WATER-CATALYSED HYDROLYSIS OF p-NITROBENZYL CELLULOSE XANTHATE

EDUARDO HUMERES* AND LUIZ FERNANDO SEQUINEL

Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil

MAURICÉA NUNES AND CÉLIA M. S. OLIVEIRA

Departamento de Química, Universidade Federal de Minas Gerais, Pampulha, 31270 Belo Horizonte, MG, Brazil

AND

PATRICK J. BARRIE

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

The spontaneous hydrolysis of p-nitrobenzyl cellulose xanthate (CelXNB) with a degree of substitution (DS) in the range 2–9 was studied in 10% aqueous ethanol at pH 10, and was followed spectrophotometrically by the appearance of p-nitro-α-toluenethiol, in a continuous-flow system where the reactor was shaken. CelXNB was characterized by solid-state ^{13}C NMR spectra. The reaction occurs through two parallel processes due to two xanthate ester groups with different reactivities. The fast hydrolysis was ascribed to the reaction of the C-2 + C-3 isomers, whereas the slow hydrolysis was due to the C-6 isomer. The percentage of the latter is much higher than C-2 + C-3. The solvent isotope effect of the fast hydrolysis ($k_{H_2O}^f/k_{D_2O}^f$) was $2 \cdot 22 \pm 0 \cdot 16$ and the proton inventory indicated that there is only one proton transfer involved in the transition state, where a second water (or a neighbouring OH group) acts as a general base. The entropy of activation of the fast hydrolysis was only $3 \cdot 3 \pm 0 \cdot 8$ e.u., suggesting that the water molecules involved are highly oriented with respect to the coordinates required to reach the transition state. It is proposed that they form part of the three-dimensional hydrogen-bonded ice-like structure that involves the cellulose matrix.

INTRODUCTION

Hydrolyses of xanthate esters are characterized by profiles showing a pH-independent process or water-catalysed spontaneous hydrolysis, followed by a specific base-catalysed reaction at higher pH.[1] The first-order rate constants show general base catalysis, and when extrapolated to zero buffer concentration, k_{obs} is expressed by the equation

$$k_{obs} = k_0 + k_{OH}[OH] \qquad (1)$$

where k_0 is the spontaneous water-catalysed rate constant and k_{OH} is the second-order rate constant for the specific base catalysis. The pH–rate profile of the hydrolysis of p-nitrobenzyl cellulose xanthate (2) also follows equation (1), with a pH-independent spontaneous hydrolysis region at pH $< 10 \cdot 5$.[2] This region is similar to that found for analogues such as p-

nitrobenzyl ethylxanthate (NBEX) or methyl-α-D-glucopyranoside-6-(S-p-nitrobenzylxanthate).[1,2] For these simple xanthate esters, the spontaneous hydrolysis is a slow process, but CelXNB showed an unexpectedly high rate constant, about 3000 times faster than that for NBEX, although the reactivity with respect to external nucleophiles such as hydroxide ion and amines is similar to that of NBEX.[2]
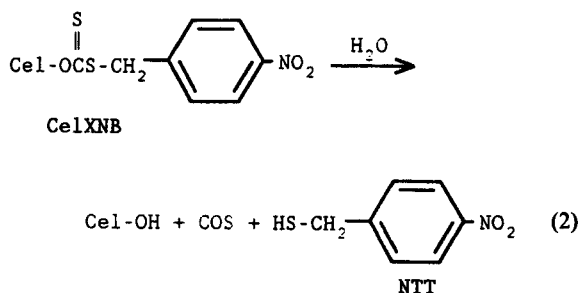
The interaction of carbohydrates with water through the hydrogen bonding of the sugar hydroxyls should be highly dependent on the precise spatial arrangements of those groups, such as the conformation of the carbohydrate, but is is not known if the structure of water maximizes the extent of hydrogen-bonded interactions of the solute.[3] Kinetic medium effects induced by carbohydrates give some insight into the specificity of the stereochemical interaction with water.[4,5] The purpose of this work was to study the effect of the water interaction on the reactivity of a moiety covalently bound to a polysaccharide system, looking for a detailed description of a reaction occurring on the liquid–solid interface of cellulose. Further papers will compare these results with the behaviour of small analogue molecules.

