The Hydrolysis of Cellulose Part I. The Fine Structure of Egyptian Cotton

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INTRODUCTION

Previous hydrolytic studies¹ have established the presence in cellulose of a fraction which is more readily degraded than the remaining material. and it has been reasonably supposed that this fraction represents the disordered or noncrystalline segments of the chain molecules. If these accessible regions are degraded to low molecular weight products and hence removed by dissolution in the hydrolyzing acid, the corresponding decrease in weight of the cellulose under investigation can be related to its accessibility.² However, although the amount of disordered material which is hydrolytically accessible is of fundamental interest in characterizing a sample of cellulose, there are several objections to the existing methods^{1,2} for determining this quantity. Firstly, severe acid conditions are necessary, producing high degrees of degradation, when it is likely that there is an increase in crystallinity during hydrolysis. This has been shown to be true in the case of regenerated celluloses,³ but for natural celluloses the results are not conclusive.³⁻⁵ The second disadvantage of the method is that in many cases the initial weight loss corresponding to the accessible fraction is quite small, and the distinction between this and the subsequent less rapid decrease in weight of the ordered regions can only be achieved by an arbitrary extrapolation.

However, whereas the initial weight loss is small and arbitrary, the fall in degree of polymerization is usually great, and it was thought that an investigation of the rate of chain breakdown during hydrolysis might provide a sensitive means for determining accessibility. The results of such a kinetic study for the case of Egyptian cotton are considered in this paper, and it will be shown that accessibility values can be determined by using a method which is free from the objections considered above. It will be assumed that the course of hydrolysis is not influenced by the presence of extranormal linkages of the types proposed by Schulz⁶ and Pacsu.⁷ The validity of this assumption will be discussed in Part II.¹⁵

METHOD

If it is assumed, by analogy with cellobiose, that the hydrolysis of cellulose is an acid catalyzed reaction of the first order, then:

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$$d[N_t - N_0(1 - \alpha)]/dt = k[N_t - N_0(1 - \alpha)]t$$

where N_t is the number of bonds at time t, α the fraction of bonds available for hydrolysis, and k the hydrolysis rate constant for the conditions used. This can be integrated (cf. af Ekenstam⁸) to give:

$$\ln\left(1 - \frac{1}{(\bar{P}_n)_0}\right) - \ln\left(1 - \frac{1}{(\bar{P}_n)_0} + \frac{1}{(\bar{P}_n)_0\alpha} - \frac{1}{(\bar{P}_n)_t\alpha}\right) = kt \quad (1)$$

where $(\bar{P}_n)_t$ is the number-average degree of polymerization at time t. As it will not be necessary to consider high degrees of degradation, the following approximation can be used:

$$\frac{1}{(\bar{P}_{n})_{t}} - \frac{1}{(\bar{P}_{n})_{0}} = k\alpha t$$
(2)

Estimation of the accessibility, α , thus involves determinations of $(\bar{P}_n)_i$ at various times during the hydrolysis. The advantage of this over the Nickerson method lies in the fact that by studying the initial stages of degradation, α can be evaluated accurately before recrystallization occurs. In addition, degradation proceeds with measurable rapidity under very mild conditions, N/10 H₂SO₄ at 50°C. being used in the following experiments.

Determination of k

The rate constant, k, for the completely accessible intermonomeric linkages in cellulose was found experimentally from results on the hydrolysis of cellopentaose. The latter is the highest soluble member of the cellulose series and in dilute solution it is assumed that all the bonds are available for hydrolytic attack. Interpretation of the results is complicated by the fact that cellopentaose hydrolyzes at a slightly different rate from cellulose, owing to the effect of the terminal linkages. However, Freudenberg⁹ has determined the rate constants of cellulose and various oligosaccharides in 51% sulfuric acid solutions, and from these data the ratio k_5/k , can be found by interpolation, k_5 being the initial rate constant for cellopentaose. The value of this ratio at 50°C., is 1.38 \pm 0.05 and it is assumed to be independent of acid concentration.

