Thermochimica Acta, 43 (1981) 213—219
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

PYROLYSIS AND COMBUSTION OF α-CELLULOSE: EFFECT OF DIHYDRAZINIUM PHOSPHATE $(N_2H_5)_2HPO_4$ *

K.C. PATIL, J.P. VITTAL and C.C. PATEL

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012 (India)

(Received 7 July 1980)

ABSTRACT

A strip of Whatman filter paper (α-cellulose) dipped in an aqueous solution of dihydrazinium phosphate, $(N_2H_5)_2HPO_4$(DHP), and dried, carbonized without flame when ignited. The observed flame retardancy of DHP on α-cellulose has been studied using TG, DTA and mass spectrometry. Dihydrazinium phosphate appears to catalyze the dehydration of α-cellulose, minimizing the depolymerization which produces flammable tars, with the formation of water and char. Flame retardancy of DHP is compared with that of diammonium phosphate and phosphoric acid.

INTRODUCTION

Phosphorus-containing compounds are well known as flame retardants of cellulose and cellulosic polymers, and the flame retardant properties of ammonium phosphates were investigated as early as 1786 [1]. Since wood and fabric are cellulosic materials, much attention has been given to the study of flame retardants of cellulose [2]. The most effective flame retardants are the salts of phosphoric acid with weak bases, e.g. $NH_4H_2PO_4$, $(NH_4)_2HPO_4$. However, the salts of phosphoric acid with strong bases like sodium hydroxide, e.g. NaH_2PO_4, Na_2HPO_4, are not good flame retardants [3]. Since hydrazine is a weaker base than ammonia, it was thought interesting to study the flame retardant properties of hydrazinium phosphates, $N_2H_5H_2PO_4$ and $(N_2H_5)_2$-HPO_4. The flame retardant property of $N_2H_5H_2PO_4$ on α-cellulose has already been studied [4]. Presently we report the effect of $(N_2H_5)_2HPO_4$ (DHP) on the pyrolysis and combustion of cellulose (Whatman filter paper). For this purpose we have made use of thermal analysis techniques such as thermogravimetry (TG) and differential thermal analysis (DTA) and mass spectrometry. The flame retardant properties of DHP have been compared with those of diammonium phosphate and phosphoric acid.

---

* This paper was presented at the Second National Symposium on Thermal Analysis held at Bhabha Atomic Research Centre, Trombay, Bombay, 10—11 Jan. 1980.

EXPERIMENTAL

Dihydrazinium phosphate $(N_2H_5)_2HPO_4$ (DHP) was prepared by the reaction of stoichiometric quantities of diammonium phosphate, $(NH_4)_2HPO_4$, with hydrazine hydrate by the method described earlier [5] for the preparation of hydrazinium salts. The product was characterized by chemical analysis (% hydrazine observed 39.58, calcd. 39.54; % phosphate observed 60.12, calcd. 58.69) and IR spectra ($\nu_{N—N}$ 980 cm^{-1}).

$$(NH_4)_2HPO_4(s) + 2\ N_2H_4H_2O(l) \rightarrow (N_2H_5)_2HPO_4(s) + 2\ H_2O(g) + 2\ NH_3(g) \qquad (1)$$

Whatman filter paper No. 42 was used as cellulose. The ash content was 0.01%. Same weight of the cellulose was treated with the same volume of aqueous solutions of DHP of known concentration (2, 5 and 10%) for 2 min and air-dried at room temperature (27°C) for 12 h so that the amount of DHP adsorbed in the cellulose was proportional to the concentration of the solution used. For the preparation of DHP, DAP and phosphoric acid treated cellulose samples containing the same percentage of phosphorus, the following procedure was adopted. First, the cellulose was treated with phosphoric acid and air-dried at room temperature. The phosphorus content was estimated by the method of Fiske and Subbarow [6]. Cellulose samples containing almost the same percentage of phosphorus for DHP and DAP were also prepared by a similar method (1.90 ± 0.20% P). The percentage of nitrogen was calculated on the basis of percentage of phosphorus in DHP and DAP.

Thermogravimetric analysis (TG) of the DHP treated and untreated cellulose samples was carried out using a Stanton-Redcroft TG-750 thermobalance. About 8 mg of the samples were used for each experiment. A heating rate of 5°C min^{-1} was employed.

