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Study on the thermal degradation of cotton cellulose ammonium phosphate and its metal complexes ☆

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Abstract

The thermal degradation of cellulose, and of cellulose ammonium phosphorylate and its metal complex products was studied by thermal analysis, infrared spectroscopy, elemental analysis and chemical analysis. The kinetic parameters were obtained using the equation of Brodio. The values of activation energies for decomposition of the cellulose, cellulose ammonium phosphorylate and its metal complexes were calculated. Experimental data for cellulose ammonium phosphorylate and its metal complexes show that for these samples there is a decrease in the activation energy for decomposition and an increase in char yield compared with pure cellulose.

Keywords: Cotton cellulose ammonium phosphate; Degradation; DTA; Flame retardant; Pyrolysis; TA

1. Introduction

The effects of fire retardants on both smoke generation and the toxicity of combustion products have become of particular importance as fire-retardant compositions have been reported to produce denser smoke than untreated compositions [1,2].

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In previous papers [3,4], compounds of transition metals have been found to be the most effective smoke retarders.

However, to date complexes of cellulose ammonium phosphate with transition metals such as lanthanum, ytterbium and holmium have not been reported.

In this paper, coordinate complexes of ammonium phosphate with various transition metal ions were prepared and their thermal properties investigated. In order to understand the mechanism of the thermal degradation of cellulose ammonium phosphate and its metal complexes, infrared (IR) spectroscopy, thermal analysis and elemental analysis have been carried out and the phosphorus and chlorine contents in the samples have been determined by chemical analysis. This study shows that the combustibility of the treated cotton cellulose is reduced with the introduction of the elements P, Cl and N. Experimental data for cellulose ammonium phosphate and its metal complexes show that for these samples there is a decrease in the activation energy for decomposition and an increase in char yield compared with pure cellulose.

2. Experimental

2.1. Material

The following samples of cellulose, cellulose ammonium phosphate and its metal complexes were selected for the present work. Sample (i) was cotton cellulose (Hebei Province Dingzhou Sanitary Plant, China), dried in vacuo at 333 K for 1 h. Sample (ii), cellulose ammonium phosphate was obtained by treating dried cellulose (4.86 g) and carbamide (7.20 g) with phosphorus oxychloride (6.89 g) in pyridine at 388 K for 24 h. The product was filtered, washed thoroughly with water and dried in vacuo. Samples (iii)-(xi) were prepared by treating the cellulose phosphate with 5% copper sulphate, zinc sulphate, cobalt sulphate, iron sulphate, cerium nitrate, lanthanum nitrate, ytterbium nitrate and holmium nitrate, respectively. Each reaction mixture was stirred at ambient temperature for 72 h.

2.2. Thermal analysis

The differential thermal analysis (DTA) and thermogravimetry (TG) were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). The DTA and TG curves were run under static air at a scanning rate of 10 K min^{-1}. Calcined alumina was taken as the reference material.

