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THERMAL STUDIES ON CELLOBIOSE AND CELLOBIOSE HALOBENZOATES

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ABSTRACT

Cellobiose 2-chlorobenzoate, 2-bromobenzoate and 2-iodobenzoate samples with different degrees of substitution (DS) were prepared. The DS in each sample was determined from the respective halogen content. The samples were subjected to DTA, TG and DTG studies in air from ambient temperature to 800 °C. The decomposition temperatures for cellobiose halobenzoate samples are found to decrease with increasing DS and size of the halogen atom. Various kinetic parameters for the different stages of the thermal degradation of the treated cellobiose samples were calculated from the TG thermograms using Broido's method. The energies of activation for the decomposition of cellobiose and its halobenzoate samples were found to be in the range 120–194 kJ mol^{-1}. Further, with increasing DS and the size of the halogen atom, the activation energies were found to decrease. The IR spectra of the partially charred residues of cellobiose 2-chlorobenzoate indicated elimination of the acid and formation of compounds containing carbonyl groups. A mechanism for thermal degradation of cellobiose halobenzoates has been proposed.

INTRODUCTION

The thermal degradation of cellulose and its derivatives has been studied by various investigators [1–9] in order to ascertain the mechanism that renders compounds more resistant to heat and flame. Although some investigations were carried out on the chemical degradation of cellobiose in the presence of acids and bases, little attention has been paid so far to its behaviour at higher temperatures. Gardiner [10] and Kato [11] pyrolysed cellobiose, cellulose and other carbohydrates and volatile products were detected. Heyns and Klier [12] have reported that cellobiose, cellulose and a number of other carbohydrates give the same volatile products on thermal degradation. Puddington [13] studied the thermal degradation of cellobiose in vacuo and reported the various products of the degradation and the energy of activation. Recently, Bhatnagar and co-workers [14–17] have

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studied the kinetics of the thermal degradation of cellobiose as a model compound for cellulose and of various cellobiose esters.

In the present study, cellobiose halobenzoate samples were obtained by treatment of cellobiose with various 2-halobenzoyl chlorides and the kinetics of the thermal degradation of the treated cellobiose samples were studied in air atmosphere from ambient temperature to 800 °C using DTA, TG and DTG techniques in order to elucidate the mechanism of thermal degradation.

EXPERIMENTAL

The following samples of cellobiose and cellobiose halobenzoates with different degrees of substitution were selected for the thermal studies: (i) cellobiose (Koch-Light, England) was dried in vacuo over P_2O_5 at 80 °C; samples (ii), (iii) cellobiose 2-chlorobenzoate; (iv), (v) cellobiose 2-bromobenzoate; and (vi), (vii) cellobiose 2-iodobenzoate. These samples had different DS.

Halobenzoylated cellobiose samples were prepared by treating cellobiose (3.42 g) in pyridine (50 ml) with the respective 2-halobenzoyl chloride (2-chlorobenzoyl chloride, 14.00 g; 2-bromobenzoyl chloride, 17.55 g; and 2-iodobenzoyl chloride, 21.32 g) at the desired temperature for a given period and the products, obtained by precipitating in ice-cold water, were extracted with ethanol, and ether in a Soxhlet apparatus. The samples, after purification, were dried in vacuo over P_2O_5. The reaction temperature for samples (ii) and (iii) was kept at 95 °C for 6 and 12 h, respectively; for samples (iv) and (v), it was kept at 80 and 95 °C, respectively, for 16 h; and samples (vi) and (vii) were obtained at 60 and 70 °C, respectively, for 16 h.

The samples were characterized by their IR and NMR spectra.

Halogen content

The chlorine, bromine, and iodine content of the treated cellobiose samples were estimated gravimetrically by the Carius method [18]. The degree of substitution (DS) of the different samples, given in Table 1, were determined from the halogen content (in per cent) using eqn. (1) [19]

$$S_1 = \frac{342X}{(100W_x - XW_I)} \tag{1}$$

where 342 is the molecular weight of the cellobiose unit, X is the percentage of halogen present in the sample, W_x is the atomic weight of the halogen and W_I is the net increase in the molecular weight of cellobiose resulting from the introduction of one substituent group, i.e., xC_6H_4CO-.

TABLE 1

Nature of the peaks and peak temperatures in the DTA thermograms of cellobiose and its halobenzoate samples in air

Sample No.	Sample	Degree of substitution	Nature of the peak	Peak temperatures (°C)		
				Initiation	Maximum	Termination
(i)	Cellobiose	–	Endo (large)	222	248	282
			Exo (large)	282	364	440
(ii)	Cellobiose 2-chlorobenzoate	6.14	Exo (small)	220	276	300
			Exo (large)	300	349	429
			Exo (large)	429	542, 589	665
(iii)	Cellobiose 2-chlorobenzoate	6.99	Exo (small)	200	272	298
			Exo (large)	298	343	425
			Exo (large)	425	538, 585	660
(iv)	Cellobiose 2-bromobenzoate	5.54	Exo (small)	175	240	278
			Exo (large)	278	322	400
			Exo (large)	400	630	730
(v)	Cellobiose 2-bromobenzoate	6.08	Exo (small)	196	235	273
			Exo (large)	273	318	410
			Exo (large)	410	527, 570	648
(vi)	Cellobiose 2-iodobenzoate	4.19	Exo (small)	210	257	275
			Exo (large)	275	305	370
			Exo (large)	370	468	550
(vii)	Cellobiose 2-iodobenzoate	4.76	Exo (small)	200	253	278
			Exo (large)	278	319	380
			Exo (large)	380	485	621

Thermal analysis

The differential thermal analysis (DTA), thermogravimetry (TG) and derivative thermogravimetry (DTG) thermograms for the samples were obtained using a MOM derivatograph (Paulik–Paulik–Erdey, Budapest). The thermograms were recorded from ambient temperature to 800 °C under a dynamic dried air atmosphere flowing at a rate of 100 ml min^{-1} and at a linear heating rate of 10 °C min^{-1}. The DTA measurements were relative to calcined alumina.

