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ACTIVATION ENERGY FOR THE SALT CATALYZED HETEROGENEOUS DILUTE ACID HYDROLYSIS OF THE DIFFICULTLY ACCESSIBLE PORTIONS OF MICROCRYSTALLINE CELLULOSE

Abstract

The apparent rate constants, K_c, for the heterogeneous dilute acid hydrolysis of the difficulty accessible portions of microcrystalline cellulose in 0.3 M, 1.0 M and 1.3M HCl containing 0.00 M, 0.08 M and 0.20 M KCl at 60, 70, 75 and 80°C were determined by the loss-in-weight method, and the activation energy, E_a, calculated from the ln K_c versus 1/T curves, where T = absolute temperature. When hydrolysis was carried out in 0.3 M HCl only, a value 25 of kcals obtained for E_a. In the presence of KCl as added electrolyte Ea was found to be constant with a average value of 12.6 = 0.5 kcals·mole^{-1}, and, in the range of concentrations studied, did not depend on the concentration of the added electrolyte. A possible mechanism to account for the low activation energy is presented.

Introduction

The heterogeneous dilute acid hydrolysis of cellulosic materials is characterized by an initial fast rate of hydrolysis in the "amorphous" region of the material, which then decreases until a constant value is reached in the crystalline portion of the material. The slow rate of hydrolysis in the crystalline portion has been attributed to (a) the intensity of inter- and intra-chain H-bonds, and (b) restrictions to the conformational changes necessary for the hydrolytic reaction to occur [1].

The "amorphous" region of cellulose is often assumed to be "freely" accessible to the hydrolysing medium, so that the Arrhenius activation energy calculated from the temperature dependence of the rate of hydrolysis in this region corresponds to that associated with breaking the glycosidic bond in the cellulose chains. The activation energy for the hydrolysis of the crystalline portion, on the other hand, should include an additional quantity of energy related to the breaking of inter and intra-chain H-

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bonds, as well as energy required to overcome restrictions to conformational changes necessary for hydrolysis to occur [1-3].

Different rate laws have been proposed for the heterogenous hydrolysis of cellulose. Meller4 proposed a zero order rate law for the hydrolysis of the difficultly accessible portions of cellose when determined by the loss-in-weight method:

$$\frac{dx}{dt} = k \tag{1}$$

where x = % loss in weight, t = time and k is a constant represented by the slope of the straight portion of the rate plot. Using this law Meller obtained activation energies of 28-29 kcal/mole for the hydrolysis of cotton linters, acetate grade pulp and viscose grade pulp. Nelson3 used the same rate law to show that for cotton linters, mercerized cotton, decrystallised cotton and viscose rayon, the apparent activation energy for both the amorphous and crystalline regions ranges from 31.5 to 33.0 kcal/mole.

When the extent of hydrolysis is followed by the change in degree of polymerization (DP), it was found that data on change in DP with duration of hydrolysis fitted an empirical hyperbolic equation of the type:

$$\frac{1}{kt} = \frac{1}{P_t - P_o} + \frac{1}{P_m - P_o} \tag{2}$$

where k is the empirical rate constant applicable over the entire range of extent of reaction, P_t is the DP at time t, P_o is the initial DP, and P_m is the level-off DP (LODP). Using this empirical rate law Nelson [3] obtained average activation energies for cotton linters and rayon of 30 and 34 kcal/mole respectively. Similar approaches were used by several workers prior to Nelson. Sharples [2] used this approach and obtained activation energies of 31 kcal/mole for the homogeneous hydrolysis of cellobiose and 28 kcal/mole for the accessible fraction in cotton and 38 kcal/mole for the crystalline portion of cotton. Foster and Wardrops obtained a value of 38 kcal/mole for the crystalline fraction of halocellulose. Gibbons [6], and Higgins [7], obtained values ranging from 27 to 35 kcal/mole for clifferent cellulosic materials.

