

DTA and IR Studies on Cellobiose Treated with Phosphorus Oxychloride-N, N-Dimethylformamide Mixture

SATISH BHATNAGAR, S L AGNISH & HARI L BHATNAGAR

Department of Chemistry, Kurukshetra University, Kurukshetra 132 119

Received 1 September 1980; accepted 8 December 1980

Phosphorylation of cellobiose, a basic unit of cellulose, was carried out in a mixture of N,N-dimethylformamide and phosphorus oxychloride at different temperatures in the range 40-80°C and the products of the reaction were subjected to DTA studies. The thermograms show an endothermic activity in the region 170-230°C in air. The single endotherm at 200°C in air has been found to be shifted to 180°C in nitrogen atmosphere. This lowering of the peak temperature is attributed to the effect of synergism of nitrogen gas in combination with phosphorus present in the phosphorylated products of cellobiose. The IR spectra of the residues, obtained after partial or complete charring of the phosphorylated products in the vicinity of 180°C, together with elemental analyses provide evidence of dehydration attributable to O-H and C-H stretching in the region 3400-2880-cm⁻¹.

The study of a thermally induced chemical reaction for a cellulose substrate is difficult because of (i) the existence of a large portion of the substrate as crystalline material which is not easily accessible to the reagent being studied, and (ii) secondary reactions which may occur with primary degradation products or with intermediates resulting from disintegration of the gross polymeric structure. It was, therefore, advantageous to select a model system such as cellobiose, a basic unit of cellulose, for understanding the reaction process. In continuation of our earlier work¹, cellobiose was phosphorylated and chlorinated with a mixture of phosphorus oxychloride (POCl₃) and N,N-dimethylformamide (DMF) at different temperatures in the range 40-80°C for 1 hr. The samples obtained were subjected to DTA studies for evaluating the effectiveness of organo-phosphorus compounds as flame retardants. IR spectra of the partially/completely charred samples, near DTA peak temperatures, were taken to study the char patterns of these samples.

Materials and Methods

Cellobiose supplied by M/s Aldrich & Thomas Laboratories was dried in vacuum over P₂O₅. DMF (Anala R) and POCl₃ (E. Merck) were distilled before use.

Pure cellobiose (2 g) was stirred continuously with a mixture of DMF (38.7 ml) and POCl₃ (1.52 g; density, 1.675 g/ml) in a three-necked flask fitted with a mercury sealed stirrer, a water condenser having a guard tube at its open end and immersed in an oil thermostat (constancy, ±0.5°C) at the desired temperature for 1 hr. The product was filtered using a

G-3 sintered glass funnel, washed with benzene, and dried initially in air and then in a vacuum drier using benzene as solvent.

Paper chromatography was used to identify and separate the products formed in the reaction of cellobiose with POCl₃-DMF mixture.

Phosphorylated cellobiose (about 100 mg) was dissolved in ethyl alcohol (20%) and the solution was loaded with glass capillary over a strip of Whatman chromatographic paper No. 4. The paper strip was hung in a jar containing the solvent system ethyl acetate-pyridine-water (2:1:2). The strip was then allowed to run overnight and the spots were developed with a mixture of phthalic acid (1.66 g), aniline (0.9 ml) and water saturated *n*-butanol (100 ml). The strip of paper was finally heated at about 100°C to develop spots.

IR spectra of cellobiose and of the products of phosphorylation of cellobiose were obtained employing KBr-pellet technique using Beckman spectrophotometer (Model IR-20).

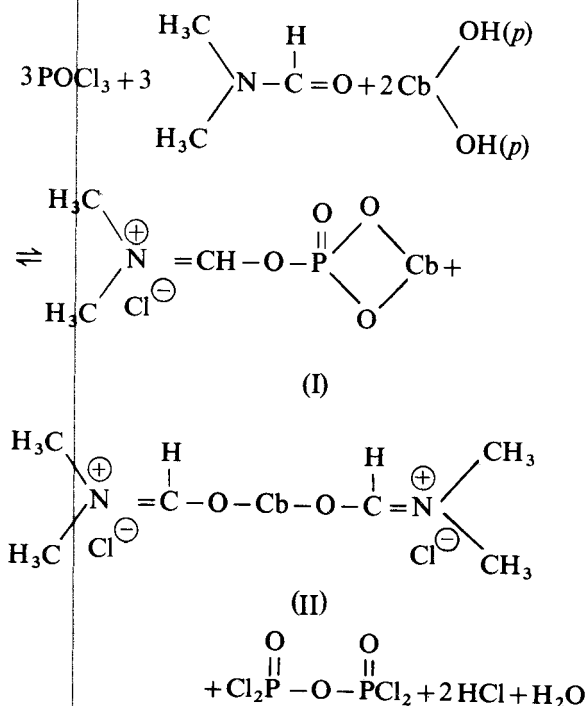
NMR spectra of pure cellobiose and of cellobiose treated with POCl₃-DMF mixture were obtained in D₂O solvent using DSS as the internal standard. The spectra were recorded on Perkin-Elmer R-32, 90 MHz spectrophotometer.