2.3. Infrared spectrometry

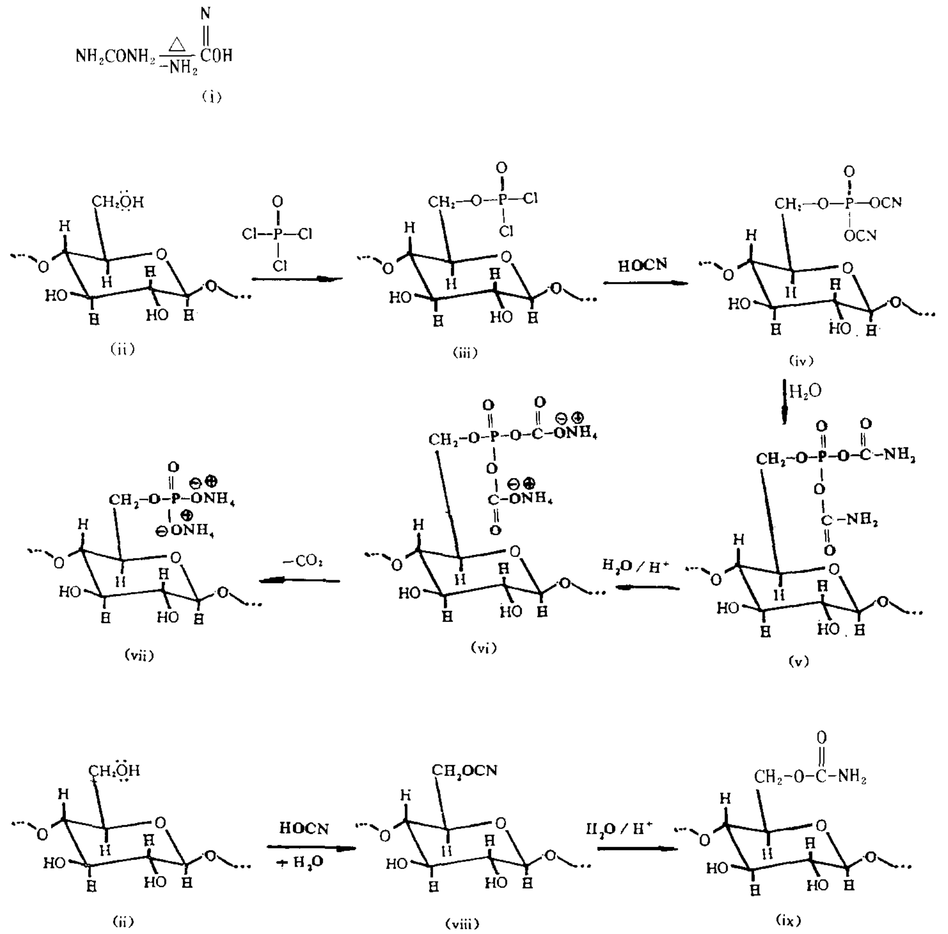
For the IR studies (Hitachi 260-50 IR spectrometer, Japan), the residue of phosphorylated cellulose was analyzed by the KBr technique. The residual samples were prepared by heating them in a DTA cell. The heating temperatures were 298, 373, 423, 473 and 573 K respectively.

2.4. Elemental analysis

The elemental analysis was carried out using a PE-2400 Elemental Analyzer (USA). The percentages of C and H were obtained from the elemental analyzer by chemical analysis.

2.5. Characterization of cellulose ammonium phosphate

Cellulose, on reaction with phosphorus oxychloride and urea in pyridine followed by hydrolysis with water, forms cellulose ammonium phosphate as shown in Scheme 1. During this reaction cellulose carbamate is also formed as a side product, as evidenced by a peak at 1720 cm^{-1} due to C–O groups in the IR spectrum [5].



Scheme 1. Reaction of cellulose with phosphorus oxychloride and urea in pyridine, followed by hydrolysis with water, forming cellulose ammonium phosphate.

Table 1
Analytical data for cellulose, cellulose ammonium phosphate and metal complexes of cellulose ammonium phosphate

Sample no.	Compound	Color	P/%	Cl/%	Char yield/ wt%	C:H
i	Cellulose	White	–	–	0.49	6.4
ii	Cellulose ammonium phosphate (CAP)	White	4.92	1.14	4.08	6.1
iii	Cu(II) complex of CAP	Light green	2.93	0.02	14.2	6.0
iv	Zn(II) complex of CAP	Brown	1.76	0.5	13.7	6.2
v	Fe(II) complex of CAP	Yellow	3.37	0.54	18.6	6.4
vi	Co(II) complex of CAP	Brown	3.97	0.19	14.6	5.7
vii	Cr(III) complex of CAP	Green	3.41	1.7	13.8	6.1
viii	Ce(III) complex of CAP	White	1.22	0.11	19.5	6.1
ix	La(III) complex of CAP	White	1.96	0.08	18.6	5.2
x	Y(III) complex of CAP	White	2.75	0.14	19.6	6.4
xi	Ho(III) complex of CAP	White	1.97	–	20.5	6.1

3. Results and discussion

The percentages of phosphorus in samples (ii)–(xi) are given in Table 1. The data show that the amount of phosphorus in sample (ii) is higher than in the metal-containing products (iii)–(xi). When heated strongly, phosphorus acid yields polyphosphorus acid, which is more effective in catalyzing dehydration and charring. This is the main reason why all phorphorus-containing samples are effective flame retardants.

