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THE MECHANISM OF THE ACID-CATALYSED HYDROLYSIS OF POLYSACCHARIDES

YURII V. MOISEEV, NIKOLAI A. KHALTURINSKII, AND GENNADII E. ZAIKOV
Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)
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ABSTRACT

The kinetics of homogeneous and heterogeneous acid-catalyzed hydrolysis of polysaccharides has been studied. The hydrolysis of *O*-methylcellulose in solutions of hydrochloric, sulfuric, and perchloric acids, and the acetolysis of cellulose triacetate were found to follow the mechanism established earlier for glycosides. Degradation of *O*-ethylcellulose films in hydrochloric acid vapour occurred in the kinetic region.

INTRODUCTION

In studying the kinetics and mechanism of the acid-catalysed degradation of polysaccharides, the following questions may be posed: (*a*) can the acid-catalysed degradation be regarded as the sum of the more-simple processes, *e.g.*, acid diffusion into the polymer and the hydrolysis of glycoside bonds; and (*b*) to what extent is the mechanism of hydrolysis established for glycosides of low molecular weight valid for cleavage of glycoside bonds in the polymer? The hydrolysis of polysaccharides has therefore been investigated first under homogeneous conditions free of diffusion phemonena, and then under heterogeneous conditions.

DISCUSSION

Degradation under homogeneous conditions

Unlike glycosides of low molecular weight, polymers may have bonds of different reactivities. The degradation of the cellulose molecule and its derivatives may involve three types of glycosidic bonds of different reactivity, namely, internal, terminal, and weak bonds.

Some investigators[1] have assumed the glycoside bonds to be equivalent on the basis of kinetic data and the molecular-weight distribution of the fragments formed on degradation. Others have concluded[2] that the terminal bonds are more reactive because of the higher degradation rate of polysaccharides having a lower d.p. The mechanism of glycoside hydrolysis[3] involves a change of pyranose conformation on formation of an oxonium–carbonium ion in the rate-limiting step. The conformational transition in a sugar residue at an end of a polymeric molecule might be expected to require lower free energy than for an internal unit.

Feather and Harris[4] have shown that, for cellotriose, the reactivities of the two glucosidic bonds differ 1.5-fold. Considering cellotriose as a model for cellulose, it may be assumed that the homogeneous hydrolysis of cellulose will be described by two rate constants that differ negligibly from each other, and thus the effect of increasing hydrolysis rate should be observed only at the higher extents of hydrolysis.

On the basis of analysis of the molecular weight distribution of cellulose nitrates prepared from a cellulose hydrolysate, Schulz and Husemann[5] have concluded that polysaccharide molecules may have weak bonds. Glycoside bonds may be weak in acyclic derivatives[6].

Thus, in spite of a large number of studies, the mechanism of polysaccharide degradation in acid is not yet fully established. For elucidating the mechanism of degradation of polysaccharides, it is necessary to study the change in molecular weight distribution during the course of degradation of the polymer. By using light scattering and spectropolarimetry, we have determined this parameter for the homogeneous hydrolysis of *O*-methylcellulose in aqueous hydrochloric acid.

Examination of the light scattering by *O*-methylcellulose in aqueous hydrochloric acid demonstrated that the second virial coefficient is close to zero ($A_2 \approx O$). The scattering intensity $I = Kc\bar{M}_w$, where $I = R - R_0/R_b$; R, R_0, and R_b are the scatterings of the solution, solvent, and pure benzene, respectively, at $\theta = 90°$; c is the concentration in g/ml; and K is given by equation *1*. Table I shows the values of I specifying the change of $\bar{M}_w$ with time for the degradation of *O*-methylcellulose. For this reaction, the change of $\bar{M}_n$ with time may also be found.

$$K = \frac{2\pi n_0^2 \left(\frac{\partial n}{\partial c}\right)^2}{\lambda^4 N_A} = 9.87 \times 10^{-8} \tag{1}$$

Assuming that the terminal, reducing polymeric units contribute α_1 to the specific rotation, and that all other units (middle and terminal non-reducing) make a contribution α_2, then if the number of monomeric units is j, and the number of molecules of type j is n_j, the rotation angle of the polymer in solution may be given by equation *2*.

$$[\alpha] = \alpha_1 \sum_{j=1}^{\infty} n_j + \alpha_2 \sum_{j=1}^{\infty} (j-1) n_j \tag{2}$$

By definition,

$$\sum_{j=1}^{\infty} j n_j / \sum_{j=1}^{\infty} n_j = P \tag{3}$$

By substitution of equation *3*, equation *2* gives equation *4*.

$$[\alpha] = \frac{\alpha_1 - \alpha_2}{\bar{P}_n} \sum_{j=1}^{\infty} jn_j + \alpha_2 \sum_{j=1}^{\infty} jn_j \tag{4}$$

Since the total number of monomeric units in the system is constant, then $\sum_{j=1}^{\infty} jn_j$ is constant, and we have equation *5*, $[\alpha] = A/\bar{P}_n + B$, where $A = (\alpha_1 - \alpha_2)$. constant, and $B = \alpha_2$.constant. Analysis of literature data on specific rotation and the number-average d.p. for cellulose derivatives and its oligomers confirms this assumption[7]. Thus, the change of specific rotation may be related to a decrease of $\bar{M}_n$. The values $[\alpha]$ for the degradation of *O*-methylcellulose are listed in Table I.