Thermograms of the samples were recorded in both air and nitrogen atmospheres using DTA apparatus (02-Universal Model, GDR) at a heating rate of 12.5°C/min.

Phosphorus and chlorine in the phosphorylated samples of cellobiose were estimated by the methods of Pons *et al.*² and Carius³ respectively.

Results and Discussion

Paper chromatographic separation—Three distinct spots with R_f values 0.35, 0.46 and 0.57 were obtained. The first two spots may be due to compounds (I) and (II) formed⁴ as follows:



Only primary $-\text{OH}(p)$ groups of cellobiose are assumed to react. The spot with R_f value 0.57 is due to unreacted cellobiose.

Infrared examination—From the study of the IR spectra of pure cellobiose and cellobiose treated with POCl_3 -DMF (8%) at 80°C for 1 hr, an additional band at 1720 cm^{-1} has been found which is assumed to be the result of substitution at the hydroxyl groups of the cellobiose molecule.

NMR examination—NMR spectrum of cellobiose shows two doublets at $\delta=4.45$, $J_{12}=7.5$ cps and $\delta=5.72$, $J_{12}=4.0$ cps characteristic of anomeric protons in two anomeric forms^{5,6}, whereas NMR spectrum of the product gives one doublet (3 protons each) at $\delta=2.9$ and 2.75 and a sharp singlet (6 protons) at $\delta=2.6$, probably due to the four methyl groups of the compound II.

DTA studies—The thermograms of pure cellobiose and its phosphorylated products in both air and dynamic nitrogen atmosphere are shown in Figs 1 and 2. The maxima in ΔT vs T are presented in Table 1.

The DTA thermogram for pure cellobiose exhibits two major regions of thermal activity. The first, an endotherm near 240°C , corresponds to the melting point of the pure compound. The second indicates

endothermic decomposition, followed by a small exotherm and then an endotherm near 300°C .

The DTA thermograms for cellobiose treated with POCl_3 -DMF mixture at different temperatures in the range 40 – 80°C show an endothermic activity in the region 170 – 230°C in air. The single endothermic peak at 200°C is suggestive of the formation of new bonds. The area of this peak increases with rise in the reaction temperature, indicating that the heat of reaction (ΔH) involved in the above process also follows the same

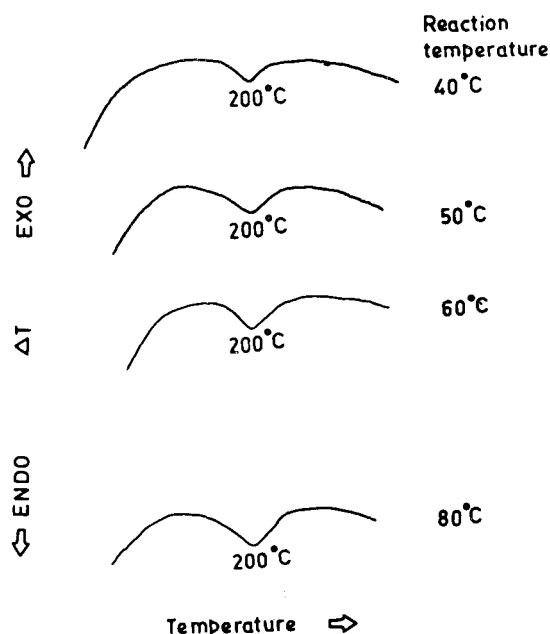


Fig. 1—DTA curves of cellobiose treated with POCl_3 and DMF in air

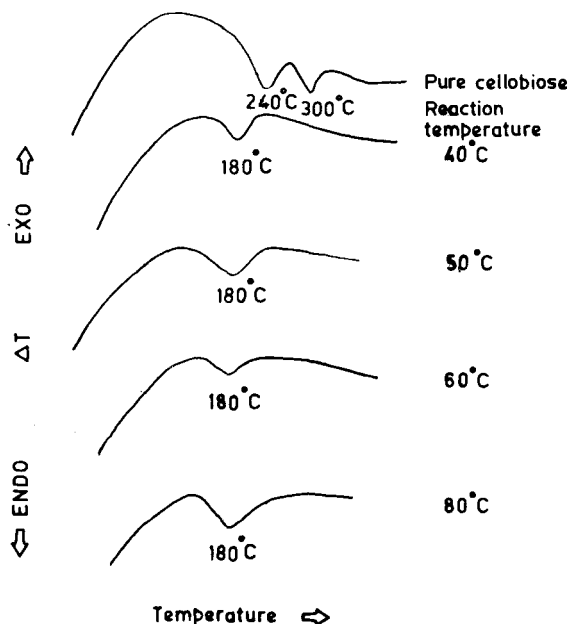


Fig. 2—DTA curves of cellobiose treated with POCl_3 and DMF in nitrogen

Table 1—Maxima in the DTA Thermograms for Cellobiose and Its Phosphorylated Products

