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THE MECHANISM OF THE ACID-CATALYSED HYDROLYSIS OF GLUCOSIDES

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ABSTRACT

The kinetics of hydrolysis of β-cellobiose, methyl α-D-glucopyranoside, and sucrose over a wide range of concentrations of hydrochloric, sulfuric, and phosphoric acids have been studied by the polarimetry technique. Transition of the protonated form from the chair to half-chair conformation (a cyclic carbonium ion being formed) was found to be the rate-determining step of pyranoside hydrolysis. The interaction of a glycoside molecule with the medium, estimated from the proton chemical shifts ($\Delta\nu$), was found to have a marked effect on this step. An equation relating the changes in rate constant to the acidity function (H_0) and the value $\Delta\nu$ has been derived.

INTRODUCTION

The mechanism of the acid-catalysed hydrolysis of glycosides has attracted investigators for many years. The hydrolysis of sucrose was one of the first reactions studied by means of the Hammett acidity function H_0, and is now a classical example of the monomolecular A-1 mechanism[1]. Subsequent investigations have shown that data for the hydrolysis of some other glycosides could not be interpreted rigorously by the A-1 mechanism. However, these data have been explained by possible experimental inaccuracy[2], or because of the incursion of the bimolecular A-2 mechanism of hydrolysis.

Therefore, the kinetics of hydrolysis of cellobiose, sucrose, and methyl α-D-glucopyranoside and the state of these compounds in aqueous, acid solutions have been subjected to a detailed investigation.

DISCUSSION

The state of glucosides in acid media

The term "state" connotes the collective data on protonation, conformation, and solvation. The state of cellobiose and its hydrolysis product, D-glucose, was investigated by p.m.r. and o.r.d. methods.

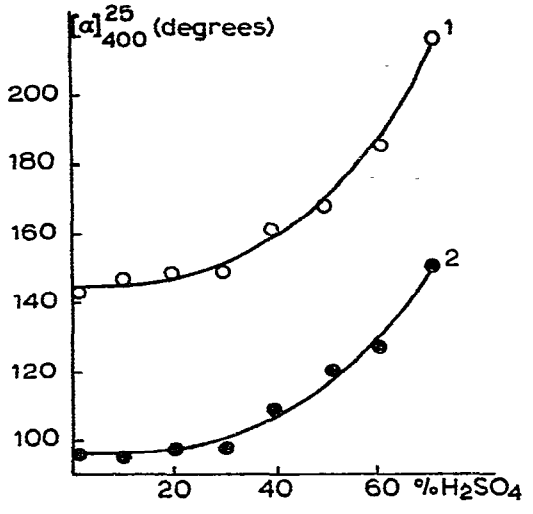

Fig. 1. The specific rotation of D-glucose (1) and cellobiose (2) in H_2SO_4.

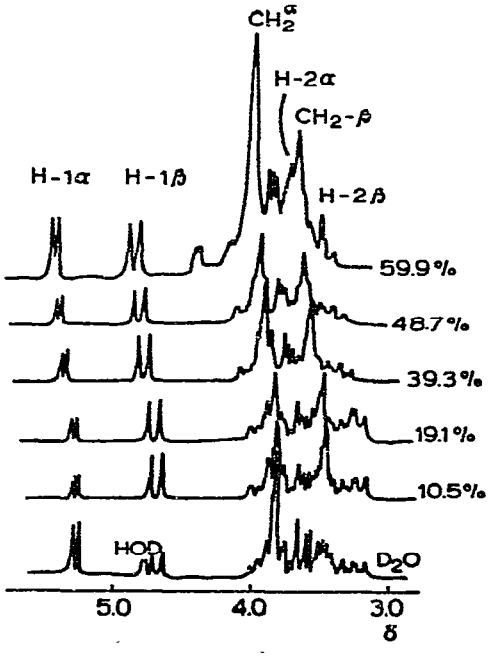

Fig. 2. The p.m.r. spectra of D-glucose in D_2SO_4 at 25°.

Figure 1 shows the dependence of $[\alpha]_{400}^{25}$ of equilibrium mixtures of D-glucose and cellobiose on the concentration of sulphuric acid, and Fig. 2 contains the p.m.r. spectra of D-glucose in D_2O–D_2SO_4 mixtures of various concentrations. The assignments in Fig. 2 are based on the data of Lemieux *et al.*[5]. An increase in the concentration of D_2SO_4 results in enhancement of the H-1, H-2, and H-6,6′ signals for the α-pyranose form, as well as a progressive downfield shift of the p.m.r. signals.