Infrared spectroscopy

The technique employed in our study for obtaining the IR spectra by Beckman spectrophotometer IR-20 (U.S.A.) involved the dispersion of the charred samples in discs of potassium bromide. A feature of the disc preparation was that the mass of the charred sample mixed with KBr was the same (2 mg) for each experiment. The charred samples were prepared by heating sample (ii) in air at the desired temperature and the residues, after cooling, were transferred into sample containers.

Evaluation of kinetic parameters

The energies of activation and the frequency factors from the TG thermograms were evaluated by Broido's method [20]. According to this method, the energy of activation, E_a, and the frequency factor, Z, can be evaluated using eqn. (2)

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

where R_H is the rate of heating, T_m is the temperature of maximum reaction velocity and y is the fraction of the number of initial molecules not yet decomposed. The value of y at any time t was determined using eqn. (3)

$$y = \frac{(W_t - W_\infty)}{(W_0 - W_\infty)} \tag{3}$$

where W_0 and W_∞ are the initial and the final weights of the sample undergoing degradation and W_t is the weight of the sample at time t of degradation.

The plots of $\ln[\ln(1/y)]$ versus $1/T$ for the various stages of thermal degradation have been found to be linear and the values of E_a and Z have been calculated from the slopes and intercepts, respectively, of these plots.

RESULTS AND DISCUSSION

The DTA, TG and DTG thermograms of samples (i–vii) were recorded in a dynamic air atmosphere and are shown in Figs. 1–7. The nature of the DTA peaks and the measured temperatures of their initiation, maximum and termination for the thermal degradation of the samples are given in Table 1.

The DTA thermogram of pure cellobiose [17] shows a sharp endotherm with a maximum at about 248 °C and a large exotherm peaking at about 364 °C. The endotherm corresponds to the melting and dehydration of cellobiose. The exotherm is due to the decomposition of cellobiose, which may include the scission of $1 \rightarrow 4\beta$-glycosidic linkages and formation of $1 \rightarrow 6\beta$-glycosidic linkages, resulting in the formation of levoglucosan and tar, conversion of tar to char and subsequent oxidation of char.

The DTA thermograms of cellobiose halobenzoate samples (ii–vii) exhibit three exotherms each. The first exotherm corresponds to the decomposition of the compounds and the temperature maxima of the peaks for samples (ii–vii) are at 276, 272, 240, 235, 257 and 253 °C, respectively. The de-esterification and dehydration reactions of the samples could not be distinguished from the decomposition reactions. It is evident from the TG thermograms that the weight losses start in the temperature region 160–210 °C. The TG thermograms show a two-stage degradation below 300 °C; the first stage is due to the scission of the halobenzoyl groups accompanied by dehydration, and the second stage is associated with the decomposition of the compounds. The corresponding weight losses are in the range 2–4% and 53–62%, respectively. Thus it appears that the endotherms due to the de-esterification and dehydration are masked by the exothermic effects due to the decomposition of the compounds. The DTG maxima (see Table 3) corresponding to the first exotherm (decomposition) are at 298, 295, 274, 271, 267 and 270 °C, respectively, for samples (ii–vii).

The second exotherm, peaking at 349, 343, 322, 318, 305 and 319 °C, respectively, for samples (ii–vii), is due to the oxidation of the products formed during the decomposition process. The third and final exotherm, showing two maxima in the case of samples (ii), (iii) and (v), represents the oxidation of the charred residual matter and the temperature maxima of the peaks for samples (ii–vii), respectively, are 542, 589; 538, 585; 630; 527, 570; 468 and 485 °C. The TG thermograms also show weight losses corresponding to the temperature range of the above exotherms and these are in the range 7–23% and 7–10%, respectively, for the third and fourth stages.

The char yields (in weight %) for cellobiose (i) and cellobiose halobenzoate samples (ii–vii) were determined from the TG thermograms at 725 K (see Table 5). From the DTA and DTG thermograms and char yields, the following observations can be made.

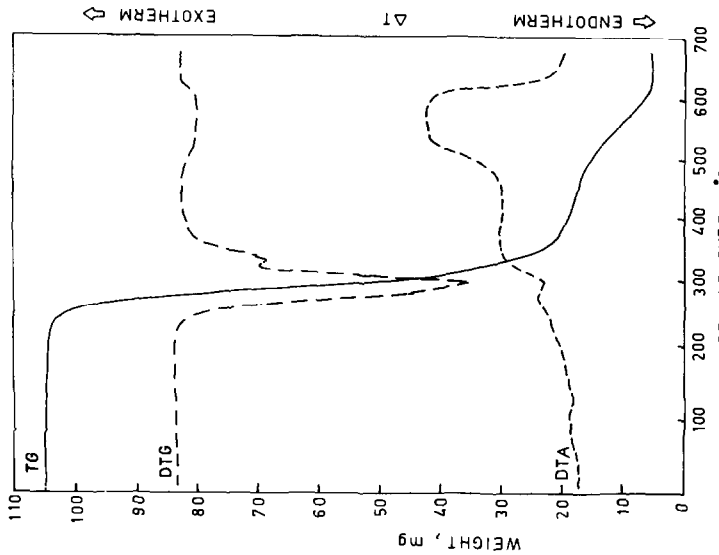


Fig. 2. DTA, TG and DTG thermograms for cellobiose 2-chlorobenzoate sample (ii) in air.