TABLE I

DEGRADATION OF *O*-METHYLCELLULOSE IN 32% HCl AT 25°

t (min)	*I×10*	*−α×10 (degrees)*	*t (min)*	*I×10*	*−α×10 (degrees)*
0	6.0	3.27	21	0.15	3.11
6	1.90	3.25	24	0.70	3.08
9	1.45	3.22	27	0.70	3.06
12	1.40	3.19	30	0.60	3.03
15	1.10	3.17	33	0.50	3.00
18	0.85	3.14			

Using equations *1* and *6*, equation *5* may be rewritten as equation *7*.

$$\bar{M}_w/\bar{M}_n = n \tag{6}$$

$$[\alpha] = \frac{A'n}{I} + B \tag{7}$$

It can be seen from Fig. 1 that the angular coefficient of dependence, $\alpha \approx i/j$, is constant (the correlation coefficient $r = 0.95$), and thus n is constant. Since a considerable change of d.p. (1-fold) does not provide a noticeable quantity of products of low molecular weight, the above condition allows the conclusion that the degradation of *O*-methylcellulose in aqueous hydrochloric acid occurs randomly[8].

Employing the Kun equation,

$$k_{\text{obs}} . t = \ln \frac{1 - 1/\bar{P}_n^0}{1 - 1/\bar{P}_n}, \tag{8}$$

and expressing $\bar{P}_n$ from equation *5* we have

$$\ln \frac{\alpha_\infty - \alpha}{\alpha_\infty - \alpha_0} = k_{\text{obs}} t, \tag{9}$$

where α, α_0, and α_∞ are rotation angles of the solution at time t, and at the start and end of the experiment. Computation from equation *9* (Fig. 2) gives $k_{\text{obs}} =$

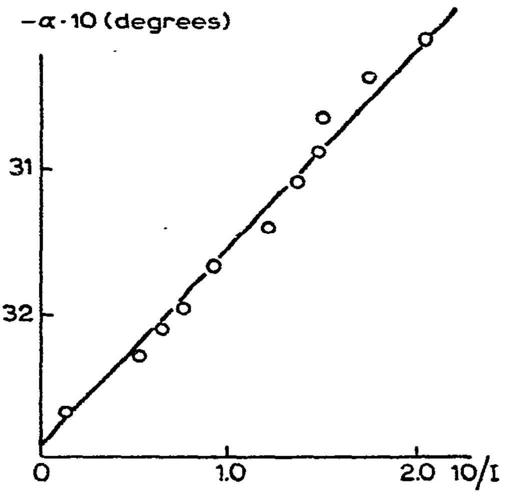

Fig. 1. A plot of α against $1/I$ for the degradation of *O*-methylcellulose in 32% HCl at 25°.

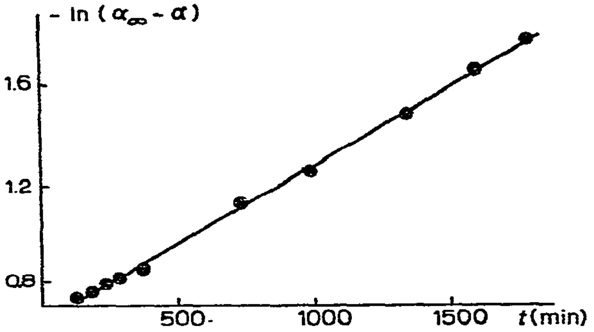

Fig. 2. Graphical solution of equation *9* for the degradation of *O*-methylcellulose in 32% HCl at 25°.

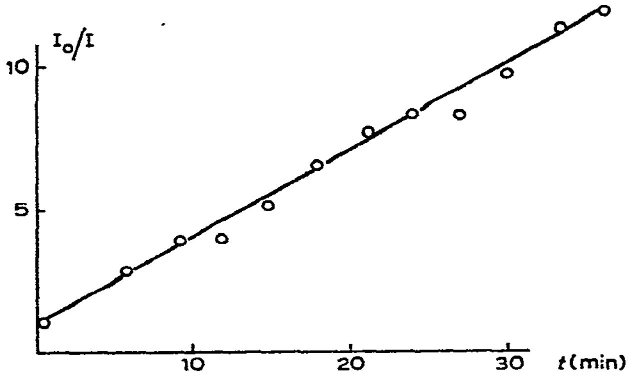

Fig. 3. A plot of I/I_0 against time at $\theta = 90°$ for the degradation of *O*-methylcellulose in 32% HCl at 25°.

$(9.5 \pm 0.5).10^{-4}$ min^{-1}; k_{obs} can be computed from data satisfying the condition $\bar{P}_w \gg 1$, obtained by means of the light-scattering method. For such a case, equation *8* may be written in the form:

$$k_{obs}t = 1/\bar{P}_n - 1/\bar{P}_n^0. \qquad (10)$$

Equation *10*, taking into account equations *1* and *6*, gives equation *11*.

$$\frac{k_{obs}}{n}\bar{P}_w^0 t = I_0/I - 1 \qquad (11)$$

By estimation from the light-scattering data (Fig. 3), the ratio $k_{obs}/n = (4.5 \pm 0.5)$. 10^{-4} min^{-1}, and taking into account that $k_{obs} = (9.5 \pm 0.5).10^{-4}$ min^{-1}, we have $n \approx 2$.

