Thermal Degradation of Cellulose and Its Phosphorylated Products in Air and Nitrogen

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Synopsis

The thermal degradation of cellulose and its phosphorylated products (phosphates, diethylphosphate, and diphenylphosphate) were studied in air and nitrogen by differential thermal analysis and dynamic thermogravimetry from ambient temperature to 750°C. From the resulting data various thermodynamic parameters were obtained following the methods of Broido and Freeman and Carroll. The values of E_a for decomposition for phosphorylated cellulose were found to be in the range 55–138 kJ mol^{-1} in air and 85–152 kJ mol^{-1} in nitrogen and depended upon the percent of phosphorus contents in the samples. The mass spectrum of cellobiose phosphate indicated the absence of the molecular ion, indicating that the compound was thermally unstable. The IR spectra of the pyrolysis residues of cellulose phosphate gave indication of formation of a compound having C=O and P=O groups. A fire retardancy mechanism for the thermal degradation of cellulose phosphate has been proposed.

INTRODUCTION

One of the textile materials frequently causing fire injuries is cotton cellulose. However, it is easily rendered flame-resistant with the application of proper condensed phase-active flame retardants. Some of the most successful commercial flame retardants for cellulose have been the organophosphorus compounds.[1-3] It has been shown that these compounds exhibit varying levels of effectiveness depending on their chemical structure. In the following, cellulose samples treated with various phosphorylating agents have been obtained by the procedure employed by Takaku et al.,[4] and the kinetics of the thermal degradation of cellulose phosphates have been studied from ambient temperature to 750°C using thermal techniques with a view to evaluating their efficiency as flame-proofing agents. The values of different kinetic parameters have been obtained employing the methods of Broido[5] and Freeman and Carroll.[6]

EXPERIMENTAL

The following samples of cellulose/cellobiose and its phosphorylated products were selected for the present work: sample (i), cellulose (from Dassel, West Germany), dried to a constant weight *in vacuo* at 60°C; samples (ii)–(iv), cellulose phosphate I, cellulose diethylphosphate, and cellulose diphenylphosphate, respectively; sample (v), cellulose phosphate II was obtained[7] by treating cellulose with phosphorus oxychloride in pyridine at 60°C for 6 h and dried over P_2O_5 *in vacuo*; sample (vi) cellobiose phosphate

I. Samples (ii)–(iv) and (vi) were prepared by the procedure of Takaku et al.,[4] who reported the formation of several alkyl dihydrogen phosphates from the reaction of alcohols with phosphorous acid and mercuric chloride. The phosphorous acid/diethylphosphite/diphenylphosphite (0.01 mol, 0.82/1.38/2.34 g) was oxidized with mercuric chloride (0.01 mol, 2.72 g) in the presence of N-methylimidazole (0.04 mol, 3.28 g) in acetonitrile (20 mL). The mixture was heated at 80°C for 1 h with vigorous stirring and the salt of N-phosphoryl-N'-methylimidazole[8] was obtained. Dry cellulose (0.05/3 mol, 2.70 g)/cellobiose (0.05/8 mol, 2.14 g) was added to the salt and the reaction mixture was stirred further at 80°C for 24 and 12 h, respectively. After removal of metallic mercury, the product was concentrated and the residue was dissolved in 95% ethanol (10 mL) and further treated with aniline (1.5 mL). A pale yellow precipitate of anilinium salt of cellulose/cellobiose phosphate was separated on keeping the mixture in a refrigerator overnight. The product was filtered, washed thoroughly with water and dried over P_2O_5 *in vacuo*.

Thermal Analysis

The differential thermal analysis, thermogravimetry, and differential thermogravimetry thermograms were obtained using a MOM derivatograph (Paulik, Paulik and Erdey, Budapest, Hungary). The DTA and TG curves were run under a dynamic air and nitrogen (dried) atmospheres flowing at 100 mL/min and at a scanning rate of 9°C/min. The DTA measurements were related to calcined alumina.

Infrared Spectroscopy

For the IR studies (Beckman spectrophotometer, IR-20, United States), 2% charred samples of cellulose phosphate I were prepared by the KBr technique. The charred samples were prepared by heating them in a DTA cell. Heating was stopped at the desired temperature, and the residues were allowed to cool and quickly transferred to a stoppered sample container.

Mass Spectrometry

Mass spectrum of cellobiose phosphate I was recorded on a KRATOS MS-45 Mass Spectrometer at 70 eV using a direct insertion probe. The temperature of oven and chamber heater was fixed at 20°C higher than the melting point of the compound.