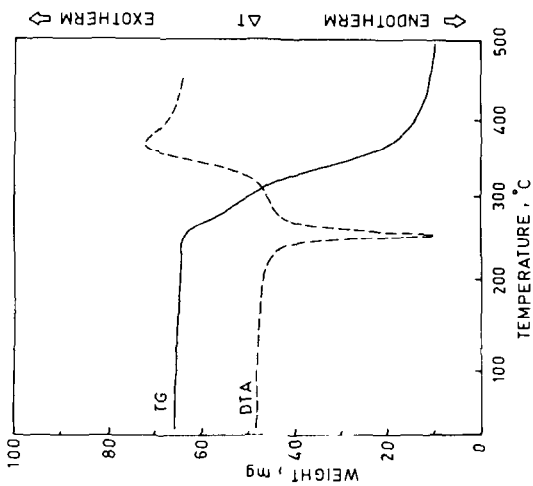


Fig. 1. DTA and TG thermograms for cellobiose in air.

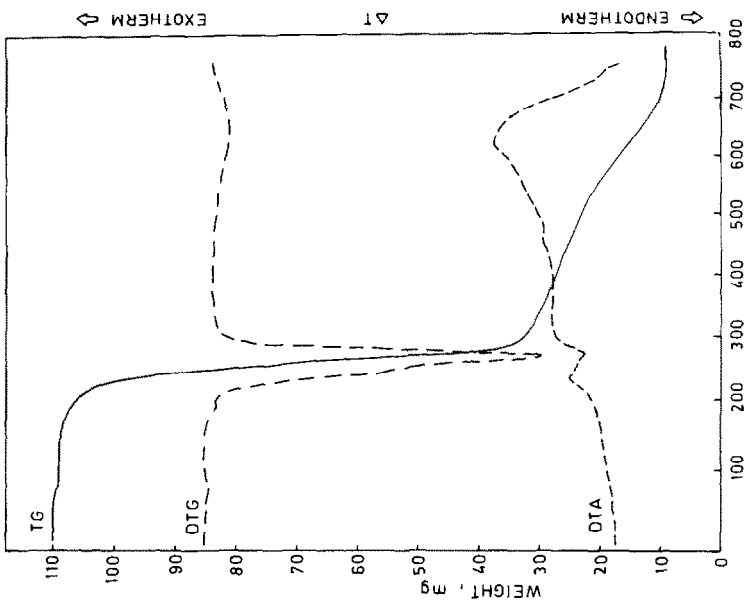


Fig. 4 DTA, TG and DTG thermograms for cellobiose 2-bromobenzoate sample (IV) in air.

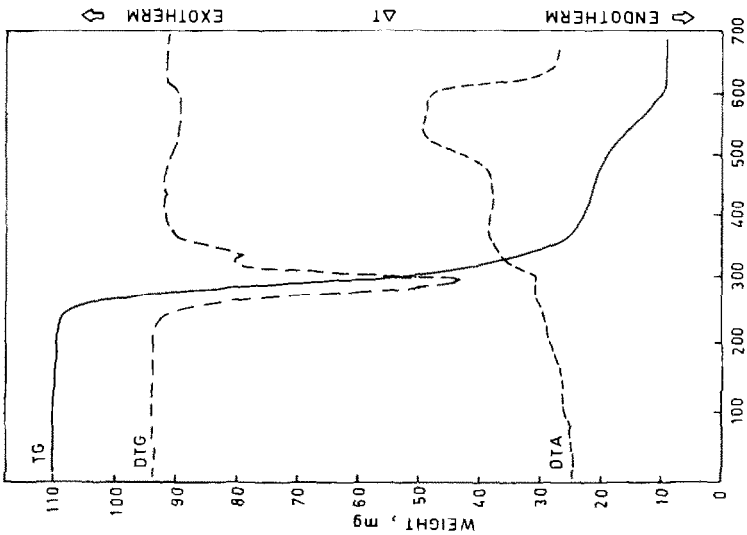


Fig. 3. DTA, TG and DTG thermograms for cellobiose 2-chlorobenzoate sample (III) in air.

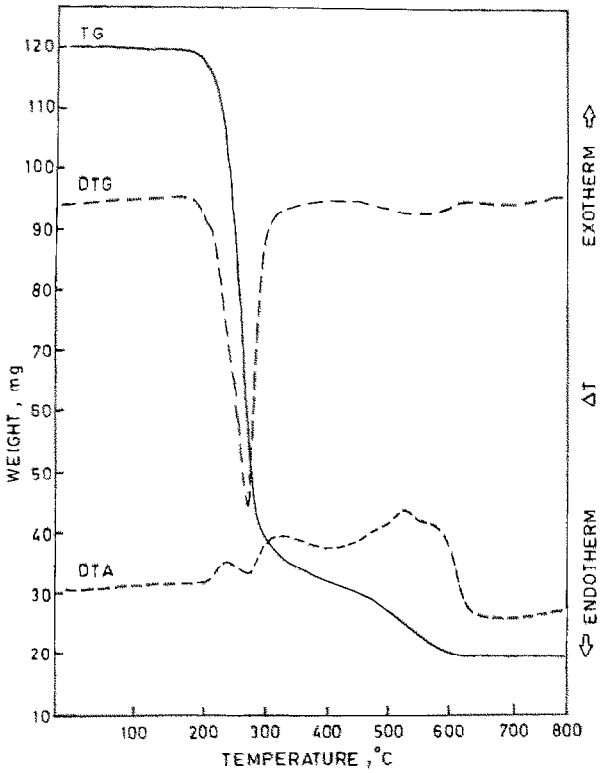


Fig. 5. DTA, TG and DTG thermograms for cellobiose 2-bromobenzoate sample (v) in air.

