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Thermal and spectroscopic studies on cellulose and its organophosphorus derivatives

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Abstract

The thermal behaviour of cellulose and its organophosphorus derivatives in air has been studied by DTA, TG and DTG techniques from ambient temperature to 700°C. From the resulting data, the energies of activation and the frequency factors were calculated for various stages of thermal degradation. The IR and EPR spectra of the chars were used in elucidating the flame retardancy mechanism for the thermal degradation of cellulose-6-(1-pyrrolidinyl) phosphate (CPP).

Keywords: Cellulose, phosphorylation, degradation, thermal property, spectroscopic study.

1. Introduction

The function of flame retardant in polymers is to alter the course of decomposition in such a way that a lower percentage of flammable volatiles is produced and a correspondingly larger quantity of char is formed. Some of the most successful commercial flame retardants for cellulose have been the organophosphorus compounds[1–4]. Although the thermal degradation of cellulose and its various derivatives was extensively investigated both in air and in an inert atmosphere[5–10], no attempt has been made to study the thermal behaviour of cellulose treated with 1-pyrrolidine phosphorus oxychloride (PPOC). This paper describes the preparation of cellulose derivatives of PPOC and the kinetics of the thermal degradation of cellulose and its phosphates in air from ambient temperature to 700°C using Broido's method[11]. The composition of the charred products has been studied by IR and EPR spectra, to elucidate the mechanism of pyrolysis.

2. Materials and methods

2.1. *Materials*

The following samples were selected for the present work, (i) cellulose (Dassel, Germany), dried in vacuum over P_2O_5 at 80°C, (ii–vi) cellulose-6-(1-pyrrolidinyl) phosphate (CPP) samples, obtained by treating cellulose with PPOC at 80, 90, 100, 110 and 120 ± 0.5°C for 6 h.

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Table I
Analytical data and description of DTA curves

Sample no.		*Per cent*			*Nature of the peak*	*Peak Temp. (°C)*			*Percentage char yield at 550°C*
		N	*P*	*Cl*		*Initiation*	*Maximum*	*Termination*	
(i)	Cellulose	—	—	—	Endo	120	148	210	1.9
					Exo	210	298	371	
					Exo	371	462	471	
(ii)	Cellulose treated with PPOC at 80°C for 6 h	1.16	2.80	0.74	Endo	117	138	200	15.9
					Exo	200	272	351	
					Exo	351	459	610	
(iii)	Cellulose treated with PPOC at 90°C for 6 h	1.37	3.00	0.88	Endo	115	132	190	17.5
					Exo	190	265	349	
					Exo	349	458	605	
(iv)	Cellulose treated with PPOC at 100°C for 6 h	2.15	3.75	1.02	Endo	112	130	188	20.6
					Exo	188	262	345	
					Exo	345	452	600	
(v)	Cellulose treated with PPOC at 110°C for 6 h	2.33	4.15	1.36	Endo	110	128	185	25.3
					Exo	185	260	240	
					Exo	340	450	595	
(vi)	Cellulose treated with PPOC at 120°C for 6 h	2.73	4.25	1.52	Endo	105	125	180	26.4
					Exo	180	260	338	
					Exo	338	470	592	

2.2. *Preparation of PPOC*

This was obtained by dropwise addition of dry pyrrolidine (0.5 mol) to phosphorus oxychloride (2 mol), with constant stirring under cold conditions (<10°C). The reaction mixture was refluxed and distilled at 68°C to get PPOC.

2.3. *Preparation of CPP*

Samples (ii–vi) were prepared by treating cellulose (1.62 g, 0.01 mol) in pyridine (50 ml) with PPOC (0.03 mol) at 80, 90, 100, 110 and 120°C, respectively, for 6 h. Products obtained were filtered, rinsed with excess pyridine, washed thoroughly with water, and dried over P_2O_5 under vacuum (Scheme 1).