RESULTS AND DISCUSSION

The DTA thermograms of (i) cellulose, (ii) cellulose phosphate I, (iii) cellulose diethylphosphate, (iv) cellulose diphenylphosphate, (v) cellulose phosphate II, and (vi) cellobiose phosphate I were recorded in air atmosphere and are shown in Figures 1–6. The peak temperatures for various endotherms and exotherms were measured and are given in Table I. An endotherm below 80°C in all the compounds is due to the evaporation of the moisture. For samples (ii)–(iv) having phosphorus content <5.2%, the second endotherm is in the range of 142–222°C, depending upon the percent of phosphorus
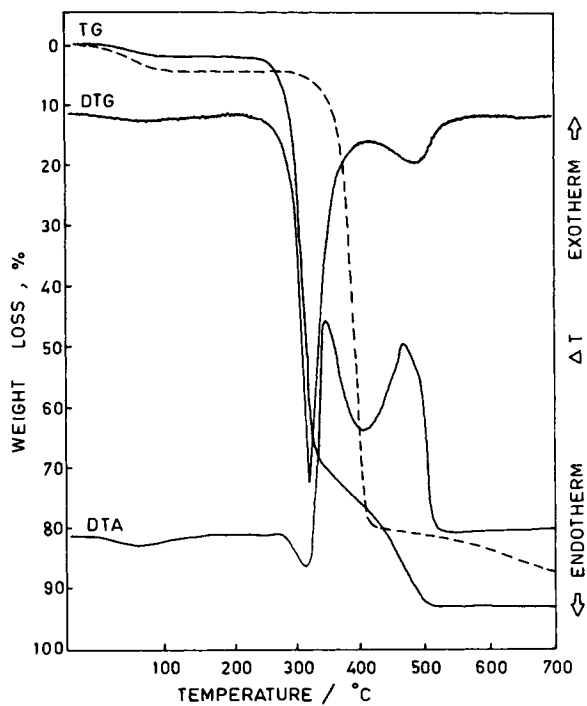
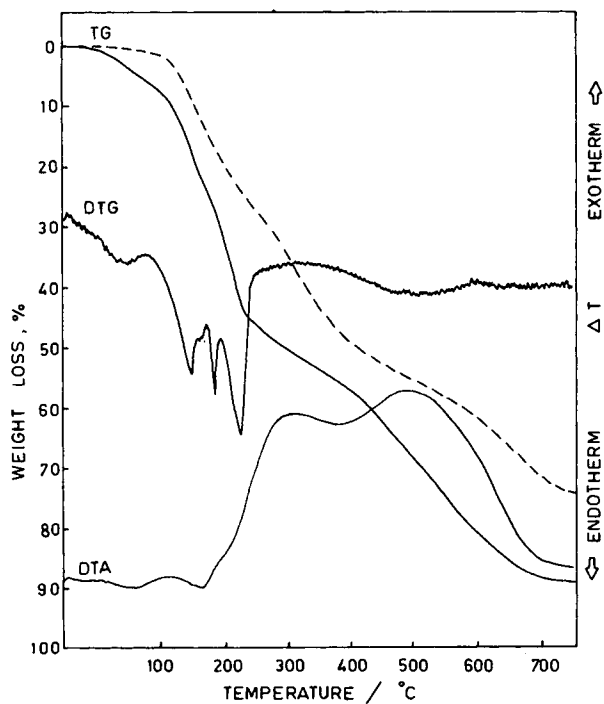Fig. 1.   Thermal analysis of cellulose in air (—) and in nitrogen (- - -).

Fig. 2.   Thermal analysis of cellulose phosphate I in air (—) and in nitrogen (- - -).
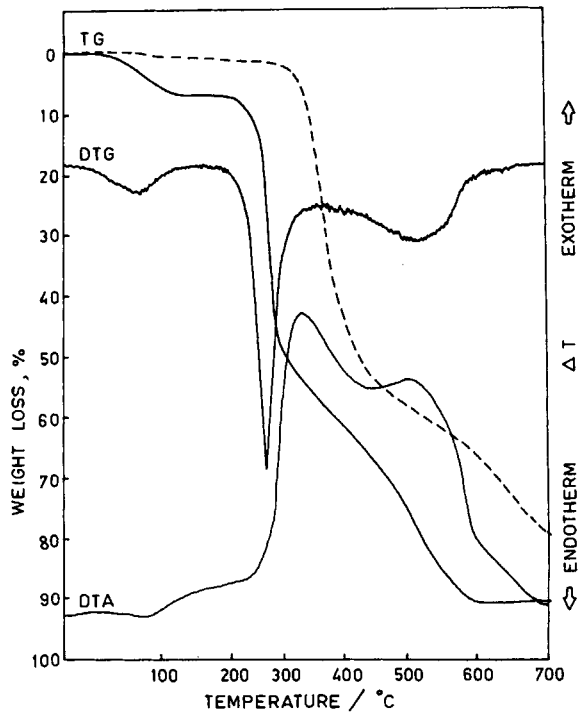
Fig. 3. Thermal analysis of cellulose diethylphosphate in air (—) and in nitrogen (- - -).
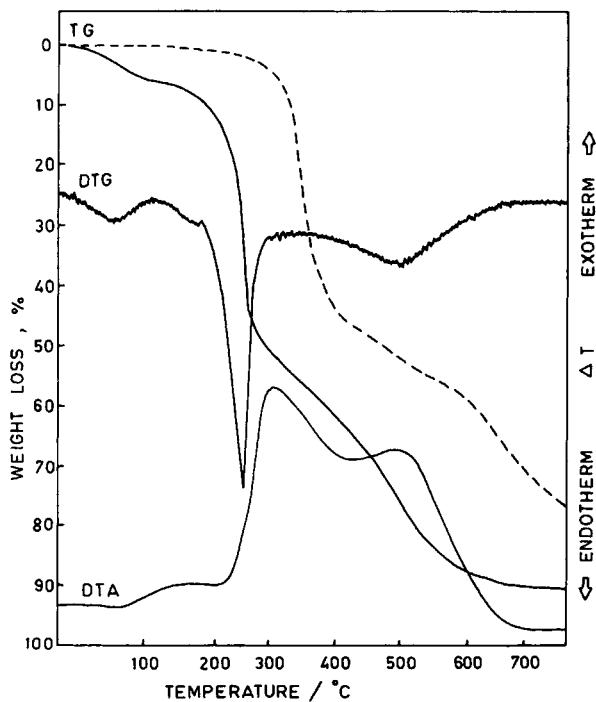

