Thermal and spectral studies on cellulose modified with various cresyldichlorothiophosphates

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Abstract

Various cresyldichlorothiophosphates have been synthesized and applied as flame-retardant formulations on cellulose. Thiophosphorylated cellulose samples have been investigated by DTA and TG techniques from ambient temperature to 600°C in a static air atmosphere. On the DTA trace of each sample, three or four peaks were observed. The first peak was endothermic and the others were exothermic. The first exotherm was caused by the decomposition process and was lower than that of pure cellulose. The Broido method was used to obtain various kinetic and thermodynamic parameters from the TG curves. The values of the activation energy for the decomposition stage of thiophosphorylated cellulose samples were in the range of 78 to 120 kJ mol^{-1} and are lower than that of pure cellulose (193 kJ mol^{-1}). The EPR signals indicated the formation of very few free radicals during the thermal degradation of these samples. Char yields of these samples, at decomposition temperatures, indicated that the formation of char is brought about at the expense of decrease in the decomposition temperature of the relevant exothermic peak. Further, higher char yields of different cellulose cresylthiophosphate samples, compared to cellulose phenylthiophosphate and cellulose itself, lead to the conclusion that cellulose cresylthiophosphates are good flame retardants.

Keywords: Activation energy; Cellulose derivative; DTA; Flame retardant; Spectral; TGA; Thermal

1. Introduction

Textile materials are used extensively to make life pleasant, comfortable, and colourful. Unfortunately, with exceptions, they are flammable and a fire hazard. In the

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United Kingdom, statistics [1] shows that textiles are the materials ignited in 25% of fires reported annually. However, such fires result in 50% of the consequent deaths. The disproportionate fatality rate emphasises the importance of the development of successful flame-retardant systems for textile materials [2,3].

Flame-retardant systems commonly applied to cotton fabrics function in the condensed and/or vapour phase depending on their chemical nature. Phosphorus- and nitrogen-containing retardants function in the condensed phase by reducing the temperature at which pyrolysis occurs and enhance char formation in preference to the evolution of flammable volatiles.

This paper is concerned with the results of thermal degradation of cellulose cresylthiophosphate samples in air. The kinetic parameters such as the energy of activation, the frequency factor, the entropy, the enthalpy and the free energy of activation for the thermal decomposition of cellulose derivatives have been determined. A mechanism for the thermal degradation of cellulose cresylthiophosphate samples has been proposed on the basis of current information concerning char yields, infra-red spectra of the chars obtained at different temperatures and kinetic parameters.

2. Experimental

The following samples were investigated for the present work: (i) cellulose powder (from Aldrich and Thomas Laboratories, Wal Mum), (ii) cellulose phenylthiophosphate, (iii) cellulose o-cresylthiophosphate, (iv) cellulose p-cresylthiophosphate, (v) cellulose m-cresylthiophosphate and (vi) cellulose 4-chloro-m-cresylthiophosphate. Samples (ii–vi) were prepared as noted below:

2.1. Preparation of Aryldichlorothiophosphates [4]

Phenyldichlorothiophosphate was prepared by the reaction of 0.5 mol (46 g) C_6H_5OH with 2.5 mol (425 g) of $PSCl_3$ in the presence of anhydrous $MgCl_2 + Cu_2Cl_2$ (0.5 g each) as catalyst. After a reaction time of 36 h, excess $PSCl_3$ was removed by distillation under atmospheric pressure. The residue on fractionation gave $C_6H_5OPSCl_2$ in the temperature range 198–203°C at 190 mm of Hg.

Various cresyldichlorothiophosphates were prepared by the reaction of the relevant $ArOPCl_2$ (where Ar = o-, p-, or m-CH_3–C_6H_4- and 4-Cl-3-CH_3-C_6H_3-), 0.54 mol and S, 0.5 mol in 0.1 mol s-$C_2H_2Cl_4$. The reaction mixture was refluxed for 3 h and then fractionated at 190 mm of Hg and the samples of o-CH_3-$C_6H_4OPSCl_2$, p-CH_3-$C_6H_4OPSCl_2$, m-CH_3-$C_6H_4OPSCl_2$ and 4-Cl-3-CH_3-$C_6H_3OPSCl_2$ were obtained in the temperature range 220–225, 225–230, 215–225 and 235–240°C, respectively.