EXPERIMENTAL

All reagents were of analytical grade and were used without further purification. Deuterium oxide from Sigma Chemical was 99·8 atom-% D.

p-Nitrobenzyl cellulose xanthate (CelXNB). About 3 g of cotton tissue was first washed with 1 M hydrochloric acid for 2 h and then exhaustively with water and subsequently treated with 100 ml of 1 M sodium hydroxide for 5 h with shaking. A solution of 20 g of carbon disulphide in 100 ml of acetone was added and it was allowed to react for 3 h with continuous shaking. After filtering, the product was washed several times with 0·1 M sodium monohydrogenphosphate at pH 8. The cellulose xanthate was treated with a solution of 3 g of *p*-nitrobenzyl bromide in 100 ml of acetone and shaken for 14 h. The product was washed with cold water, ethanol and diethyl ether to eliminate any adsorbed impurity, followed by treatment with 0·1 M hydrochloric acid to decompose non-esterified xanthate groups, repeating the washing with cold water, ethanol and diethyl ether. Finally, the CelXNB was dried under vacuum over phosphorus pentoxide and stored in a freezer. It was characterized by the degree of substitution (*DS*), defined as the average number of xanthate ester groups per 100 glucoanhydropyranose units in the cellulose, and determined as described previously.[2] In general, the *DS* of CelXNB was in the range 3–4, when following the procedure described above, but higher values were obtained on increasing the concentration of NaOH.

Solid-state ^{13}C NMR spectra of CelXNB were obtained with a Bruker MSL–300 spectrometer, using CP/MAS TOSS (total side-band suppression), with a total acquisition time of about 12 h. The contact time used was 2 ms and the recycle delay between scans was 4 s.

Kinetics. Experiments were carried out in a continuous-flow system. A 30 ml thermostated double-walled reactor was mechanically stirred. A peristaltic pump kept a constant flow through a UV cell that allowed continuous absorbance readings against time. A small overpressure of nitrogen in the reactor produced an inert atmosphere to avoid oxidation of the *p*-nitro-α-toluenethiol (NTT) produced in the hydrolysis. For the same reason, all water used in the solutions was previously deoxygenated by boiling and cooling in inert atmosphere. The reaction was followed by the appearance of NTT at 280 nm. Typically in a run, about 50 mg of CelXNB were introduced into the reactor where 25 ml of the kinetic solution were thermally equilibrated.

This continuous reading system indicated that the spontaneous hydrolysis absorbance vs time curves were not strictly first order. After a first fast increase, a slower rate was observed towards the theoretical infinity absorbance value A_∞, calculated from the *DS*. These two reactions produced the same product (NTT) as observed from the UV spectrum, and can be analysed kinetically according to the equation

$$\text{CelXNB} -\left[\begin{array}{c} X' \xrightarrow{\ k'\ } \\ X'' \xrightarrow{\ k''\ } \end{array}\right] \longrightarrow \text{NTT} \qquad (3)$$
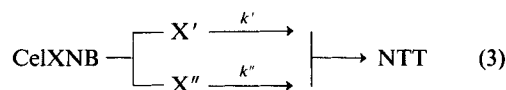
where $k' \geqslant k''$ and X' and X'' are two xanthate ester groups with different reactivities. At any time the observed absorbance A is given by

$$A = A_\infty - A_0'e^{-k't} - A_0''e^{-k''t} \qquad (4)$$

where A_0' and A_0'' are the NTT absorbances proportional to the initial concentrations X_0' and X_0'' of both esters. The ratio A_0''/A_0' is equal to X_0''/X_0'. The term $A_0' \exp(-k't) = A'$ decreases much faster than $A_0'' \exp(-k''t) = A''$, and from a plot of $\ln(A_\infty - A)$ vs time, k'' and A_0'' can be obtained (Figure 1). Since the term $A_0'' \exp(-k''t)$ can be calculated for any time, a plot of $\ln A'$ vs time produced k' from the slope and $\ln A_0'$ from the intercept. In order to calculate A_0' and A_0'', the zero time for the absorbance vs time plots was defined as the moment of contact of the CelXNB sample with the solution, although readings started about 1 min later. The sum of A_0' and A_0'' is equal to A_∞, and the ratio A_0''/A_0' indicates the relative distribution of the two groups. In general, the values of k'' were less accurate than those of k'.