Differential thermal analysis (DTA) of all the samples was carried out using the automatic recording DTA-02 Universal Instrument manufactured by Franz-Wagner Industrielle elektronik of G.D.R. A heating rate of 7°C min^{-1} was employed. About 24 mg of the samples were used for DTA. Both TG and DTA experiments were carried out in air, and platinum cups were used as sample holders in both cases.

Mass spectrometric analysis was carried out for cellulose samples treated with phosphoric acid, DAP and DHP using an AEI MS-10 model instrument. Approximately 2—3 mg of cellulose samples were pyrolyzed at 500 ± 5°C in vacuum and the products were analyzed.

RESULTS

A strip of Whatman filter paper (α-cellulose) dipped in an aqueous solution of DHP and dried, carbonized without flame when ignited. This observation is similar to that for $N_2H_5H_2PO_4$ [4] and Takayuki and Motoji's [7] mixture. The DTA and TG curves of cellulose and DHP treated cellulose are shown in Figs. 1 and 2, respectively. The DTA of cellulose exhibits a large

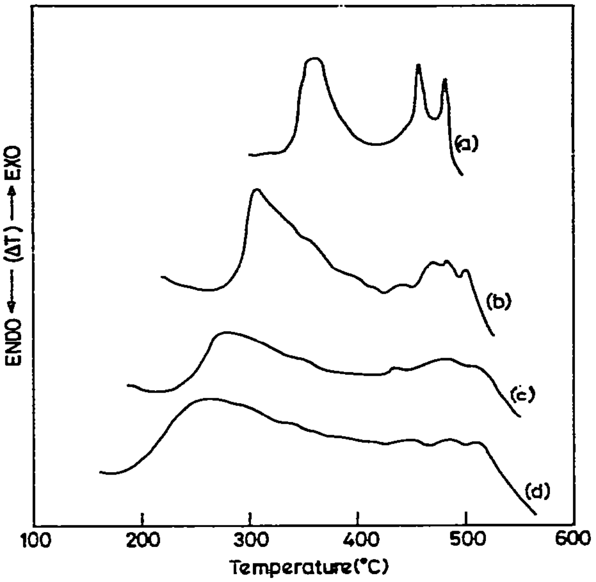

Fig. 1. DTA curves (in air) of cellulose untreated and treated with $(N_2H_5)_2HPO_4$. (a) Untreated; (b) 2% DHP treated; (c) 5% DHP treated; (d) 10% DHP treated.

exotherm at 377°C and two small exotherms at 460 and 488°C. The 2% DHP treated cellulose exhibits the first exotherm at a lower temperature (300°C). The lowering is maximum in the case of 10% DHP treated cellulose, i.e. from 377 to 266°C. However, the last two exotherms are shifted to