2.2. Thiophosphorylation of cellulose

Thiophosphorylation of cellulose was carried out by the reaction of 0.03 mol cellulose and 0.09 mol of the relevant aryldichlorothiophosphate in 100 ml pyridine as solvent. The reaction mixture was heated at 90°C for 6 h with constant stirring. The

product was filtered through a G-3 sintered glass funnel and washed first with pyridine and then thoroughly with distilled water and then dried *in vacuo* over P_2O_5.

2.3. Elemental analysis [5]

Elemental analysis of phosphorus was carried out colorimetrically using a Shimadzu spectrophotometer, model UV-140-02. The results obtained are given in Table 1.

2.4. Thermal analysis

DTA and TG traces of all the samples were recorded in a static air atmosphere from ambient temperature to 600°C at a heating rate of 10°C/min using a Stanton Redcroft (U.K.) thermal analyser.

2.5. Spectroscopic studies

IR spectra of these compounds and those of chars of cellulose derivatives were obtained by the KBr pellet technique using a Pye-Unicam SP-3-300 IR spectrophotometer. EPR spectra of the charred samples of cellulose derivatives were recorded on Varian model EPR E-112 spectrophotometer operating at 9.4 GHz. The 1,1-diphenyl-2-picrylhydrazyl (DPPH) signal was used as a standard for 'g' values.

3. Results and discussion

DTA and TG traces of cellulose (i), cellulose phenylthiophosphate (CPSP) (ii), cellulose *o*-cresyl-, *p*-cresyl-, *m*-cresyl- and 4-chloro-*m*-cresylthiophosphate samples (iii–vi) were recorded in air and only the representative traces for three samples viz (i–iii) are given (Fig. 1–3)

3.1. DTA studies

The initiation (T_i), maximum (T_m) and final (T_f) temperatures for various endotherms and exotherms are presented in Table 1. Besides an endotherm near 100°C due to evolution of sorbed moisture in all the samples, the DTA trace of sample (vi) shows an endothermic peaking at 270°C due to dehydration and depolymerization of cellulose. This endotherm was absent in the other samples (i–v). This endotherm was not discernible probably because of its overlapping with first exotherm and that it might be occurring at somewhat different temperatures in cellulose and the other samples (ii–v).

The first exotherm in the cellulose occured at 355°C which represents its decomposition to a carbonaceous mass and was accompanied by a mass change to a definite value. In the treated cellulose samples (ii–vi) this exotherm occurred at 340, 242, 250, 250, and 300°C, respectively. The second exotherm of significance in the treated cellulose samples (iii–vi) occurred at 340, 330, 335, and 325°C, respectively. This exotherm corresponded to the total gasification of the carbonaceous material (modified by the
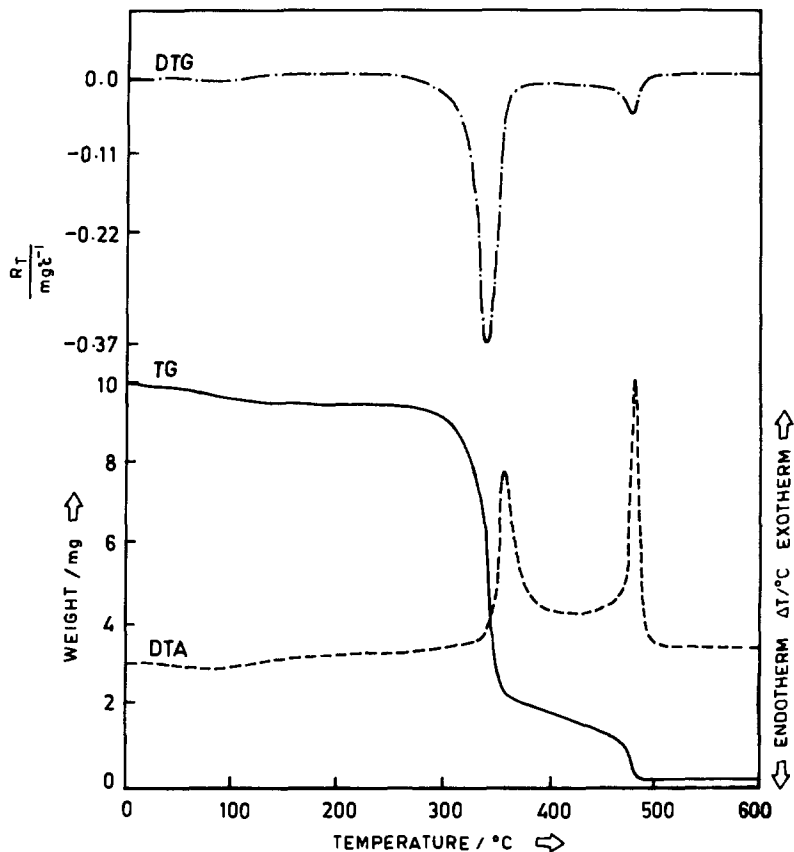
Fig. 1. DTA, TG and DTG traces of cellulose.

residue from the inorganic components of the flame retardants). This exotherm was not observed in cellulose (i) and CPSP (ii), probably due to its overlapping the first exotherm in these samples.