Several experiments were made in order to find out whether the second reaction was an artifact or a true reaction. Control tests in which the cellulose was treated under the same conditions to obtain CelXNB, but without using CS_2 and *p*-nitrobenzyl bromide, showed constant absorbance readings. When a sample of CelXNB was allowed to hydrolyse for 10 half-lives of the fast reaction (k'), a fast increase in absorbance was observed when a solution of ethylamine was added. The
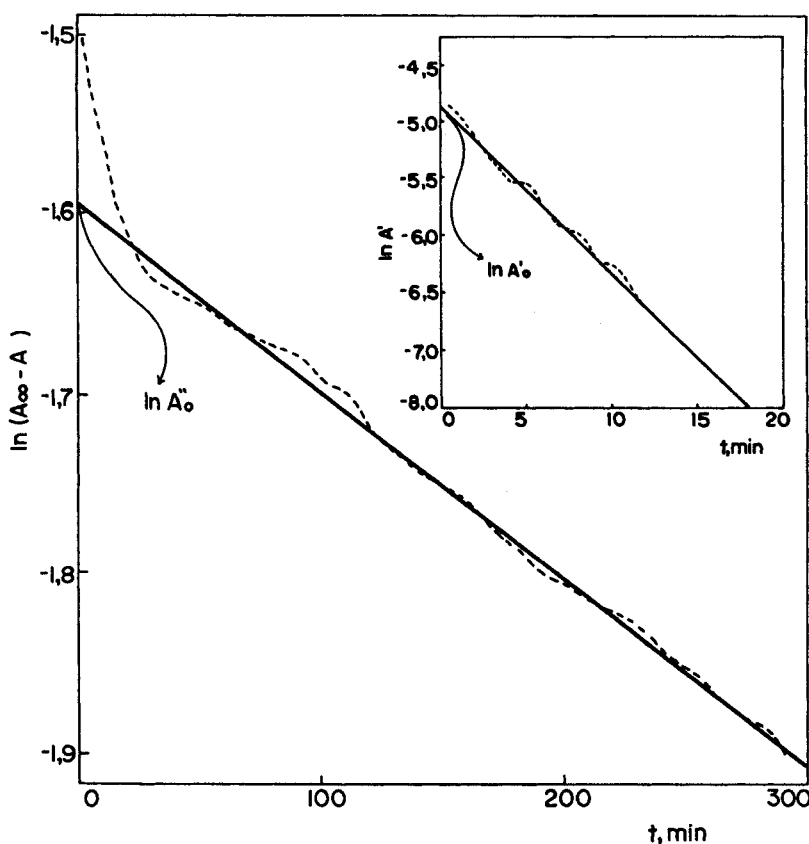
Figure 1. Plot of $\ln(A_\infty - A)$ and $\ln A'$ vs time for the hydrolysis of CelXNB at 25 °C, pH 10·0, 0·10 M carbonate, $\mu = 0·6$ (KCl), in 10% aqueous ethanol. The solid line was calculated from the least-squares fit

final reading was about the same as the expected infinity reading considering the DS.

The pH–rate profile of the fast hydrolysis was previously studied and it is similar to that for other xanthate esters.[1,2] Since there is a close correlation between the DS calculated from the aminolysis of CelXNB and that calculated from the ^{13}C NMR spectrum (see below), in another set of experiments CelXNB was allowed to react at room temperature at pH 10·0 (0·10 M carbonate) in 10% aqueous ethanol. Samples were taken at different times, washing with 50% aqueous ethanol, then with pure ethanol and finally with dry ethyl ether, and then dried under vacuum. The first sample was taken after 50 min, approximately 10 half-lives of the fast hydrolysis, and the second after 128 h, following the same procedure as for the first sample (Figure 2). After 50 min there was only partial hydrolysis of the p-nitrobenzyl xanthate and only a small decrease of the DS to 6·30 was observed. After 128 h the reaction was almost complete and the DS had now

decreased to 0·95. These results support the theory that there are two kinds of xanthate ester groups in CelXNB.

On the other hand, the base hydrolysis is strictly second order. Addition of ethylamine does not produce a change in the experimental infinity reading, which at the same time agrees with that calculated from the DS value.

The hydrolysis and aminolysis of CelXNB were also studied in 20% aqueous methanol at 35 °C, $\mu = 0·1$ (NaCl), except for the basic hydrolysis, which was run in 1 M NaOH.