Thus, up to the degree of conversion 0.1, the degradation of *O*-methylcellulose in solution in aqueous hydrochloric acid occurs randomly, and the reactivity of the various glucoside bonds (for a small degree of conversion) may be given by the same rate constant. Thus, practically, no difference may be observed in the kinetic dependences for the polymer and species of low molecular weight.

Figure 4 shows a plot of log k_{obs}/h_0 against $\Delta\nu$ for the degradation of *O*-methylcellulose in solution in aqueous hydrochloric, perchloric, and sulphuric acids at 25°. The same Figure gives a similar dependence for the degradation of cellulose under homogeneous conditions in aqueous sulphuric acid; the data are taken from Refs. 1 and 9–13. It can be seen from Fig. 4 that the experimental data are described satisfactorily by the same equation for polysaccharide degradation in aqueous acid solutions and for the hydrolysis of glucosides of low molecular weight.

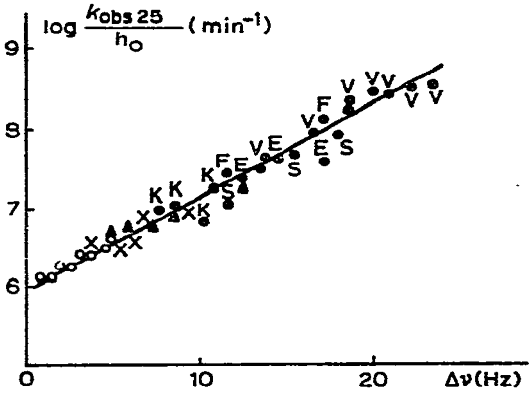

Fig. 4. A plot of log k_{obs}/h_0 against $\Delta\nu$ for the degradation of *O*-methylcellulose in aqueous solutions of HCl (○), $HClO_4$ (×), H_2SO_4 (▲), and cellulose in H_2SO_4 (●). Other data: K, Ref. 9; V, Ref. 10; F, Ref. 11; E, Ref. 12; and S, Ref. 13.

The degradation of cellulose esters in solution in anhydrous acid has been investigated in relation to cellulose acylation[14–16]. We have studied the kinetics of degradation of cellulose triacetate in solution in sulphuric acid in binary and ternary mixtures of organic solvents. The acidity function of acylating systems has been determined[17]. Figure 5 shows a plot of H_0 of 0.1M sulphuric acid solutions against solvent composition. It can be seen from the diagram that the highest acidity is observed in solutions having a high content of acetic anhydride. The kinetics of degradation of cellulose triacetate in acylating mixtures in the presence of sulphuric and perchloric acids was investigated directly by the viscosimetric method.

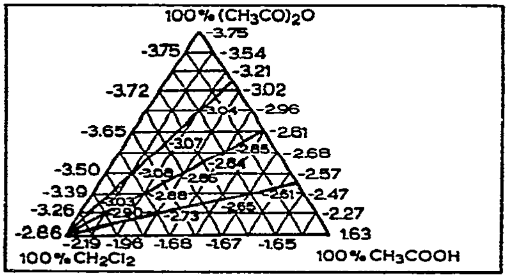

Fig. 5. A plot of H_0 of 0.1M sulphuric acid against solvent composition.

It was first shown that there is a linear correlation between d.p. and intrinsic viscosity in the acylating mixtures. This provided a direct determination of the rate constant from viscosimetric measurements, using equation *12*.

$$1/[\eta]_t = 1/[\eta]_0 + k/k'.t, \tag{12}$$

where $[\eta]_t$ and $[\eta]_0$ are the intrinsic viscosities at time t and the starting time, and k is the observed, first-order, reaction rate constant; $k' = 1.35.10^{-2}$.

Figure 6 shows a plot of log k_{obs} against H_0 with the slope close to unity, *i.e.*, the equation obtained for the hydrolysis of glucosides of low molecular weight is

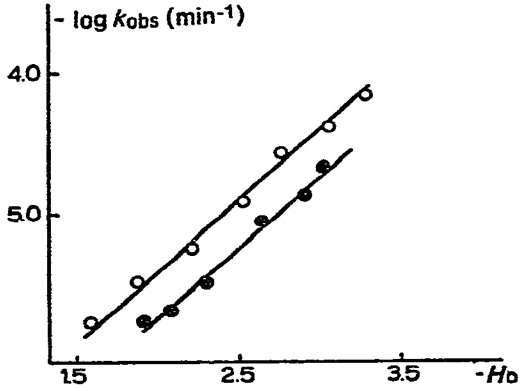

Fig. 6. A plot of k_{obs} against H_0 for the degradation of cellulose triacetate in various acylating mixtures at 25°: H_2SO_4 (●), $HClO_4$ (○).

again valid. For sulphuric and hydrochloric acids, parallel lines were obtained, which show that the acid anion plays a significant role in the formation of the reactive species; in anhydrous media, the acids may add to the reagent in the form of ionic pairs or nondissociated. It is interesting that the activation energy for the degradation of cellulose triacetate depends on the nature of the acylating system (Table II).