Although there is some variation in the values of E_a reported for different cellulosic materials and different acids used, it is now commonly accepted that the activation energy for the homogeneous acid hydrolysis of cellulose is 28-29 kcal/mole [8]. This is attributed to the energy required to break the glycosidic bond. The activation energy for the hydrolysis of the crystalline region is about 38 kcal/mole, since additional energy is required to break H-bonds in addition to the glycosidic bonds. The energy of an H-bond is often between 3 and 9 kcal/mole [8].

Zaranyika and his co-workers [9, 10] demonstrated that the rate of the heterogeneous dilute acid hydrolysis of cellulose is enhanced considerably by the addition of an electrolyte, and that the kinetics of the reaction can be described in terms of a model based on Donnan's theory of membrane equilibria. According to tly port this model, the rate of hydrolysis of the difficultly accesible portion of cellulose is given by:

$$(dp/dt)_c = k_c[H^+]_c[s] \qquad (3)$$

$$= K_c''D\,[H^+]_s[X^-]_s[S] = k_c\,[H+]_s[X^-] \qquad (4)$$

Where P denotes products, D is the diffusion coefficient of any added electrolyte MX in the solution phase of the system, $[H^+]$, $[X^-]$ and $[S]$ are the hydrogen ion, and counter ion and reaction site concentrations respectively, the subscript C and S denotes cellulose and solution phases of the system respectively, K_c'' is a "form factor" relating the diffusion coefficient, D', of the added electrolyte in the cellulose phase of the system to D, the diffusion coefficient of the electrolyte in the solution phase of the system, and $k_c = K_c''D$, the apparent rate constant for the reaction.

From the brief review above it is apparent that the effect of added electrolyte on activation energy for the hydrolysis of cellulose has not been studied. The aim of the present work was therefore to study the effect of added electrolyte on the activation energy for the hydrolysis of the crystalline regions of microcrystalline cellulose. The effect of changing the concentration of the added electrolyte used are also investigated.

Experimental

Equipment

The equipment used in these experiments was described previously [9].

Materials

The following materials were used: MN - cellulose powder 300 for thin layer chromatography with averages particle size of 10 µm (Macheren Nagel and Co., U.K.); potassium chloride and hydrochloric acid - A.R. grade.

Procedure

The loss-in-weight method of Meller for the determination of the hydrolysis rate was used in these experiments. The detailed experimental procedures followed were described previously [9]. Percentage loss-in-weight figures obtained are plotted against time in figures 1. The rate of hydrolysis, V_c, given by the slope of the straight portion of the hydrolysis curve for the crystalline portion is converted to units of moles of glucose per second (Ms^{-1}). The rate constant, K_c"D, is calculated (Table 1) and plotted against 1/T in figures 2 and 3.

Table 1

Apparent rate constants, k_c, for the hydrolysis of the difficultly accessible portions of microcrystalline cellulose at various temperatures as a function of acid and added electrolyte concentrations

[HCl]	Temp. (°C)	k ($x10^{-8}$ $mol^{-1}s.^{-1}$)		
		0.00 M. KCl	0.08 M. KCl	0.20 M. KCl
0.3 M.	60 70 75 80	1.02 1.53 3.82 9.90	21.1 34.6 56.9 63.2	17.6 29.0 36.6 52.6
1.0 M.	60 70 75 80		2.7 4.6 6.2 7.9	1.4 8.7 12.2 12.6
1.3 M.	60 70 75 80	0.86 1.10 2.20 2.30		

Results and discussion

Figures 1 to 3 show that the plot of ln k_c versus 1/T for the crystalline portion of cellulose is linear. We conclude therefore that the hydrolysis of the difficulty accessible portion follows an Arrhenius type equation. Ea values calculated from the slope of the ln k_c' versus 1/T curves are shown in table 2. Table 2 shows that when hydrolysis is carried out in 0.3M H Cl a value of 25 kcals/mole is obtained for E_a, in close agreement with the values of 27-29 Kcals by Meller4 reported. When hydrolysis is carried out in the presence of added electrolyte a constant value of Ea of 12.6 kcal/mole is obtained. This appears to be constant irrespective of the concentration of added salt.

