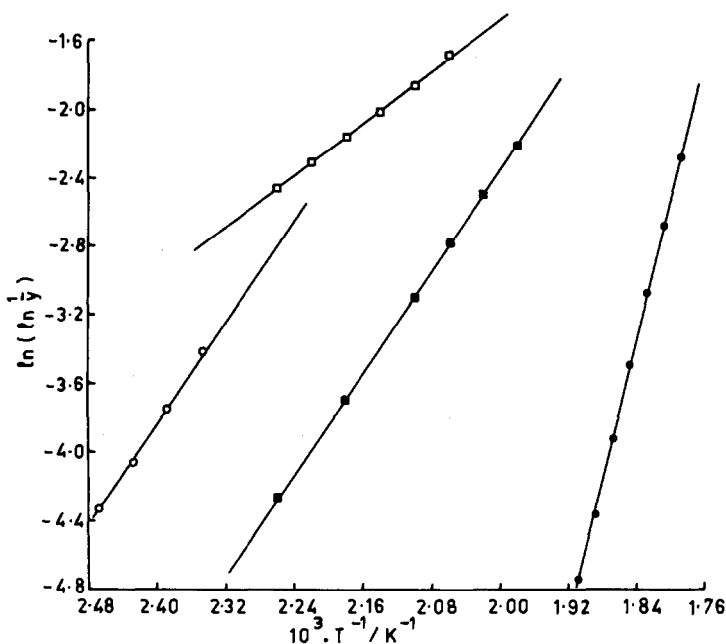


Fig. 7. Plots of $\ln[\ln(1/y)]$ vs. $10^3 T^{-1}$ (K^{-1}) using the Broido equation for cellulose (●), cellulose tritylate (■), cellulose phosphate (○) and phosphate of cellulose tritylate (□) in air for the first stage of thermal degradation.

cellulose (Table 3), the former show a much higher char yield as compared to the latter. This may be attributed to the presence of a phosphoryl group in the secondary position which, probably, changes the decomposition mechanism, making for a more effective flame retardant.

The secondary phosphoryl groups of cellulose not only affect the decomposition temperature and char yields but also the composition of the final chars. These last effects have been studied by the IR spectra of chars prepared at different temperatures (150–400°C). The changes in the IR spectra of chars of untreated and treated cellulose are as follows. At low temperature (150–250°C), where an initial mass loss was observed in TG, the decrease in 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), 1370, 1200, 1180 (C–SO₂–O–C str), 1110 (C–O–C str) and 1250 cm^{-1} (P=O str) show that dehydration and elimination of acid take place during the initial thermal degradation reaction of cellulose and its primary and secondary substituted derivatives. On heating near the intermediate temperatures of the second (decomposition) stage of thermal degradation, a new absorption band appears at 1720 cm^{-1} (C=O str) and the band due to cellulose chains becomes weak. At still higher temperature (400°C), Fig. 10 shows that the bands due to untreated and treated cellulose almost disappear, the absorption band at 1720 (C=O str), 1000 (C=C) and 1250 cm^{-1} (P=O str, for primary and secondary substituted phosphate of cellulose)