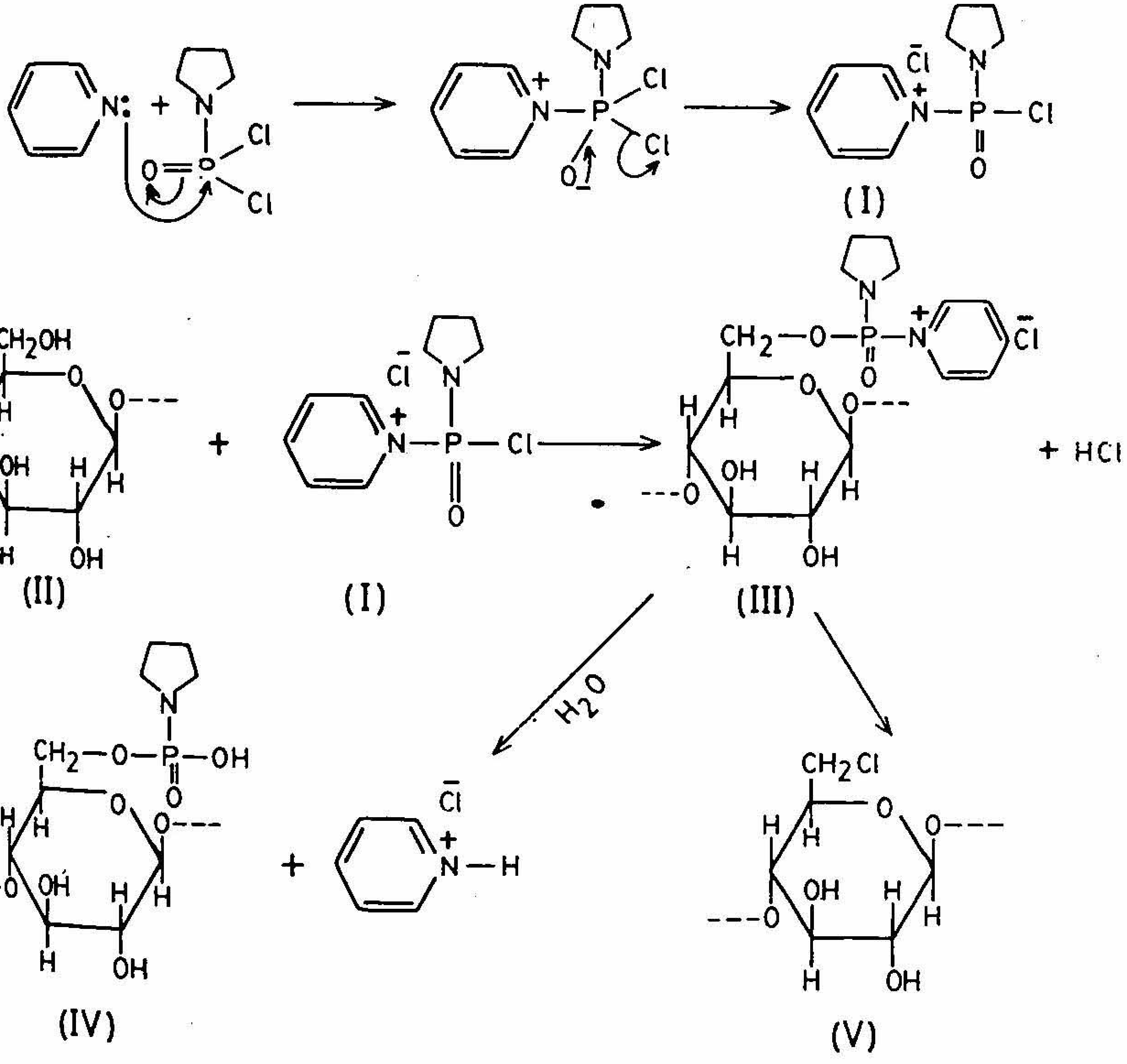
2.4. *Physical measurements*

P, Cl and N were estimated colorimetrically[12], gravimetrically[13] and by using Kjeldahl's method, respectively. The DTA, TG and DTG thermograms were obtained using an

STA-780 series derivatograph (Stanton Redcroft, London), in static air at a heating rate of 10°C min^{-1}. IR spectra of samples and their chars were recorded on a Beckman IR-20 spectrophotometer using KBr pellet technique. EPR spectra were recorded on a Varian E-112 EPR spectrophotometer operating at 9.5 GHz, using 1-1-diphenyl-2-picryl-hydrazyl signal as a standard for *g* values.

2.5. *Characterization of the samples*

Formation of CPP was confirmed by its IR spectrum and elemental analysis. Reaction of PPOC with cellulose forms CPP (IV) and chlorodeoxy cellulose (V)[14] (Scheme 1). However, the high percentage of P (Table I) indicates that predominantly CPP is formed. Owing to the method employed, the pyridinium complex is also formed in small amounts.



SCHEME 1. Formation of CPP (IV) and chlorodeoxy cellulose (V).

3. Results and discussion

3.1. *Thermal analysis*

As an illustration, DTA, TG and DTG thermograms of cellulose and CPP obtained at 80°C are shown in Figs 1 and 2, respectively. The peak temperatures for various endo- and exotherms of DTA curves are given in Table I. In the case of cellulose, endotherm is due to dehydration process followed by exotherms due to decomposition and oxidation of volatile and charred products, respectively[5, 6]. DTA thermograms of CPP samples (ii–vi) show endotherms, due to dephosphorylation, acid-catalysed dehydration and dehydrohalogenation reactions, followed by exotherms due to decomposition process leading to the formation and evaporation of the volatile products[15]. The decomposition temperatures of CPP samples (ii–vi) are found to be lower than that of cellulose and decrease with increasing percentage of P (Table I). Last exotherm appears due to the oxidation of the volatile products and charred residual matter[15, 16].