Muhlethaler [11] has proposed that crystalline cellulose is composed of cellulose microfibrils, each consisting of 36 cellulose molecule chains from 1 000 to 15000 glucose units. These molecules are oriented in the same direction, are parallel to one another, and are connected by means of interchain or intermolecular H-bonds between OH-3 in one chain to OH-6 in another to form a layer structure in the A-C plane. In addition intrachain or intramolecular H-bonds exist between the hydroxyls on C-2 and C-6, and OH-3 and the pyranose ring oxygen of successive glucose units. In the A-B plane, the space between the layers, which are held together by weak Van der Waals forces, is hydrophobic, the "amorphous" regions occurring at chain-ends or interruptions in the microfibrils.

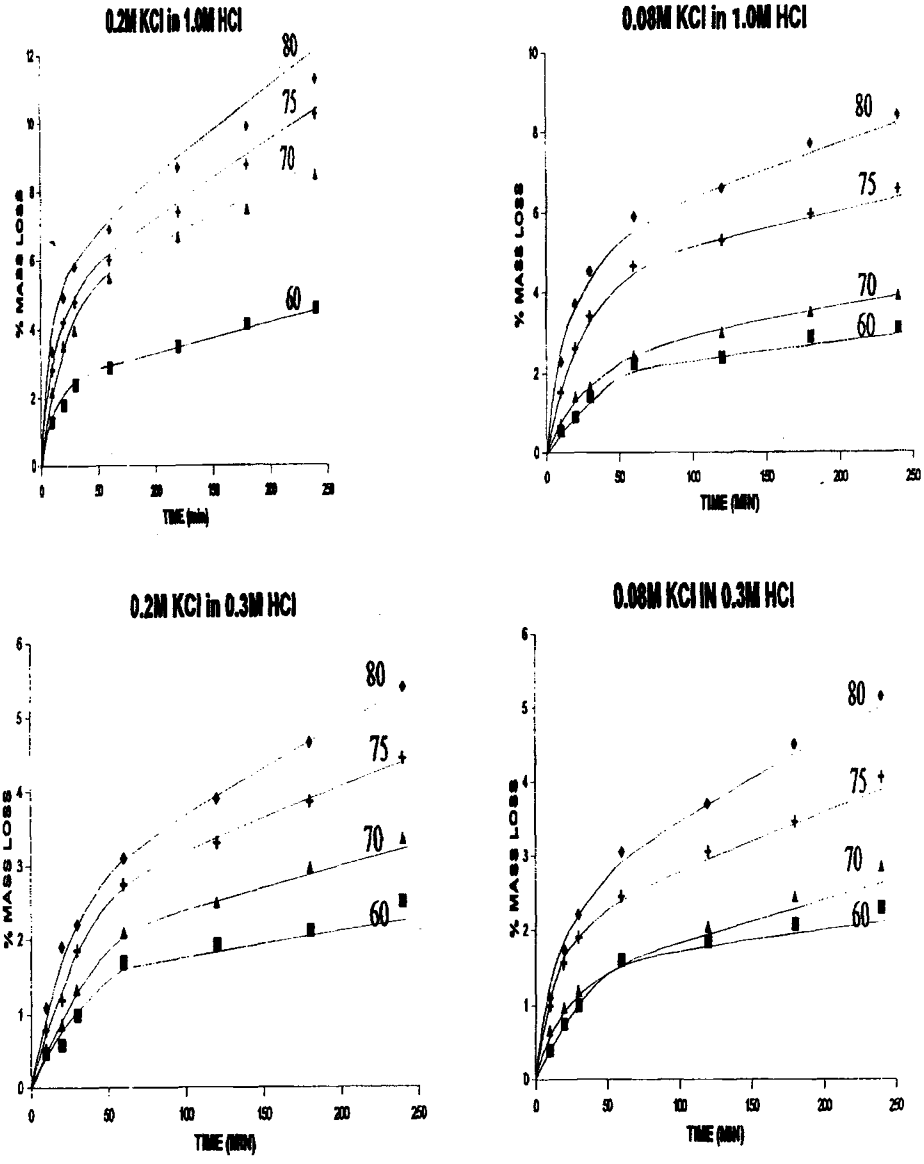

Fig. 1. Plot of percentage-loss-in-weight versus time for the dilute acid hydrolysis of microcrystalline cellulose at different temperatures.