Fig. 4. Thermal analysis of cellulose diphenylphosphate in air (—) and in nitrogen (- - -).
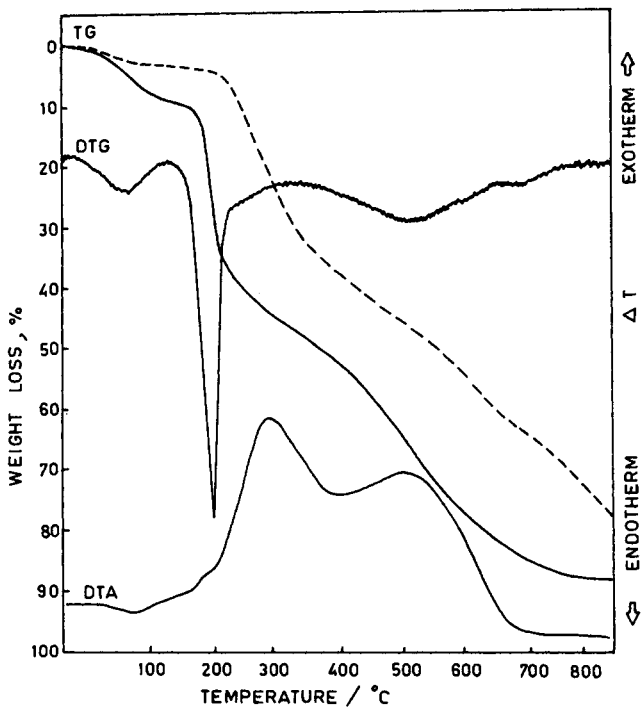
Fig. 5. Thermal analysis of cellulose phosphate II in air (—) and in nitrogen (- - -).
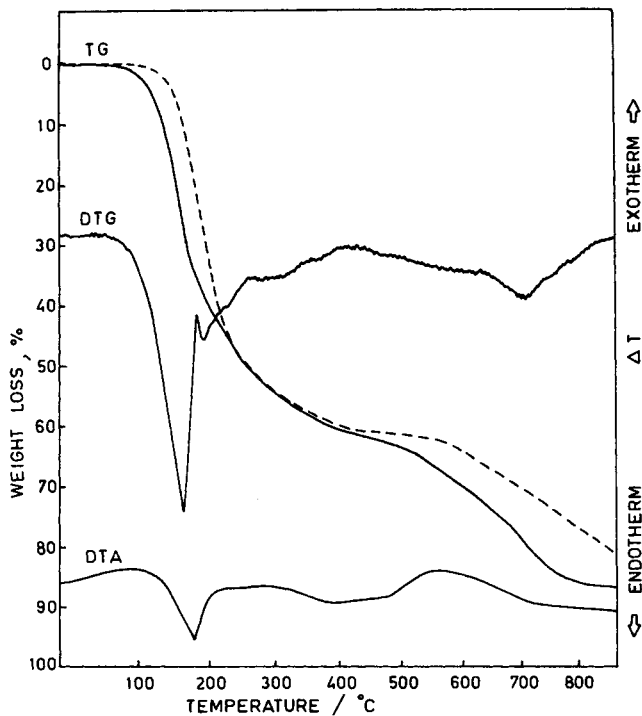

Fig. 6. Thermal analysis of cellobiose phosphate I in air (—) and in nitrogen (- - -).

TABLE I
Peak Temperatures in the DTA Thermograms for Cellulose and Phosphorylated Cellulose/Cellobiose in Air[a]

Sample no.	Compound	P (%)	N (%)	Cl (%)	DTA curve			Nature of the DTA peak	Char yield at 975 K (wt %)
					Initiation temperature (°C)	Peak temperature (°C)	Termination temperature (°C)		
(i)	Cellulose	—	—	—	—	75	—	Endo, large	7.76
					260	274	280	Exo, small	(12.68)
					280	314	325	Endo, large	
					325	350	405	Exo, large	
					405	468	520	Exo, large	
(ii)	Cellulose phosphate I	5.15	6.68	—	—	65	—	Endo, small	12.41
					114	142	188	Endo, small	(28.88)
					—	159	—	Exo, large	
					188	310	380	Exo, large	
					380	500	730	Endo, small	
(iii)	Cellulose diethylphosphate	1.10	2.56	—	—	73	—	Endo, small	9.56
					170	222	251	Exo, large	(20.78)
					251	333	440	Exo, large	
					440	505	690	Endo, small	
(iv)	Cellulose diphenylphosphate	2.44	3.31	—	—	63	—	Endo, small	10.70
					173	202	233	Exo, large	(28.61)
					233	308	428	Exo, large	
					428	500	690	Endo, small	
(v)	Cellulose phosphate II	8.03	—	2.42	—	77	—	Endo, small	16.28
					120	160	182	Exo, large	(37.23)
					182	290	390	Exo, large	
					390	508	715	Endo, small	
(vi)	Cellobiose phosphate I	12.41	11.29	—	92	172	235	Endo, large	20.81
					235	275	400	Exo, small	(29.36)
					475	553	780	Exo, large	

[a] Values in parentheses were determined in nitrogen.

and nitrogen. It is suggested that, for these samples, the initial reactions are dephosphorylation and that the released acids then catalyze the decomposition of cellulose.

For sample (v) prepared from cellulose treated with phosphorus oxychloride, the endotherm at 160°C is associated with dephosphorylation and dehydrohalogenation. For anilinium salt of cellobiose phosphate I [sample (vi)], the endotherm initiating at 92, terminating at 235 and peaking at 172°C is large and the next exotherm is small. This indicates that, in this temperature range, dephosphorylation and simultaneous decomposition by the catalytic effect due to the released acid is taking place. This is supported by a large weight loss > 47% at 235°C. The next exotherm at 350°C, 310°C, 333°C, 308°C, 290°C, and 275°C for samples (i)–(vi), respectively, are due to the oxidative decomposition of the products. The last exotherm in the temperature range 380–780°C is due to the oxidation of the charred residue.

Dynamic TG and DTG for samples (i)–(vi) in air and TG in nitrogen were also obtained and are shown in Figures 1–6. Maxima in DTG curves in air for dephosphorylation and decomposition for phosphorylated cellulose/cellobiose samples are in the range of 143–255°C, depending on the percent of P, N, and Cl contents in the compounds (Table III). Next DTG curves for the oxidation of the char residues for phosphorylated cellulose samples are in the range of 505–515°C. The corresponding DTG maximum for cellobiose phosphate I lies at 707°C. The char yields (wt %) for these samples in air and nitrogen atmospheres were calculated at 975 K from TG curves and are given in Table I.

Flame retardancy of a particular cellulose derivative is generally measured in terms of the following:

(i) Lowering in decomposition temperature of the treated cellulose sample. This factor will give a lower percent of flammable volatile products and correspondingly higher amount of char yield.

(ii) Alternatively, the higher char yield may be due to some other factors.

From DTA, DTG thermograms and Table I, it is evident that there is a lowering in decomposition temperature of the phosphorylated cellulose/cellobiose samples with increasing percentage of phosphorus both in air and nitrogen atmospheres, indicating that all the phosphorylated samples are effective flame retardants. If we compare the char yield of cellulose phosphate I (prepared from cellulose and phosphorous acid) and cellulose phosphate II (prepared from cellulose and POCl₃), the latter gives higher char yield as compared to the former, although the decomposition temperature of the former is lower than that of the latter. This may be due to the presence of chlorine atom in the cellulose phosphate II. According to Lai et al.[9] such compounds on pyrolysis release the volatile fraction of HCl produced by dehydrohalogenation, which catalyzes the decomposition reactions. It appears that the role of halogen begins after the initial dephosphorylation of cellulose.