(i) The decomposition temperatures for the thermal degradation of cellobiose halobenzoate samples are lower than that for cellobiose and the lowering in decomposition temperatures increases with increasing degree of substitution and size of the halogen atom.
(ii) There is a decrease in the temperature at which the maximum rate of weight loss takes place with increasing size and amount of the halogen atom.
(iii) The char yields for the thermal degradation of samples (ii–vii) increase with increasing DS as well as size of the halogen atom.

From these observations, it can be inferred that the thermal stability of cellobiose halobenzoate samples decreases with increasing DS and size of the halogen atom present on the benzene ring.

The lowering in decomposition temperatures and higher char yields for the thermal degradation of the cellobiose halobenzoate samples (ii–vii) compared with those for cellobiose may be due to the presence of halogen atoms in the cellobiose matrix. In these cases, dehydrohalogenation takes place resulting in the formation of hydrogen halides [21–25] which then accelerate the decomposition of these compounds giving comparatively large

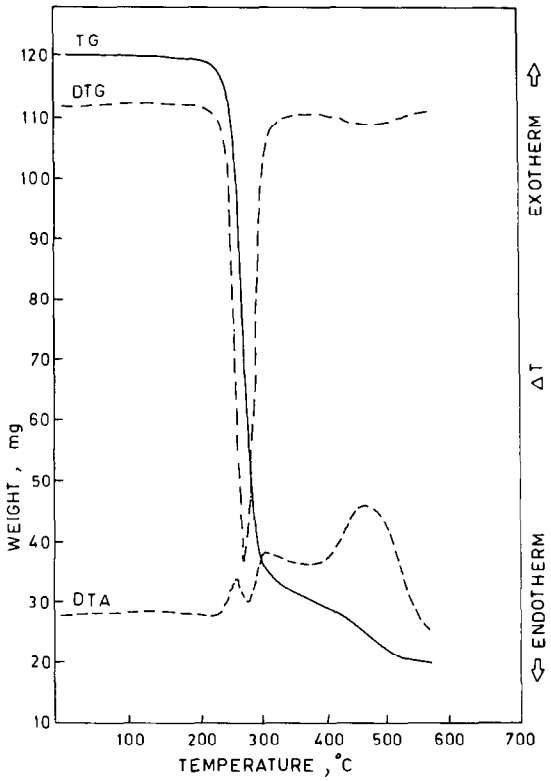


Fig. 6. DTA, TG and DTG thermograms for cellobiose 2-iodobenzoate sample (vi) in air.

amounts of char. These inferences conform with the observations made by Shafizadeh et al. [25,26], Bhatnagar et al. [7,8] and others [27,28]. Probably the release of hydrogen halide takes place only after the initial dissociation of the respective halobenzoic acid.

The weight versus temperature curves (TG thermograms) for cellobiose (i) and its halobenzoate samples (ii–vii) are shown in Figs. 1–7. In some cases, a small initial weight loss, attributed to the sorbed moisture, was observed and was neglected. The kinetic parameters for the first stage (de-esterification and dehydration), second stage (decomposition), third stage (oxidation of the decomposition products) and fourth stage (oxidation of the charred residual matter) of the thermal degradation of these samples were evaluated using eqn. (2), as described by Broido [20]. The values of the energy of activation, E_a, and the frequency factor, Z, for the various stages of the thermal degradation have been determined from the slopes and intercepts, respectively, of the linear plots (Figs. 8–11) of $\ln[\ln(1/y)]$ versus $1000/T$ and also by using the method of least squares.

The values of E_a and Z for the various stages of the thermal degradation of the cellobiose samples (i–vii) are presented in Tables 2–5. It can be seen

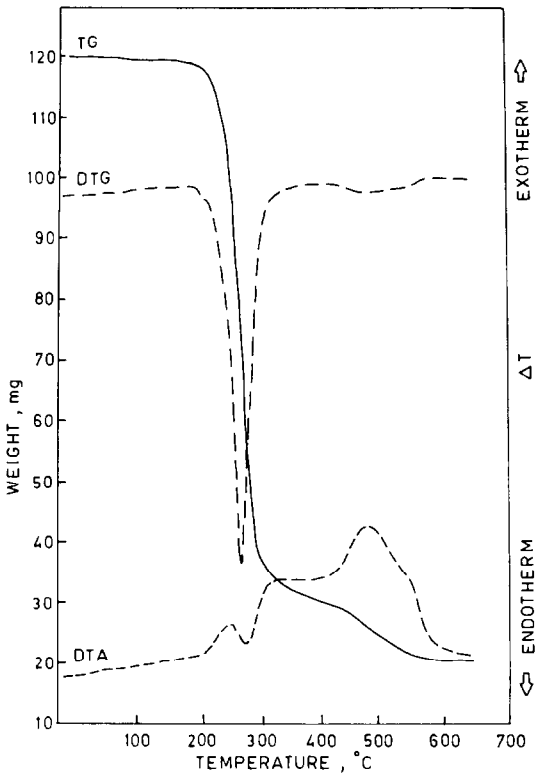


Fig. 7. DTA, TG and DTG thermograms for cellobiose 2-iodobenzoate sample (vii) in air.

from Table 2 that the energies of activation for the first stage (de-esterification and dehydration) of degradation of samples (ii–vii) are lower than that for cellobiose and the magnitude of the lowering depends upon DS and size

TABLE 2

Energies of activation and frequency factors (evaluated by Broido's method) for the first stage of the thermal degradation of cellobiose and its halobenzoate samples in air

Sample No. [a]	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})
(i)	230–270	217.20	5.21×10^{18}
	270–310	150.60	1.28×10^{12}
(ii)	–	–	–
(iii)	210–245	121.63	2.70×10^{5}
(iv)	160–220	74.40	2.47×10^{1}
(v)	175–210	152.92	9.98×10^{9}
(vi)	200–240	154.64	3.10×10^{9}
(vii)	–	–	–

[a] See Table 1.