In some cases (e.g. Fig. 3) this latter process was extended over a large mass change and temperature range, and produced smaller but less significant exothermic events (Table 1).

3.2. TG studies

TG traces of these samples (except cellulose) show four important areas of weight loss, known as the four stages of thermal degradation. Broido [6] method was used to calculate kinetic parameters from each TG curve. The equation used is given below:

$$\ln \left[\ln \left(1/y\right)\right] = -\frac{E_a}{R} \cdot \frac{1}{T} + \left[\frac{R}{E_a}\frac{Z}{\beta} \cdot T_m^2\right]$$
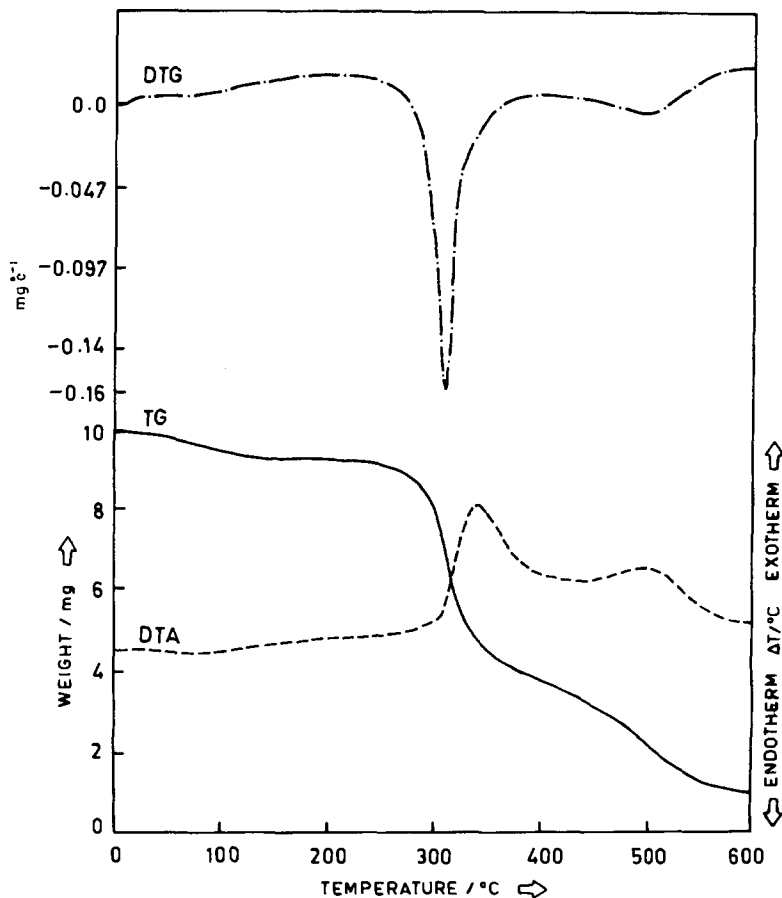
Fig. 2. DTA, TG and DTG traces of cellulose phenylthiophosphate.

where y is the fraction of number of initial molecules not yet decomposed and is determined from the expression