The kinetic parameters for various stages of pyrolysis of cellulose and phosphorylated cellulose/cellobiose samples were determined using the methods described by Broido.[5] The method of Freeman and Carroll[6] was applied to decomposition stage only. The equations involved in Broido [eq. (1)] and Freeman and Carroll [eqs. (2)–(3)] methods can be written as
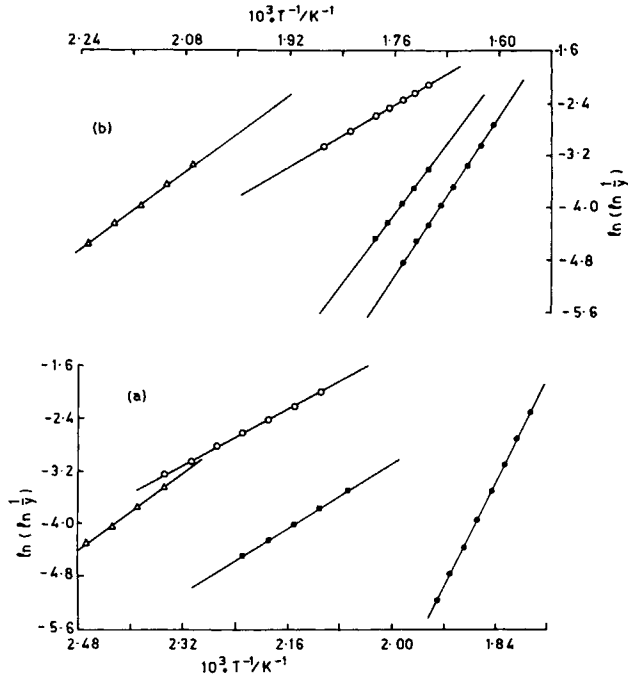
Fig. 7.   Plots of ln(ln 1/y) vs. $10^3 \times T^{-1}$ (K^{-1}) using Broido equation for cellulose (●), cellulose diethylphosphate (■), cellulose diphenylphosphate (○), and cellulose phosphate II (△) in air (a) and in nitrogen (b) for first stage of pyrolysis.
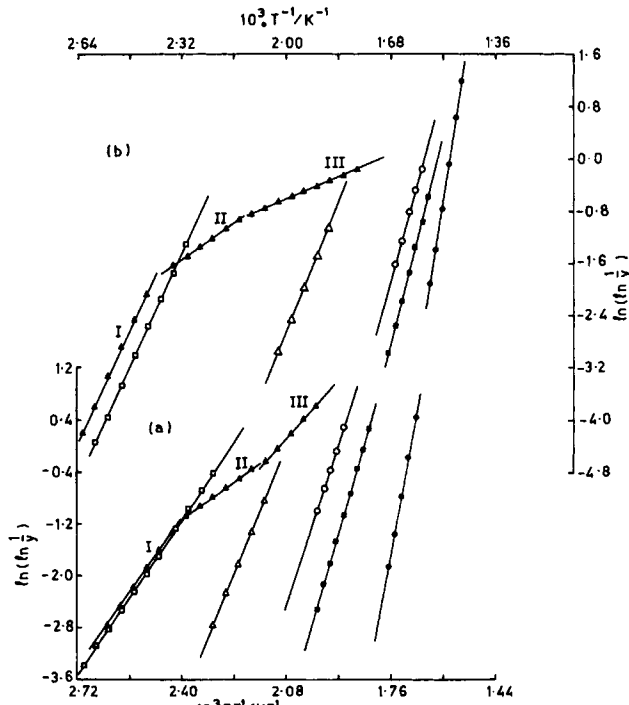

Fig. 8.   Plots of ln(ln 1/y) vs. $10^3 \times T^{-1}$(K^{-1}) using Broido equation for cellulose (●), cellulose phosphate I (▲), cellulose diethylphosphate (■), cellulose diphenylphosphate (○), cellulose phosphate II (△), and cellobiose phosphate I (□) in air (a) and in nitrogen (b) for second stage of pyrolysis.
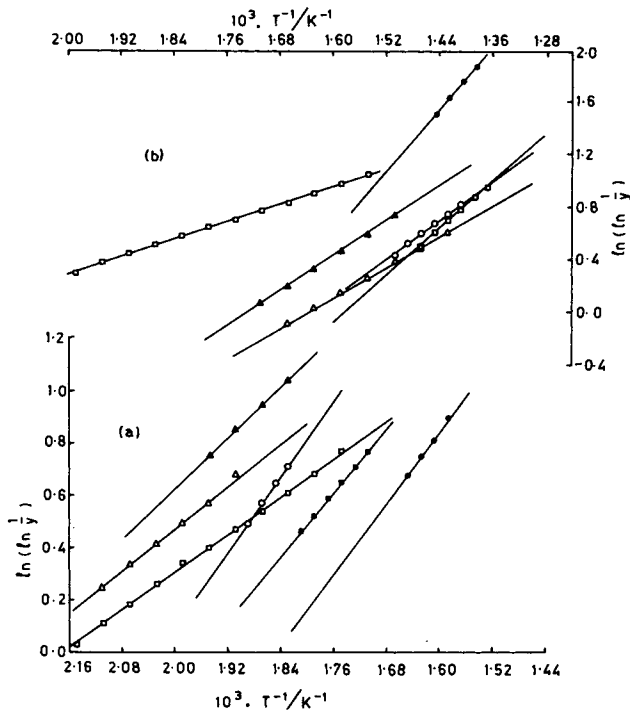
Fig. 9. Plots of ln(ln 1/y) vs. $10^3 \times T^{-1}$ (K^{-1}) using Broido equation for cellulose (●), cellulose phosphate I (▲), cellulose diethylphosphate (■), cellulose diphenylphosphate (○), cellulose phosphate II (△), and cellobiose phosphate I (□) in air (a) and in nitrogen (b) for third stage of pyrolysis.