Figure 3 shows partial p.m.r. spectra of cellobiose; in the region 2–4 p.p.m., the spectra closely resemble that of D-glucose. The chemical shifts and coupling constants of H-1α and H-1β are the same as those of the corresponding protons in D-glucose. The coupling constant (J 7.2 Hz) for H-1β is less affected by the medium. As with D-glucose, an increase in the concentration of D_2SO_4 causes a downfield shift of the signals for cellobiose.

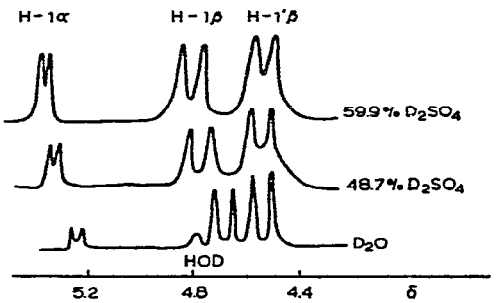

Fig. 3. The p.m.r. spectra of cellobiose in D_2SO_4 at 25°.

Protonation

The protonation of O-1 and O-5 in glycopyranosides may yield reactive entities. The electron densities at oxygen for various glycosides have been reported[6]; for cellobiose, the electron densities at O-1 and O-5 are −0.264.

No quantitative data are available for the protonation of glycosides. Their closest structural analogues, ethers, have[7] pK_{BH^+} values ranging from −3 to −4. The inductive effect of oxygen leads to a decrease in basicity and the pK_{BH^+} of glycosides should be less than −4. Thus, glycosides would be protonated only in strongly acid media ($H_0 < -4$), where a study of protonation is complicated by simultaneous hydrolysis and irreversible chemical transformations[8]. The p.m.r. spectra of cellobiose also demonstrate that probably no essential protonation occurs, as there is no substantial change in chemical shifts or coupling constants.

Conformation

The changes of specific rotation and p.m.r. spectra of D-glucose and cellobiose with increase in concentration of sulphuric acid may be due to changes in conformation.

The analysis of o.r.d. curves for solutions of α-D-glucose and β-cellobiose in

water* shows that they conform satisfactorily to a one-term Drude equation[9]. Therefore, the equilibrium mixtures of D-glucoes and cellobiose in water should obey equation *1*,

$$[\alpha] = c_\alpha \frac{A}{\lambda^2 - \lambda_\alpha^2} + c_\beta \frac{B}{\lambda^2 - \lambda_\beta^2}, \qquad (1)$$

where A and B are constants, λ_α and λ_β are the wavelengths of absorption maxima of an optically active chromophore, and c_α and c_β are the equilibrium concentrations of the anomeric forms of D-glucose and cellobiose. These parameters have the following values: D-glucose, A 3.4×10^{-7}, B 6.4×10^{-6}, λ_α 161 nm, λ_β 155 ± 2 nm; cellobiose, A 2.3×10^{-7}, B 5.9×10^{-6}, λ_α 127 nm, λ_β 120 ± 2 nm. A comparison of these data with far-u.v. spectral data showed that the values λ_α and λ_β computed for D-glucose are in good agreement with the respective spectral values.

Equation *1* also describes the results for different acids.

Table I shows the proportions of the α and β forms of D-glucose and cellobiose in water and sulphuric acid of various concentrations, computed from o.r.d. curves and p.m.r. spectra. Similar results were obtained for solutions in hydrochloric, perchloric, and phosphoric acids[10].

TABLE I

THE ANOMERIC COMPOSITION OF D-GLUCOSE AND CELLOBIOSE IN WATER AND SULPHURIC ACID

	Water	*Sulphuric acid* (%)					
		10	*20*	*40*	*50*	*60*	*70*
D-*Glucose*							
α	35	36	37	38	41	45	53
β	65	64	63	52	59	55	47
Cellobiose							
α	35	35	36	39	40	45	52
β	65	65	64	51	60	55	48

Equation *2* describes the concentrations of the α and β anomers of D-glucose and cellobiose in acid solutions[10],

$$\ln \frac{c_\beta}{c_\alpha} = \ln K_x^0 - \frac{1}{3} \cdot \frac{e^2}{KT\varepsilon a^4} (M_\alpha^2 - M_\beta^2) X_s^2, \qquad (2)$$

where M is the molecular dipole moment, e is the electronic charge, ε is the dielectric permeability of the medium, a is the ion-dipole distance, K is the equilibrium constant at infinite dilution, and X is the ion molarity.

*During the time of dissolution, preparation, and spectrum registration, mutarotation proceeded to extents of 10 and 15%, respectively, for D-glucose and cellobiose.

No accurate data are available on the dipole moments of the α and β anomers of D-glucose and cellobiose, but computations show that $M_\alpha > M_\beta$. This is the driving force that shifts the equilibrium towards the α-anomeric forms with increasing concentration. In the more-concentrated acid solutions, the values ε and a change negligibly, and the ratio of α and β anomers depends only on the molarity of the ions in solution.