$$y = N/N_0 = W_t - W_f/W_0 - W_f$$

where N_0 and N are the number of initial molecules, at any time, t and W_0, W_t and W_f are the initial, at any time t, and final weight of the sample, respectively. β is the heating rate (°C/min), T_m is the temperature at maximum reaction rate and temperature T is expressed in kelvin. Using the Broido equation, plots of $\ln (\ln 1/y)$ vs $1/T$ for various stages of thermal degradation were plotted and only representative plots for the second stage of thermal degradation of cellulose and its derivatives (ii–vi) are shown in Fig. 4. The activation energies and frequency factors calculated from the slopes and intercepts, respectively, of these plots are given in Table 2.
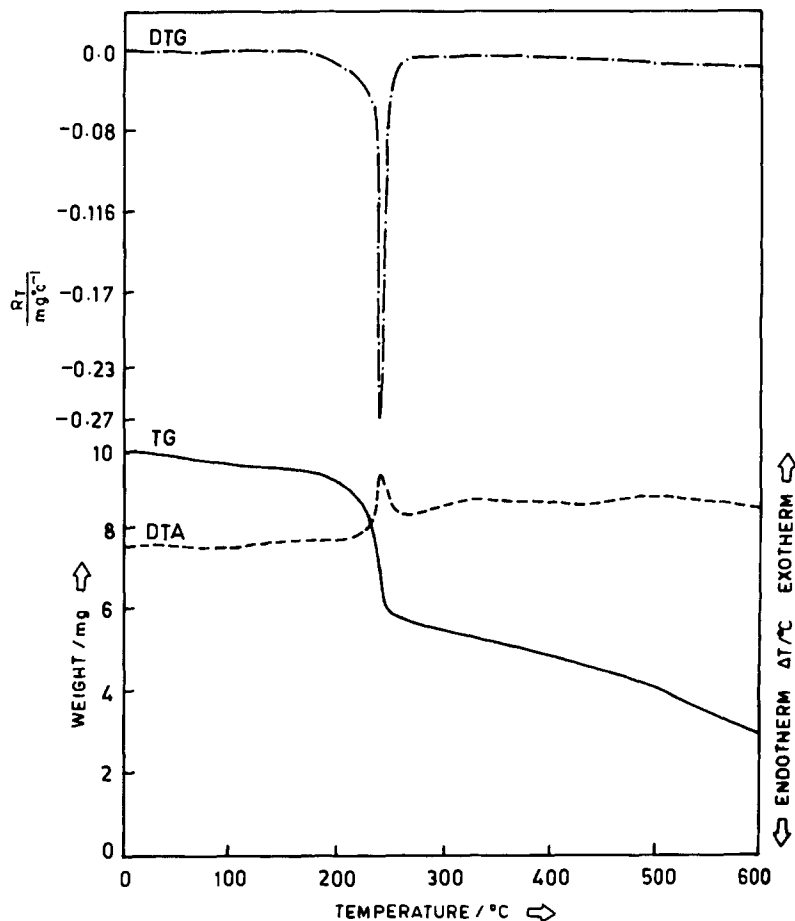
Fig. 3. DTA, TG and DTG traces of cellulose o-cresylthiophosphate.

3.3. First stage of thermal degradation

Besides the weight loss near 100°C due to sorbed moisture, the weight loss occurring up to 130°C was not described as first stage of thermal degradation. For cellulose the weight loss of 1.0% in the temperature span of 140–265°C was due to the dehydration of anhydroglucopyranose chain segments. For thiophosphorylated cellulose samples (ii–vi), the weight loss of 1.0–7.0% (130–250°C) was probably the consequence of acid catalysed dehydration reactions. The activation energies E_a, of these samples (i–vi) were 8.0, 21.3, 34.4, 41.6, 57.7 and 5.4 kJ mol^{-1}, respectively.

3.4. Second stage of thermal degradation

This stage is primarily due to chain decomposition process. Cellulose showed a weight loss of 76.0% due to thermal decomposition of the anhydroglucose polymeric

Table 1
Description of DTA traces of cellulose (i), CPSP (ii) and cellulose cresylthiophosphate samples (iii–vi)

Sr. No.	Compound	Temperature °C			Nature of peak
		Initial T_i	Maximum T_m	Final T_f	
(i)	Cellulose	–	80	130	Endo
		315	355	415	Exo
		415	480	500	Exo
(ii)	Cellulose phenylthiophosphate	–	100	135	Endo
		290	340	430	Exo
	(CPSP)(P% = 1.50)	430	500	600	Exo
(iii)	Cellulose o-cresylthiophosphate	–	72	120	Endo
		205	242	260	Exo
	(P% = 2.60)	260	340	415	Exo
		430	520	620	Exo
(iv)	Cellulose p-cresylthiophosphate	–	90	125	Endo
		220	250	270	Exo
	(P% = 2.67)	280	330	420	Exo
		420	530	630	Exo
(v)	Cellulose m-cresylthiophosphate	–	80	100	Endo
		230	250	265	Exo
	(P% = 2.80)	265	335	435	Exo
		435	535	640	Exo
(vi)	Cellulose 4-chloro-	–	95	135	Endo
	m-cresylthiophosphate	245	270	280	Endo
	(P% = 1.58)	280	300	310	Exo
		310	325	395	Exo
		440	495	560	Exo

chain in the temperature span 265–355°C with an activation energy of 193 kJ mol^{-1}. For thiophosphorylated cellulose samples (ii–vi), the corresponding weight loss was 32.0–45.0% (180–350°C). For this stage, activation energies were in the range of 78–120 kJ mol^{-1}. The weight loss in this stage corresponded to the first exotherm in the DTA traces.