From Table 1, it is evident that the Cl content in treated cellulose is higher than that in cellulose. On pyrolysis, the Cl-containing cellulose samples release volatile HCl, which can catch free radicals. This is why chlorine-containing cellulose samples show good flame retardancy.

The residual char from pyrolysis of samples (i)–(xi) is given in Table 1. The data show that the char yields of samples (iii)–(ix) are more than that of the original cellulose, especially in the case of samples (iii)–(xi) which were treated with metallic cations. This indicates that the combustibility of the cellulose ammonium phosphate treated with metal cations is reduced, especially those treated with Ce^{3+} and Ho^{3+}.

Thermal analysis of cellulose in air is shown in Fig. 1. Two exothermic peaks appear at 638 and 734 K. The first exotherm is due to the dehydration, decomposition and rearrangement of the products. The second exotherm is due to the cross-bridging and aromatic cyclization of charred residue. From Fig. 2, the first exotherm at 589, 582, 613, 550, 590, 578, 611, 606, 592 and 585 K for samples (ii)–(xi), respectively, is due to the dehydration, dehydrohalogenation and dephosphorylation. This is supported by the weight loss indicated by the TG curve. The

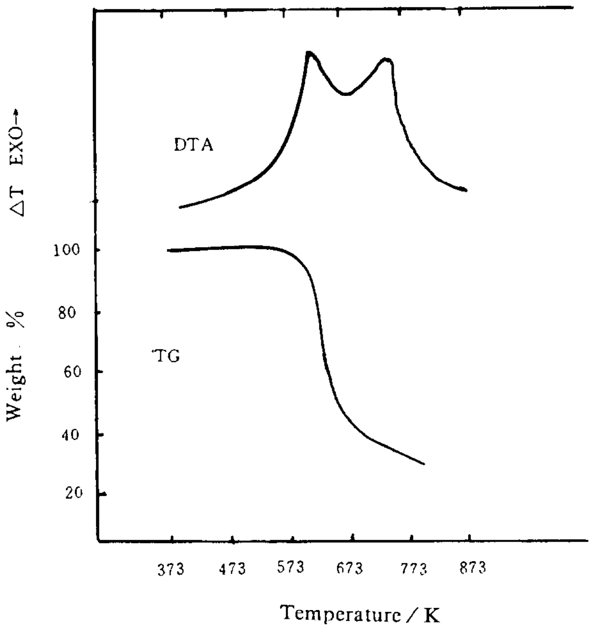


Fig. 1. The thermal analysis of cellulose in air.

second exotherm at 734, 786, 772, 695, 762, 709, 767 and 759 K is due to the oxidation and aromatic cyclization of the charred residue, and the decomposition of the polyphosphorus acid [6].

The kinetic parameters for the various stages of pyrolysis of samples (i)–(xi) were determined using the methods described by Broido [7]. The Broido method equation can be written as

$$\ln(\ln 1/y) = -\frac{E}{R}\frac{1}{T} + \ln\left(\frac{R}{E}\frac{Z}{\beta}T^2\right) \qquad (1)$$

where y is the fraction of initial molecules not yet decomposed, T the temperature of maximum reaction velocity, β the rate of heating (K min^{-1}), Z the frequency factor and E the activation energy.

Using the Broido method, plots of $\ln(\ln 1/y)$ versus $1/T$ for various stages of pyrolysis are given in Fig. 3. The values of the energies of activation E can be determined from the slopes. Table 2 presents activation energies E for the various stages for samples (i)–(xi). For the two stages of pyrolysis, the energies of activation (Table 2) for CAP and its metal complexes samples (ii)–(xi) are low compared to pure cellulose. The reason is that flame retardants catalyze the decomposition reaction [8].

Fig. 4 shows the changes in the IR spectrum of pure cellulose in air medium. When the temperature is raised, the band at 3200 cm^{-1} is decreased, the band at 2900 cm^{-1} (C–H) disappears and a new band appears at 1640 cm^{-1} (C=C).