This conclusion was confirmed by investigation of the anomeric equilibrium in aqueous solutions of lithium chloride. Figure 4 shows the linear dependence of c_β/c_α on X_s^2 for D-glucose.

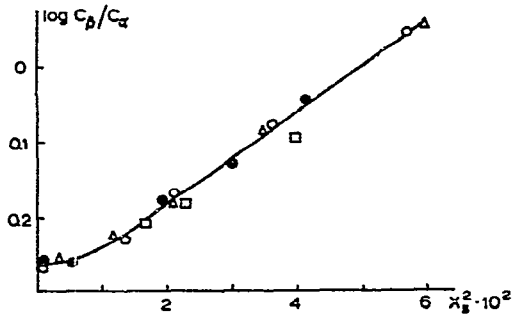

Fig. 4. Plot of log c_β/c_α against X_s^2 for aqueous solutions of LiCl (●), H_2SO_4 (○), HCl (△), and $HClO_4$ (□) at 25°.

It is therefore concluded that as the concentration of acid increases, there is a $\beta \rightarrow \alpha$ shift in the anomeric equilibrium, owing to an electrostatic interaction with the medium.

Solvation

It is known that glycosides having polar groups may form complexes with acidic solvents having acidic protons, or with some salts[11]. The concentration and stability of zinc chloride–β-D-glycopyranoside complexes increase with increasing concentrations of salt[12].

Complex formation affects the chemical shifts (~2 Hz) of H-1,2,3,4,5, and it is assumed that this change in D-glucose and cellobiose is a result of complex formation between the sugar hydroxyl groups and aqueous acids.

Table II shows the chemical shifts and coupling constants for cellobiose in different acids at 25°. As an example, Fig. 5 shows a plot of the chemical shifts for H-2 in cellobiose against the acidity function H_0; the specific interaction of HO-2 with the medium plays an important role in glycoside hydrolysis (see below). The dependence shown in Fig. 5 was also observed for methyl α-D-glucopyranoside and methyl α-L-arabinofuranoside.

The following two conclusions may be drawn on the basis of these results. (*a*) The extent of interaction is determined by the nature of the acid. From Fig. 5, it

TABLE II

PROTON CHEMICAL SHIFTS FOR CELLOBIOSE IN ACID SOLUTION AT 25°

Acid concentration (%)	*Chemical shifts*			
	H-1' ($J_{1,2}$ 7.2 Hz)	*H-1β* ($J_{1,2}$ 7.8 Hz)	*H-1α* ($J_{1,2}$ 3.3 Hz)	*H-2* ($J_{2,3}$ 8.5 Hz)
Sulphuric acid				
0	131	145	204	6
30	134.5	152	210	13.5
40	134.5	153.5	210	17.5
48.7	134.5	151	210	23
50	135	158	213	24
60	135	159	215	33
64	137	161.5	217	38
70	137	163	223	45
Hydrochloric acid				
9.6	131	147	203	7
14.7	131	148	204	7
19.8	132	150	204	8
21.6	133	151	205	10
24.5	134	152	205	13
33.9	135	153	211	18
Perchloric acid				
30		150		10
45		153.5		17.5
56		157.5		23
63		159.5		34
Phosphoric acid				
30		148.5		9
45		151		13
60		155		20
68.5		158		24
75		161		37
87.5		165		47

is seen that the strongest interaction occurs with phosphoric acid and the weakest interaction with hydrochloric acid. (*b*) The plot of $\Delta\nu$ against H_0 is practically the same for various types of glycosides (cellobiose and methyl α-D-glucopyranoside). At present, the nature of the interaction between glucosides and aqueous acid remains unexplained.

It is of interest to compare the heats of solvation of glucosides under standard conditions. It is known that the heat of solvation (H) is given by $H = L + U$, where L is the heat of dissolution, and U is the energy of the crystal lattice. The energy of the crystal lattice of the glucosides investigated may be assumed to be constant for different media. It is then reasonable to compare the heats of dissolution of methyl α-D-glucopyranoside in aqueous acid solutions at $H_0 = -2.4$ and 25°. The following values are obtained: $L = 2.65$ (21.8% HCl), 2.36 (39.9%, $HClO_4$), 2.01 (39.9%

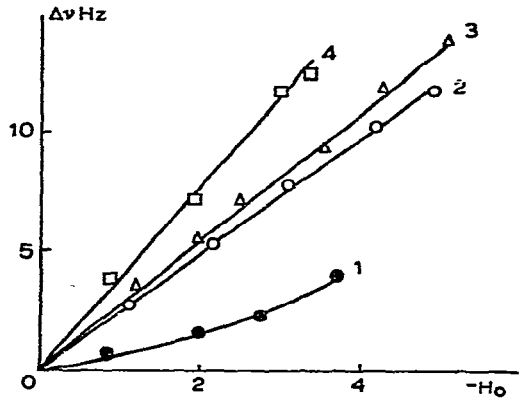

Fig. 5. Plot of chemical shift differences for cellobiose (νH_2) against acidity function H_0 in aqueous solutions of HCl (1), $HClO_4$ (2), H_2SO_4 (3), and H_3PO_4 (4) at 25°.