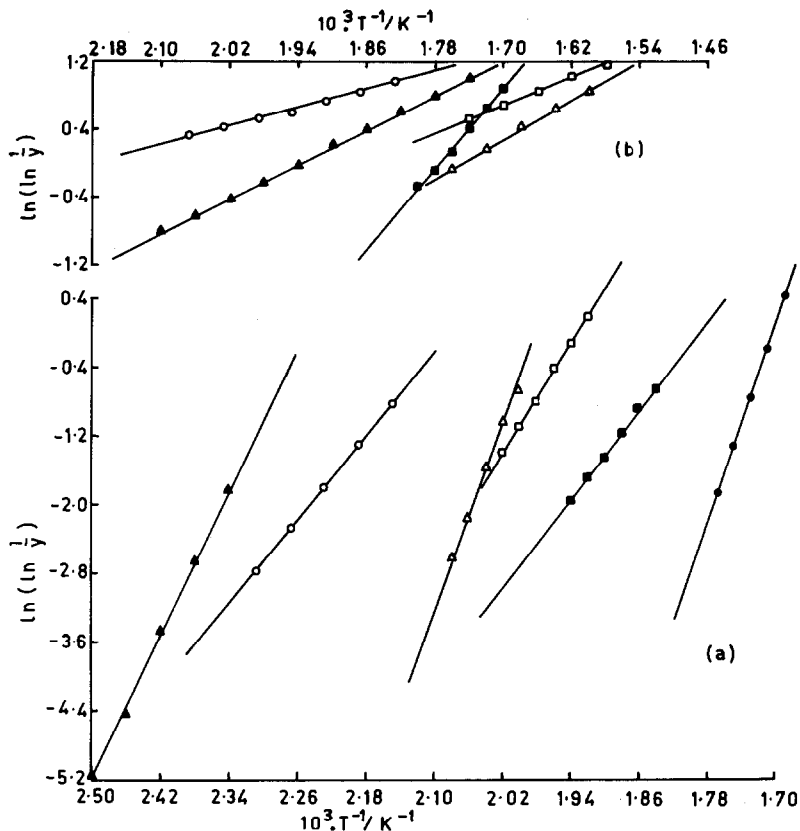


Fig. 8. Plots of $\ln[\ln(1/\gamma)]$ vs. $10^3 T^{-1}$ (K^{-1}) using the Broido equation for cellulose (●), cellulose tosylate (▲), cellulose tritylate (■), cellulose phosphate (○), phosphate of cellulose tosylate (Δ) and phosphate of cellulose tritylate (□) in air for the second stage of thermal degradation: (a) low temperature range; (b) high temperature range.

TABLE 2

Activation energies and frequency factors for first stage of thermal degradation of cellulose and its primary and secondary substituted derivatives in air (Broido method)

Sample No.	Compound	Temperature range ($^{\circ}C$)	E_a ($kJ\ mol^{-1}$)	Z (s^{-1})
(i)	Cellulose	240–285	172.1	1.36×10^{13}
(ii)	Cellulose tosylate	—	—	—
(iii)	Cellulose tritylate	160–235	61.1	1.10×10^3
(iv)	Cellulose phosphate	130–160	60.6	5.64×10^3
(v)	Phosphate of cellulose tosylate	—	—	—
(vi)	Phosphate of cellulose tritylate	160–215	32.0	1.36

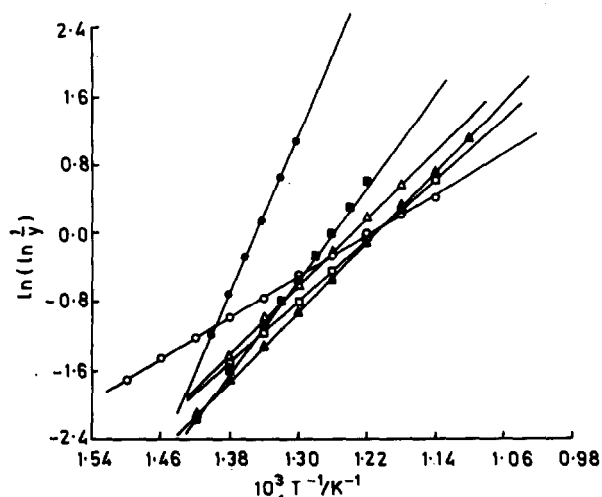


Fig. 9. Plots of $\ln[\ln(1/y)]$ vs. $10^3 T^{-1}$ (K^{-1}) using the Broido equation for cellulose (●), cellulose tosylate (▲), cellulose tritylate (■), cellulose phosphate (○), phosphate of cellulose tosylate (△) and phosphate of cellulose tritylate (□) in air for the third stage of thermal degradation.

become intense and the absorption band at 1640 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 derivatives and the

TABLE 3

Activation energies and frequency factors for the second (decomposition) stage of thermal degradation of cellulose and its primary and secondary substituted derivatives in air (Broido method)

Sample No.	Compound	DTG maxima (°C)	Temperature range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})
(i)	Cellulose	321	285–335	238.4	2.18×10^{19}
(ii)	Cellulose tosylate	155	125–180	176.5	1.16×10^{19}
		245	180–310	41.7	5.09×10^1
(iii)	Cellulose tritylate	272	235–280	109.3	1.25×10^8
		303	280–330	96.9	5.60×10^6
(iv)	Cellulose phosphate	194	160–205	102.6	1.37×10^9
		–	205–300	21.9	4.98×10^{-1}
(v)	Phosphate of cellulose tosylate	219	190–240	203.7	1.71×10^{19}
		312	240–360	47.2	5.62×10^1
(vi)	Phosphate of cellulose tritylate	237	215–265	134.2	3.61×10^{11}
		326	265–360	35.2	5.22