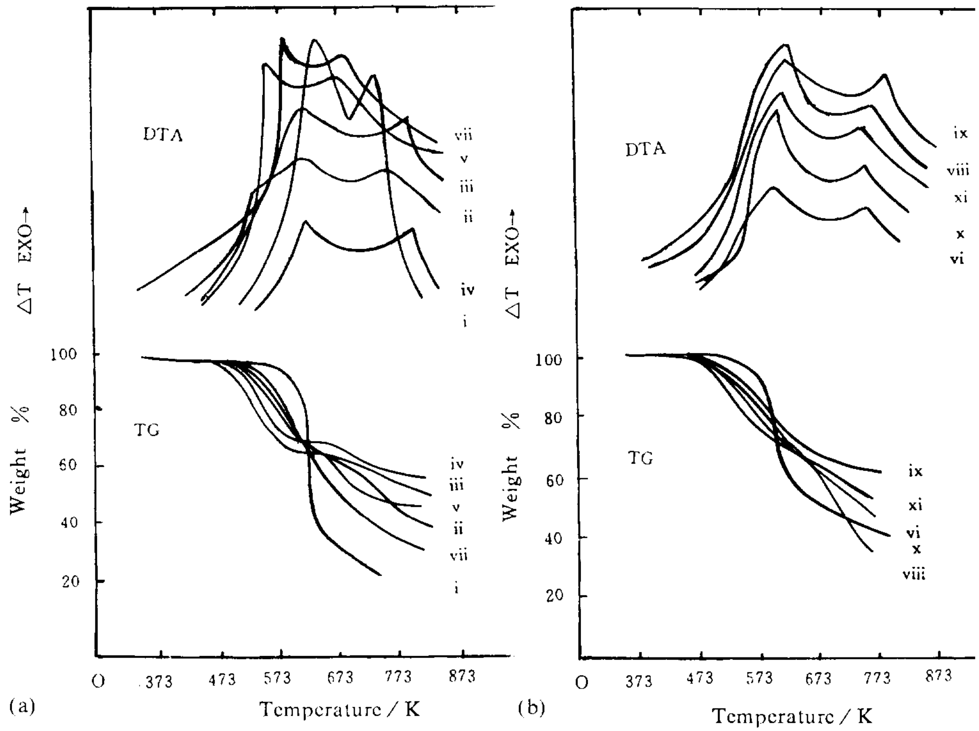


Fig. 2. The thermal analysis of samples (ii)–(xi) in air.

Table 2
Activation energies for the first and second stage of thermal degradation of cellulose, cellulose ammonium phosphate and metal complexes of cellulose ammonium phosphate in air using the Broido method

Sample no.	Compound	First stage		Second stage	
		Exotherm/K	E/(kJ mol^{-1})	Exotherm/K	E/(kJ mol^{-1})
i	Cellulose	638	227.8	734	20.1
ii	Cellulose ammonium phosphate (CAP)	589	169.4	734	20.5
iii	Cu(II) complex of CAP	582	50.8	786	11.4
iv	Zn(II) complex of CAP	613	71.6	772	13.9
v	Fe(II) complex of CAP	550	218.5	695	16.6
vi	Co(II) complex of CAP	590	131	762	16.5
vii	Cr(III) complex of CAP	578	192.6	709	29.1
viii	Ce(III) complex of CAP	611	40.5	767	16.5
ix	La(III) complex of CAP	606	73.3	767	20.8
x	Y(III) complex of CAP	592	152.1	769	20.4
xi	Ho(III) complex of CAP	585	112.6	759	15.0