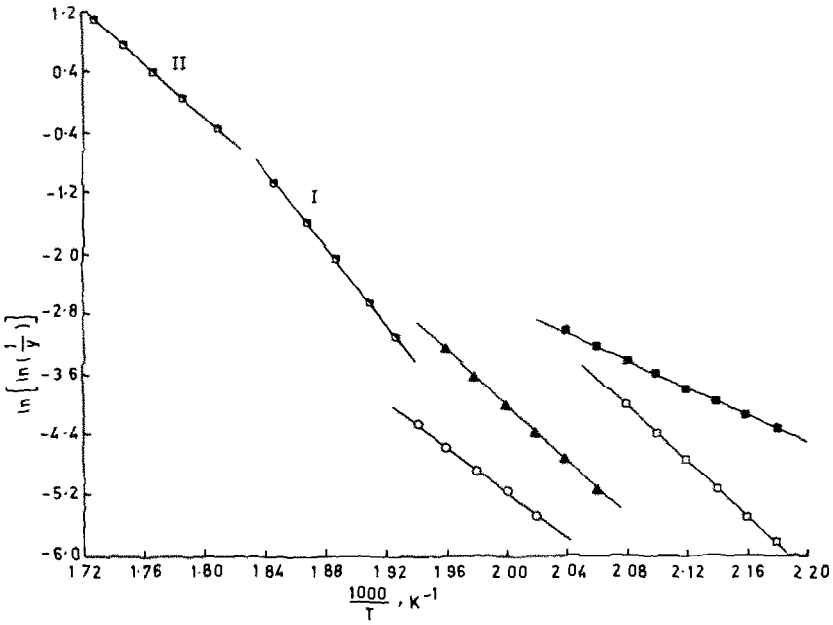


Fig. 8. Plots of $\ln[\ln(1/y)]$ vs. $1000/T$ for evaluation of E_a by Broido's method for the first stage of thermal degradation of cellobiose (◹), cellobiose 2-chlorobenzoate sample (iii) (○), cellobiose 2-bromobenzoate samples (iv) (■) and (v) (□), and cellobiose 2-iodobenzoate sample (vi) (▲).

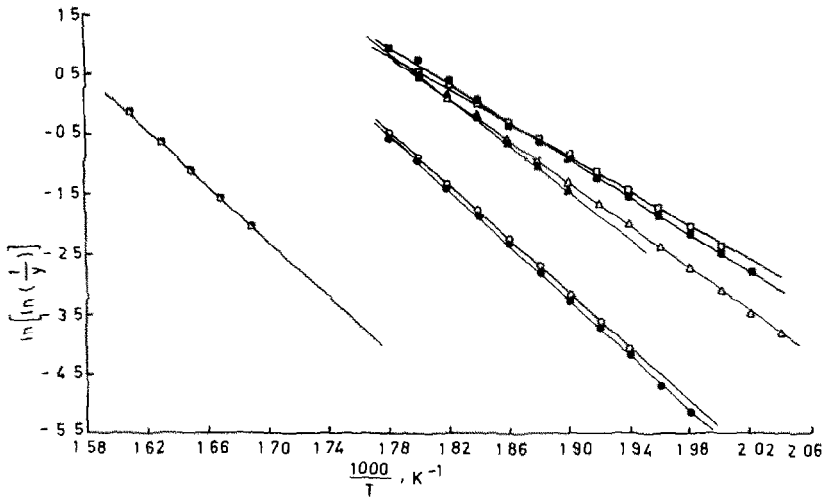


Fig. 9. Plots of $\ln[\ln(1/y)]$ vs. $1000/T$ for evaluation of E_a by Broido's method for the second stage of thermal degradation of cellobiose (◹), cellobiose 2-chlorobenzoate samples (ii) (●) and (iii) (○), cellobiose 2-bromobenzoate samples (iv) (■) and (v) (□), and cellobiose 2-iodobenzoate samples (vi) (▲) and (vii) (△).

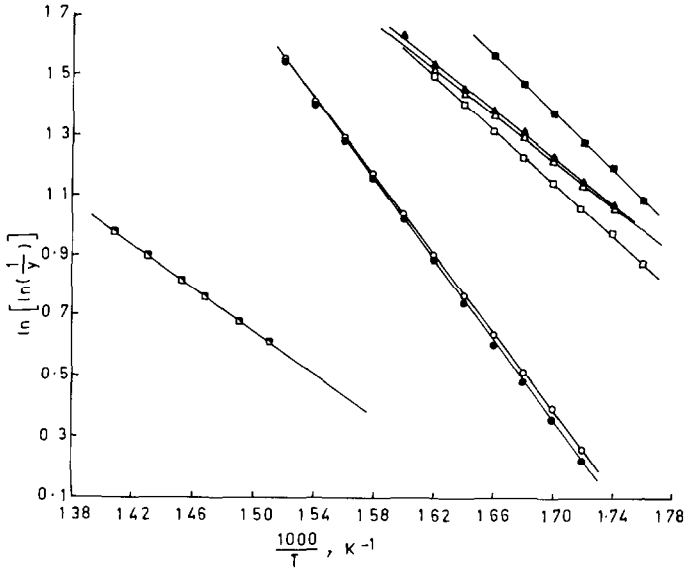


Fig. 10. Plots of $\ln[\ln(1/y)]$ vs. $1000/T$ for evaluation of E_a by Broido's method for the third stage of thermal degradation of cellobiose (◥), cellobiose 2-chlorobenzoate samples (ii) (●) and (iii) (○), cellobiose 2-bromobenzoate samples (iv) (■) and (v) (□), and cellobiose 2-iodobenzoate samples (vi) (▲) and (vii) (△).