H_2SO_4), and 1.06 kcal.mol^{-1} (68.4% H_3PO_4). It therefore follows that the heat of solvation changes in the series: HCl, $HClO_4$, H_2SO_4, H_3PO_4.

Kinetics and mechanism of glucoside hydrolysis

Figure 6 shows a plot of log k_{obs} against H_0 for the hydrolysis of cellobiose over a large concentration range of different acids. The deviation from linearity increases with increase of acid concentration and is outside the range of experimental error. Similar dependencies have been observed for methyl β-D-glucopyranoside[2], methyl α-D-glucopyranoside[13], and sucrose[13–15]. The results obtained may have the following explanations.

1. Glucoside protonation. On the assumption that the data concerning the absence of noticeable glucoside protonation are incorrect and that the essential

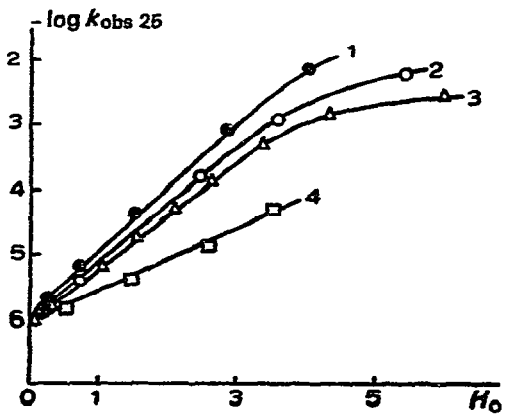

Fig. 6. Plot of log kM against H_0 for the hydrolysis of cellobiose in aqueous solutions of HCl (1), $HClO_4$ (2), H_2SO_4 (3), and H_3PO_4 (4) at 25°.

glucoside protonation causes the deviation from linearity in Fig. 6, then two facts remain unexplained: (*a*) the marked effect of the nature of the acid on the slope of the plot k_{obs} against H_0; (*b*) for solutions in aqueous sulphuric acid, a deviation from linearity is observed within a four-order interval in H_0. If protonation of cellobiose is the reason for this deviation from linearity of $\log k_{obs}$ against H_0, then the dependence would reach a plateau within a two-order interval in H_0.

Thus, an essential glycoside protonation, even if it occurred, cannot explain the experimental data.

2. Bimolecular mechanism. On the basis of empirical criteria, Bunnett[3] concluded that some glycosides are hydrolyzed *via* an A-2 mechanism (participation of the water molecule in the limiting step). Deviation from linearity in the plot of $\log k_{obs}$ against H_0 may then be explained by a decrease of water activity in concentrated acid solutions.

If glycoside hydrolysis involves the A-2 mechanism, the expression for the reaction rate may be represented by two identical equations:

$$G + H_2O + H^+ \overset{K_p}{\rightleftharpoons} M^{\ddagger} \rightleftharpoons M \xrightarrow{k_{tr}} \text{reaction products};$$

$$W = K_{obs} \cdot c_0 = k'_{tr} \frac{a^{\ddagger}}{f^{\ddagger}} \begin{cases} \longrightarrow k_{tr} \dfrac{a_G a_{H_3O^+}}{f^{\ddagger}}, & (3) \\ \longrightarrow k^{\ddagger}_{tr} \dfrac{a_{GH^+} a_{H_2O}}{f^{\ddagger}}, & (4) \end{cases}$$

where c_0 is the total reagent concentration, K_p is the equilibrium constant for formation of the intermediate complex M which decomposes into the reaction products by a monomolecular mechanism, $M^{\ddagger}$ is an activated complex, k_{tr} is the true rate constant, and a_{H_2O} and $a_{H_3O^+}$ are the activities of water and hydroxonium ion, respectively. According to equation *3*, the relationship *5* holds where $f_{H_3O^+}$ and f_G are the activity coefficients of hydroxonium ion and nonionized glycoside, respectively.

$$k_{obs} = k_{tr} \frac{c_G}{c_0} \cdot c_{H_3O^+} \cdot \frac{f_{H_3O^+} f_G}{f^{\ddagger}} \qquad (5)$$