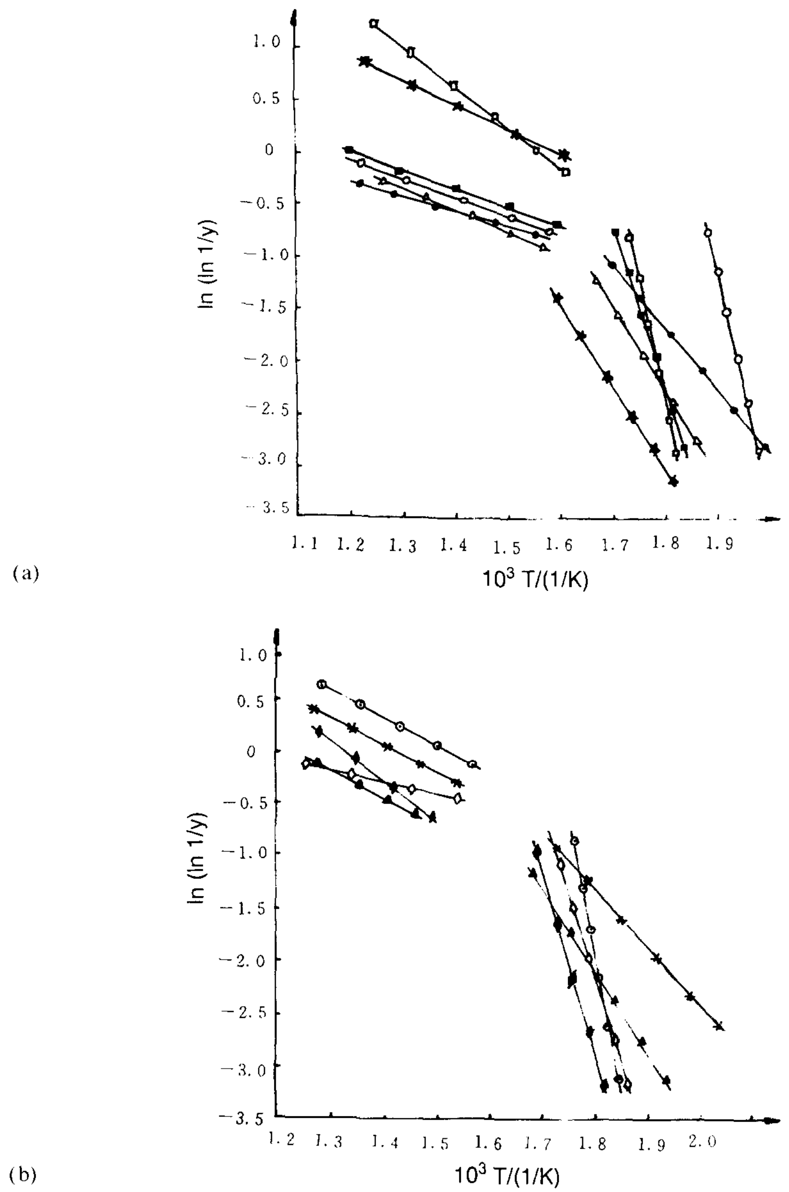


Fig. 3. Broido's plots for various stages of pyrolysis: ✱, cellulose; ○, CAP; ●, Cu(II); △, Zn(II); ■, Co(II); □, Cr(III); ⊙, Fe(II); *, Ce(III); ▲, La(III); ◆, Y(III); ◇, Ho(III).

From Fig. 5, the changes in the IR spectrum of cellulose ammonium phosphate in air medium can be described. At 423 K, bands at 3400 and 1380 cm^{-1} decrease and new bands at 1630 and 1000 cm^{-1} (C=C) appear. At 473 K, new bands at 1720 cm^{-1} (C=O) and 1250 cm^{-1} (P=O) appear, indicating that skeletal rearrangement

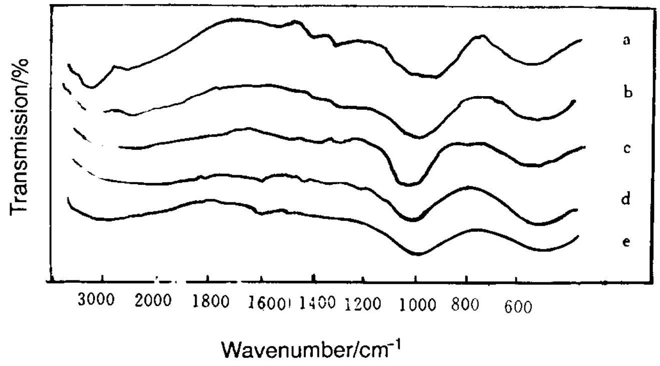


Fig. 4. The changes on heating in air of the IR spectrum of cellulose: a, pure cellulose; b–e, chars of cellulose at 373, 423, 473 and 573 K, respectively.