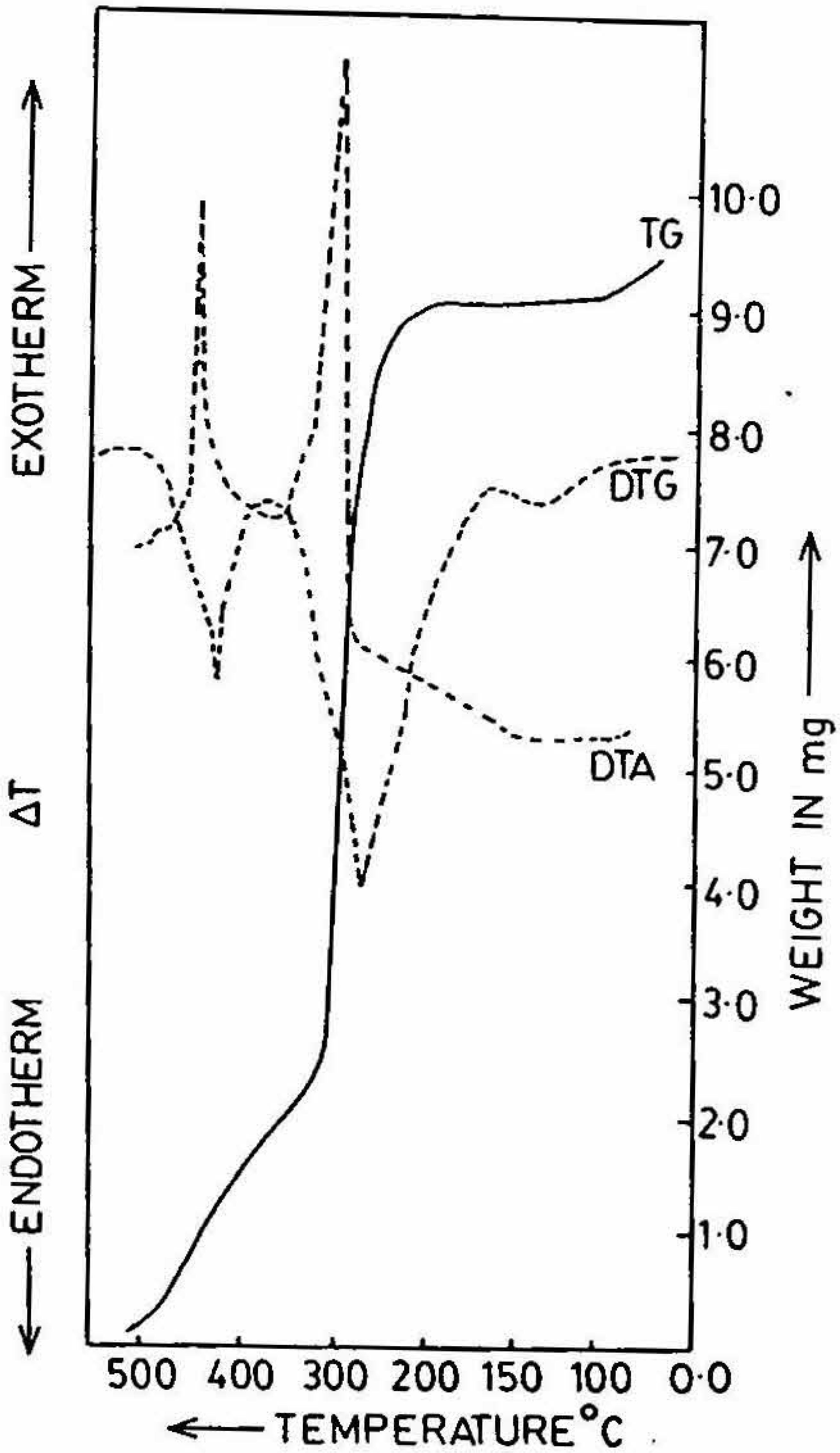


FIG. 1. TG. DTA and DTG curves of cellulose (i) in static air.