TABLE II

THE ACTIVATION ENERGY (E) OF CELLULOSE TRIACETATE DEGRADATION AS A FUNCTION OF SOLVENT COMPOSITION

0.1M H_2SO_4 (vol. %)[a]	60–40	30–70	10–90
E (kcal. mol^{-1})	26 ±1	22 ±1	21 ±1

[a]In a mixture of acetic anhydride–acetic acid.

Degradation under heterogeneous conditions

The degradation of polysaccharides under heterogeneous conditions is a complex physical and chemical process, involving acid diffusion into the polymer and the breaking of glycoside bonds. The degradation of polysaccharides has been reviewed[18]. For elucidating the mechanism of degradation, the following points must be considered. (*a*) A detailed mechanism for the hydrolysis of glycoside bonds. This problem has been solved in the preceding paper for glycosides of low molecular weight; (*b*) the type of degradation of the polymeric molecule (*i.e.*, random or otherwise); and (*c*) the diffusion of acid into the polymer.

The degradation of polysaccharides under heterogeneous conditions has been studied by Manley *et al.*[19]. On the basis of a structural model where the cellulose molecules have a folded conformation of protofibrils, with nearly eight elementary units in each folding[20], a higher reactivity of the glycoside bonds at the vertices of the foldings may be assumed.

The original experiments on the acid-catalysed degradation of cellulose under heterogeneous conditions were repeated for confirmation. The molecular weight distribution for the products (acid-soluble and insoluble) was obtained at various times up to 70% conversion. During degradation, the cellulose molecule is cleaved into fragments having a mean d.p. of ~8, and the molecular weight distribution of the unreacted cellulose was independent of the polymer type. The results obtained confirm the assumption that there are at least two types of bond, having different reactivities in the polymer. At the vertices of the foldings, the glucoside bonds are more reactive.

Acid diffusion into polyglucosides

No quantitative data are available on diffusion.

In studying the diffusion of a bicomponent mixture into a polymer, the following problems must be solved: (*a*) determination of the concentration of each component in the polymer matrix; (*b*) elucidation of diffusion character, *i.e.*, whether it occurs independently and has different diffusion coefficients, or whether the components interact and behave as a single entity.

To solve these problems, the diffusion of vapours of aqueous hydrochloric acid of different concentration into *O*-ethylcellulose films was investigated. The quantity of acid in the polymer at various sorption times was determined by desorption of the acid into water and by a photocolorimetric method. The methods gave almost identical results.

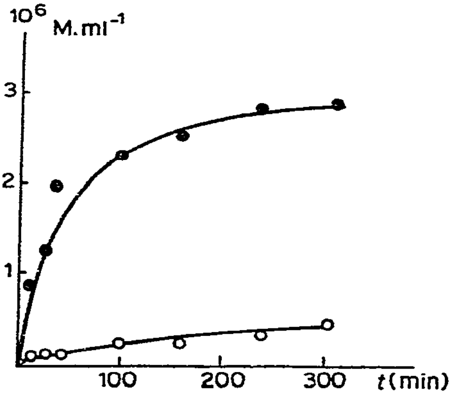

Fig. 7. A plot of the quantity of adsorbed HCl and H_2O against time of diffusion of 25% HCl vapour at 45°.

Figure 7 shows a plot of the quantity of adsorbed acid and water against time during diffusion of vapours of 28% hydrochloric acid at 45°. Similar dependencies were obtained in the temperature range 25–60° for hydrochloric acid concentrations of 28 and 36%. The water–acid ratio remained practically constant with increase of temperature, but decreased somewhat on increase of hydrochloric acid concentration (10.5 ±1 for 28% acid and 9.5 ±0.5 for 36% acid). Thus, diffusions of hydrochloric acid and water into films of *O*-ethylcellulose occur at the same rates, and the diffusion flow may be defined by the effective diffusion coefficient (*D*). The diffusion coefficients

TABLE III

THE DIFFUSION COEFFICIENTS AND ACTIVATION ENERGIES FOR THE DIFFUSION OF HYDROCHLORIC ACID VAPOURS INTO *O*-ETHYLCELLULOSE FILMS AT VARIOUS TEMPERATURES

Temperature (degrees)	$D \times 10^7$ ($cm^2.sec^{-1}$)		E ($kcal.mol^{-1}$)
	28% Acid	*36% Acid*	
25	1.0	0.8	9.5 ±0.5
45	2.8	1.4	
60	3.4	2.4	

and activation energies for diffusion of hydrochloric acid vapours into *O*-ethylcellulose films are listed in Table III.

Degradation of polysaccharides

In the general case, equation *13* applies for the rate of polysaccharide degradation in acid media:

$$W = \frac{\partial c_n}{\partial t} = K(c_n^0 - c_n)c_{HA} \cdot c_{H_2O}, \tag{13}$$

where c_n^0 is the initial concentration of glucoside bonds in the polymer, c_n is the concentration of hydrolysed glucoside bonds, and c_{HA} and c_{H_2O} are the concentrations of acid and water, respectively, in the polymer.

The acid concentration may be found from equation *14*:

$$\frac{\partial c_{HA}}{\partial t} = D_{HA} \cdot \frac{\partial^2 c_{HA}}{\partial X^2} + \sum_i^0 c_{HA} \cdot c_i \cdot K_{pi}, \tag{14}$$

where c_i is the concentration of functional group incapable of protonation, K_{pi} is the equilibrium constant of these reactions, and X is the diffusion coordinate.