Compound	Peak temperature, °C	
	air	Nitrogen
Pure cellobiose	—	240, 300(endo) large
Cellobiose phosphorylated and chlorinated for 1 hr at		
40°C	200 (endo) large	180(endo) large
50°C	do	do
60°C	do	do
80°C	do	do

Table 2—Percentage of Phosphorus and Chlorine in Treated Cellobiose

[Heating period, 1 hr]		
Temperature °C	Phosphorus %	Chlorine %
40	0.36	0.52
50	0.31	0.69
60	0.58	1.05
80	0.79	1.33

trend. This is because of the increasing percentages of phosphorus and chlorine and hence substitution in the products (Table 2). In nitrogen atmosphere, a single endotherm at 180°C is obtained. The peaks are sharper in comparison to those recorded in air. This may be due to a synergistic effect of nitrogen gas in combination with phosphorus already introduced in cellobiose. The effectiveness of organophosphorus compounds as flame retardants in nitrogen atmosphere may also be due to the fact that nitrogen might be reacting directly with the decomposition products of cellobiose^{7,8}.

Infrared examination of chars obtained in nitrogen atmosphere—IR spectra of the partially/completely charred samples of phosphorylated cellobiose obtained in a DTA cell under nitrogen atmosphere at temperatures 130, 150, 160 and 180°C were recorded (Fig. 3).

IR spectra of the residues show evidence of dehydration and skeletal rearrangements, as suggested by the decrease in absorptions attributable to hydroxyl and C—H stretching in the region 3400–2880 cm⁻¹. These frequencies practically disappear at about 200°C.

Dehydration is also evidenced by the elemental analysis of (i) residues (for pure cellobiose, C = 47.74%, H = 5.93% and for cellobiose treated with POCl₃-DMF mixture at 80°C for 1 hr, C = 57.38%, H = 4.16%,

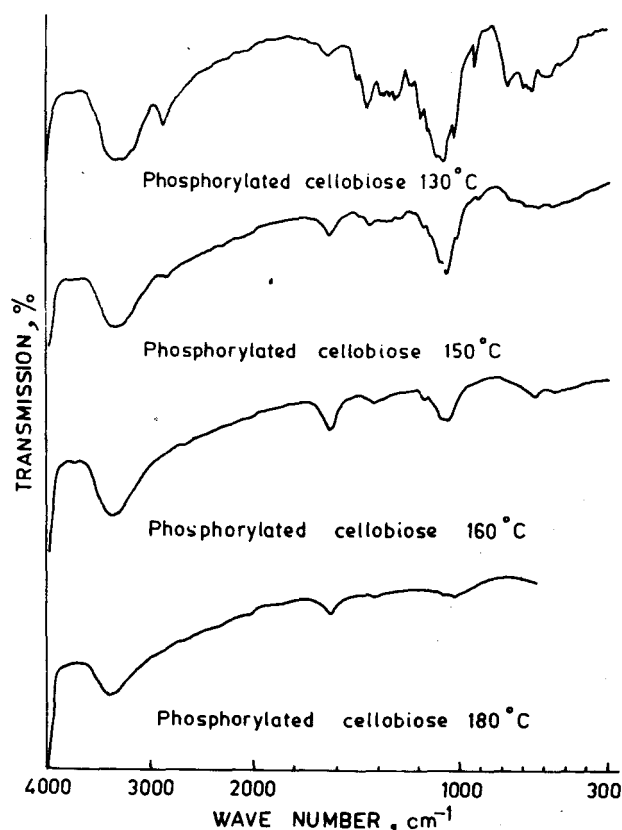


Fig. 3—IR spectra of the samples after heating in DTA cell in nitrogen

P = 3.57%), and (ii) unburnt untreated pure cellobiose (C = 42.11%, H = 6.43%). Residues from the treated cellobiose are, thus, found to be more carbonaceous than those obtained from the untreated sample of cellobiose.

Acknowledgement

Two of the authors (SB and SLA) are thankful to the United States Department of Agriculture (Far Eastern Research Service) and the University Grants Commission for granting research fellowships to them.

References

- Gupta J C, Bhatnagar S, Lal K & Bhatnagar H L, *Indian J Text Res*, **4** (1979) 43.
- Pons W A (Jr) & Guthrie J D, *Ind Engng Chem*, **18** (1946) 184.
- Mann F G & Saunders B C, *Practical organic chemistry* (Longman Ltd, London) 1960, 500.
- Vigo T L & Welch C M, *Carbohydr Res*, **32** (1974) 331.
- Casu B & Regiani M, *Tetrahedron Lett*, **39** (1964) 2839.
- van der Veen, James M, *J Org Chem*, **28** (1963) 564.
- Tesoro G C, *Textilveredlung*, **2** (1967) 435; *Chem Abstr*, **67** (1967) 82899v.
- Gupta J C, Bhatnagar S, Lal K & Bhatnagar H L, *Indian J Text Res*, **4** (1979) 40.
- Tesoro G C, Sello S B & Willard J J, *Text Res J*, **38** (1968) 245; **39** (1969) 180.