3.5. Third stage of thermal degradation

The major weight loss accompanying the second degradation stage of cellulose was complete below 355°C. The third stage, covering the temperature range of 355–475°C for pure cellulose, showed a 19.0% weight loss with an activation energy of 13 kJ mol^{-1} corresponding to the third exotherm in the DTA trace. The weight loss for treated cellulose samples was from 14.0–22.0% with activation energies varying from 8.4–17.8 kJ mol^{-1}. This stage corresponded to the third exotherm in the DTA traces of these samples.
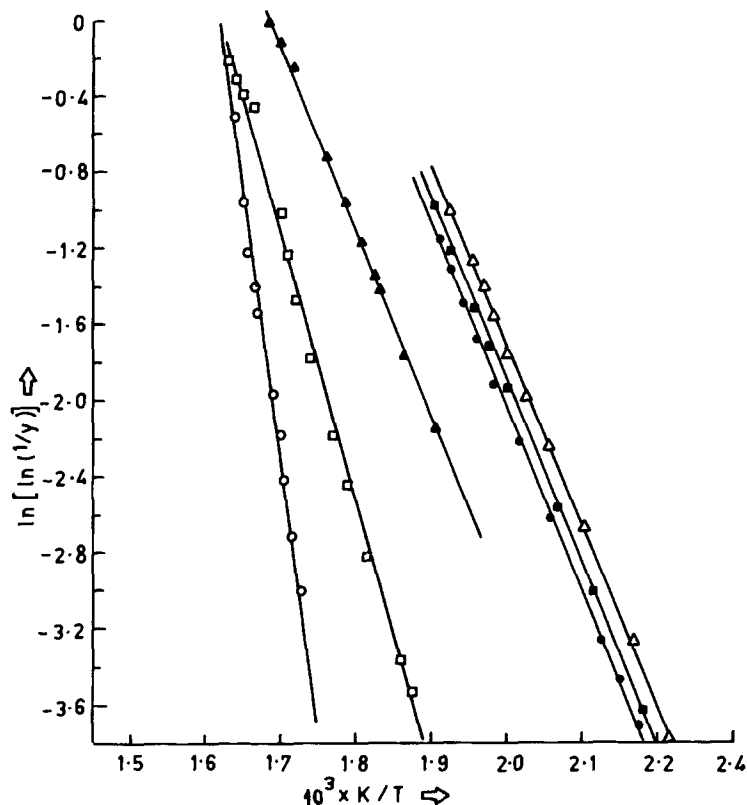
Fig. 4. Plots of $10^3 \times K/T$ vs $\ln(\ln(1/y))$ using Broido method for second stage of thermal degradation of cellulose ($\bigcirc$) and its derivatives(ii) ($\square$), (iii)($\triangle$), (iv) ($\bullet$), (v) ($\blacksquare$) and (vi) ($\blacktriangle$).

3.6. Fourth stage of thermal degradation

This stage was not observed in the pure cellulose. For the treated cellulose samples (ii–vi), the weight loss of 13.0–19.0% in the temperature range 415–595°C was due to the oxidation, crosslinking and aromatization of charred residues. The activation energy for these samples in this stage was in the range 29.5–52.6 kJ mol^{-1}.