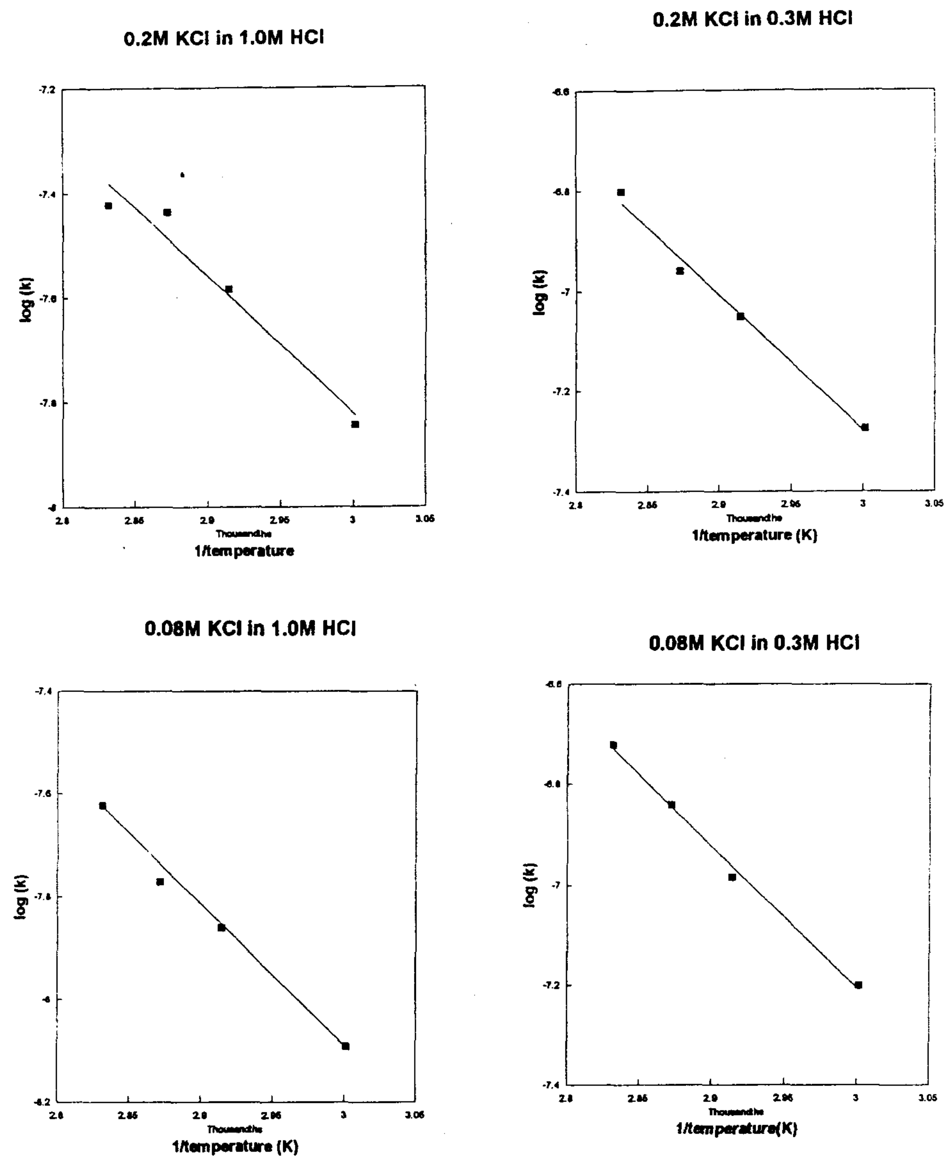

Fig. 2. Plot of ln K_c versus 1/T for the later (straight) portion of the hydrolysis curve (from Fig. 1).