Activation parameters. The fast hydrolysis rate constants k' correspond to those previously reported in pure water,[2] and are independent of pH at pH < 10·5. Hydrolyses of CelXNB were carried out in 10% aqueous ethanol at four temperatures. At each temperature the rate constants were obtained at three different concentrations of carbonate buffer (0·1, 0·2
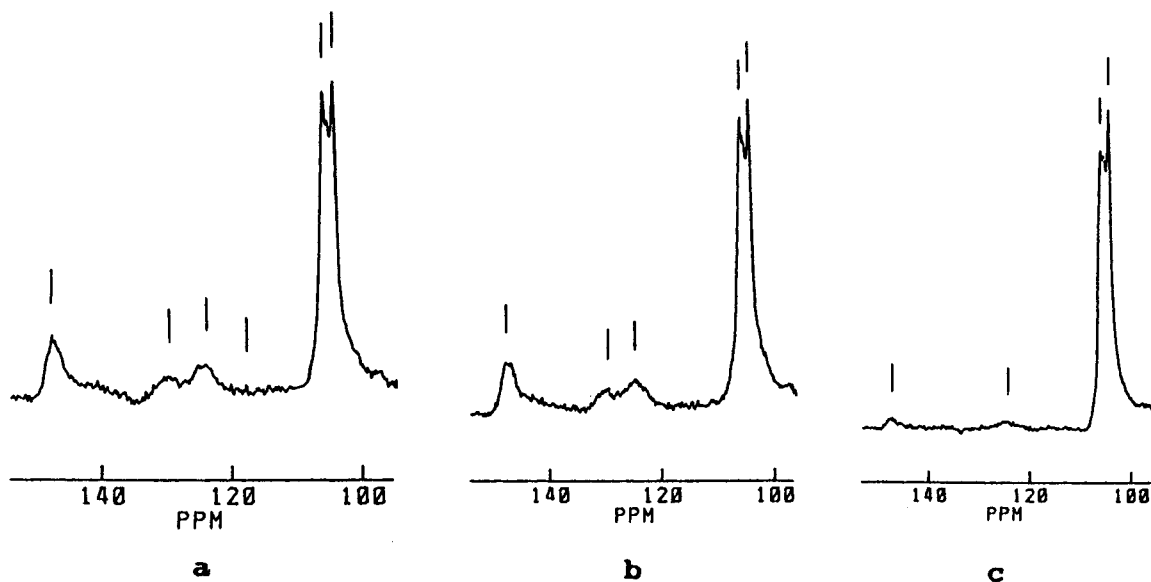
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Figure 2. ^{13}C CP/MAS TOSS NMR spectra of solid CelXNB, allowed to react at room temperature at pH $10 \cdot 0$ ($0 \cdot 10$ M carbonate) in 10% aqueous ethanol. (a) Initial ($DS = 6 \cdot 7$); (b) after 50 min ($DS = 6 \cdot 3$); (c) after 128 h ($DS = 0 \cdot 95$)

and $0 \cdot 3$ M) and the values reported were obtained by extrapolation of the buffer plot to zero buffer concentration because general base catalysis was observed for this reaction.[2]

The activation parameters were obtained by least-squares fitting from the Eyring equation:

$$\Delta G^{\neq} = RT \ln(k_B T / h k') \tag{5a}$$

$$\ln(k'/T) = (-\Delta H^{\neq}/R)(1/T) + \text{constant} \tag{5b}$$

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T} \tag{5c}$$

where k' is the rate constant and k_B and h are the Planck and Boltzmann constants, respectively.

Solvent isotope effects. All deuterated solutions and pH measurements were made inside a dry-box in a nitrogen atmosphere. The value of pH $10 \cdot 0$ was not corrected with respect to the molar fraction of D_2O because in that range the rate constants are independent of pH.[6,7] The kinetic runs were carried out at 25 °C in 10% ethanol-OD, at three different carbonate buffer concentrations and the rate constants were extrapolated to zero buffer concentration.

RESULTS

Activation parameters

In the reactions of cellulose xanthate esters with low *DS*, as is the case for CelXNB, the xanthate moiety behaves independently of the molecular mass of the cellulose matrix. It was shown that under conditions of strong mechanical shaking the rate constants are not diffusion controlled and they are first order with respect to the xanthate moiety and independent of the amount of the polymer in the system.[2] Therefore, under those conditions, the number of moles of xanthate moiety per unit volume is an intensive property of the system, regardless of the fact that some groups are bound through the polymer chain. These results allow a comparison of the reactivity of xanthate esters bound to a cellulose matrix or to small molecules through the activation parameters.

In Table 1 are given the rate constants for the fast (k') and slow (k'') spontaneous hydrolysis of CelXNB at different temperatures, along with the rate constants for the hydroxide ion-catalysed reaction (k_{OH}). The average ratio A_0''/A_0' showed that the percentage of isomer X'' (slow) in the cellulose is much higher than that of isomer X' (fast). The activation parameters for the fast spontaneous and basic hydrolysis are given in Table 2.

Solvent isotope effects

The spontaneous hydrolysis of CelXNB was also studied in water–deuterium oxide mixtures at different buffer concentrations, and the rate constants were extrapolated to zero buffer concentration. The solvent kinetic isotope effect on k' was $k_{H_2O}/k_{D_2O} = 2 \cdot 22 \pm 0 \cdot 16$ and the proton inventory produced a

Table 1. Hydrolysis of CelXNB in 10% aqueous ethanol

t (°C)	$10^3 k'$ (s⁻¹)	$10^5 k''$ (s⁻¹)[a]	A_0''/A_0'	$10^4 k_{OH}$ (l mol⁻¹ s⁻¹)[b]
20·0	—	—	—	5·63
23·0	0·64 ± 0·07	1·3 ± 0·2	24 ± 9	—
25·0	0·82 ± 0·04	1·4 ± 0·3	27 ± 2	9·28
28·0	1·24 ± 0·11	1·9 ± 0·3	26 ± 5	—
30·0	1·58 ± 0·08	2·2 ± 0·5	19 ± 6	11·46
35·0	—	—	—	16·51

[a] At pH 10·0 (carbonate buffer), $\mu = 0·6$ (KCl). The rate constants were extrapolated to zero buffer concentration. CelXNB ($DS = 4·1$), except at 25 °C, where $DS = 1·56$.
[b] In 1 M NaOH and CelXNB ($DS = 9·7$).