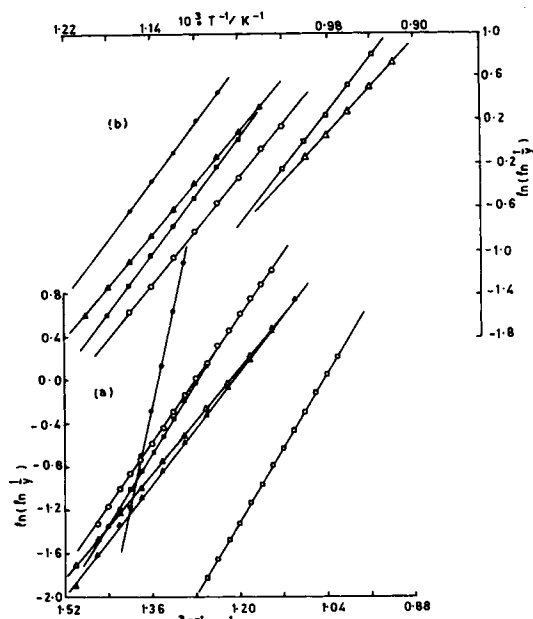Fig. 10. Plots of ln(ln 1/y) vs. $10^3 \times T^{-1}$ using Broido equations for cellulose (●), cellulose phosphate I (▲), cellulose diethylphosphate (■), cellulose diphenylphosphate (○), cellulose phosphate II (△), and cellobiose phosphate I (□) in air (a) and in nitrogen (b) for fourth stage of pyrolysis.

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

$$\frac{\Delta \log R_T}{\Delta \log W} = n - \frac{E_a}{2.303\ R}\cdot\frac{\Delta(1/T)}{\Delta \log W} \tag{2}$$

and the rate of decomposition[10] as

$$-\frac{dW}{dT} = R_T = \frac{Z}{\text{RH}}\exp\left(-\frac{E_a}{RT}\right)\cdot W^n \tag{3}$$

where y is the fraction of the number of initial molecules not yet decomposed, T_m is the temperature of maximum reaction velocity, W is the weight fraction of the material undergoing degradation at time t, RH is the rate of heating (°C/min), and Z is the frequency factor.

Using Broido method, plots of $\ln(\ln 1/y)$ vs. $1/T$ for various stages of pyrolysis are given in Figures 7–10. The values of the energies of activation E_a, and the frequency factors Z determined from the slopes and intercepts of these plots respectively are given in Tables II–IV. Using the Freeman and Carroll method for decomposition stage of cellulose and phosphorylated cellulose/cellobiose, plots of $\Delta \log R_T/\Delta \log W$ vs. $\Delta(1/T)/\Delta \log W$ were made and are given in Figure 11. The activation energies and the values of order of reaction, n, determined from the slopes and intercepts, respectively, are given in Table III. These parameters have been evaluated using the method of least squares for all the methods.

Tables II–IV present activation energies E_a and the frequency factors Z for various stages for pure cellulose and cellulose/cellobiose phosphates samples (i)–(vi) in air and nitrogen atmospheres. For the first stage of pyrolysis (mainly dephosphorylation or dehydration) the energies of activation (Table II) for the phosphorylated cellulose samples (iii)–(v) are low as compared to pure cellulose. For cellulose phosphate I and cellobiose phosphate

TABLE II
Activation Energies and Frequency Factors for First Stage of Pyrolysis of Cellulose and Phosphorylated Cellulose/Cellobiose in Air and Nitrogen (Broido Method)[a]

Sample no.	Compound	Temperature range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})
(i)	Cellulose	240–285	172.1	1.36×10^{13}
		(290–350)	(124.6)	(1.19×10^7)
(iii)	Cellulose diethylphos-phate	170–220	53.9	9.12×10^1
		(260–315)	(112.6)	(2.39×10^6)
(iv)	Cellulose diphenyl-phosphate	150–205	43.9	3.64×10^1
		(250–310)	(49.6)	(9.39)
(v)	Cellulose phosphate II	130–160	60.6	5.64×10^3
		(170–215)	(63.3)	(1.25×10^3)

[a] Values in parentheses were determined in nitrogen.

TABLE III

Activation Energies and Frequency Factors Using Different Methods for Second (Decomposition) Stage of Pyrolysis of Cellulose and Phosphorylated Cellulose/Cellobiose in Air and Nitrogen

Sample no.[a]	Temperature range (°C)	DTG maxima (°C)	E_a (kJ mol^{-1}) Broido	E_a Freeman and Carroll	Z (s^{-1}) Broido	Z Freeman and Carroll	n
(i)	285–335	321	238.4	212.8	2.18×10^{19}	1.82×10^{18}	1.05
	(350–410)		(263.2)	(214.1)	(5.18×10^{18})	(1.86×10^{15})	(1.00)
(ii)	100–145	143	60.2	55.3	7.98×10^{4}	8.93×10^{5}	1.11
	(100–150)		(90.3)	(85.5)	(3.84×10^{8})	(2.63×10^{8})	(1.15)
	145–185	179	29.7	—	5.05	—	—
	(150–195)		(28.6)		(1.78)		
	185–235	222	43.6	—	2.25×10^{2}	—	—
	(195–290)		(16.3)		(3.33×10^{-2})		
(iii)	220–275	255	146.3	138.5	1.36×10^{12}	1.35×10^{13}	1.11
	(315–390)		(167.6)	(152.6)	(2.72×10^{11})	(4.69×10^{10})	(1.06)
(iv)	205–255	243	133.7	130.3	2.87×10^{11}	6.28×10^{12}	0.96
	(310–375)		(156.0)	(148.2)	(6.70×10^{10})	(2.20×10^{10})	(1.04)
(v)	160–200	194	102.6	98.4	1.37×10^{9}	1.86×10^{10}	1.14
	(215–300)		(100.4)	(96.4)	(1.64×10^{7})	(1.54×10^{7})	(0.89)
(vi)	95–190	155	62.3	58.7	1.52×10^{5}	5.84×10^{6}	1.08
	(100–200)		(90.7)	(85.4)	(2.33×10^{9})	(9.87×10^{7})	(0.99)

[a] Compounds referred to as samples nos. (i)–(vi) are the same as in Table I. Values in parentheses were determined in nitrogen.