In the preceding paper, using the p.m.r. method, we found that the model polyglucosides undergo negligible protonation, so that the second term in equation *14* may be ignored and equation *15* results:

$$\frac{\partial c_{HA}}{\partial t} = D_{HA} \cdot \frac{\partial^2 c_{HA}}{\partial X^2}. \tag{15}$$

Since the glucoside bonds are cleaved with participation of water, its concentration may be found from equation *16*:

$$\frac{\partial c_{H_2O}}{\partial t} = D_{H_2O} \cdot \frac{\partial^2 c_{H_2O}}{\partial X^2} - K(c_n^0 - c_n) \cdot c_{HA} \cdot c_{H_2O}. \tag{16}$$

By applying these equations to the degradation of *O*-ethylcellulose films, the rates of HCl and water diffusions were found to be equivalent, *i.e.*, $D = D_{HCl} = D_{H_2O}$.

The following assumptions may then be considered: (*a*) the system *O*-ethylcellulose–acid is rather dilute with respect to the acid (the HCl and water solubilities do not exceed 1.5×10^{-4} mol/ml and 1.5×10^{-3} mol/ml); thus D may be regarded as independent of concentration of the respective components in the polymer; (*b*) K may be regarded as constant because of the low solubility of aqueous acid in the polymer; (*c*) the hydrolysis of glucoside bonds is virtually irreversible; this condition is satisfied in degradations to a low degree of conversion (<0.02) where the concentration of glucoside bonds is almost constant, *i.e.*, $c_n^0 - c_n \approx c_n^0$; (*d*) the polymer properties are isotropic. *O*-Ethylcellulose is amorphous, and thus the mean rate over the total polymer volume and volume concentrations can be used. Thus, determination of the rate of cleavage of glucoside bonds in the polymer under the action of hydrochloric acid vapour involves a combined solution of equations *13* and *16*. Solving these equations on the basis of the above assumptions gives the general equation *17* for the concentration of glucoside bonds broken in the polymer:

$$c_n = k_{\text{obs}} c_{\text{HCl}} \cdot t \left\{ 1 - \frac{8}{\pi l} \sum_{m=1}^{\infty} \frac{k_{\text{obs}}(B_m^2 D + k_{\text{obs}}) + B_m^2 D[1 - \exp-(B_m^2 D + k_{\text{obs}}) . t]}{(2m-1) B_m (B_m^2 D + k_{\text{obs}})^2 t} \right\}, \tag{17}$$

where $B_m = \pi(2m-1)/l$. The concentration of cleaved bonds may be found from equation *18*:

$$c_n = m(1/\bar{M}_n - 1/\bar{M}_n^0), \tag{18}$$

where $\bar{M}_n$ and $\bar{M}_n^0$ are the number-average molecular weights at time t and initially, and m is the molecular weight of the unit.

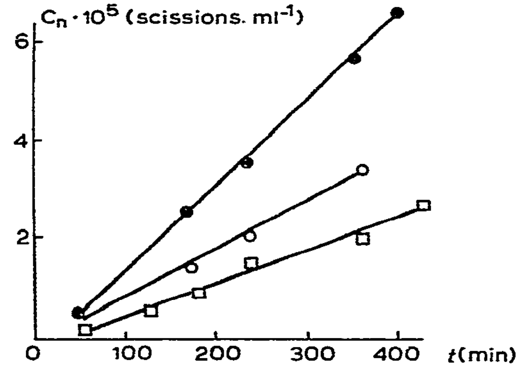

Fig. 8. A plot of c_n against time for the degradation of *O*-ethylcellulose films in 28% HCl vapour at 25, 40, and 60°.

Figure 8 shows part of the experimental data in c_n–t coordinates. It can be seen that, eventually, the plot of c_n against t is linear, *i.e.*, the polymeric matrix is entirely saturated with the acid:

$$(B_m^2 D + k_{\text{obs}}) . t \gg 1, \tag{19}$$

and equation *17* takes the form:

$$c_n \approx k_{\text{obs}} c_{\text{HCl}} \cdot t, \tag{20}$$

where $k_{\text{obs}} = Kc_n^0$.

According to this equation, the number of glucoside bonds cleaved in the polymer is determined by K, time, and the concentration of acid in the polymer.

The values of k_{obs}, activation energy, and entropy are listed in Table IV.

TABLE IV

THE RATE CONSTANTS OF GLUCOSIDE BOND CLEAVAGE, ACTIVATION ENERGY, AND ENTROPY FOR THE DEGRADATION OF *O*-ETHYLCELLULOSE IN HYDROCHLORIC ACID VAPOUR

HCl conc. (*wt.* %)	*Temperature* (*degrees*)	*Time* (*min*)	$c_n \times 10^5$ (*mol scissions.ml*$^{-1}$)	$c_{HCl} \times 10^5$ (*mol.ml*$^{-1}$)	k_{obs} (*min*$^{-1}$)	E (*kcal.mol*$^{-1}$)	S (*e.u.*)
28	35	60	0.2	8	0.11		−50 ±2
		90	0.4	11	0.09		
		180	0.6	12	0.07		
	45	90	0.5	10	0.12	5.5 ±1.0	
		180	1.0	12	0.11		
		240	1.3	12	0.11		
	60	180	2.4	13	0.22		
		240	3.2	14	0.21		
36	35	180	1.3	11	0.14		−50 ±2
		240	1.7	12	0.13		
		360	2.3	12	0.12		
	45	120	1.0	11	0.16	5.5 ±1.0	
		180	1.6	11	0.15		
		240	2.3	13	0.16		
		360	3.5	14	0.16		
	60	120	1.8	15	0.23		
		180	2.8	13	0.26		
		240	3.8	15	0.23		
		360	5.9	16	0.23		