3.7. Char yields

Char yields (in weight%) for cellulose (i) and its thiophosphorylated samples (ii–vi) were calculated from TG traces at the respective decomposition temperatures of each sample (Table 3) and at 475°C where cellulose ceases to show any significant weight loss (Table 4). An appraisal of Table 3 indicates that the formation of char is brought about at the expense of a decrease in the decomposition temperature of the relevant exothermic peak. From Table 4, it is obvious that the char yields of the treated cellulose

Table 2
Activation energies and frequency factors for all stages of thermal degradation of cellulose, CPSP (ii) and cellulose cresylthiophosphate samples (iii–vi)

Sr. No.	Compound	Stage	DTG maxima/°C	Temperature range/°C	Weight loss/%	E_a/kJ mol^{-1}	Z/s^{-1}
(i)	Cellulose	First		140–265	1.0	8.00	8.10×10^{-1}
		second	335	265–355	76.0	193.32	3.00×10^{11}
		Third		355–475	19.0	13.04	9.60×10^{-6}
(ii)	Cellulose phenyl-thiophosphate (CPSP)	First		135–235	1.0	21.34	3.80×10^{-6}
		Second	315	235–335	45.0	120.10	1.10×10^5
		Third		335–460	22.0	17.82	2.40×10^{-5}
		Fourth		460–555	19.0	52.63	1.30×10^{-2}
(iii)	Cellulose o-cresylthiophosphate	First		130–180	1.0	34.48	7.60×10^{-4}
		Second	242	180–245	32.0	81.06	3.40×10^2
		Third		245–445	19.0	8.49	2.30×10^{-6}
		Fourth		445–580	15.0	33.05	3.50×10^{-4}
(iv)	Cellulose p-cresylthiophosphate	First		130–180	1.0	41.60	5.30×10^3
		Second	250	180–260	34.0	78.14	1.00×10^2
		Third		260–450	15.0	8.38	2.70×10^{-6}
		Fourth		450–595	13.0	32.33	3.00×10^{-6}
(v)	Cellulose m-cresylthiophosphate	First		140–180	1.0	57.72	4.10×10^{-1}
		Second	242	180–260	35.0	81.21	2.60×10^{-2}
		Third		260–475	14.0	8.41	7.00×10^{-7}
		Fourth		475–575	14.0	29.51	1.40×10^{-4}
(vi)	Cellulose 4-chloro-m-cresyl-thiophosphate	First		150–250	7.0	5.40	3.60×10^{-7}
		Second	–	250–350	44.0	80.77	8.10×10^1
		Third		350–415	18.0	14.77	1.30×10^{-5}
		Fourth		415–560	14.0	44.73	4.60×10^{-3}

samples (20.0–46.0%) were higher than that of pure cellulose (2.0%) indicating a reduction in the amounts of low molecular weight gases formed during degradation. From these studies, it may be concluded that the cellulose cresylthiophosphate system is a good flame retardant in that it lowers the decomposition temperature, reduces the flammable volatiles and correspondingly increases char yield [7].

The values of the entropies (ΔS^*), the enthalpies (ΔH^*) and the free energies of activation (ΔG^*) were calculated at the respective temperature of maximum reaction rate of thermal degradation of each sample. The values obtained are presented in Table 4. Various thiophosphorylated samples (ii–vi) of cellulose show variation in the values for entropy of activation (-162 to -221 J K^{-1} mol^{-1}), but this variation is compensated by a corresponding change in the values of the enthalpy of activation (73 to 115 kJ mol^{-1}), leading to almost similar values of the free energy of activation (184 to 210 kJ mol^{-1}). This shows that the basic step involved in the deccomposition (second stage of thermal degradation) of the CPSP (ii) and cellulose cresylthiophosphate samples (iii–vi) was the same.

Table 3
Char yield at ignition temperature of each sample

Sample	Temperature/°C	Residue at end/mg
Cellulose	355	2.2/10
(ii)	340	4.9/10
(iii)	242	6.2/10
(iv)	250	6.0/10
(v)	250	6.2/10
(vi)	300	5.1/10

Table 4
The entropies, the enthalpies and the free energies of activation for second stage of thermal degradation of cellulose, CPSP (ii) and cellulose cresylthiophosphate samples (iii–vi)

Sr. No.	Compound	T_m/K	ΔS^*/ J K^{-1}	ΔH^*/ kJ mol^{-1}	ΔG^*/ kJ mol^{-1}	Char yield at 748K/%
(i)	Cellulose	608	−42.0	198.40	223.90	2.0
(ii)	Cellulose phenylthiophosphate (CPSP)	588	−162.20	115.20	210.60	20.0
(iii)	Cellulose o-cresyl-thiophosphate	515	−209.40	76.80	184.60	42.0
(iv)	Cellulose p-cresyl-thiophosphate	523	−218.90	73.80	188.30	44.0
(v)	Cellulose m-cresyl-thiophosphate	515	−211.80	76.90	187.60	46.0
(vi)	Cellulose 4-chloro-m-cresylthiophosphate	523	−221.35	85.10	200.90	25.0