The total activation energy of 25-30 kcal/mole obtained in the absence of the salt catalyst includes the excess energy required to break H-bonds between cellulose chains. The breaking of intermolecular (or inter-chain) H-bonds occurs by intercalation of H_2O molecules into the H-bonds between cellulose chains resulting in inter crystalline swelling. A notable feature of this inter-crystalline swelling is that from the crystalline region outwards, the sorbed water molecules become progressively more loosely bound to the cellulose chains, and that even in these regions of more loosely bound water molecules, the intramolecular H-bonds can remain intact depending on the reaction conditions [12].

Table 2

Activation energy values at different levels of HCl and added KCl concentrations

[KCl]	Activation Energy (kcal/mole)		
	1.3 M. HCl	1.0 M. HCl	0.3 M. HCl
0.00 M.		30.7*	25.8
0.08 M.		12.66	13.57
0.20 M.	12.6	12.03	12.43

* Literature value for celobiose [4].

The activation energy results obtained above throw some light on the mechanism of the hydrolysis of the glycosidic bond in the heterogeneous dilute acid hydrolysis of cellulose. The kinetic model on which the results are based assumes the following elementary steps [9]:

$$H_3O^+ + S \rightleftarrows S.(H_3O)^+ \rightarrow P \qquad (5)$$

where S is the reaction site and P denotes products. Since heterogeneous dilute acid hydrolysis of cellulose involves breaking intermolecular H-bonds, intra-molecular H-bonds and the glycosidic bonds, S can be (a) the intermolecular H-bond, (b) the intramolecular H-bond, or (c) the glycosidic bond, as shown in table 3, where the corresponding reactions are indicated.

As discussed in the preceeding paragraph the activation energy study results obtained in the present work can distinguish between (a) and (c), but cannot distinguish between (a) and (b), or (b) and (c). Nevertheless, assuming the minimum activation energy of 12-13 Kcal relates to the breaking of the glycocidic bond, then since this activation energy is close in magnitude to the activation for breaking H-bonds, we conclude that the activated complex involved is the protonated glycosidic bond, and that the formation of products, P, from this complex must involve even lower activation energy step(s).

Two mechanisms were proposed for the hydrolysis of glycosides by Edward [13] and Bunton et al. [14] respectively. The mechanism proposed by Edward involves protonation of the oxygen of the aglycone and the formation of a cyclic carbonium-oxonium ion as the rate determining step. Bunton et al proposed a mechanism initiated by protonation of the ring oxygen followed by formation of an acyclic carbonium ion intermediate again as the rate determining step. Both mechanisms are not consistent with the low activation energy of 12-13 kcal/mole obtained in the present work. The formation of the carbonum-oxonium ions is expected to involve high activation energy in order to break the C-0 bond, and to overcome restrictions to conformational changes necessary for the formation of these ions [3, 4].

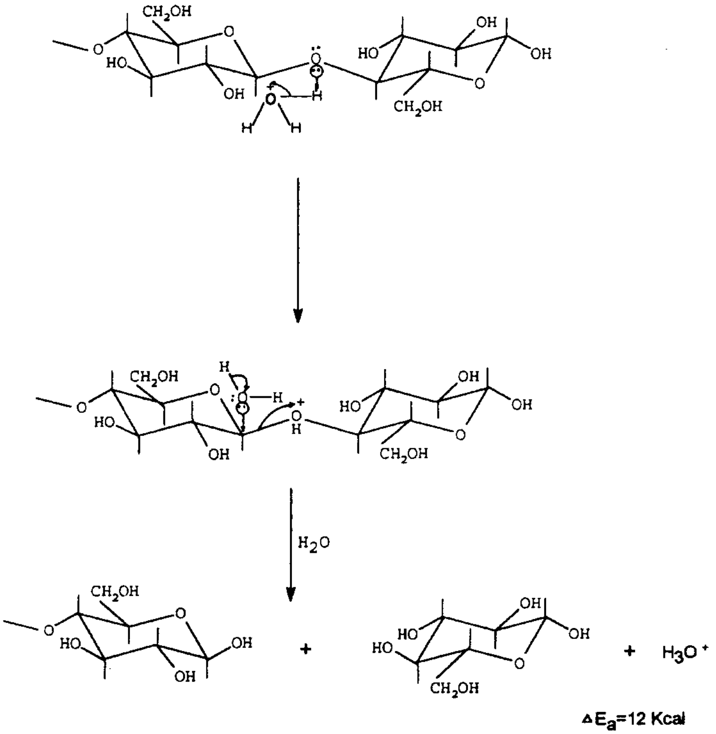

Fig. 3.