TABLE IV

Activation Energies and Frequency Factors for the Third and Fourth Stages of Pyrolysis of Cellulose and Phosphorylated Cellulose/Cellobiose in Air and Nitrogen (Broido Method)

Sample no.[a]	Third stage			Fourth stage		
	Temperature range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})	Temperature range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})
(i)	335–370	30.4	1.34	425–500	187.1	1.03×10^{11}
	(410–450)	(49.9)	(5.00×10^{1})	(550–660)	(112.5)	(8.90×10^{9})
(ii)	235–280	19.9	3.51×10^{-1}	390–640	54.5	5.03
	(290–390)	(28.0)	(1.33)	(550–725)	(99.2)	(8.42×10^{2})
(iii)	275–315	26.0	7.96×10^{-1}	410–540	68.9	8.91×10^{1}
	(390–460)	(37.6)	(2.18)	(570–700)	(113.3)	(5.06×10^{6})
(iv)	255–280	31.3	4.49	400–600	61.4	2.59×10^{1}
	(375–450)	(29.7)	(4.87×10^{-1})	(570–700)	(102.7)	(8.29×10^{2})
(v)	200–255	17.7	1.78×10^{-1}	380–620	50.1	2.51
	(300–425)	(24.6)	(1.89×10^{-1})	(550–660)	(112.5)	(4.16×10^{9})
(vi)	190–315	15.0	7.12×10^{-2}	520–730	71.2	1.16×10^{1}
	(200–370)	(14.0)	(4.88×10^{-2})	(650–800)	(110.7)	(1.24×10^{9})

[a] Compounds referred to as samples nos. (i)–(vi) are the same as in Table I. Values in parentheses were determined in nitrogen.

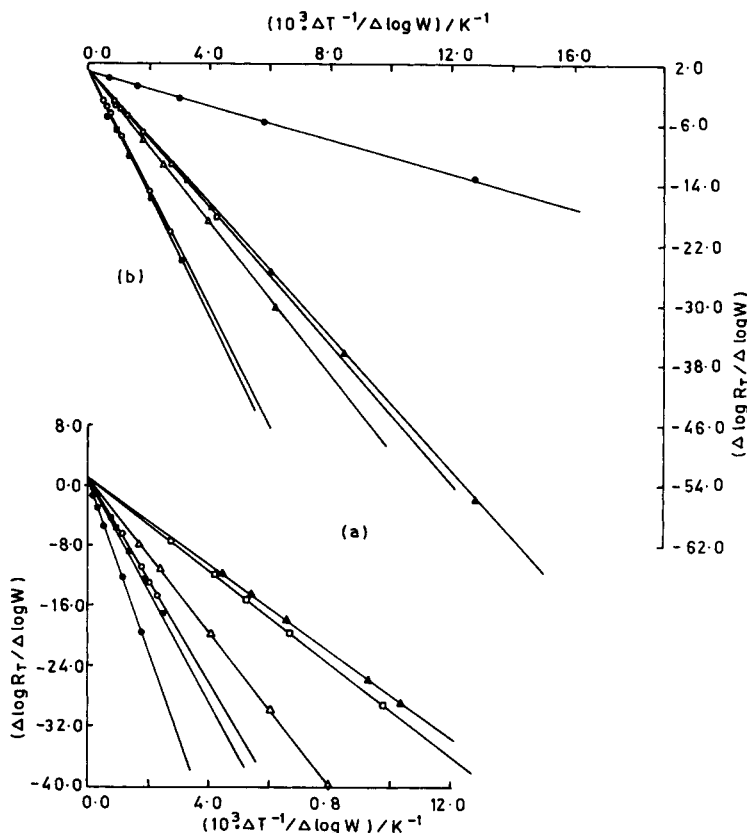Fig. 11. Plots of (Δ log R_T/Δ log W) vs. ($10^3 \times \Delta T^{-1}$/$\Delta$ log W) (K^{-1}) using Freeman and Carroll equation for cellulose ($\bullet$), cellulose phosphate I ($\blacktriangle$), cellulose diethylphosphate ($\blacksquare$), cellulose diphenylphosphate ($\bigcirc$), cellulose phosphate II ($\triangle$), and cellobiose phosphate I ($\square$) in air (a) and in nitrogen (b) for second stage of pyrolysis.

I [samples (ii) and (vi)], the lowering in decomposition temperature is so high that the dephosphorylation and dehydration of the cellulose/cellobiose phosphate I occur simultaneously. From Table III, it is observed that the energy of activation for cellulose/cellobiose phosphate I for the decomposition (second) stage of pyrolysis decreases considerably as compared to cellulose. The activation energies of the phosphorylated samples (ii)–(vi) lie in the range of 55–138 kJ mol^{-1} in air and 85–152 kJ mol^{-1} in nitrogen (Freeman and Carroll method) and depend upon the percent of phosphorus contents in the samples. The values of activation energies obtained in air atmosphere are generally lower than those in nitrogen atmosphere as explained by Lewin et al.,[11] the oxygen in air plays the role of a catalyst in enhancing the pyrolysis of cellulose derivatives. After the decomposition stage, the residual material of cellulose/cellobiose phosphates are found to pyrolyze further in the temperature range of 190–315°C in air and 200–460°C in nitrogen. The activation energies and other parameters for the third stage are listed in Table IV.

In air atmosphere, high temperature exotherms > 380°C for pure cellulose and cellulose/cellobiose phosphates (fourth stage) are due to oxidation of char residues whereas in nitrogen atmosphere the fourth stage corresponds

to production and evaporation of volatile char products. Activation energies and frequency factors for this stage are presented in Table IV.