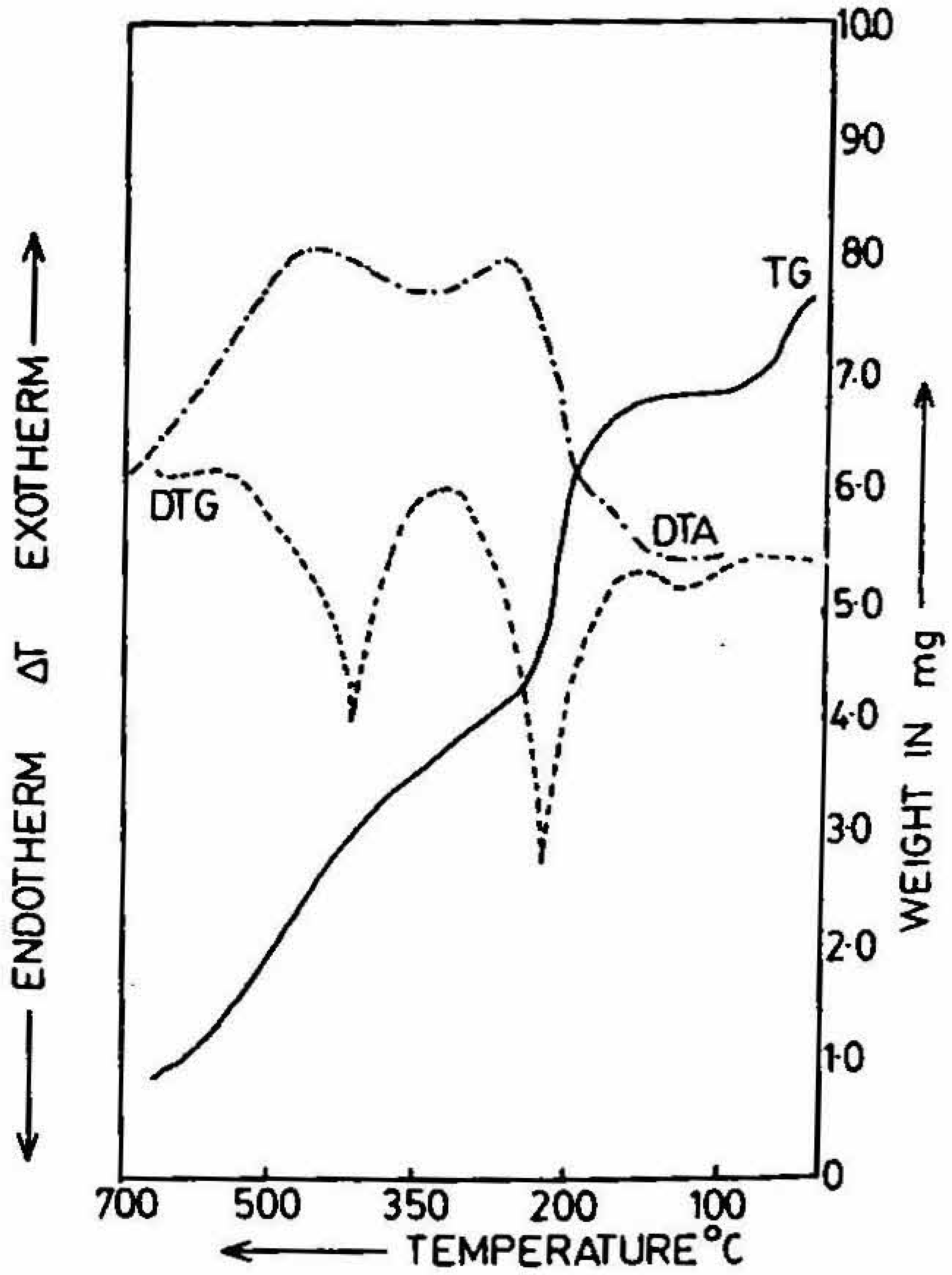


FIG. 2. TG, DTA and DTG curves of phosphorylated cellulose sample (ii) [%P = 2.80] in static air.

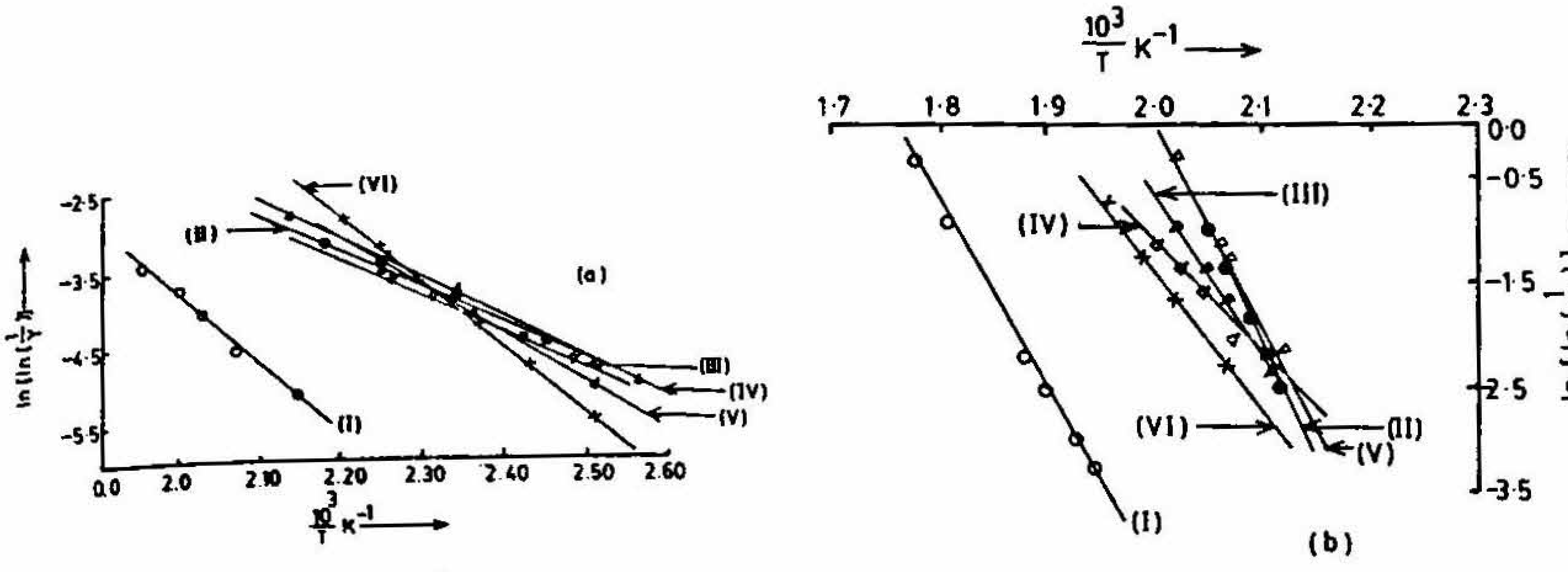


FIG. 3. Plots of ln [ln(1/y)] *vs* $\frac{10^3}{T}K^{-1}$ using Broido equation for the thermal degradation of cellulose (i) in air [o] and treated cellulose samples (ii) [•], (iii) [∇], (iv) [Δ], (v) [▲], (vi) [x], for (a) first and (b) second stages.