In order to take into account the change of activity coefficient of an activated complex, $f^{\ddagger}$, the following assumptions have been made[16]: (*a*) the ratio of activity coefficients $f_M/f^{\ddagger}$ is constant, and (*b*) the activity coefficients of an activated complex and complex M obey the relation *6*:

$$f_M = f^{\ddagger} = f_G^{\beta} f_{H_3O^+}^{\alpha} \cdot \text{constant}, \qquad (6)$$

where α and β are the medium-independent parameters. Expressing c_G/c_0 through h_0 and K_{GH^+}, we obtain:

$$k_{obs} = k_{tr} K_p \frac{c_{H_3O^+} f_G^{(1-\beta)} f_{H_3O^+}^{(1-\alpha)}}{1 + h_0/K_{GH^+}}. \qquad (7)$$

If $c_G \gg c_{GH^+}$, then equation *8* is obtained.

$$k_{obs} = k_{tr}/K_p \cdot c_{H_3O^+} \cdot f_G^{(1-\beta)} \cdot f_{H_3O^+}^{(1-\alpha)} \qquad (8)$$

The value f_G may be found approximately by using the solubilities of cellobiose in acid solutions. Since the solubility is not essentially affected by the nature of the acid and its concentration (0.2–0.3 mol/l), then $f_G^{(1-\beta)}$ may be assumed to be almost constant, and equation *7* takes the form

$$k_{obs} = k_{tr}/K_p c_{H_3O^+} \cdot f_{H_3O^+}^{(1-\alpha)}. \qquad (9)$$

It is seem from Fig. 7 for plots of $\log k_{obs}/c_{H_3O^+}$ against $\log f_{H_3O^+}$ (the values $f_{H_3O^+}$ are taken from Ref. 17) that lines with different slopes are observed for various acids. According to the A-2 mechanism, this parameter should be independent of the acid nature, and hence the hydrolysis of cellobiose does not follow the A-2 mechanism.

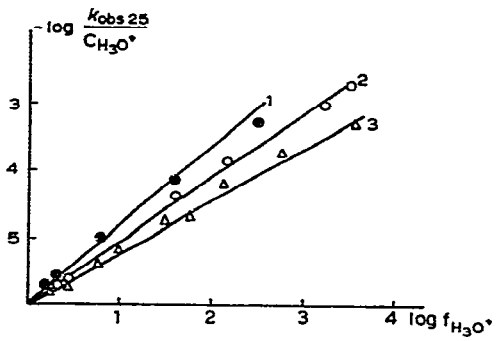

Fig. 7. Plot of $\log k_{obs}/c_{H_3O^+}$ against $\log f_{H_3O^+}$ for the hydrolysis of cellobiose in aqueous solutions of HCl (1), $HClO_4$ (2), and H_2SO_4 (3) at 25°.

Existing data[18] tend to support the A-1 rather than the A-2 mechanism of glucoside hydrolysis.

The mechanism of glycoside hydrolysis

We therefore conclude that glycoside hydrolysis should follow the A-1 mechanism. In general, the equation for such a process (for $c_G \gg c_{GH^+}$) has the form:

$$k_{obs} = \frac{k_{tr}}{K_{GH^+}} h_0 \frac{f_{InH^+}}{f_{In}} \cdot \frac{f_G}{f_{GH^+}} \cdot \frac{f_{GH^+}}{f^{\ddagger}}, \qquad (10)$$

where f_{In} and f_{InH^+} are the activity coefficients of the indicator and its protonated form, respectively. This equation may be simplified by using the Hammett postulate, and the ratio $f_{GH^+}/f^{\ddagger}$ remains constant in different media; the Hammett postulate is expected to be as valid for glycosides as for simple acetals.

For glycosides, the protonated form and activated complex have similar compositions and charges, but their structures are not similar. It has been assumed that an activated complex is a half-chair form for glycopyranosides[19] and planar for furanosides[18]. The rate-limiting step involves heterolysis of the exocyclic oxygen. For furanosides, the active-complex formation also should not involve a cyclic rearrangement; it is presently accepted that the hydrolysis of pyranosides and furanosides involves cyclic intermediates[18], and there is no conclusive evidence for the acyclic mechanism.

The parameter $f_{GH^+}/f^{\ddagger}$ may be written in terms of the change of free energy of transition from protonated form to activated complex: $\log f_{GH^+}/f^{\ddagger} = \Delta\Delta F$. The value of $\Delta\Delta F$ includes the free-energy change associated with the chair to half-chair conversion for pyranosides, and for the corresponding changes in furanoside rearrangement. The value $\Delta\Delta F$ will increase upon enhancement of the interaction of the glucoside with the medium. The equation[18] where $f_{GH^+}/f^{\ddagger}$ is variable may be written in the forms *11* and *12*.

$$\log k_{obs} + H_0 = \log \frac{f_{GH^+}}{f^{\ddagger}} + \log \frac{k_{tr}}{K_{GH^+}} \qquad (11)$$

$$\log k_{obs}/h_0 = \Delta\Delta F + \log k_{tr}/K_{GH^+} \qquad (12)$$

The change of $\Delta\Delta F$ may be estimated from the change of interaction of the glucoside molecules with the medium, as manifested by the change of proton chemical shifts.