Mass Spectrum of Anilinium Salts of Cellobiose Phosphate I

In the mass spectrum of anilinium salt of cellobiose phosphate I, a large number of peaks in the mass range 16–122 were obtained (Fig. 12). The parent molecular ion peak was missing in its mass spectrum, indicating that the compound was thermally unstable and decomposes to give a large number of products. A very intense peak at m/z 28 indicates the evolution of carbon monoxide gas. A peak at m/z 44 shows the formation of carbon dioxide. An intense peak at m/z 93 shows that aniline splits from the anilinium salt. The intense peaks at m/z 66 and 65 are due to the hydrocarbons produced after the loss of HCN and H_2CN from aniline. This is supported from the peaks from HCN and H_2CN at m/z 27 and 28, respectively. The prominent peak at m/z 39 may be due to $(C_3H_3)^+$ as suggested by Lam et al.[12]

Infrared Spectra of Residual Products of Phosphorylated Cellulose

The acceleration of the thermal reaction of cellulose phosphate was also confirmed by the IR spectroscopy. Cellulose phosphate I was subjected to pyrolysis in air and the IR spectra of the residual products at different temperatures were recorded (Fig. 13). From Fig. 13, the changes in the IR spectrum of cellulose phosphate I in air medium are as follows. At a temperature of 125°C, where an initial weight loss was detected, the band at
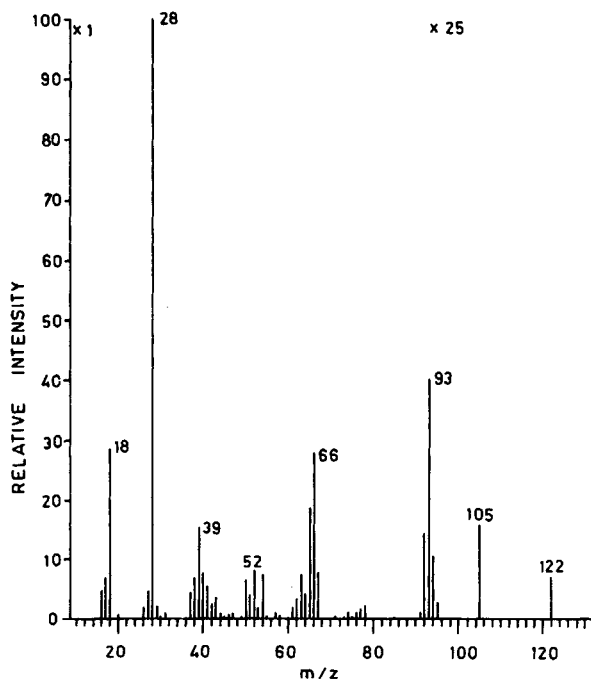

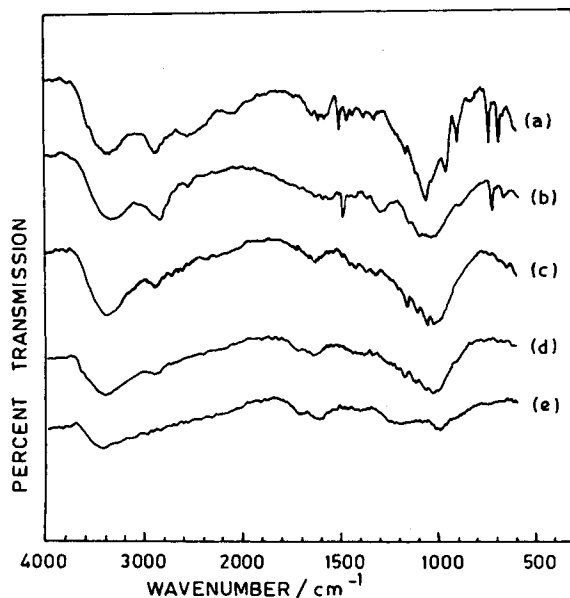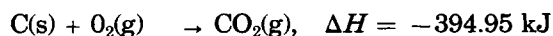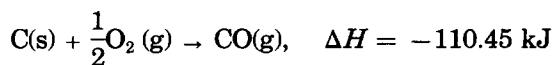Fig. 12.   Mass spectrum of cellobiose phosphate I.

Fig. 13. IR spectra of (a) cellulose phosphate I and (b–e) chars of cellulose phosphate I at different temperatures: (b) 125°C; (c) 150°C; (d) 200°C; (e) 250°C.

2560 cm^{-1} (P—OH) decreases. At 150°C, the band at 2560 cm^{-1} (P—OH) disappeared and new band at 1630 (C=C) and 1000 cm^{-1} (C=C) appeared. At 200°C, the intensity of all the normal bands due to cellulose phosphate I decreased and bands at 1720 cm^{-1} (C=O) and 1250 cm^{-1} (P=O) appeared, indicating that the skeletal rearrangement and the evolution of volatile products commence only at higher temperatures. At 250°C, the bands due to cellulose phosphate I disappeared and the intense absorption at 1720, 1250, and 1000 cm^{-1} remained. At this temperature, the absorption band at 1630 cm^{-1} shifted to 1600 cm^{-1} (due to conjugated C=C), suggesting the extension of conjugation of the C=C bonds in the residue from cellulose phosphate I and formation of compounds containing C=O and P=O groups.

The reduction in the thermal stability of the polymers by phosphorus fire retardants[13] and the presence of phosphorus in the residual char of the cellulose phosphate strongly support the above mechanism.[14,15]

The presence of phosphorus in the char has a special role to play. It is known that the char is essentially carbon and its oxidation causes after glow. Phosphorus-containing celluloses are particularly effective in inhibiting char oxidation. The oxidation of carbon takes place through either of the following reactions:

$$C(s) + \frac{1}{2}O_2 \ (g) \rightarrow CO(g), \quad \Delta H = -110.45 \ \text{kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g), \quad \Delta H = -394.95 \ \text{kJ}$$

Phosphorus containing cellulose causes the first reaction to be prevalent. Oxidation of CO is not sufficiently exothermic to maintain the after glow of the char:

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g), \quad \Delta H = -284.5 \text{ kJ}$$
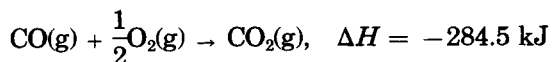
Fire Retardancy Mechanism for Cellulose Phosphates