TG thermograms show four significant areas of weight loss termed as four stages of thermal degradation. Broido's method[11], having the following equation, is used to evaluate the kinetic parameters for each stage.

$$\ln[\ln(1/y)] = -\frac{E_a}{RT} + \ln\left[\frac{RZ}{E_a\beta}T_m^2\right]$$

where y is the fraction of number of initial molecules not yet decomposed, β, the heating rate, Z, the frequency factor and T_m, the temperature at maximum reaction rate. From the plots of ln[ln(1/y)] *vs* 1/T (Figs 3 and 4) the values of activation energies (E_a) and frequency factors (Z) have been calculated (Table II).

During the first stage of thermal degradation, the per cent weight loss occurring in CPP samples (ii–vi) is in the range 3.6–6.9. In DTA curves, this stage corresponds to

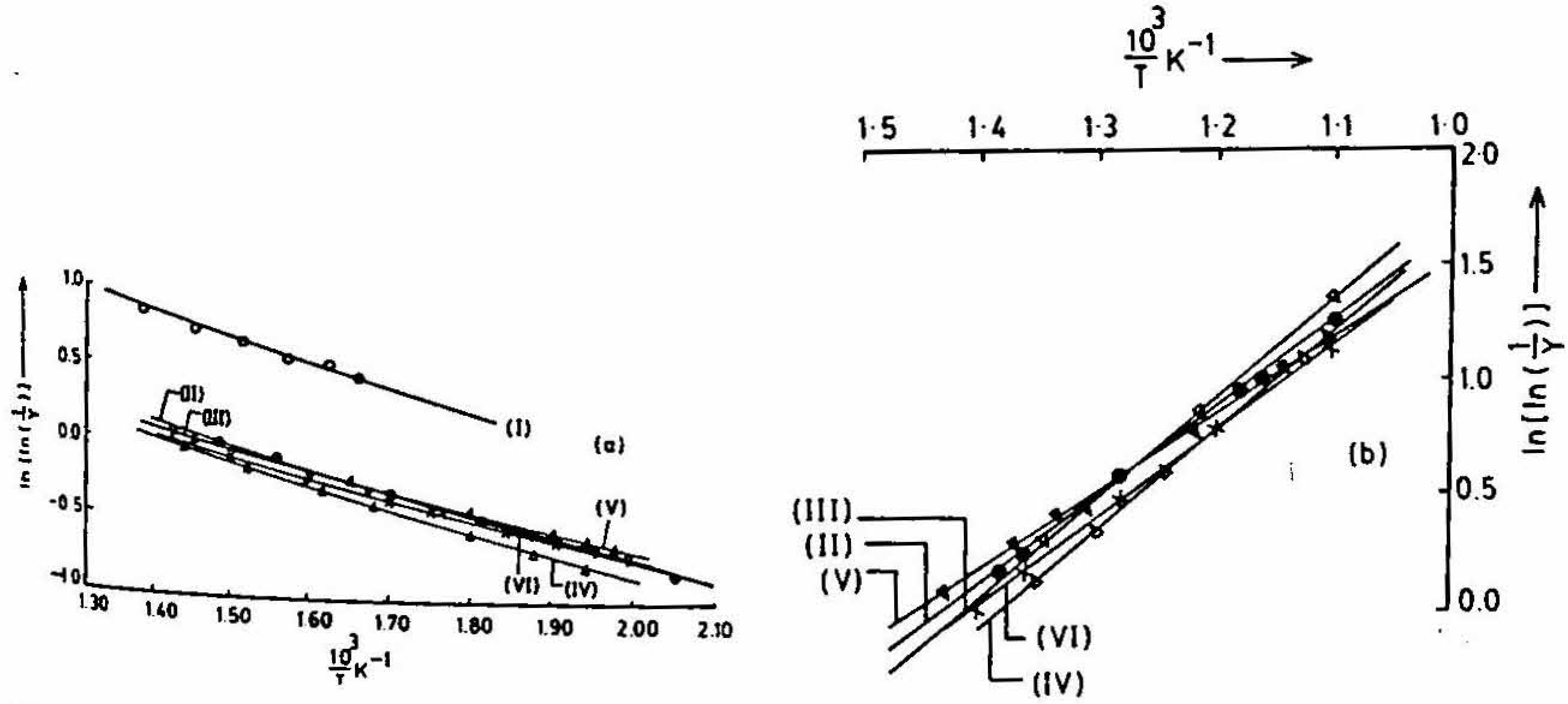


FIG. 4. Plots of ln [ln(1/y)] *vs* $\frac{10^3}{T}K^{-1}$ using Broido equation for the thermal degradation of cellulose (i) in air [o] and treated cellulose samples (ii) [•], (iii) [∇], (iv) [Δ], (v) [▲], (vi) [x], for (a) third and (b) fourth stages.

Table II
Activation energies and frequency factors for all stages of thermal degradation of cellulose and cellulose derivatives (Broido method)