As a first approximation, we may assume $\Delta\Delta F \approx \Delta\nu$, where $\Delta\nu$ is the change in chemical shift of glycoside protons occurring with change of medium; the aqueous solution is taken as standard. Equation *12* then takes the form *13*.

$$\log k_{obs}/h_0 \approx \Delta\nu + \log k_{tr}/K_{GH^+} \qquad (13)$$

Glycosides interact with the medium through hydroxyl groups, and it is interesting to identify the hydroxyl group that plays the most significant role in the hydrolysis.

In Table III, $\log k_{tr}/K_{GH^+}$ is listed for cellobiose, methyl α-D-glucopyranoside, and some methyl α-D-glucopyranosides having hydroxyl groups substituted by

TABLE III

THE EFFECT ON THE HYDROLYSIS RATE OF HYDROXYL GROUPS AT DIFFERENT POSITIONS OF THE PYRANOSE RING

Compound	$-\log (k_{tr}/K_{GH^+})^a$
Cellobiose	6.1
Methyl α-D-glucopyranoside	7.0
Methyl 2-deoxy-α-D-*arabino*-hexopyranoside	3.1[b]
Methyl 3-deoxy-α-D-*ribo*-hexopyranoside	6.6[b]
Methyl α-D-xylopyranoside	6.3[b]

[a]At 25°. [b]The data are taken from Ref. 18.

hydrogens in different positions. Replacement of HO-2 by hydrogen increases the rate constant by nearly 10^4. Similar replacement of HO-3 and HO-6 affects the rate constant to a negligible extent. According to De Bruyne *et al.*[20], the replacement of HO-2 in *p*-nitrophenyl β-D-xylopyranoside considerably changes the rate constant of base hydrolysis.

Thus, the hydrolysis of pyranosides is principally influenced by interaction of the molecules with the medium *via* HO-2. Such a conclusion, however, does not exclude the influence of steric and inductive effects of the hydroxyl group on pyranoside reactivity.

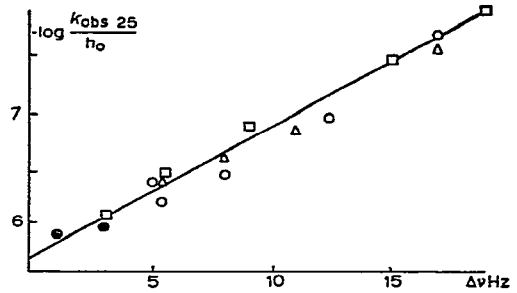

Fig. 8. Plot of log k_{obs}/H_0 against $\Delta\nu$ for the hydrolysis of cellobiose in aqueous solutions of HCl (●), $HClO_4$ (○), H_2SO_4 (△), and H_3PO_4 (□) at 25°.

Figure 8 contains a plot of log k_{obs}/h_0 against $\Delta\nu$ and shows that there is a linear relationship for methyl α-D-glucopyranoside, sucrose, and methyl β-D-glucopyranoside[2]. On the basis of the data obtained, it is concluded that the acid hydrolysis of glucosides occurs by the A-1 mechanism, with the principal role being played by interaction of the glucoside with the medium.

EXPERIMENTAL

Reagents. — β-Cellobiose was twice crystallized from absolute ethanol and had m.p. 225°, $[\alpha]_D^{25}$ +18°; lit.[21] m.p. 225°, $[\alpha]_D^{25}$ +24.4°; the difference in the rotation may be explained by the presence of the α-form of cellobiose in solution[21]. Other compounds used were α-D-glucose, m.p. 83°, $[\alpha]_D^{25}$ +112°; β-D-glucose, m.p. 83°, $[\alpha]_D^{25}$ +20.5°; methyl α-D-glucopyranoside, m.p. 167°, $[\alpha]_D^{25}$ +159°; and sucrose, m.p. 185°, $[\alpha]_D^{25}$ +66.5°.

Solutions of sulphuric, hydrochloric, phosphoric, and perchloric acids, and lithium chloride were prepared by using doubly distilled water.

O-Deuterated derivatives of cellobiose and D-glucose were prepared by repeated concentration of 10% solutions in D_2O (isotope content, 99.7%) with subsequent drying *in vacuo*.