Table 3

Types of reaction sites in heterogeneous dilute acid hydrolysis of cellulose

S	Reaction
a. Inter-molecular H-bond	Intercalation of H_2O
b. Inter-molecular H-bond	Intercalation of H_2O
c. Glycosidic bond	Hydrolysis

The mechanism in Figure 3 would be consistent with the low activation energy of 12-13 kcal/mole obtained in the present work, and is put forward as a plausible mechanism for the hydrolysis of the glycosidic bond in cellulose. In heterogenous dilute acid hydrolysis of cellulose, the glycocidic bond can be approached by the hydroxonium ion in the A - C plane only because the space between cellulose layers in the A - B plane is hydrophobic. This means that the glycosidic bond is protected by the intra-molecular H-bonds between the hydroxyls on C-2 and C-6, and OH-3 and the pyranose ring oxygen. In turn the intramolecular H-bonds are protected by the intermolecular H-bonds. For breaking intermolecular H-bonds penetration of the H_3O^+ ions into the crystallites is very slow and, in the absence of added salt, is rate limiting. Addition of an inert electrolyte catalyses the penetration of the H_3O^+ ions into the crystallites and the breaking of the glycocidic bond becomes rate limiting. Further support of the mechanism proposed above comes from the fact that high levels and rates of hydrolysis are obtained when heterogeneous dilute acid hydrolysis of cellulose is carried out under pressure [15].

Table 1 shows that the rate constant for the salt catalysed heterogeneous dilute acid hydrolysis of cellulose decreases us the concentration of the added electrolyte increases. The rate constant, $k_c = k_c''d$ (see eqn 4), is identifiable with the flux of the hydrolysing medium into the crystallites. By definition the flux is given by

$$\text{Flux} = \text{Mobility} \times \text{concentration} \times \text{total driving force}$$

The total driving force is composed of an electrical term and an osmotic term. The electrical term is the basis of the Donnan Theory, and has a positive effect on the rate constant, i.e. an increase in the electrical term should lead to an increase in the rate constant. The osmotic term on the other hand tends to reduce the flux of the hydrolysing medium into the crystallites, so that at high electrolyte concentrations, the rate constant begins to drop as the effect of the osmotic term becomes greater than the effect of the electrical term. In previous paper we showed that this point is reached at a concentration of 0.028 molar added salt in the case of Li Cl catalyst [10].

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ENERGIA AKTYWACJI KATALIZOWANEJ SOLAMI HETEROGENNEJ HYDROLIZY ROZCIEŃCZONYM KWASEM TRUDNO DOSTĘPNYCH CZĘŚCI MIKROKRYSTALICZNEJ CELULOZY

Streszczenie

Wyznaczano pozorne stałe szybkości, K_c, heterogennej hydrolizy rozcieńczonym kwasem trudno dostępnych części mikrokrystalicznej celulozy w 0,3, 1,0 i 1,3 M kwasie solnym zawierającym 0,00, 0,08 i 0,20 M KCl w 60, 70, 75 i 80°C posługując się metodą ubytku wagi. Energie aktywacji E_a obliczono z krzywych ln K_c-1/T gdzie T jest temperaturą absolutną. Gdy hydrolizę przeprowadzano w 0,3 M kwasie solnym otrzymano dla E_a zaledwie 25 kcal/mol. Wobec dodanego KCl jako elektrolitu E_a nie zmieniała się, a średnia wartość 12,6 = 0,5 kcal/mol i w badanym zakresie była niezależna od stężenia dodanego elektrolitu. Przedstawiono prawdopodobny mechanizm odpowiadający za niską energię aktywacji.