Sample no.	*Compound*	*Stage*	*DTG max. (°C)*	*Temp. range*	E_a *(KJ mol⁻¹)*	$Z(s^{-1})$
(i)	Cellulose	1st	—	141–240	74.83	9.86×10^{10}
		2nd	279	240–310	160.74	1.11×10^{30}
		3rd	—	310–340	12.15	6.53×10^{2}
		4th	427	340–485	—	-
(ii)	Cellulose treated with PPOC at 80°C for 6 h	1st	—	120–198	37.23	8.88×10^{6}
		2nd	224	198–253	125.63	7.28×10^{27}
		3rd	—	253–403	10.14	2.86×10^{-2}
		4th	424	403–600	42.63	6.09×10^{7}
(iii)	Cellulose treated with PPOC at 90°C for 6 h	1st	—	112–190	38.74	1.57×10^{7}
		2nd	222	190–243	123.31	1.46×10^{23}
		3rd	—	243–400	10.02	2.29×10^{-2}
		4th	423	400–640	38.12	1.27×10^{7}
(iv)	Cellulose treated with PPOC at 100°C for 6 h	1st	—	110–186	40.23	2.35×10^{7}
		2nd	213	186–240	120.73	1.44×10^{21}
		3rd	—	240–427	9.72	1.63×10^{-2}
		4th	420	427–650	34.05	5.85×10^{6}
(v)	Cellulose treated with PPOC at 110°C for 6 h	1st	—	108–180	42.83	4.96×10^{7}
		2nd	206	180–238	118.62	1.18×10^{19}
		3rd	—	238–415	8.63	7.70×10^{-3}
		4th	418	415–660	30.12	2.13×10^{6}
(vi)	Cellulose treated with PPOC at 120°C for 6 h	1st	—	100–175	46.17	7.00×10^{7}
		2nd	202	175–233	115.81	2.74×10^{17}
		3rd	—	233–410	7.37	5.64×10^{-3}
		4th	416	410–666	27.07	1.08×10^{5}

the respective endotherms due to dephosphorylation, dehydrohalogenation and acid-catalysed dehydration, while for cellulose this is mainly due to dehydration[15]. The second stage of thermal degradation is due to the decomposition process and the major weight loss occurs in this stage. Cellulose loses 66.7% weight, whereas CPP samples (ii–vi) lose 22.0–28.8%. These weight losses correspond to the first exotherms in the DTA curves and are also supported by first DTG peaks (Table II). Third stage of thermal degradation is attributed to the oxidation of volatile products of decomposition and charred residues[15, 16]. In this stage, the per cent weight loss for CPP samples (ii–vi) is in the range 16.2–25.0 and this corresponds to the second exotherms in the DTA curves. The fourth stage is more predominant in CPP samples and is attributed to oxidation, crosslinking and aromatisation of char[17–20]. This stage corresponds to the last exotherm in DTA curves and is also supported by second DTG peaks. From Table II, it is clear that activation energies of CPP samples (ii–vi) are lower than that of cellulose for all the stages of thermal degradation.

The char yields for cellulose (i) and CPP samples (ii–vi) were determined from the TG thermograms at 550°C and are given in Table I. CPP samples give more char yields than cellulose, indicating a reduction in the amounts of low molecular weight flammable