Deuterated sulphuric acid was obtained by saturation of D_2O with sulphur trioxide. The solvents employed were purified by the literature procedures[22].

Methods. — P.m.r. spectra were obtained with a Varian HA-100 spectrometer at 25°, with hexamethyldisiloxane (external) and tetramethylammonium chloride (internal) standards. Solutions were prepared and spectra determined within 10–15 min, which practically excluded reagent decomposition. Reagent concentrations were 0.1–0.2 mol/l.

U.v. spectra were obtained with a vacuum VMR-2 spectrometer at 25° and 140–190 nm. Films on a polished LiF plate were prepared by multiple coating with a saturated, ethanolic solution of D-glucose, with subsequent evaporation of the solvent.

O.r.d. spectra were obtained with a Carey-60 spectropolarimeter, within 185–600 nm, at 25°. The pathlength was 1 mm, and concentrations of cellobiose and D-glucose were 0.03–0.06 mol/l. Solutions were prepared and spectra measured within 10–15 min.

The kinetics of hydrolysis of cellobiose, methyl α-D-glucopyranoside, and sucrose were studied polarimetrically using a SPUE spectropolarimeter. Experiments were carried out in thermostatted (±0.1°) quartz cuvettes at reagent concentrations of 30–70 mmol/l. At these concentrations, the effect of the reagents on the thermodynamic properties of the medium was negligible. The kinetics of hydrolysis of cellobiose, methyl α-D-glucopyranoside, and sucrose were studied for solutions in aqueous acid where the hydrolysis products (D-glucose and D-fructose) were stable during the time of experiment. The hydrolysis rate constants were computed from the first-order equation

$$k_{obs} = 2.3/t \,.\, \log \frac{(\alpha_\infty - \alpha)}{(\alpha_\infty - \alpha_0)}, \qquad (14)$$

where α, α_0, and α_∞ are the angles of rotation for the solution at time t, at the start, and at the end of the experiment, respectively.

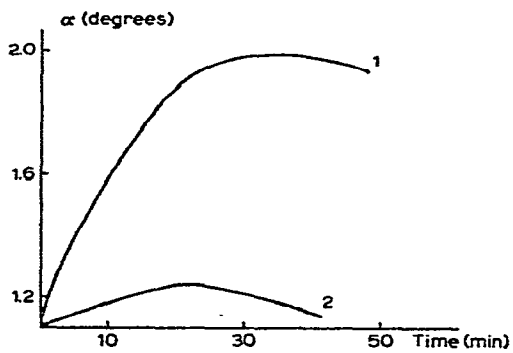

Fig. 9. Change of rotation (α) with time for cellobiose (1) and D-glucose (2) in 71% H_2SO_4 at 50°.

In the study of the kinetics of hydrolysis of the above-mentioned compounds in concentrated acid, D-glucose and D-fructose undergo complex transformations.

For example, Fig. 9 shows the change in rotation of cellobiose and D-glucose with time in 71% H_2SO_4 at 50°. D-Glucose yields an intermediate product having a large rotation with respect to that of D-glucose. Then the rotation decreases because of formation of optically inactive substances; in this case, the solution is strongly coloured by 5-hydroxymethyl-2-furaldehyde. Thus, the following consecutive reactions take place in the system:

$$A \xrightarrow{k_1} 2B \xrightarrow{k_2} 2C \xrightarrow{k_3} 2D,$$

where A is cellobiose, B is D-glucose, C is an unknown product, and D is 5-hydroxymethyl-2-furaldehyde. The rate constants were computed by solving the system of equations:

$$dA/dt = -kA; \qquad dB/dt = 2k_1A - k_2B; \qquad dC/dt = k_2B - k_3C;$$

$$[\alpha] = A[\alpha]_A + 2B[\alpha]_B + 2C[\alpha]_C.$$

The rate constants for hydrolysis of cellobiose, methyl α-D-glucopyranoside, and sucrose at various acid concentrations and temperatures are shown in Table IV.