Table 2. Activation parameters for the hydrolysis of CelXNB in 10% aqueous ethanol

Catalyst	$\Delta H^{\neq}$ (kcal mol⁻¹)	$\Delta S^{\neq}$ (e.u.)
H₂O, fast hydrolysis[a]	22·6 ± 0·2	3·3 ± 0·8
OH⁻[b]	11·8 ± 0·7	− 33·4 ± 2·8

[a] Rate constants extrapolated to zero buffer concentration, $\mu = 0·6$ (KCl).
[b] In 1 M NaOH.

Table 3. Spontaneous hydrolysis of CelXNB ($DS = 4·1$) in water–deuterium oxide[a]

n_{D_2O}	[Carbonate] (M)	$10^3 k$ (s⁻¹)
0·00		
	0·20	3·27
	0·10	2·19
	0·05	1·36
	0·00	0·82 ± 0·04[b] (0·82)[c]
0·277		
	0·20	1·95
	0·10	1·38
	0·05	0·98
	0·00	0·70 ± 0·02[b] (0·70)[c]
0·544		
	0·20	1·98
	0·10	1·26
	0·05	0·93
	0·00	0·57 ± 0·01[b] (0·58)[c]
0·998		
	0·18	1·97
	0·10	1·29
	0·05	0·80
	0·00	0·37 ± 0·02[b] (0·37)[c]

[a] 25·0 °C, $\mu = 0·6$ (KCl), pH = 10·0, in 10% aqueous ethanol.
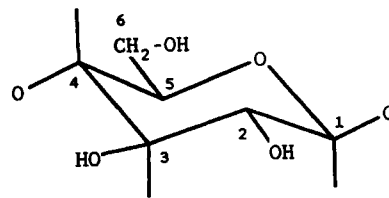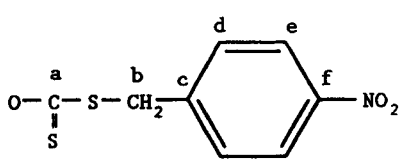[b] Extrapolated value.
[c] Calculated from the Gross–Butler equation for $n = 1$.

straight line, which according to the Gross–Butler equation indicates that only one proton transfer is involved in the transition state (Table 3).

Characterization of CelXNB by solid-state NMR

CelXNB with higher DS was obtained by increasing the concentrations of NaOH and CS₂, in order to obtain

Table 4. ¹³C chemical shifts of CelXNB[a]

Carbon	Chemical shift (ppm)			

C-1	106·2[b]	105·5[c]	104·5[b]	
C-4	89·3[b]	84·3[c]		
C-2, -3, -5	75·3	74·7	72·9	71·8
C-6	65·5[b]	63·2[c]		

C-a	213·6
C-b	39·8
C-c, -f	147·7
C-d	131·9
C-e	124·9

[a] CP/MAS TOSS.
[b] From crystalline components.[8]
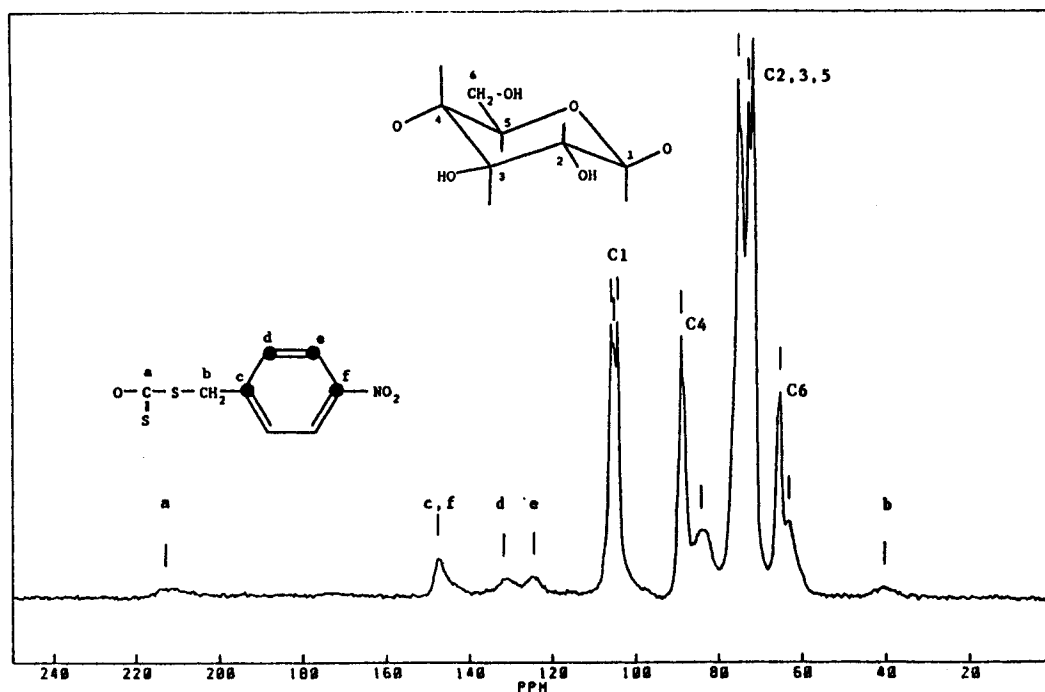[c] From non-crystalline components.[8]