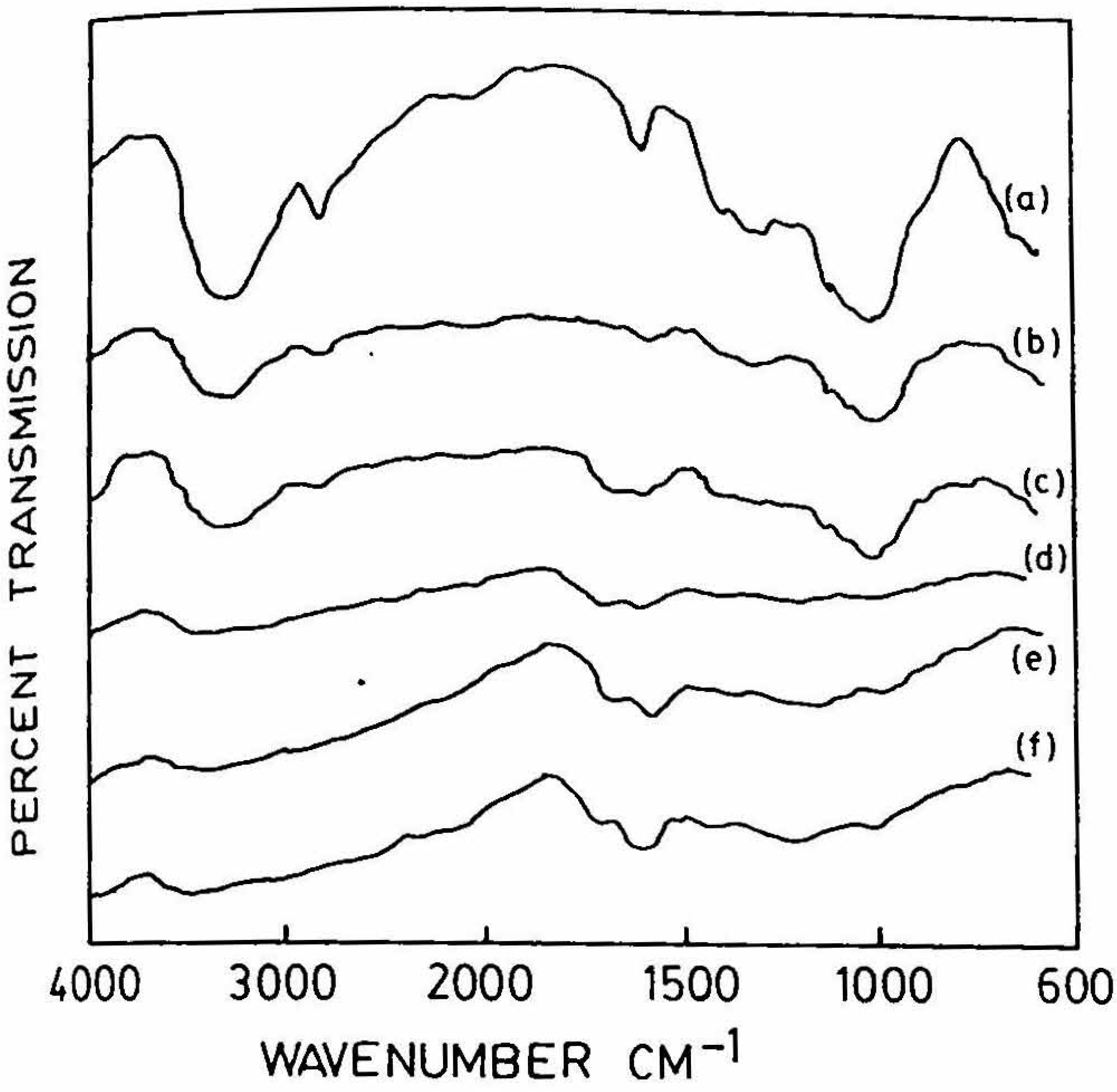


Fig. 5. IR spectra of (a) phosphorylated cellulose sample and (b–f) chars of phosphorylated cellulose sample at 200, 225, 250, 300 and 350°C, respectively.

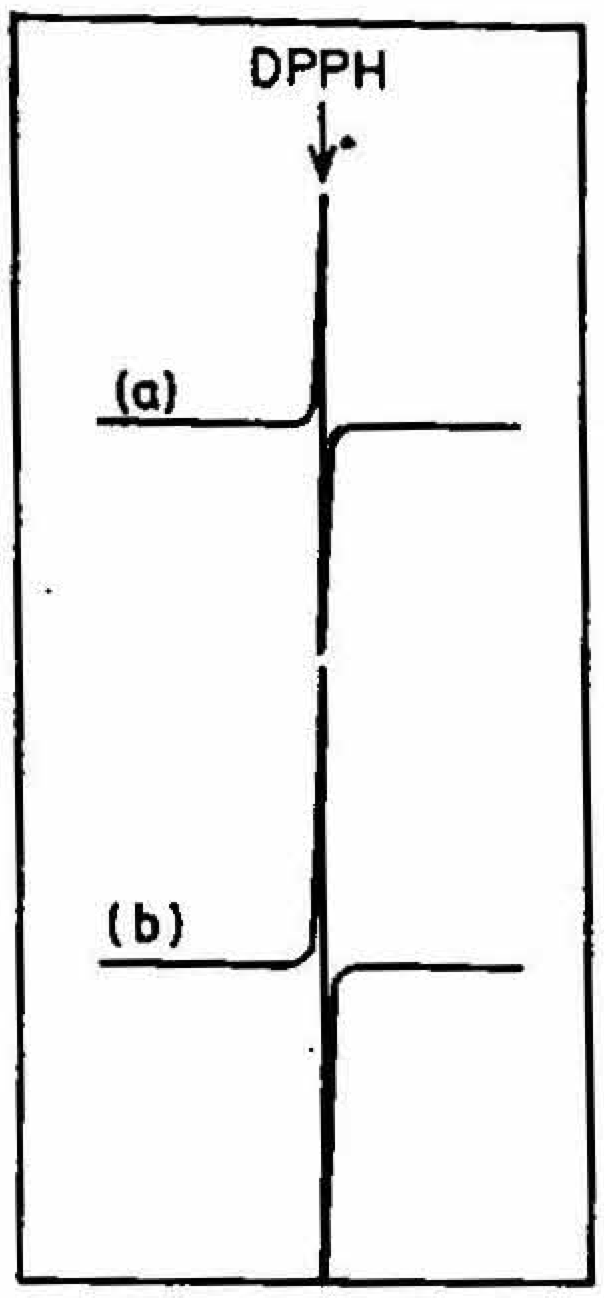
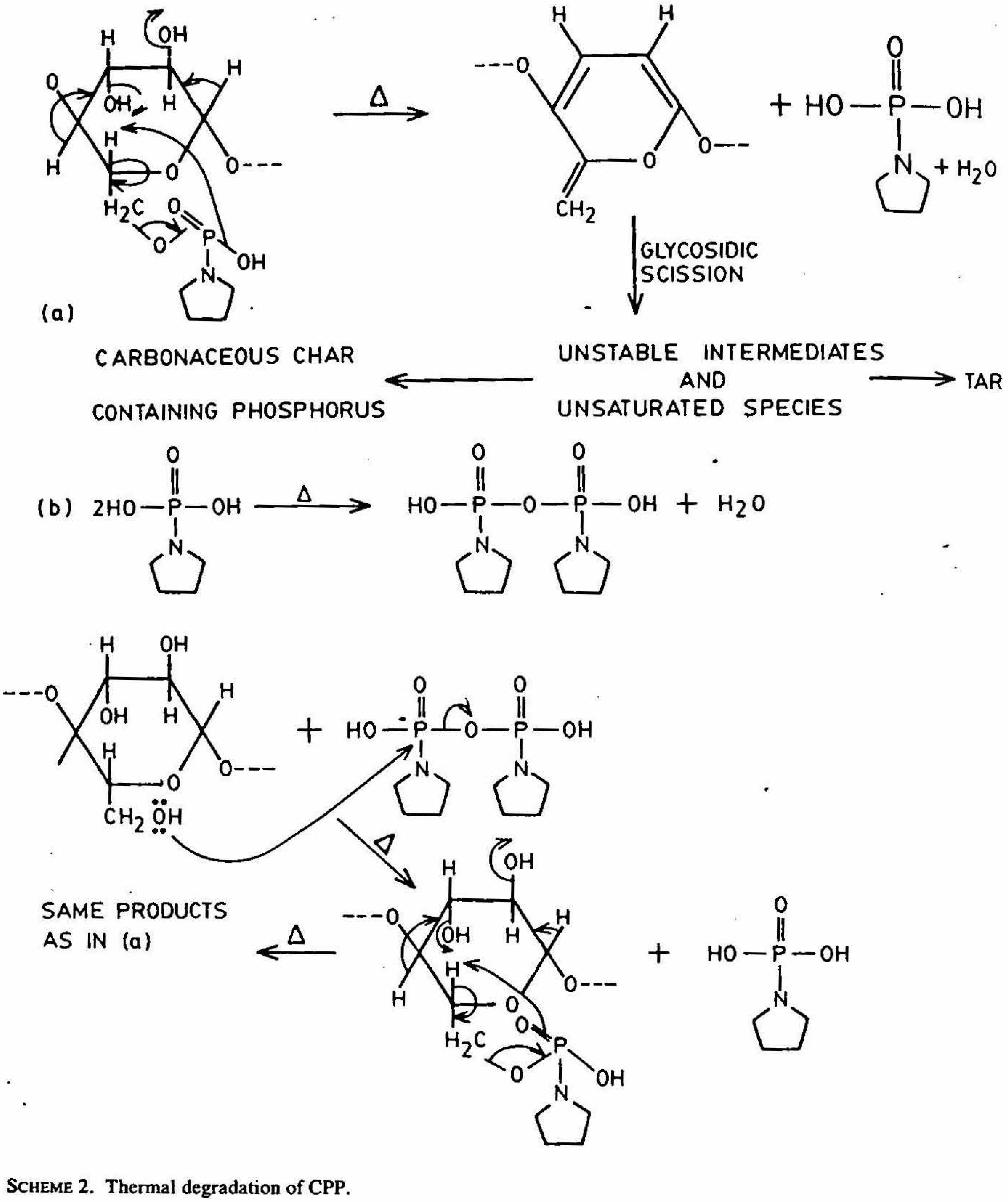