3.8. IR studies

IR spectra of the chars of cellulose m-cresylthiophosphate obtained at different temperatures (up to 350°C) were recorded. For chars obtained at 200°C compared to the IR spectra of the original material, the intensities of the bands at 3450 (–OH stretching); 1380 (–OH bending); 1250 (P = O stretching or P–OH deform.); and 780,750,735 (P = S stretching) decreased and a new band at 1700 cm^{-1} (C=C stretching or C=O strertching) emerged (Fig. 5). Diminishing intensities of the bands, particularly at 3450 and 750 cm^{-1} region, were observed which show that dehydration and dethio- phosphorylation reactions took place in the initial stages of thermal degradation.

At 250°C, the bands at 1160, 1060, 1035 (skeletal vibrations involving C–O stretching) almost vanished and a new band at 1705 cm^{-1} (C=O stretching) appeared suggesting that the decomposition of the sample occurred at this stage. At this temperature the peak at 1250 (P=O stretching or P–OH deformation.) moved to 1220 cm^{-1} and peaks at 780, 750, 735 cm^{-1} (P=S stretching) transformed into a broad band.
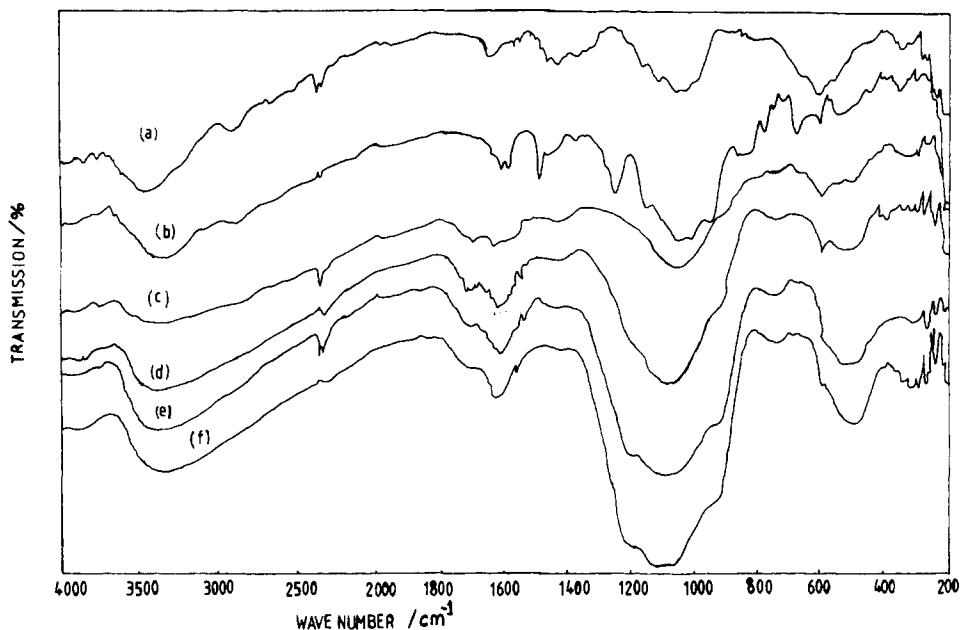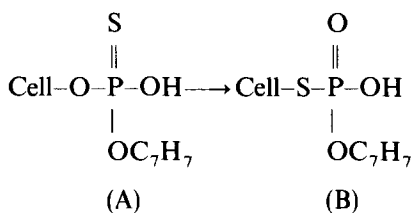
Fig. 5. IR spectra of cellulose(a), cellulose m-cresylthiophosphate(b), and its chars obtained at 200(c), 250(d), 300(e) and 350 (f) °C, respectively.

It is believed that the transformation of structure (A) into structure (B) took place at lower temperature

$$
\begin{array}{cc}
\text{S} & \text{O} \\
\parallel & \parallel \\
\text{Cell--O--P--OH} \longrightarrow \text{Cell--S--P--OH} \\
| & | \\
\text{OC}_7\text{H}_7 & \text{OC}_7\text{H}_7 \\
\text{(A)} & \text{(B)}
\end{array}
$$

and at higher temperature the mixture of both structures (A) and (B) underwent degradation [8,9].