Figure 3. CP/MAS TOSS ^{13}C solid-state NMR spectrum of CelXNB ($DS = 5 \cdot 7$)

better NMR spectra. In Figure 3 the solid-state ^{13}C CP/MAS TOSS NMR spectrum of a sample of CelXNB with $DS = 5 \cdot 7$ is shown. The chemical shifts of the individual carbons of cellulose in Table 4 were assigned according to Hirai *et al.*[8] for cotton. The thiocarbonyl carbon C-a of the xanthate ester group should have a chemical shift similar to that of CS_2 (200 ppm) or that of cellulose xanthate (233–232 ppm) because they were observed in solution.[9] The other assignments are straightforward.[10]

At this level of substitution, the solid-state NMR spectra do not allow any estimation of the isomer distribution on positions 2, 3 and 6 of the glucopyranose ring, as has been made for cellulose xanthate.[9] However, integration of the signals in the 120–150 ppm region corresponding to the six aryl carbons, and those in the 90–110 ppm region corresponding to C-1, allows the calculation of DS:

$$(DS)_{NMR} = \frac{100(\text{aryl area})/6}{(C\text{-}1 \text{ area})}$$

These results agree reasonably well with the DS calculated from the aminolysis method.[2] The plot of DS vs $(DS)_{NMR}$ gave a straight line with slope $0 \cdot 98$ ($r = 0 \cdot 983$).

DISCUSSION

Hydrolysis of CelXNB occurs through two mechanisms. At pH < $10 \cdot 5$ the reaction proceeds through a spontaneous hydrolysis and at higher pH the pH–rate profile shows that base-catalysed mechanism predominates.[2]

According to Table 1, there are two different isomers in the CelXNB that hydrolyse spontaneously with rate constants k' and k'', where the first is about 60 times faster than the second, at 25 °C.

A fair estimate of the isomer distribution can be obtained from the A_0''/A_0' ratio (Table 1). This ratio indicates that CelXNB contains about 96% of the slower isomer, although this distribution might depend on the preparation procedure of CelXNB.

It is expected that the C-6 isomer predominates over the C-2 + C-3 isomer. The reaction of methyl-α-D-glucopyranoside with carbon disulphide in alkaline solution produced 88% of the C-6 isomer.[11] There is significant migration of the thiolthionocarbonyl group from positions 2 and 3, and the final composition depends on the basicity of the medium and the time of reaction. After ripening, only the C-6 isomer was found in cellulose xanthate.[9] One can conclude that the ratio A_0''/A_0' represents the relative concentration of the C-6

isomer with respect to the sum of C-2 and C-3 isomers, and consequently the slowest isomer to hydrolyse spontaneously is the 6-substituted isomer and the C-2 and C-3 isomers hydrolyse faster.