Fig. 6. EPR spectra of chars of (a) cellulose and (b) CPP.

gases. From the above studies, it may be concluded that PPOC is a good flame retardant for cellulose, as it lowers the decomposition temperature, reduces the percentage of flammable volatiles and correspondingly increases char yield[17–19].

3.2. *IR and EPR studies of chars*

The IR spectra of chars of CPP sample (iii) obtained at different temperatures (up to 350°C) were recorded (Fig. 5). At 200°C, the intensities of peaks at 3360 (O–H str.), 1380, 1330 (O–H bending) and 660 cm^{-1} (C–Cl str.) decrease and bands at 1635 (absorbed H_2O), 1240 cm^{-1}($P=O$ str.) vanish and new band at 1620 cm^{-1} ($C=C$) emerges. These observations show that dephosphorylation, dehydration and dehydrohalogenation reactions take place in the initial stages of thermal degradation[5,6]. At 225°C, the bands at 2880 (C–H str.), 1160 (C–O–C str.), 1055, 1020 cm^{-1} (skeleton vibrations involving C–O str.) show decrease in intensity and a new low intense band at 1690 cm^{-1} ($C=O$ str.) appears, which indicates that decomposition of CPP takes place[6]. At 300°C, the bands due to cellulose disappear, and new bands at 1250 ($P=O$ str.), 1000 cm^{-1} (P–O–P str.) appear due to polymerisation of pyrrolidinyl phosphoric acid[5, 6, 21]. At 350°C,



SCHEME 2. Thermal degradation of CPP.

intense bands at 1700 (C = O), 1590 (C = C) and 1240 cm^{-1} (P = O) remain, suggesting the formation of compounds having these groups[4–6, 22].

EPR spectra of chars of cellulose and CPP obtained at 250°C were recorded in air (Fig. 6). The relative intensities of EPR spectral lines were computed by Wertz and

Bolton method[23]. The relative intensities thus calculated and hence the relative concentration of free radicals[24] in the chars of cellulose and CPP are found to be in the ratio of 1.0 : 1.3. It is obvious that there is formation of trapped free radicals to a small extent during the decomposition of cellulose and CPP[21, 25]. As the number of free radicals formed for CPP is much smaller in comparison to those compounds having free radical mechanism, the latter is not dominant in the degradation of CPP[26, 27].

3.3. *Mechanism of thermal degradation of CPP*

Thermal degradation of CPP commences with the generation of pyrrolidinyl phosphoric acid which alters the decomposition of the cellulose backbone to such an extent that the primary decomposition route favours the formation of carbonaceous char[5, 28]. At higher temperatures, pyrrolidinyl phosphoric acid polymerises, which is more effective in catalysing the dehydration[4–7] (Scheme 2). Chlorodeoxy cellulose which is formed as the side product during the formation of CPP also affects the mechanism of degradation by the release of HCl[5]. A similar mechanism has been suggested by Shafizadeh *et al.*[29]

Acknowledgement

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