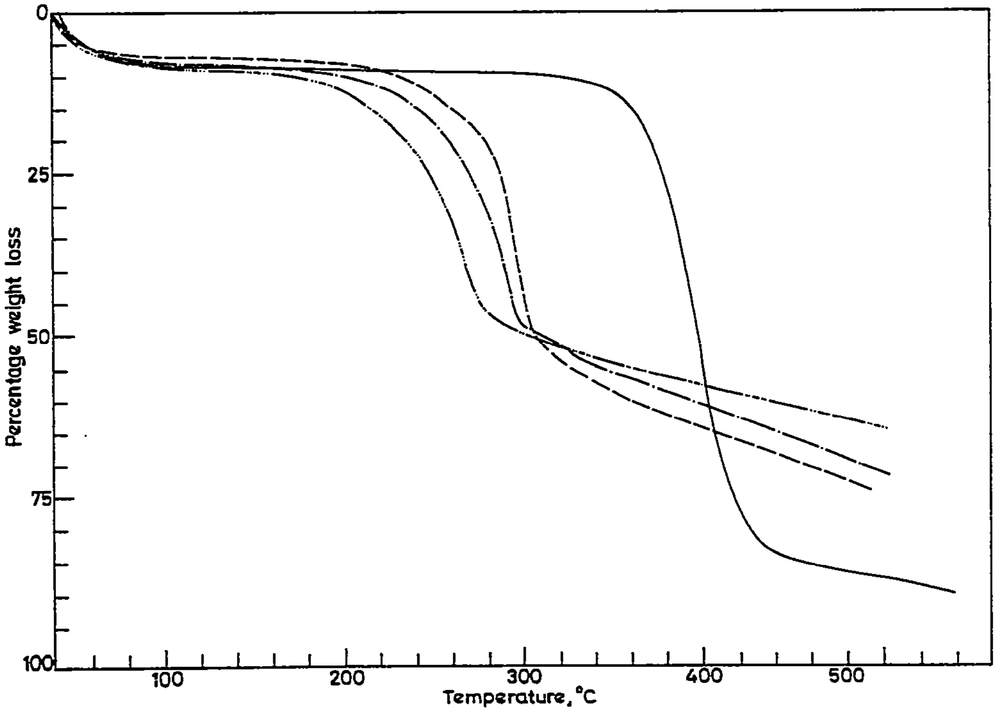

Fig. 2. TG curves of untreated cellulose (———) and filter paper treated with 2% (— — —), 5% (· — · — ·) and 10% (— ·· — ·· — ·· —) $(N_2H_5)_2HPO_4$.

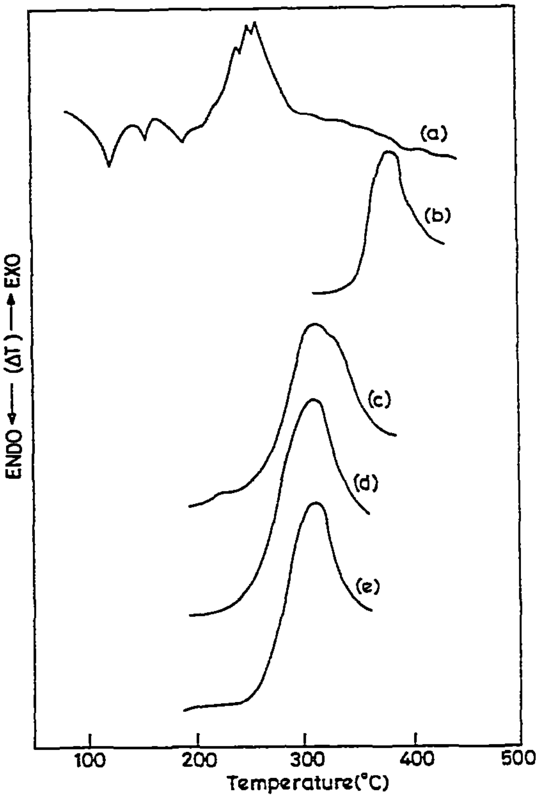

Fig. 3. DTA curves (in air) of (a) pure dihydrazinium phosphate; (b) untreated cellulose; (c) cellulose + phosphoric acid (1.87% P); (d) cellulose + diammonium phosphate (1.94% P + 1.76% N); (e) cellulose + dihydrazinium phosphate (1.88% P + 3.40% N).

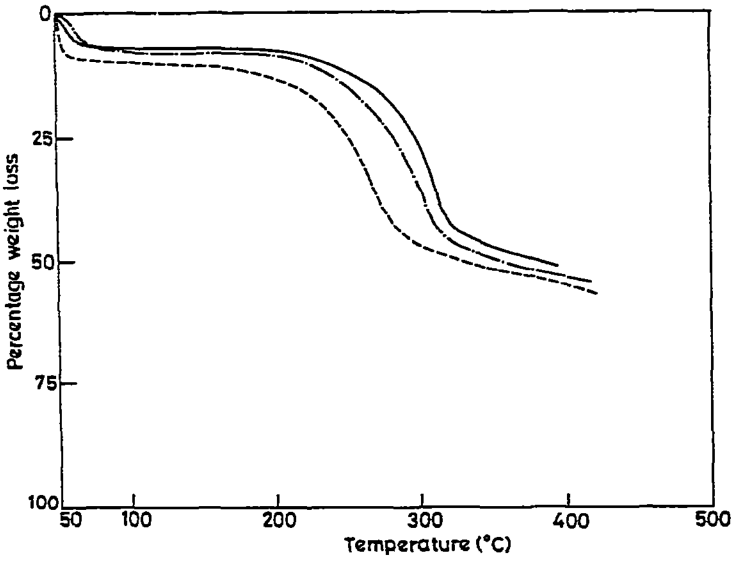

Fig. 4. TG curves of cellulose treated with phosphoric acid (1.87% P) (— — —), diammonium phosphate (1.94% P + 1.76% N) (· — · — ·), and dihydrazinium phosphate (1.88% P + 3.40% N) (———).