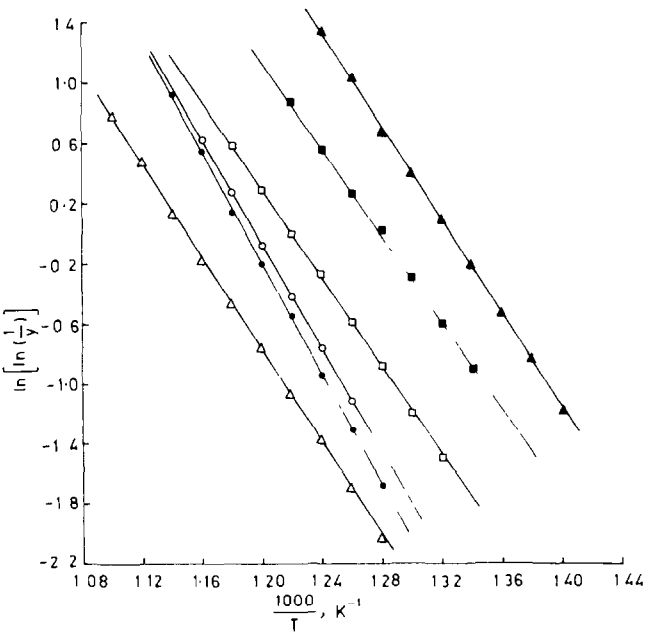


Fig. 11. Plots of $\ln[\ln(1/y)]$ vs. $1000/T$ for evaluation of E_a by Broido's method for the fourth stage of thermal degradation of cellobiose 2-chlorobenzoate samples (ii) (●) and (iii) (○), cellobiose 2-bromobenzoate samples (iv) (△) and (v) (□), and cellobiose 2-iodobenzoate samples (vi) (▲) and (vii) (■).

TABLE 3

DTG maxima, and energies of activation and frequency factors (evaluated by Broido's method) for the second stage (decomposition) of the thermal degradation of cellobiose and its halobenzoate samples in air

Sample No. [a]	DTG maximum (°C)	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})
(i)	–	310–370	194.30	1.86×10^{14}
(ii)	298	210–305	191.75	4.99×10^{12}
(iii)	295	245–305	185.68	1.35×10^{12}
(iv)	274	220–290	132.10	4.62×10^{7}
(v)	271	210–290	120.51	2.98×10^{6}
(vi)	267	240–290	167.94	1.20×10^{11}
(vii)	270	200–295	149.58	1.83×10^{9}

[a] See Table 1.

TABLE 4

Energies of activation and frequency factors (evaluated by Broido's method) for the third stage of the thermal degradation of cellobiose and its halobenzoate samples in air

Sample No. [a]	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})
(i)	370–440	30.00	6.20×10^{-1}
(ii)	305–400	54.80	3.04×10^{-1}
(iii)	305–400	53.82	2.51×10^{-1}
(iv)	290–340	39.21	2.76×10^{-2}
(v)	290–360	36.27	1.08×10^{-2}
(vi)	290–360	32.96	5.31×10^{-3}
(vii)	295–360	31.47	3.76×10^{-3}

[a] See Table 1.

TABLE 5

Energies of activation and frequency factors (evaluated by Broido's method) for the fourth stage of the thermal degradation of cellobiose and its halobenzoate samples in air

Sample No. [a]	Temp. range (°C)	E_a (kJ mol^{-1})	Z (s^{-1})	Char yield at 725 K (wt. %)
(i)	–	–	–	17.84
(ii)	475–610	154.09	1.65×10^{4}	16.90
(iii)	475–610	144.77	4.59×10^{3}	19.32
(iv)	480–650	129.31	2.02×10^{2}	23.20
(v)	450–600	124.12	3.06×10^{2}	25.83
(vi)	400–540	130.22	4.78×10^{3}	21.66
(vii)	425–560	122.51	6.34×10^{2}	23.33

[a] See Table 1.

of the halogen atom. For example, higher DS (6.99) of sample (iii) lowers the activation energy from 217.20 kJ mol^{-1} for cellobiose to 121.63 kJ mol^{-1}, while for sample (vi) with DS 4.19, the lowering in E_a is small, i.e., from 217.20 to 154.64 kJ mol^{-1}.

It can be observed from Table 3 that the energies of activation for the second stage (decomposition) of the thermal degradation are less than that of cellobiose and decrease with increasing DS and size of the halogen atom. Although the DS for cellobiose 2-chlorobenzoate samples (ii and iii) are high, the lowering in activation energies is small. For cellobiose 2-bromobenzoate samples (iv and v) with DS 5.54 and 6.04, the decrease in activation energy is higher, i.e., from 194.3 kJ mol^{-1} for cellobiose to 132.1 and 120.5 kJ mol^{-1}, respectively, for samples (iv) and (v). The energy of activation for samples (vi) and (vii) (cellobiose 2-iodobenzoate) decreases from 167.9 to 149.5 kJ mol^{-1} as the DS increases from 4.19 to 4.76. The higher values for samples (vi) and (vii) compared with those for samples (iv) and (v) may be due to a lower degree of substitution in the former.