The most generally accepted mechanism for phosphorus fire retardancy in cellulose is considered to occur in the condensed phase. Phosphorous acid thermally generated from the fire retardant apparently alter the pyrolytic decomposition of the substrate to such an extent that the primary decompositon products are changed by dehydration from levoglucosan and other flammable products of cellulose to carbonaceous char.[16]

The generation of the phosphorous acid is easily explained as resulting
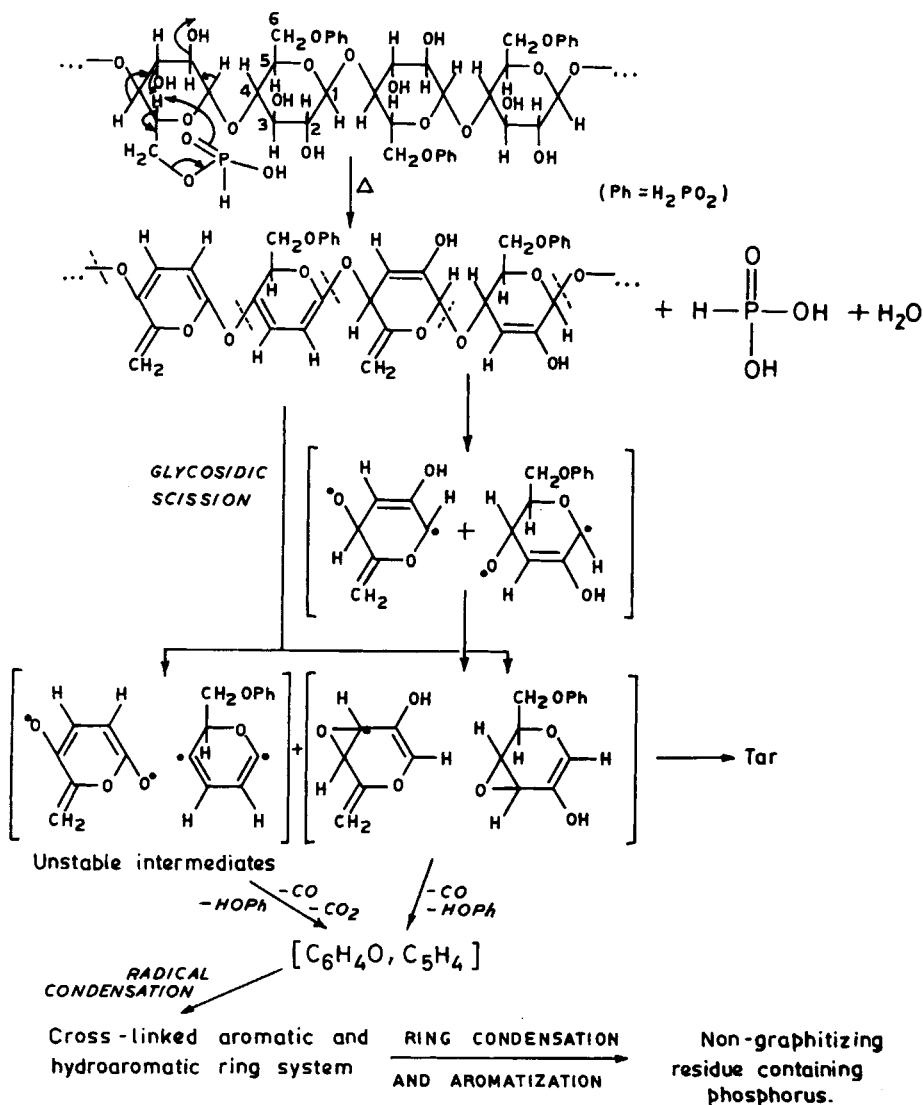
Scheme I. Thermal degradation of cellulose phosphates.

from the known thermal decomposition of the alkyl phosphorus esters to an olefin and the corresponding acid. This reaction, together with the postulated char-forming dehydration of cellulose, is depicted Scheme I. The mechanism has been discussed in detail elsewhere[17].

When strongly heated, the phosphorous acid yields polyphosphorous acid, which is more effective in catalyzing dehydration. The flame-retardant action of phosphorus compounds in cellulose proceeds by way of initial phosphorylation of the cellulose. Phosphorylated cellulose then breaks down to give water, phosphorous acid, and an unsaturated cellulose analogue and eventually char by repetition of these steps (Scheme II).
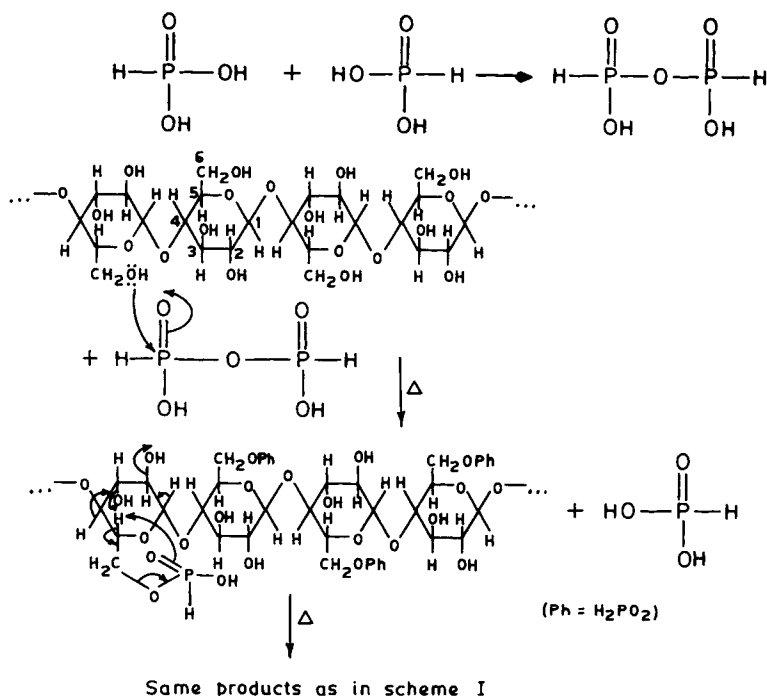
Scheme II. Thermal degradation of cellulose phosphates.

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