TABLE 1

Mass spectrometry results of cellulose pyrolyzed at 500°C and 10^{-8} torr

Sample	Peak hts. of molecular ions m/e			Peak ht. ratio of mass 18 to 44 (H_2O/CO_2)
	18	28	44	
DHP treated cellulose	59.04	21.4	7.44	7.9355
DAP treated cellulose	51.47	13.7	6.84	7.5249
Phosphoric acid treated cellulose	44.69	13.0	5.51	8.1107

higher temperatures in the case of 2% DHP treated cellulose and almost completely disappear in the case of the 10% DHP treated cellulose sample.

The TG of α-cellulose and DHP treated cellulose (Fig. 2) shows an initial weight loss (~9%) at ~50°C due to dehydration. α-Cellulose starts decomposing slowly at ~300°C and weight loss is rapid between 340 and 430°C. The final weight loss at ~480°C is ~85%, leaving behind 15% char. The DHP treated cellulose decomposes at lower temperatures. The weight loss is rapid between 200 and 300°C. There is a break in the TG curves of DHP treated cellulose at 300°C, corresponding to ~50% weight loss. Further weight loss is very slow and continues beyond 500°C. Both DTA and TG results are in good agreement.

The flame retardancy of DHP on α-cellulose has been compared with that of diammonium phosphate (DAP) and phosphoric acid. The results of DTA and TG of DHP, DAP and phosphoric acid treated cellulose are shown in Figs. 3 and 4 respectively. The oxidation degradation exotherm of cellulose is lowered to the same extent (i.e. from 377°C to 310°C) in all cases. TG results also do not show a marked difference in the amount of char formed (weight loss 50% at 310°C). Results of the mass spectrometric studies of cellulose treated with DHP, DAP and phosphoric acid are summarized in Table 1. It can be seen that DHP treated cellulose produced more water, nitrogen and carbon dioxide compared with the other two.

DISCUSSION

During the decomposition of cellulose, solid carbonaceous char and ill-defined tar which decomposes further with the formation of flammable gases are produced. The flammable products of depolymerization of tar are: 1, 4 anhydro-*D*-glucopyranose, 1, 6 anhydro-*D*-glucofuranose, laevoglycosan, etc. [8]. The phosphorus containing flame retardant materials by themselves or by producing some species, perhaps Lewis acids or other dehydrating agents, alter the pyrolysis of cellulose in such a way as to reduce the amount of the above mentioned flammable gases. In other words, flame retardancy is brought about by dehydration and char formation. Therefore, any good flame retardant should increase the char formation, lower the concentration of combustible gases by dehydration, dehydrogenation or by the formation of a glassy coating [9].

This type of acid catalyzed dehydration is observed in the case of phosphoric acid and ammonium phosphates [3,10]. Similar behaviour is also observed in the case of cellulose treated with DHP. The main exothermic peak in DTA (Fig. 1) for pure cellulose at 377°C is assigned to the oxidative degradation of cellulose and the oxidation of 'tarry products' produced from the pyrolysis of cellulose. The latter two exotherms could be due to the glowing of char in the condensed phase [11]. The DHP treated cellulose samples decompose at lower temperatures. The first exothermic peak temperature is lowered from 377°C for pure cellulose to 266°C for 10% DHP treated cellulose. This sensitization clearly visualizes the acid catalyzed decomposition of cellulose. However, the decomposition temperature of the last two exotherms are higher but the peak area is considerably reduced, almost disappearing for 5% and 10% DHP treated cellulose. Since the percentage of phosphorus is more and more, the oxidation and hence glowing of char is completely prevented in the above cases.

All cellulose samples show ~9% weight loss initially due to dehydration (Fig. 2). The percentage of weight loss of cellulose (~85%) decreases to a greater extent when treated with DHP. This shows that the phosphate acting in the condensed phase minimizes tar formation and maximizes char formation.

Since DHP is the salt of a weak base, namely hydrazine, having a hydrophilic hydrazinium cation and a higher percentage of nitrogen than DAP, it is interesting to compare its flame retardant properties with those of DAP and phosphoric acid.

Dihydrazinium phosphate melts around 125°C and decomposes exothermically at 270°C (Fig. 3). The exotherm for the oxidative degradation of cellulose is lowered to the same extent from 377°C to 310°C when treated with DHP, DAP or phosphoric acid (Fig. 3). TG results (Fig. 4) show that there is not much difference in the weight loss around 350°C. However, cellulose treated with phosphoric acid decomposes at a lower temperature than the other. This appears to envisage the view [12,13] that free phosphoric acid, which offers a more acidic environment in the thermal state, causes dehydration and degradation at a lower temperature.