The reactivities of glucoside bonds in polysaccharide degradation in the solid state and in solution

It is of interest to compare the kinetic parameters (Table V) for the degradation of the cellulose derivatives in the solid state (*O*-ethylcellulose films in hydrochloric acid vapour) and in solution (*O*-methylcellulose in aqueous hydrochloric acid); such comparison is justified since methyl and ethyl D-glucopyranosides have practically the same kinetic parameters[21]. For the solid-state system, the rate constants were computed by using equation *20*. For the solution, involving an excess of hydrochloric acid, the rate constants were found from the first-order equation but equated to unit catalyst concentration.

TABLE V

THE KINETIC PARAMETERS OF ACID-CATALYSED DEGRADATION OF *O*-METHYLCELLULOSE AND *O*-ETHYLCELLULOSE

Compound	$k_{35°}$ (*min^{-1}.mol^{-1}.ml*)	E (*kcal.mol^{-1}*)	S (*e.u.*)
O-Methylcellulose	5×10^{-6}	30	+4
O-Ethylcellulose	1.2×10^{-1}	5.5	−50

As a first approximation, one may assume that the degradation of *O*-ethylcellulose occurs in "solution", and it is of interest to identify the property of the solution that is reponsible for the change of kinetic parameters. Figure 9 shows the change of activation energy associated with the degradation of cellulose esters in media having different dielectric permeability ε. The activation energy is inversely proportional to 1/ε. Thus, a model may be proposed for the chemical degradation reaction in the solid state by means of reactions in solvents having identical physical parameters. Further examples are needed to validate this approach.

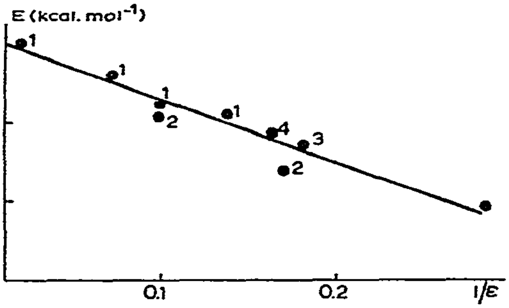

Fig. 9. A plot of *E* against 1/ε; 1, our data; 2, Ref. 16; 3, Ref. 15; 4, Ref. 21.

EXPERIMENTAL

Reagents. — *O*-Methylcellulose was twice precipitated from solution in water with alcohol. [Found: OMe, 33.3%; $\bar{M}_w = (1.3 \pm 0.1) \times 10^5$].

Cellulose triacetate was twice precipitated from dichloromethane; characteristics of the samples are shown in Table VI.

TABLE VI

CHARACTERISTICS OF THE SAMPLES OF CELLULOSE TRIACETATE

Sample	*Acetyl number*[a]	$\bar{P}_n^b$	$\bar{P}_v^c$
1	61.60	156	280
2	59.70	215	390
3	61.36	288	530
4	61.53	396	710
5	61.26	500	950

[a]Measured by the method of Timell[22]. [b]The number-average d.p. ($\bar{P}_n$) was computed from the intrinsic viscosity in chloroform[23]. [c]The mean viscosity d.p. ($\bar{P}_v$) was determined by the viscosimetric method[24].

O-Ethylcellulose was twice precipitated from solution in butanone with water (Found: OEt, 52.4%; $\bar{M}_n = 3.6 \times 10^4$); 30–180-μm films were prepared from 3–5% polymer solutions in dichloroethane by solvent evaporation at room temperature, and dried (at 10^{-7} torr) to constant weight before use.

Degradation kinetics. — The degradation kinetics of *O*-methylcellulose were investigated by polarimetry. A solution of the polymer in water was stored for 5–6 days at 5° and then concentrated. Acid was added to the solution before each experiment. The polymer concentration was measured by refractometric and polarimetric methods.

Since *O*-methylcellulose forms an aggregate in aqueous solutions[25], the concentration and temperature regions were selected for acid solutions having practically no aggregates of the polymer. The polymer concentration was 0.5–0.8%.

The degradation kinetics of cellulose triacetate were studied by viscometry, using an Ostwald viscometer. The polymer sample was rapidly dissolved (3–10 min, depending on the initial $\bar{P}_n$) in acetic acid at 110–115° or in dichloromethane at 25°, and then the computed quantities of the other components were added. The intrinsic viscosity was found from the Maron equation[26], the validity of which was proved for all the mixtures investigated.

The degradation kinetics of *O*-ethylcellulose films were measured by means of molecular weight determination after desorbing with hydrochloric acid. The viscosity was determined in chloroform at 25°. The number-average molecular weight was computed from equation *21*[27]: $[\xi] = \bar{M}_n.K$, where $K = 3.71 \times 10^{-5}$.