The energies of activation (Tables 4 and 5) for the third stage (oxidation of decomposition products) and fourth stage (oxidation of the charred residual matter) of the thermal degradation of cellobiose halobenzoate samples (ii–vii) are also found to decrease with increasing size and content of the halogen atom present in the cellobiose matrix.

It may be inferred from the above discussion that activation energies for thermal degradation of the cellobiose samples (ii–vii) decrease with increasing DS and size of the halogen atom. This indicates that the incorporation of halogen into the cellobiose matrix decreases activation energy and thereby thermal stability, thus reducing the amount of volatile products formed during the thermal degradation. In other words, the amounts of char (Table 5) formed are found to increase with increasing size and content of the halogen. This is in agreement with the findings of Shafizadeh et al. [26] and Bhatnagar et al. [7,8].

Infrared spectral studies of char residues

To study the nature of the products of the thermal degradation of cellobiose halobenzoate samples, only cellobiose 2-chlorobenzoate with DS 6.14 (sample (ii)) was subjected to heating at 250, 275, 290, 300, 325 and 350 °C in air and the IR spectra of the original sample (ii) and the resultant residual materials, shown in Fig. 12, were recorded. The IR spectrum of the residue obtained on heating showed that up to 290 °C, the intensity of the bands at 3450 (O–H stretching), 3040 (aromatic =C–H str.), 2920 (aliphatic C–H str.) and 1730 cm^{-1} (C=O str. of ester group) decreased, indicating that during the initial stages of degradation, cellobiose 2-chlorobenzoate undergoes thermolysis eliminating carboxylic acid and water. At 300 °C, the intensity of all the bands due to cellobiose 2-chlorobenzoate became fairly

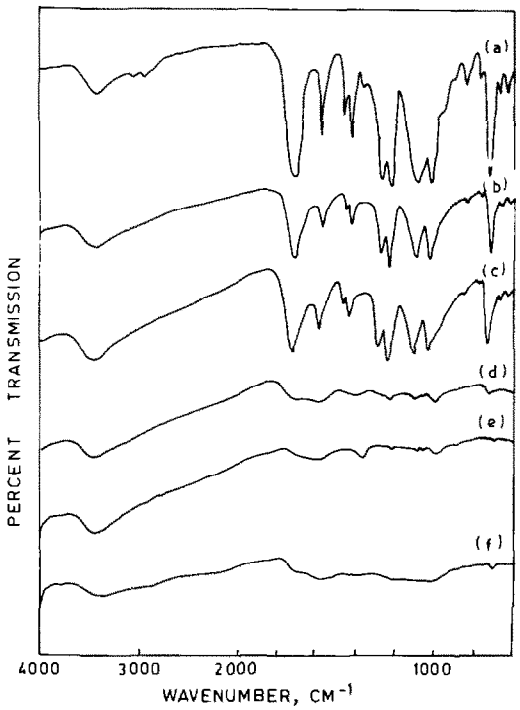
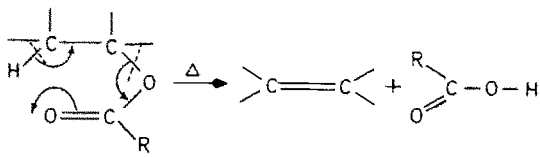


Fig. 12. IR spectra of (a) cellobiose chlorobenzoate and (b–f) chars of cellobiose chlorobenzoate at 250, 290, 300, 325 and 350 °C, respectively.

small suggesting that the residue starts cleaving. Further, at 325 °C, all the bands due to cellobiose 2-chlorobenzoate almost disappeared indicating the evolution of volatile products at higher temperatures. The spectrum of the residue obtained at 350 °C showed broad bands with low intensity at 1710 (C=O str.) and 1600 cm^{-1} (C=C conjugation). These bands suggest skeletal rearrangement, formation of carbonyl compounds and extension of the conjugation of the C=C bonds in the residue from cellobiose 2-chlorobenzoate.

Mechanism of thermal degradation

Bhatnagar et al. [17] have reported that the mass spectrum of cellobiose acetate shows an abundance of fragments with m/z 28 and 44, indicating the formation of CO and CO_2. Significant constituents of the volatile fractions appeared at m/z 60 and 18, due to CH_3COOH and H_2O, respectively. Scotney [29] has also made similar observations during the thermal degradation of cellulose triacetate. According to this author, the early evolution of higher amounts of oxides of carbon is due to the extensive breakdown of the pyranose ring. Scotney [29] also found an initial elimination of acetic acid (de-acetylation) to leave an unsaturated tarry material



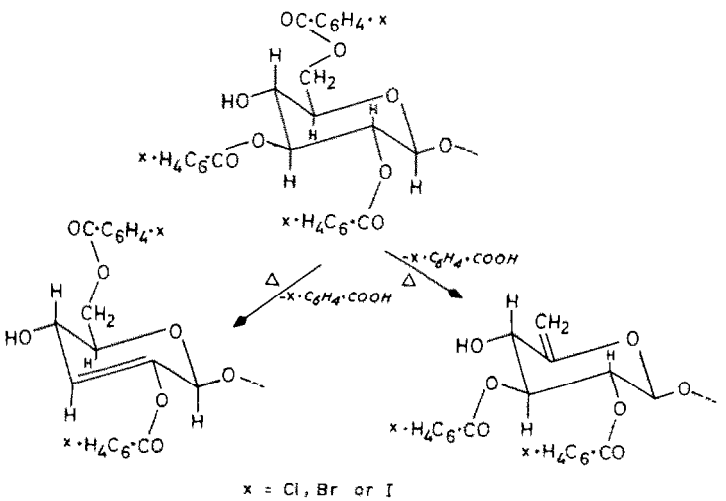
Scheme 1.

and assumed that de-acetylation in the polymer chain is one of the main degradation processes. The elimination of the acid, as proposed by Grassie [30], can be represented by Scheme 1.