An experimental determination of k_5 was made in N/10 H₂SO₄ at 50°C., *i.e.*, under the conditions used in the experiments to be described later on the hydrolysis of cotton. The results are given graphically in Figure 1, and it can be seen that they conform to the modified version of equation (1), obtained by putting α equal to unity:

$$\ln\left(1-\frac{1}{(\bar{P}_n)_0}\right) - \ln\left(1-\frac{1}{(\bar{P}_n)_i}\right) = k_5 t$$

It is known⁹ that the slope of the curve increases during hydrolysis, but for the limited range of \bar{P}_n considered in these experiments, no significant deviation from linearity is apparent. The value of k_5 found was 2.17 \pm 0.06×10^{-8} sec.⁻¹; hence k is equal to $1.57 \pm 0.10 \times 10^{-8}$ sec.⁻¹.



Fig. 1. Hydrolysis of cellopentaose in N/10 H₂SO₄ at 50 °C.

RESULTS AND DISCUSSION

Values of \bar{P}_n can be determined from osmotic experiments, but the results are not very accurate in the high molecular weight range. Weight average degrees of polymerization (\bar{P}_w) , on the other hand, can be determined with great accuracy from viscosity measurements, ^{10,11} but the results are not necessarily related in a simple manner to values of \bar{P}_n . However, it has been shown¹² that random degradation of an initially monodisperse polymer results in a distribution of degrees of polymerization, the ratio of the two moments, \bar{P}_w/\bar{P}_n , being equal to two over a wide range of degrees of degradation.

The values of \bar{P}_w/\bar{P}_n determined experimentally for various stages in the hydrolysis of Egyptian cotton are given in Table I, and it is apparent that there is no significant deviation from 2. The modified version of equation (2):

$$\frac{2}{(\bar{P}_{w})_{t}} - \frac{2}{(\bar{P}_{w})_{0}} = k\alpha t$$
(3)

is therefore considered to be applicable and the more accurate weight average results, determined from viscosity experiments, are used in the construction of rate curves. Probable reasons for the lack of agreement between the results given in Table I and those found by Schulz¹² are given in Part II.¹⁵

$ar{P}_w/ar{P}_n$ at	VARIOUS	STAGES IN	тне І	YDROLYSIS	OF EGYPTIA	IN COTTON
\overline{P}_n		$\overline{P}_w/\overline{P}_n$		\overline{P}_n	$\overline{P}_{w_{\ell}}$	\overline{P}_n
2300	2.	04 ± 0.26		620	1.97 =	E 0.13
1320	2.	18 ± 0.17		573	1.83 =	E 0.13
1260	1.	90 ± 0.14		426	2.02 =	Ŀ 0.13
1050	1.	97 ± 0.13		384	2.03 =	E 0.13
753	2.	03 ± 0.13		371	2.09 =	± 0.13
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TABLE I

Fig. 2. Hydrolysis of Egyptian cotton in N/10 H₂SO₄ at 50 °C.—first stage. Abscissa, time $\times 10^{-4}$ sec.

12

16

20

24

0

4

8

Hydrolysis of Egyptian Cotton-First Stage

The results for the initial stage of cotton hydrolysis are expressed in Figure 2. Below a value of 1870 for $\bar{P}_w/2$ (or \bar{P}_n) the rate plot is linear, and the slope of the most probable straight line is $0.170 \pm 0.007 \times 10^{-8}$ sec.⁻¹. Hence, from equation (3), the accessibility can be calculated to be $10.8 \pm 1.0\%$. It will be noticed that the value of $2/\bar{P}_w$ for unhydrolyzed cotton does not lie on the curve. This is considered to arise from the presence of abnormally acid-sensitive linkages and is discussed in greater detail in the second part of this paper.¹⁵

It is of interest to speculate on the nature of the hydrolytically accessible material determined by the above method. The suggestion has been made¹ that the accessible chain segments lie not only in the intercrystalline regions, but also on the surfaces of the crystallites, although there is no conclusive evidence to substantiate this point. However, Rånby⁵ has calculated that, for cotton, the fraction of chains in the crystal surfaces is about 20%, so that if degradation is taking place here, it must be at a reduced rate. Of further interest in this connection are the results given in Figure 3 for the

hydrolysis of a sample of bacterial cellulose grown from A. acetigenum. Although the crystalline regions in this type of cellulose are of similar dimensions to those in cotton,⁵ the accessibility calculated from Figure 3 is only 3%. As part of this small fraction of accessible material must be accounted for by the intercrystalline regions, the extent of the reaction occurring on the crystallite surfaces would appear to be negligible. This can be explained by assuming that ruptured chains in these areas are held in positions sterically favourable for resynthesis. The difference in accessibility between cotton and bacterial cellulose is thus accountable for solely in terms of the differences in amounts of disordered material.