The sorption kinetics of the vapour of the aqueous hydrochloric acid solutions was studied by using a McBen balance with a sensitive quartz spiral (0.5–0.7 mg/mm).

TABLE VII

THE RATE CONSTANTS FOR DEGRADATION OF *O*-METHYLCELLULOSE

Acid (%)	*Temp. (degrees)*	k_{obs} (*min*$^{-1}$)	*Acid* (%)	*Temp. (degrees)*	k_{obs} (*min*$^{-1}$)
HCl					
4.2	70	4.7×10^{-4}	25.9	40	3.1×10^{-3}
	80	1.4×10^{-3}		50	1.1×10^{-2}
	90	3.4×10^{-3}		60	4.0×10^{-2}
				70	1.7×10^{-1}
8.5	70	2.6×10^{-3}	29.0	30	1.1×10^{-3}
	80	5.6×10^{-3}		40	5.3×10^{-3}
	90	1.7×10^{-2}		50	2.4×10^{-2}
12.3	60	4.6×10^{-3}		60	6.3×10^{-2}
	70	1.2×10^{-2}		70	1.3×10^{-1}
	80	3.6×10^{-2}	32.0	25	1.4×10^{-3}
17.0	60	8.5×10^{-3}		30	2.5×10^{-3}
	70	2.7×10^{-2}		40	1.0×10^{-2}
	80	7.0×10^{-2}		50	3.9×10^{-2}
21.5	60	2.4×10^{-2}		60	1.0×10^{-1}
	70	7.9×10^{-2}			
	80	1.8×10^{-1}			
$HClO_4$					
22.2	60	8.6×10^{-4}	45.2	50	5.0×10^{-3}
	70	3.8×10^{-3}		60	2.1×10^{-2}
	80	1.4×10^{-2}		70	8.9×10^{-2}
	88	2.9×10^{-2}	57.2	30	2.5×10^{-3}
31.3	60	3.3×10^{-3}		40	1.7×10^{-2}
	70	8.2×10^{-3}		50	9.1×10^{-2}
	80	3.3×10^{-2}	63.5	30	2.5×10^{-2}
	90	9.7×10^{-2}		40	1.1×10^{-1}
35.0	60	4.2×10^{-3}		50	3.6×10^{-1}
	70	1.4×10^{-2}			
	80	4.6×10^{-2}			
H_2SO_4					
26.2	25	5.9×10^{-6}		70	4.4×10^{-2}
31.0	50	6.0×10^{-4}		80	1.3×10^{-1}
	60	3.0×10^{-3}	54.2	50	1.7×10^{-2}
	70	7.3×10^{-3}		60	6.0×10^{-2}
	80	2.2×10^{-2}		70	1.7×10^{-1}
36.1	60	7.4×10^{-3}	62.0	40	9.6×10^{-3}
	70	1.7×10^{-2}		50	3.9×10^{-2}
	80	5.2×10^{-2}		60	1.5×10^{-1}
43.7	60	1.2×10^{-2}	70.7	30	6.1×10^{-3}
				40	2.4×10^{-2}
				50	1.0×10^{-1}

TABLE VIII

THE OBSERVED RATE CONSTANTS FOR THE DEGRADATION OF CELLULOSE TRIACETATE SAMPLES HAVING DIFFERENT MOLECULAR WEIGHTS

P_v	CH_3CO_2H (vol. %)	$(CH_3CO)_2O$ (vol. %)	Medium CH_2Cl_2 (vol. %)	H_2SO_4 (mol/l)	$HClO_4$ (mol/l)	Temp. (degrees)	Polymer conc. (g/100 ml)	k_{obs} 10^5 (sec^{-1})
280	100	—	—	0.1	—	25	0.2	0.15
	100	—	—	0.2	—	25	0.2	0.29
	90	10	0.1	0.1	—	25	0.2	0.89
	70	30	—	0.1	—	25	0.2	1.40
	70	30	—	0.1	—	15	0.2	0.38
	70	30	—	0.1	—	40	0.2	7.80
	50	50	—	0.1	—	25	0.2	2.40
	20	80	—	0.1	—	25	0.2	5.40
390	80	—	20	0.1	—	25	0.2	0.18
	70	30	—	0.1	—	25	0.2	1.32
	70	30	—	0.1	—	25	0.1	1.33
	60	20	20	0.1	—	25	0.2	1.65
	20	60	20	0.1	—	25	0.1	5.42
530	70	30	—	0.1	—	25	0.1	1.35
	70	30	—	0.1	—	25	0.1	1.30
710	70	30	—	0.1	—	25	0.2	1.38
	70	30	—	0.1	—	25	0.1	1.34
950	100	—	—	0.2	—	25	0.1	0.27
	80	—	20	0.1	—	25	0.1	0.16
	96	4	—	0.1	—	25	0.1	0.38
	90	10	—	0.1	—	25	0.1	0.73
	90	10	—	0.1	—	15	0.1	0.22
	90	10	—	0.1	—	40	0.1	5.10
	70	30	—	0.1	—	25	0.1	1.35
	70	30	—	0.1	—	15	0.1	0.34
	70	30	—	0.1	—	40	0.1	8.60
	70	30	—	0.1	—	25	0.2	1.39
	70	30	—	0.1	—	25	0.06	1.33
	70	30	—	0.1	—	25	0.03	1.28
	40	60	—	0.1	—	25	0.1	2.47
	40	60	—	0.1	—	15	0.1	0.64
	40	60	—	0.1	—	40	0.1	17.5
	80	20	—	—	0.01	25	0.1	0.20
	70	30	—	—	0.01	25	0.1	0.23
	50	50	—	—	0.01	25	0.1	0.32
	40	60	—	—	0.01	25	0.1	0.43
	20	80	—	—	0.01	25	0.1	0.89
	20	80	—	—	0.02	25	0.1	2.10
	20	60	20	—	0.01	25	0.1	1.40

The temperature in the sorption cell was maintained at ±0.1°. The diffusion coefficient was found from the equation given in Ref. 28.