In the case of DHP, since phosphoric acid must be formed at a higher temperature, the decomposition occurs at a comparitively higher temperature.

The efficiency of matching the decomposition temperature of flammable substrate and the flame retardant additive has been cited as one of the keys to good flame retardancy [14,15], referred to as the 'right place at the right time' theory. Also the decomposition of the additives should be endothermic to lower the heat supply for the decomposition of the flammable substrate. The decomposition temperature of DHP is comparable with that of the flammable substrate of cellulose, but it suffers from the disadvantage that it decomposes exothermically at 270°C. This disadvantage appears to be more than compensated for by the hygroscopic property of DHP which promotes dehydration more efficiently and limits the production of combustible hydrocarbon gases.

Mass spectrometric analysis has been carried out with a view to analyzing the decomposition gaseous products of DHP, DAP and phosphoric acid treated cellulose. The results are summarized in Table 1. The ratio of the intensity of mass 18 to 44 for water and carbon dioxide, respectively, shows that the ratio is more for DHP than for DAP although it is not significant. Considering mass 28 to be due to nitrogen alone (carbon monoxide can also be produced) it seems that more nitrogen is produced in the case of DHP. Therefore it appears that $N_2H_5^+$ in DHP is not reacting with phosphate, forming P—N bonds which facilitate phosphorylation. From the point of view of the gas theory of fire retardancy, it appears that nitrogen which is produced during pyrolysis of cellulose, being noncombustible, alters the flammability by dilution of the flammable gases, but the contribution to the flame retardation may not be significant.

CONCLUSIONS

Dihydrazinium phosphate, ammonium phosphate and phosphoric acid are equally good as flame retardants for cellulose. Although DHP decomposes exothermically, the hydrophilic nature of the hydrazinium ion more than compensates for it to be equally as good as other phosphates in retarding cellulose burning.

It appears that the excess nitrogen produced during the pyrolysis of DHP treated cellulose alters the flammability by dilution of flammable gases. From comparative studies of DAP, DHP and phosphoric acid it can be seen that the formation of phosphoric acid would degrade the cellulose at a lower temperature.

REFERENCES

1 F. Ward, J. Soc. Dyers Colour., 71 (1955) 569.
2 R.W. Little, Flame Proofing Textile Fabrics, Am. Chem. Soc., Monogr. Ser., Reinhold, New York, 1947.
3 Kwang-Shuan Huang, Kee-Chuan Pan and Chao-Nan Perng, J. Chin. Chem. Soc. (Taipei), 22 (1975) 57.
4 K.C. Patil, J.P. Vittal and C.C. Patel, J. Fire Retard. Chem., 7 (1980) 3.
5 K.C. Patil, R. Soundararajan and V.R. Pai Verneker, Proc. Indian Acad. Sci., Sect. A, 87 (1978) 281.
6 H. Varley, Practical Clinical Biochemistry, Arnold—Heinemann, India, 1975, 4th edn, p. 446.
7 M. Takayuki and Y. Motoji, Chem. Abstr., 88 (1978) 107553b.
8 F. Shafizadeh, Adv. Carbohydr. Chem., 23 (1968) 419.
9 J.J. Pitts, in W.C. Kuryla and A.J. Papa (Eds.), Flame Retardancy of Polymeric Materials, Vol. 1, Dekker, New York, 1973, p. 135.
10 J.E. Hendrix, J.E. Bostic Jr., E.S. Olson and R.H. Barker, J. Appl. Polym. Sci., 14 (1970) 1701.
11 W.K. Tang, in R.C. McKenzie (Ed.), Differential Thermal Analysis, Vol. 2, Academic Press, London, 1972, pp. 538, 547.
12 R. Hindersinn, in Herman F. Mark, Norman G. Gaylord and Norbert M. Bikales (Eds.), Encyclopaedia of Polymer Science and Technology, Suppl., Vol. 2, Wiley, New York, 1977, p. 270.
13 J.W. Lyons, J. Fire Flammability, 1 (1970) 302.
14 J.A. Rhys, Chem. Ind. (London), (1969) 187.
15 H.C. Gulledge and G.R. Seidel, Ind. Eng. Chem., 42 (1950) 442.