There is no difference in the reactivity among the isomers for the reaction with respect to external nucleophiles such as hydroxide ion and amines. The reaction is strictly pseudo-first order with respect to CelXNB. The rate-determining step for the aminolysis of simple xanthate esters is the formation of the tetrahedral intermediate, whereas for the base-catalysed hydrolysis it is the breakdown of the intermediate.[1] Also, the reaction of CelXNB with hydroxide ion is slower than that of the p-nitrobenzyl O-ethylxanthate analogue and the same trend is followed by the aminolysis reaction (Figure 4). Therefore, it is surprising that only the spontaneous hydrolysis of CelXNB is faster than that of other analogues. It was proposed that this acceleration could be a consequence of the highly ordered cybotactic region formed by the water around
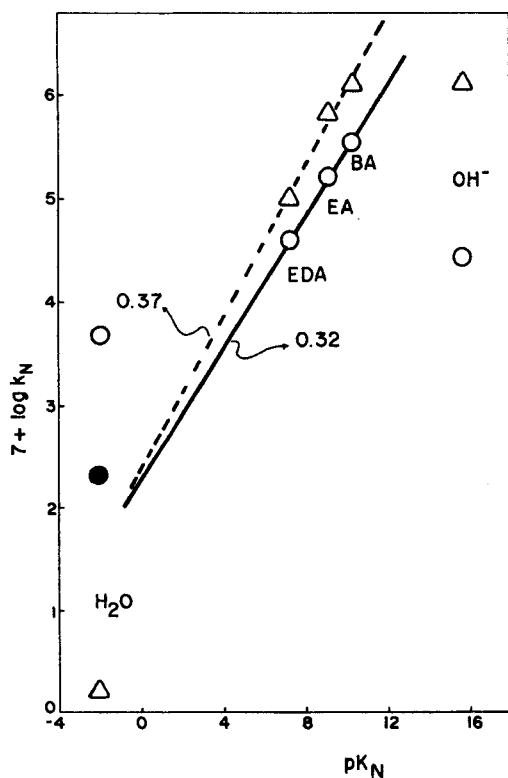

Figure 4. Brønsted plot for nucleophilic reactions of CelXNB (○, this work) and p-nitrobenzyl ethylxanthate (△ , Ref. 1) at 35 °C in 20% aqueous methanol, $\mu = 0 \cdot 1$ (NaCl). CelXNB and water: open circle, k'; solid circle k''. EDA, ethylenediamine; EA, ethanolamine; BA, n-butylamine

the cellulose, predicting that in that case the entropy of activation should be near zero.[2] The entropy of activation is only $3 \cdot 3 \pm 0 \cdot 8$ e.u. for the fast spontaneous hydrolysis reaction of CelXNB. Unfortunately, the values of k'' are not accurate enough to calculate reliable activation parameters. Anyhow, that value for the entropy of activation is unique in the literature for water-catalysed hydrolyses of esters and amides which are characterized by large negative entropies of activation, often in the range -30 to -40 e.u.[12-14] The near-zero value is strong support for the proposal that there is little or no solvent reorganization between initial and transition state for the reaction.

The basic hydrolysis of CelXNB, on the other hand, occurs with a strongly negative entropy of activation of $-33 \cdot 2$ e.u. (Table 2), as expected from a bimolecular mechanism, and it does not discriminate between the different positional isomers of CelXNE3.

Another feature of the spontaneous hydrolysis of carboxylic esters and amides is the fairly substantial kinetic solvent isotope effect (KSIE) which arises from a general catalysis by water of the spontaneous hydrolysis, involving proton transfer to or from water molecules in the transition state of the rate-determining step.[12-14] The KSIE of the fast spontaneous hydrolysis of CelXNB is $k_{H_2O}/k_{D_2O} = 2 \cdot 22 \pm 0 \cdot 16$, a typical value for carboxylic ester hydrolysis, where water molecules act as general base catalysts.[12] The linear change of k' with the molar fraction of deuterium oxide indicates that there is only one proton transfer involved in the transition state and also signifies that there is little proton transfer to the water molecule acting as general base, or, in other words, the protons of this molecule have very little hydronium character and therefore their fractionation factor is essentially $1 \cdot 0$ and consequently no secondary isotope effect was observed.[15] Only the protons undergoing transfer should show a change in fractionation factor between reagent and transition state.[16,17]