Chars obtained at 300°C had spectra that did not show characteristic bands of cellulose and bands at 520 (P–S–P stretching); 1220 (P=O stretching or P–OH deformation) and 1705 cm^{-1} (C=O stretching.) were observed. At this temperature, the peak at 1220 (P=O stretching), 1160, 1060, 1035 cm^{-1} (skeletal vibration involving C=O stretching) overlapped with each other and a very large absorption band was observed in 1300–900 cm^{-1} region. The band at 750 cm^{-1} (P=S stretching) remained and a peak at 1705 cm^{-1} (C=O stretching) became less intense and the peak at 1610 cm^{-1} more intense (C=C conjugation), indicating skeletal rearrangements and evolution of volatile compounds.

At still higher temperatures (at 350°C), the bands at 1705 (C=O stretching); 1610 (C=C stretching conjugated); 1220 (P=O stretching or P–OH deformation); 520 (P–S–P stretching) and 750 cm^{-1} (P=S stretching) remained, suggesting the formation of compounds containing C=O, C=C, P–S–P and P=O groups.

3.9. EPR studies

EPR spectra of chars of pure cellulose (obtained at 300°C) and treated cellulose samples (ii–vi) (obtained at 250°C) were recorded at ambient temperature. The values of relative intensities of the EPR spectral lines were calculated by Wertz and Bolton technique [10]. The relative intensities and hence relative concentrations of free radicals of the chars of the cellulose (i) and its thiophosphorylated samples (ii–vi) are found to be in the ratio of 1.0:0.45:0.39:0.64:1.08:1.08 (Fig. 6).

The formation of free radicals is associated with char formation during the decomposition of cellulose compounds [11]. As the number of free radicals generated for cellulose is small [12], so little char is obtained during the thermal degradation of cellulose. Similarly as the number of free radicals generated is the same or less for thiophosphorylated cellulose samples (ii–vi), when compared with cellulose, a small char yield for these samples would be expected. However, char yields were very high for treated cellulose samples (ii–vi), when compared to cellulose. This shows that a free radical mechanism is not operative during the thermal degradation of these thiophosphorylated cellulose samples. They degrade by some alternate mechanism briefly described below.
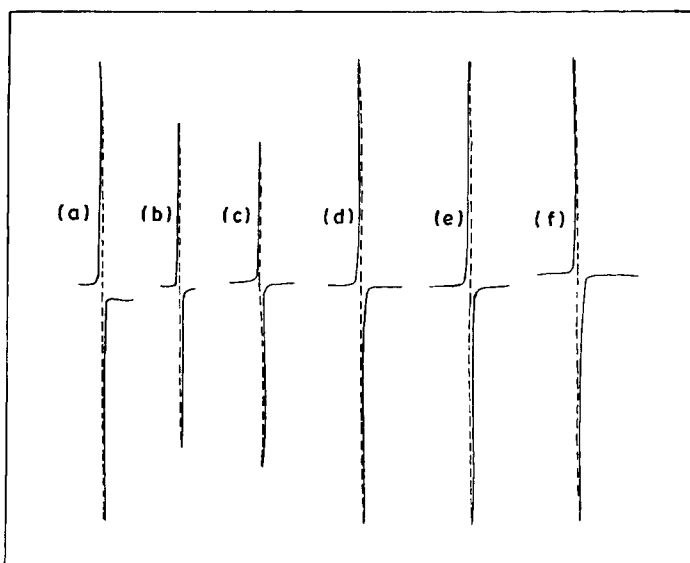

Fig. 6. EPR spectra of (a) Cellulose, (b) Cellulose phenyl-, (c) Cellulose o-cresyl-, (d) Cellulose p-cresyl-, (e) Cellulose m-cresyl- and (f) Cellulose 4-chloro-m-cresylthiophosphate.

4. Mechanism of thermal degradation

Thermal degradation of a cellulose cresylthiophosphate begins with the release of cresylthiophosphoric acid which then alters the decomposition of the cellulose backbone to such an extent that the primary decomposition route promotes formation of carbonaceous char. At higher temperatures, cresylthiophosphoric acid polymerises. The polyacid formed is more effective in catalysing the dehydration. A plausible mechanism of acid-catalysed thermal degradation of cellulose esters has been discussed in detail by Shafizadeh et al. [13] and Bhatnagar et al. [14].

Chlorodeoxycellulose, produced during thiophosphorylation of cellulose, may also affect the mechanism of degradation. The first step of thermal degradation of chlorodeoxycellulose involves the dehydrohalogenation reaction. The released hydrochloric acid then catalyses a series of heterolytic and homolytic reactions leading ultimately to a carbonaceous char [15].

Acknowledgement

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