Fig. 3. Hydrolysis of bacterial cellulose in N/10 H₂SO₄ at 50 °C. Abscissa, time $\times 10^{-4}$ sec.

Hydrolysis of Egyptian Cotton-Second Stage

In Figure 4, results are given for the hydrolysis of cotton over a wider range of degrees of polymerization, and significant deviation from linearity in the rate plot is apparent. Before the decrease in slope can be interpreted in terms of recrystallization, however, corrections must be applied for the effect of nonrandom degradation occurring when the probability of making more than one cut in the accessible segment of a chain cannot be neglected. The length of the ordered regions in Egyptian cotton was determined from measurements of the limiting degree of polymerization. Experiments in 2 N HCl at 50°C. gave a weight-average result of 200 \pm 10 and a number-average result of 120 \pm 20 units, in good agreement with the values recently determined by Nelson and Tripp.¹³ Thus the numberaverage length of the intercrystalline regions is 13 units, so that two or more cuts produce molecules which are sufficiently small either to dissolve in the hydrolyzing acid or to be ignored in subsequent molecular weight measurements. In viscometric estimations the derived weight-average result is



Fig. 4. Hydrolysis of Egyptian cotton in N/10 H₂SO₄ at 50 °C.—complete curve covering wider range of degrees of polymerization.

virtually unaffected by the presence of such small molecules and in osmometry rapid diffusion through the membrane ensures that no contribution is made to the observed pressure. Consequently, for any given intercrystalline section of a chain, only the first cut can be considered to be effective. Although the weight of these molecules is small relative to the total weight of degraded polymer (amounting to a maximum of 2% for the degrees of degradation considered in these experiments) their relative number is large, so that the effect on the rate curve is not negligible. Direct estimations of their weight and degree of polymerization cannot be made with sufficient accuracy, but the necessary corrections can be made by calculating the distributions of chain scissions at various degrees of degradation, as follows.

The probability of r cuts occurring in an intercrystalline chain segment is given by:

$$W_{r} \simeq \left[\left(\frac{Q-1}{Q} \right)^{QX-r} \right] \left[\left(\frac{1}{\bar{Q}} \right)^{r} \right] \left[Q_{X}C_{r} \right]$$

(where X is the average number of cuts per crystalline segment, and Q the number of segments. The degree of degradation is assumed to be small.) For all practical cases Q can be taken as equal to infinity, so that:

$$W_{\tau} = \frac{e^{-X}X^{r}}{r!}$$

 $(\bar{P}_{n})_{t}$ can be conveniently expressed as:

 $(\bar{P}_n)_t = (\bar{P}_n)_0/1 + (\text{number of cuts per chain})$

so that if all cuts are equally effective:

$$[(\bar{P}_n)_t]_{\text{true}} = \frac{(P_n)_0}{1 + YX}$$
(4)

where Y is the average number of intercrystalline segments present in the undergraded chain molecule; whereas if first cuts only are effective:

$$[(\bar{P}_n)_t]_{\text{obs.}} = \frac{(\bar{P}_n)_0}{(1 - W_0) Y + 1} \approx \frac{(\bar{P}_n)_0}{(1 - e^{-X})Y + 1}$$
(5)

From equations (4) and (5) the true hydrolysis rate curve given in Figure 4 was constructed, using a value of 1870 for \bar{P}_0 , determined from the intercept in Figure 2; Y was calculated to be 14, from a knowledge of the crystallite size (120 units) and the accessibility (10.8%) of the unhydrolyzed structure.

The decrease in slope of the true rate curve shows that appreciable recrystallization is occurring during hydrolysis. At the greatest extent of degradation considered in these experiments the accessibility calculated from equation (3) is only 5%, compared with the value of 10.8% found initially. It is rather surprising to find that the recrystallization starts at a very early stage in the hydrolysis, when the value of \bar{P}_n is approximately 900. At this point less than one-eighth of the intercrystalline chain segments have been broken.