There are several probable transition states considering only the reactant water molecules as shown by structures I–III.[12] Transition state I describes a general base-catalysed process which involves proton removal from the entering water molecule. Considering the isomers on C-2 and C-3, it is also possible that the oxygen on the neighbouring OH of the anhydropyranose ring might act as a general base, instead of a second water molecule as shown in transition state I. However, aminolysis of xanthate esters are general base catalysed,[1] and the vicinal OH could also act as such for the same reaction of CelXNB. The fact that no acceleration was observed for the aminolysis of CelXNB is evidence that the fast spontaneous hydrolysis is not due to the neighbouring group effect of OH. Work in progress using model compounds is expected to produce further evidence on this alternative. Transition state II involves the general acid-catalysed
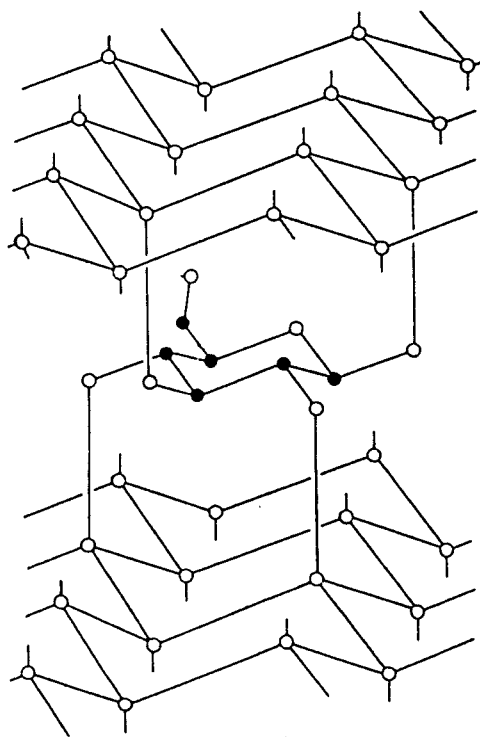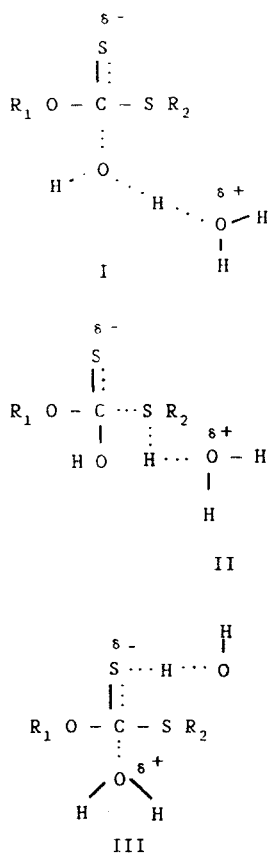
$$\delta^-$$
$$S$$
$$|\colon$$
$$R_1 \quad O - C - S \quad R_2$$
$$\vdots$$
$$O$$
$$H \cdots \overset{}{} \cdots$$
$$H \cdots \quad \delta^+$$
$$O - H$$
$$|$$
$$I \qquad H$$

$$\delta^-$$
$$S$$
$$|\colon$$
$$R_1 \quad O - C \cdots S \quad R_2$$
$$| \qquad \vdots \quad \delta^+$$
$$H \quad O \quad H \cdots \quad O - H$$
$$|$$
$$H$$

$$II$$

$$\delta^- \qquad \overset{H}{|}$$
$$S \cdots H \cdots O$$
$$|\colon$$
$$R_1 \quad O - C - S \quad R_2$$
$$\vdots$$
$$O^{\delta+}$$
$$H \qquad H$$

$$III$$

Figure 5. Insertion of β-D-glucopyranose into the water lattice. Open circles, oxygen atoms; solid circles, carbon atoms; hydrogen atoms between the oxygens are not shown. From Ref. 21

decomposition of the anionic tetrahedral intermediate and structure **III** corresponds to a general acid-catalysed hydration of the thiocarbonyl group. Transition states **II** and **III** should be rejected on the grounds that neither general nor specific acid catalysis is observed in the hydrolysis of xanthate esters.[1] Also, nucleophilic attack of the xanthate esters by weak bases such as amines and water occurs by rate-determining formation of the tetrahedral intermediate, again ruling out structure **II**.[1] Therefore, hydrolysis of CelXNB catalysed by water proceeds through transition state **I**.

Cellulose is strongly hydrated in water[3,18,19] and the β-D-glucose unit can replace almost exactly water molecules in a tridymite ice lattice, expanded to ambient temperatures.[20] Insertion of β-D-glucose into one layer of the lattice has no effect on the relative positions of the other layers (Figure 5). From this point of view, the higher reactivity with water of isomers on C-2 and C-3 might be a consequence of the highly ordered water structure of the inner solvation shell of the cybotactic region in the vicinity of the thiocarbonyl group. The extent of hydration of the oxygen on C-6 is not known, but it is also included in the cybotactic region of the cellulose, and that positon in CelXNB also hydrolyses faster than *p*-nitrobenzyl ethylxanthate (Figure 4). This is a hydrophobic molecule and in water should have a higher free energy than CelXNB. Therefore for the spontaneous hydrolysis of the latter to be faster, the transition state of CelXNB should be more stabilized as a consequence of the orientation of the water molecules. Consistent with this analysis, changing the ethyl group to methyl α-D-glucopyranoside favours the spontaneous hydrolysis.[1]

CONCLUSIONS

Spontaneous hydrolysis of CelXNB occurs through two kind of isomeric xanthate esters. The fast hydrolysis is tentatively ascribed to the sum of C-2 and C-3 isomers, and the slower reaction to the C-6-substituted ester.

The transition state of the fast hydrolysis contains one water molecule upon which a second molecule (or a neighbouring OH group) acts as a general base.

The entropy of activation of the fast process is nearly zero ($\Delta S^{\neq} = 3 \cdot 3 \pm 0 \cdot 8$ e.u.), showing that there is virtually no solvent reorganization between the initial and transition state, owing to the ice-like structure of water in the cybotactic region of CelXNB.

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