TABLE IV

THE RATE CONSTANTS FOR GLYCOSIDE HYDROLYSIS

	Acid (%)	*Temp.* (*degrees*)	k_{obs} min^{-1}	*Acid* (%)	*Temp.* (*degrees*)	k_{obs} min^{-1}
Cellobiose						
HCl	5.11	60	$5.9.10^{-4}$	25.2	40	$5.1.10^{-3}$
		80	$6.9.10^{-3}$		50	$1.6.10^{-2}$
		90	$1.2.10^{-2}$		60	$5.4.10^{-2}$
	15.2	50	$1.8.10^{-3}$		70	$1.5.10^{-1}$
		60	$7.2.10^{-3}$	34.3	30	$6.9.10^{-3}$
		70	$1.5.10^{-2}$		40	$2.8.10^{-2}$
		80	$5.6.10^{-2}$		50	$7.8.10^{-2}$
$HClO_4$	11.0	70	$2.0.10^{-3}$	41.6	40	$1.1.10^{-3}$
		80	$4.6.10^{-3}$		60	$1.4.10^{-2}$
		90	$1.8.10^{-2}$		70	$3.5.10^{-2}$
					80	$2.0.10^{-1}$
	26.0	70	$7.4.10^{-3}$	48.9	50	$1.1.10^{-2}$
		80	$3.1.10^{-2}$		60	$4.8.10^{-2}$
		90	$1.1.10^{-1}$		70	$1.4.10^{-2}$
	35.0	70	$2.5.10^{-2}$	62.3	25	$1.1.10^{-2}$
		80	$8.9.10^{-2}$		40	$7.4.10^{-2}$
		90	$2.3.10^{-1}$		50	$2.4.10^{-1}$
H_2SO_4	10.5	70	$1.6.10^{-3}$	43.2	40	$1.3.10^{-3}$
		80	$5.5.10^{-3}$		50	$6.0.10^{-3}$
		90	$1.7.10^{-2}$		60	$1.7.10^{-2}$
					70	$5.7.10^{-2}$

(Table continued on p. 36)

TABLE IV (*continued*)

	Acid (%)	*Temp.* (*degrees*)	k_{obs} min^{-1}	*Acid* (%)	*Temp.* (*degrees*)	k_{obs} min^{-1}
Cellobiose						
	19.8	60	$1.1.10^{-3}$	49.6	40	$3.2.10^{-3}$
		70	$4.7.10^{-3}$		50	$1.1.10^{-2}$
		80	$1.8.10^{-2}$		60	$4.1.10^{-2}$
		90	$5.7.10^{-2}$		70	$1.2.10^{-1}$
	27.2	50	$8.9.10^{-3}$	58.8	40	$8.9.10^{-3}$
		60	$3.1.10^{-3}$		50	$2.2.10^{-2}$
		70	$1.0.10^{-2}$		60	$6.0.10^{-2}$
		80	$3.7.10^{-2}$		70	$1.4.10^{-1}$
	37.6	40	$8.0.10^{-4}$	71.0	30	$1.0.10^{-2}$
		50	$2.5.10^{-3}$		40	$3.6.10^{-2}$
		60	$1.1.10^{-2}$		50	$1.0.10^{-1}$
		70	$3.4.10^{-2}$		60	$2.7.10^{-1}$
		80	$1.0.10^{-1}$			
		90	$3.9.10^{-1}$			
H_3PO_4	40.4	70	$1.0.10^{-3}$	69.0	70	$1.6.10^{-2}$
		80	$3.6.10^{-3}$		80	$3.3.10^{-2}$
		90	$1.3.10^{-2}$		90	$1.4.10^{-1}$
	55.0	70	$1.9.10^{-3}$	84.3	60	$7.0.10^{-3}$
		80	$7.5.10^{-3}$		70	$2.2.10^{-2}$
		90	$2.6.10^{-2}$		80	$6.5.10^{-2}$
Methyl α-D-glucopyranoside						
H_2SO_4	6.0	60	$3.8.10^{-5}$		70	$4.4.10^{-4}$
		70	$1.7.10^{-4}$		80	$1.3.10^{-4}$
		80	$7.4.10^{-4}$	60.0	40	$4.6.10^{-3}$
	35.6	60	$2.4.10^{-3}$		50	$4.1.10^{-2}$
		70	$9.3.10^{-3}$		60	$9.1.10^{-2}$
		80	$3.0.10^{-2}$			
	50.2	45	$2.0.10^{-3}$	63.9	25	$5.3.10^{-3}$
		50	$3.9.10^{-3}$		30	$8.5.10^{-3}$
		60	$1.4.10^{-2}$		40	$3.1.10^{-2}$
					50	$1.3.10^{-1}$
Sucrose (25°)						
HCl	5.0		$2.3.10^{-2}$	15.0		$2.7.10^{-1}$
H_2SO_4	10.1		$1.9.10^{-2}$	20.0		$6.4.10^{-2}$
	15.0		$3.1.10^{-2}$	25.2		$1.1.10^{-1}$
$HClO_4$	11.1		$1.9.10^{-2}$	29.9		$2.5.10^{-1}$
	20.0		$7.4.10^{-2}$			
H_3PO_4	40.0		$1.5.10^{-2}$	60.0		$6.6.10^{-2}$
	44.7		$1.9.10^{-2}$	66.0		$1.1.10^{-1}$
	55.0		$4.5.10^{-2}$			

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