has occurred. The band at 1100 cm^{-1} is due to PO_4^{3-}. At 573 and 673 K, the absorption bands at 1720 and 1100 cm^{-1} (PO_4^{3-}) and at 1000 cm^{-1} (C=C) remain. At these temperatures, the absorption band at 1630 cm^{-1} is shifted to 1600 cm^{-1} (due to conjugated C=C).

The changes in the IR spectrum of Cu(II) complex of CAP (Fig. 6) are similar to those of CAP.

As the temperature is increased, the disappearence of the band at 2900 cm^{-1} is due to dehydration, dephosphorylation and dehydrochlorination. The appearance of the bands at 1720 and 1100 cm^{-1} indicates the formation of C=O and $M_3^{2+}(PO_4)_2^{3-}$ (M is the metal cation).

Due to the presence of chlorine atoms in samples (ii)–(xi), pyrolysis of these compounds releases volatile HCl, which can capture the free radical of OH and produce a large quantity of non-flammable gases, separating the cellulose from air. This is the reason why chlorine-containing CAP and its metal complexes are effective flame retardants.

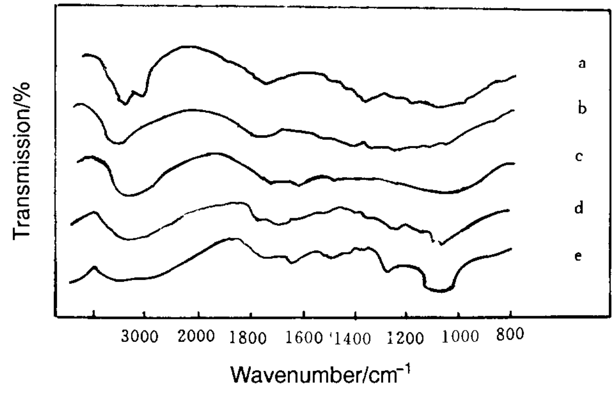


Fig. 5. The changes on heating in air of the IR spectrum of cellulose ammonium phosphate: a, CAP; b–e, chars of CAP at 373, 423, 473 and 573 K, respectively.

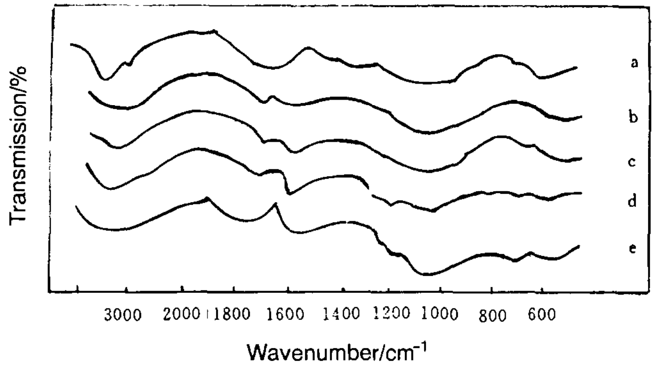


Fig. 6. The changes on heating in air of the IR spectrum of the Cu(II) complex of CAP: a, Cu(II) complex of CAP; b–e, Cu(II) complexes of CAP at 373, 423, 473 and 573 K, respectively.

When heated, samples (ii)–(xi) yield polyphosphorus acid or phosphoric anhydride, which is more effective in catalyzing dehydration and charring to eliminate or reduce the flammable gases produced. In addition, pyrolysis of phosphoric anhydride forms a glass-like melt which covers the surface of the samples. This encourages the formation of non-flammable gases such as carbon dioxide. Hence, the combustibility of the cotton cellulose is reduced.

Because the flame retardancy (or its decomposition product) is more effective in catalyzing the thermal decomposition, both the energies of activation for samples (ii)–(xi) and the decomposition temperature are much lower as compared to pure cellulose.

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