TABLE 4

Activation energies and frequency factors for the third stage of thermal degradation of cellulose and its primary and secondary substituted derivatives in air (Broido method)

Sample No.	Compound	DTG maxima (°C)	Temperature range (°C)	E_a (kJ mol ⁻¹)	Z (s ⁻¹)
(i)	Cellulose	482	425–500	187.1	1.03×10^{11}
(ii)	Cellulose tosylate	538	425–640	84.6	5.67×10^2
(iii)	Cellulose tritylate	538	430–560	116.5	1.67×10^5
(iv)	Cellulose phosphate	505	380–620	50.1	2.51
(v)	Phosphate of cellulose tosylate	524	425–580	82.6	5.62×10^2
(vi)	Phosphate of cellulose tritylate	560	430–610	74.2	1.07×10^2

formation of compounds containing C=O and P=O groups. Further, at this temperature, the secondary substituted cellulose phosphate shows a new adsorption band at 900 cm⁻¹ (due to pyrophosphate P–O–P linkage) indicating the formation of a pyrophosphate compound in the final mass

TABLE 5

Entropies and free energies of activation for the second (decomposition) stage of thermal degradation of cellulose and its primary and secondary substituted derivatives in air

Sample No.	Compound	ΔS^* (J K ⁻¹ mol ⁻¹) at 500 K	ΔG^* (kJ mol ⁻¹) at 500 K	Char yield at 975 K (mass%)
(i)	Cellulose	112.7	177.9	7.8
(ii)	Cellulose tosylate	107.5 –224.8	118.6 149.9	12.4
(iii)	Cellulose tritylate	–102.5 –128.3	156.4 157.0	12.5
(iv)	Cellulose phosphate	–82.6 –263.3	139.8 149.6	16.3
(v)	Phosphate of cellulose tosylate	110.7 –224.0	144.2 155.0	28.9
(vi)	Phosphate of cellulose tritylate	–36.3 –243.8	148.2 152.9	33.2

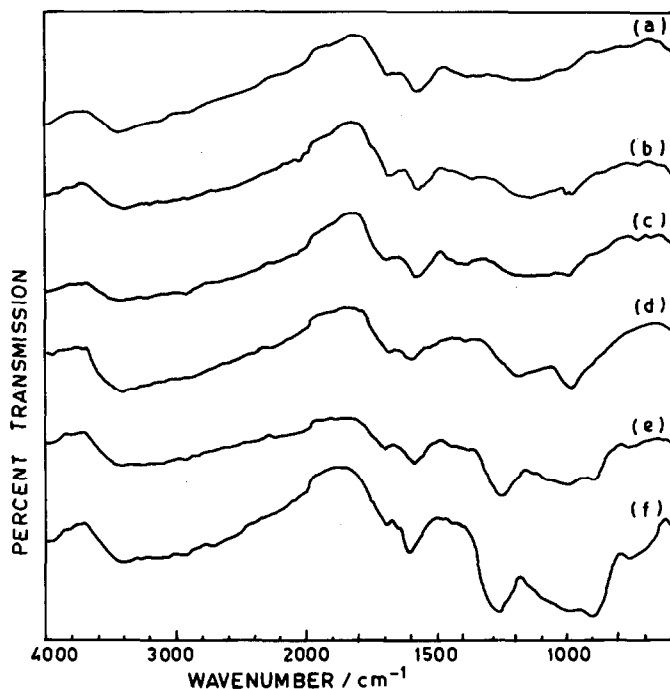


Fig. 10. IR spectra of chars of (a) cellulose, (b) cellulose tosylate, (c) cellulose tritylate, (d) cellulose phosphate, (e) phosphate of cellulose tosylate and (f) phosphate of cellulose tritylate at 400°C.

loss region of the phosphates of cellulose tosylate and cellulose tritylate. It is suggested that at high temperature the phosphoric acid, released during the first stage of thermal degradation of cellulose containing phosphoryl groups in the secondary positions, polymerizes into polymetaphosphoric acid which forms a glassy layer on the surface of burning cellulosic derivatives. This layer hinders diffusion of the volatile products to the flame and oxygen to the cellulosic residue. Thus, the char layer on the surface of the remaining residue plays the role of a heat insulator and also prevents liberation of the volatile degradation products into the gas phase. This results in a considerable increase in char yield for secondary substituted phosphoryl groups of cellulose tosylate and tritylate.

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