Kinetic results. — The degradation rate constants of *O*-methylcellulose at various acid concentrations and tempertures are listed in Table VII.

Table VIII shows the observed rate constants for the degradation of cellulose triacetate samples having different molecular weights, at various temperatures and in different acylating mixtures.

REFERENCES

1 A. Sharples, *J. Polym. Sci., Part A-2,* 13 (1954) 393–401; 14 (1954) 95–104.

2 K. Freudenberg, W. Kuhn, W. Durr, F. Bolz, and G. Steinbrunn, *Ber.*, 63 (1930) 1510–1530; M. L. Wolfrom and J. C. Dacons, *J. Amer. Chem. Soc.*, 74 (1952) 5331–5333; J. Hallo and J. Szejtli, *Stärke,* 11 (1959) 239–244.

3 J. T. Edward, *Chem. Ind. (London)*, (1955) 1102–1105.

4 M. S. Feather and J. F. Harris, *J. Amer. Chem. Soc.*, 89 (1967) 5661–5664.

5 G. V. Schulz and E. Husemann, *Z. Phys. Chem.*, B52 (1942) 1–22, 23–49.

6 N. E. Virkova, *Pap. Puu,* 41 (1959) 551–555; N. Ya. Lenshina and V. I. Ivanov, *Vysokomol. Soedin. Ser. A,* 4 (1962) 1647–1654.

7 E. E. Dickey and M. L. Wolfrom, *J. Amer. Chem. Soc.*, 71 (1949) 825–828; M. L. Wolfrom, L. W. Georges, and J. C. Sowden, *ibid.*, 60 (1938) 1026–1031; M. L. Wolfrom, J. C. Sowden, and E. N. Lassettre, *ibid.*, 61 (1939) 1072–1076.

8 A. A. Berlin and N. S. Enikolopyan, *Vysokomol. Soedin. Ser. A.*, 10 (1968) 1475–1496.

9 L. I. Novikova and A. A. Konkin, *Zh. Prikl. Khim. (Leningrad)*, 32 (1959) 1081–1086.

10 P. N. Odintsov and Ya. V. Vitol, *Izv. Akad. Nauk Latvian SSR,* (1966) 375–382.

11 K. Freudenberg and G. Blomqvist, *Ber.*, 68 (1935) 2070–2082.

12 A. Ekenstam, *Ber.*, 69 (1936) 549–553, 553–559.

13 J. Sakurada and S. Okamura, *Z. Phys. Chim. (Japan)*, A187 (1940) 289–297.

14 N. K. Pyatakina, Yu. V. Moiseev, and G. E. Zaikov, *Vysokomol. Soedin. Ser. A,* 13 (1971) 200–205.

15 M. A. Bhatti and P. Howard, *Preprint Int. Symp. Macromol.*, Helsinki, 1972, Vol. 5, pp. 43–48.

16 V. Yu. Bytenskii, E. P. Kuznetsova, and N. I. Klenkova, *Zh. Prikl. Khim.* (Leningrad), 39 (1966) 2319–2322.

17 N. K. Pyatakina, Yu. V. Moissev, and M. I. Vinnik, *Zh. Fiz. Khim.*, 44 (1970) 1985–1989.

18 J. N. BeMiller, in *Starch Chemistry and Technology,* Vol. 1, R. L. Whistler and E. F. Paschall (Eds.), Academic Press, New York, 1965, pp. 495–520.

19 M. Chang, T. C. Pound, and R. St. J. Manley, *J. Polym. Sci., Part A-2,* 11 (1973) 399–411.

20 R. St. J. Manley, *J. Polym. Sci., Part A-2,* 9 (1971) 1025–1059.

21 W. C. Frith, *Tappi,* 46 (1963) 739–744.

22 T. E. Timell, *Chem. Ind. (London)*, (1963) 1208–1209.

23 A. Sharples and H. M. Major, *J. Polym. Sci.*, 27 (1958) 433–440.

24 D. Henley, *Arkiv Kemi,* 28 (1961) 327–392.

25 W. Brock Neely, *Nature (London)*, 185 (1960) 159–160; W. Kuhn, P. Moser, and H. Majer, *Helv. Chim. Acta,* 44 (1961) 770–791.

26 S. H. Maron, *J. Appl. Polym. Sci.*, 5 (1961) 282–284.

27 W. R. More and A. M. Broun, *J. Appl. Chem.*, 8 (1958) 363–366.

28 M. M. Mikhailov, *Vlagopronitsaemost' organicheskikh dielektrikov,* Gosenergoizdat Publ. House, Moscow–Leningrad, 1960, pp. 147–149.