EXPERIMENTAL

(1) Hydrolysis of Cellopentaose

A carefully fractionated sample of cellopentaose was prepared by partially hydrolyzing a batch of commercial viscose rayon and separating the products by means of a charcoal column. The hydrolysis was carried out on a 0.1% solution in N/10 H₂SO₄ at 50°C. Molecular weights were determined by the hypoiodite method.¹⁴

(2) Hydrolysis of Egyptian Cotton

Egyptian cotton, purified by extraction with boiling alcohol and ether, was hydrolyzed for varying times in N/10 H₂SO₄ at 50°C. The samples were conditioned in distilled water at 50°C. for 18 hours before hydrolysis, and after reaction the acid was removed by suction through a filter. Washing was carried out until the conductivity of the wash liquor remained unchanged by contact with the hydrolyzate.

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Molecular weight measurements were made on the soluble nitrated products containing 14.0 \pm 0.1% N., prepared by nondegradative reaction with mixtures of nitric acid, acetic acid, and acetic anhydride.¹⁰ Viscosities of the butyl acetate solutions were determined in capillary viscometers at 25.0 \pm 0.1°C., and corrections for the effect of shear were applied when necessary. Intrinsic viscosities were converted to weightaverage degrees of polymerization by use of the equation:¹⁰

$$[\eta] = 0.0108 (\bar{P}_w)^{1.0}$$

In order to obtain an assessment of the experimental error, each hydrolyzed sample was nitrated in duplicate; the mean difference between duplicate intrinsic viscosities was observed to be 1.6%. Osmotic pressures were determined in a Fuoss-Meade type of osmometer, using acetone solutions at a temperature of $26.5 \pm 0.01^{\circ}$ C. The membranes employed were prepared from never-dried cellophane by conditioning through acetone-water mixtures. Density corrections were applied to the osmotic pressures, experiments having shown that the density of the solution is related to its concentration by:

$$\rho = 0.7838 + 0.054C$$

where C is the concentration in g./100 ml. The estimated value for the error was $\pm 5\%$ for degrees of polymerization in the range 200 to 1000. Above 1000, the small osmotic pressures involved reduced the accuracy of measurement, while below 200 diffusion through the membrane made an arbitrary extrapolation necessary, involving an unpredictable error.

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Synopsis

The kinetics of chain degradation have been studied for the heterogeneous hydrolysis of Egyptian cotton under mild acid conditions. The results have been interpreted to give estimates of accessibilities free from the defects associated with former measurements. The amount of accessible material in the undegraded cotton was found to be 10.8%, but during hydrolysis this is reduced to less than 5%. The recrystallization takes place at an early stage in the degradation, starting at a point when approximately one-eighth of the intercrystalline chain segments have been broken.

Résumé

La cinétique de dégradation en chaîne de l'hydrolyse hétérogène du coton égyptien a été étudiée en milieu acide léger. Les résultats ont été interprétés en vue d'estimer les accessibilités sans répéter les défauts qui affectaient les mesures antérieures. La quantité de matériel accessible dans le coton non-dégradé a été trouvée égale à 10.8%, durant l'hydrolyse toutefois elle est réduite à moins de 5%. La recristallisation se passe au début de la dégradation, dès qu'environ un huitième des segments intercristallins a été rompu.

Zusammenfassung

Die Kinetik von Kettenabbau wurde in der heterogenen Hydrolyse von ägyptischer Baumwolle unter leicht sauren Bedingungen untersucht. Die Resultate wurden im Hinblick auf die Abschätzung der Zugänglichkeit ausgelegt, ohne die Fehler, die mit früheren Messungen verbunden waren. Es wurde gefunden, dass die Menge an erreichbarem Material in der unabgebauten Baumwolle 10,8% ist, aber während der Hydrolyse wird dies auf weniger als 5% vermindert. Die Rekristallisation tritt bei einer frühen Stufe des Abbaus auf und beginnt, wenn ungefähr ein Achtel der interkristallinen Kettensegmente abgebrochen ist.

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