Recently, Bhatnagar et al. [9,31] have proposed a mechanism for the thermal degradation of cellulose esters using various thermal studies and their mechanism is in good agreement with the observations of Scotney [29]. Based on the above evidence, a similar mechanism to that for cellulose esters is plausible for the thermal degradation of cellobiose halobenzoate samples.

It is observed from the IR spectra of the char residues of cellobiose 2-chlorobenzoate samples that during the thermal degradation, the initial reaction is the elimination of the halobenzoic acid (de-esterification). A *cis* elimination (Scheme 2), giving a methylene group at C_5–C_6 or a double bond between C_2 and C_3 inside the ring, is supported by other workers [32]. The carboxylic acid released apparently alters thermolysis of the substrate to such an extent that the primary decomposition products are changed from levoglucosan and other products of cellobiose to carbonaceous char.

As reported by Shafizadeh [26], dehydrohalogenation takes place after the initial dissociation of the halobenzoic acid resulting in the formation of



Scheme 2.

hydrogen halide. The released hydrogen halide then catalyses a series of heterolytic reactions including dehydration, transglycosylation, etc., and results in tarry condensation products [25] which further release CO, CO_2, etc., and eventually produce large amounts of char.

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REFERENCES

1 S.L. Madorsky, V.E. Hart and S. Strauss, J. Res. Natl. Bur. Stand., 56 (1956) 343
2 K. Akita, Rept. Fire Res. Inst., Jpn., 9 (1959).
3 F. Shafizadeh, Adv. Carbohydr. Chem., 23 (1968) 419.
4 F. Shafizadeh, J. Polym. Sci., 36(C) (1971) 21.
5 F. Shafizadeh, Appl. Polym. Symp., 28 (1975) 153.
6 C. Fairbridge, R.A. Ross and S.P. Sood, J. Appl. Polym. Sci., 22 (1978) 497.
7 S. Bhatnagar, S. Lal and H.L. Bhatnagar, Indian J. Chem., 20A (1981) 839.
8 S. Bhatnagar, S.L. Agnish and H.L. Bhatnagar, Indian J. Text. Res., 7 (1982) 13.
9 R.K. Jain, K. Lal and H.L. Bhatnagar, J. Anal. Appl. Pyrol., 8 (1985) 359.
10 D. Gardiner, J. Chem. Soc. C, 17 (1966) 1473.
11 K. Kato, Agr. Biol. Chem. (Tokyo), 31 (1967) 657.
12 K. Heyns and M. Klier, Carbohydr. Res., 6 (1968) 436.
13 I.E. Puddington, Can. J. Res., 26B (1948) 415.
14 C. Kala, I.S. Gur and H.L. Bhatnagar, Indian J. Chem., 19A (1980) 641.
15 R.K. Jain, K. Lal and H.L. Bhatnagar, Indian J. Chem., 23A (1984) 828.
16 A.R. Rao, I.S. Gur and H.L. Bhatnagar, J. Indian Chem. Soc., 62 (1985) 595.
17 R.K. Jain, K. Lal and H.L. Bhatnagar, Cellulose Chem. Technol., 20 (1986) 169.
18 H.T. Clarke (Ed.), A Handbook of Organic Analysis, 4th edn., Orient Longman, London, 1970, p. 308.
19 W.E. Gloor and E.D. Klug, in E. Ott, H.M. Spurlin and M.W. Grafflin (Eds.), Cellulose and Cellulose Derivatives, Vol. V, Part III, Wiley-Interscience, New York, 1955, p. 1422
20 A. Broido, J. Polym. Sci., Part A-2, 7 (1969) 1761.
21 R.I. Thrune, Am. Chem. Soc., Div. Org. Coatings Plastics Chem., Prepr., 23(1) (1963) 15.
22 A. Fish, N.H. Franklin and R.T. Pollard, J. Appl. Chem., 13 (1963) 506.
23 J. Eichhor, J. Appl. Polym. Sci., 8 (1964) 2497.
24 P. Robitschek, J. Cellulose Plastics, 1 (1965) 395.
25 F. Shafizadeh, Y.Z. Lai and C.R. McIntyre, J. Appl. Polym. Sci., 22 (1978) 1183.
26 F. Shafizadeh, Y.Z. Lai and C.R. Nelson, J. Appl. Polym. Sci., 20 (1976) 139.
27 R.F. Simmons and H.G. Wolfhard, Trans. Faraday Soc., 51 (1955) 1211.
28 W.A. Rosser, H. Wise and H. Miller, 7th Int. Symp. on Combustion, Butterworth, London, 1959, p. 175.
29 A. Scotney, Eur. Polym. J., 8 (1972) 163.
30 N. Grassie, J. Polym. Sci., 48 (1960) 79.
31 R.K. Jain, K. Lal and H.L. Bhatnagar, Makromol. Chem., 183 (1982) 3003.
32 C.H. Depuy and R.W. King, Chem. Rev., 60 (1960) 431.