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Kinetic Study on the Alkaline Degradation of Cotton Hydrocellulose

DONALD W. HAAS, BJORN F. HRUTFIORD, and K. V. SARKANEN,
Department of Chemical Engineering, University of Washington, Seattle, Washington 98105

Synopsis

The kinetics of alkaline degradation of cotton hydrocellulose were determined in 5% NaOH at various temperatures. An activation energy of 24 kcal./mole was found for the endwise degradation reaction, while that of termination to a stable *m*-saccharinic acid endunit is 32 kcal./mole. Consequently, the DP_n of the degradable chain length is highly dependent on the reaction temperature, being 1000 at 65°C. and 140 at 132°C. At lower temperatures, the majority of degrading chains terminate to a normal reducing endgroup at the crystalline–amorphous transition region. From the data, the $\overline{DP}_n$ of cellulose chain segments participating in the amorphous regions of the original cotton fibril was calculated to be 143. This result strongly supports the classical micellar fibril structure over the folded model proposed by Manley.

INTRODUCTION

The mechanism of alkaline degradation of cellulose is now reasonably well understood.[1,2] The cellulose molecule is attacked at its reducing endgroup by the alkali as shown in Figure 1. When this happens a chain-propagation reaction results in which glucose units are progressively eliminated from the molecule. Chain termination results when the reducing endgroup is converted to a *m*-saccharinic acid group while it is still attached to the cellulose molecule, resulting in an alkali-stable structure.

The only kinetic analysis available for the alkaline degradation of cellulose has been provided by Samuelson and co-workers,[3,4] who studied the alkaline hydrolysis of cellulose at 170°C. A mathematical expression was derived for the ratio between the rates of the propagation and termination reactions which occur during the alkaline degradation, and a value of 65 was obtained for this ratio.[4] Machell and Richards[5] and Colbran and Davidson[6] have made the important observation that when hydrocellulose was degraded in sodium hydroxide at 100°C., only a part of the degrading chains terminated to *m*-saccharinic acid end units, while in others, the propagation reaction appeared to come to a standstill when the degrading chain end reached the inaccessible regions of the cellulose fiber. On the other hand, when high concentrations of strontium hydroxide were used as the basic reagent, the weight loss was substantially smaller than with sodium hydrox-

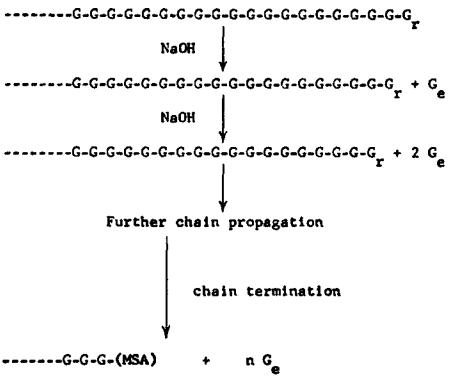

Fig. 1. Degradation mechanism of polysaccharides by NaOH as illustrated for cellulose. G = anhydroglucose unit; G_r = reducing endgroup; G_e = glucose unit eliminated by conversion to isosaccharinic acid and other degradation products; MSA = *m*-saccharinic acid endgroup.

ide and the carboxyl content was much higher. Calcium and barium hydroxides had a similar effect. It was concluded that alkaline earth hydroxides catalytically accelerate the conversion of reducing endgroups to *m*-saccharinic acid units.

EXPERIMENTAL

Preparation of Hydrocellulose

Purified cellulose was prepared from a bleached grade of cotton by the standard method described by Whistler.[7a] The cellulose was then converted to two preparations of hydrocellulose by hydrolysis in 1*N* sulfuric acid. The first preparation, referred to as hydrocellulose I, was heated at 90°C. for 3 hr. with 1*N* sulfuric acid at a liquor/cellulose ratio of 50:1. The second preparation (hydrocellulose II) was carried out under the same conditions except that the temperature of hydrolysis was 75°C. After the heating period the hydrocellulose was washed until free of acid and then allowed to become air dry at room temperature. Moisture determinations were made by heating samples at 105°C. to a constant weight. All calculations were based on moisture-free cellulose.

Alkaline Degradations

The alkaline degradations were carried out in sealed glass tubes made from 15-mm. glass tubing or in 20-ml. autoclaves when temperatures higher than 100°C. were used. When larger samples were required for the carboxyl determinations the degradation was carried out in a 200-ml. boiling flask which was stoppered and clamped shut. Water was boiled prior to preparation of all solutions to remove dissolved carbon dioxide and oxygen. A solution of 10% sodium hydroxide was prepared and standardized with 0.1*N* acid. Samples of the hydrocellulose (0.1 g.) were weighed in the

tubes and the required amounts of 10% sodium hydroxide solution and water were added to give a 5% sodium hydroxide solution and a liquid/cellulose ratio of 100:1. The air was displaced with nitrogen and the tube was sealed. The tube was shaken thoroughly and immersed in a constant temperature bath for the required length of time. A resin flask fitted with reflux condenser and filled with constant-boiling liquids was used as the constant temperature bath. The five temperatures used were the boiling points of methanol, 95% ethanol, trichloroethylene, water, and chlorobenzene. After being removed from the bath, the tubes were cooled rapidly in cold water and opened. After acidification the sample was filtered on a coarse sintered glass crucible which had been previously tared. The sample was washed with water and then dried at 105°C. and the weight loss determined. Samples (1 g.) for carboxyl determinations were converted to acid-free form as described by Whistler.[7b] The sample was dried at room temperature under vacuum and conditioned in the atmosphere for 1 day. A moisture determination was made and the weight loss calculated.

Carboxyl Determinations

Carboxyl determinations were made by using methylene blue absorption according to TAPPI standard method T237 Su63, originally developed by Davidson.[8,9] A Beckman DK-2 spectrophotometer was used to measure the methylene blue concentration.

Reducing Endgroup Determinations

Reducing endgroup determinations were made by carrying out a degradation of the hydrocellulose in 1*M* strontium hydroxide solution at 100°C. for 10 hr. The carboxyl content and the weight loss were measured. Since essentially all of the reducing endgroups are converted to *m*-saccharinic acid under these conditions, the reducing endgroup content of the original hydrocellulose can be calculated from the increase in carboxyl content as it relates to the original weight of the sample.

THEORY

To illustrate the cellulose degradation, a classical model of a cotton fibril in its original form is pictured in Figure 2*A*. When the cellulose is hydrolyzed by acid to hydrocellulose it is attacked randomly but only in the amorphous region. It is assumed that only one scission takes place for each amorphous section of molecule. All of the amorphous chains are not the same length and all are not necessarily fissioned in the hydrolysis. The newly formed reducing endgroups are randomly located at different distances from the crystalline–amorphous transition region. Accordingly, the length distribution of amorphous segments terminating to those reducing endgroups that were formed in the acidic hydrolysis may be expected to be essentially gaussian.

When the hydrocellulose is subjected to alkaline degradation, the propagation reaction proceeds and glucose units are peeled off by the alkali.

Eventually *m*-saccharinic acid groups are formed by the termination reaction. However, all of the reducing endgroups are not converted into *m*-saccharinic acid groups due to the inability of the alkali to penetrate the crystalline regions of the cellulose.

Accepting this mechanism, there are three probabilities for the conversion of each reducing endgroup which can be defined as follows: P_e = probability that the reducing endgroup will be eliminated from the cellulose chain; P_{msa} = probability that the reducing endgroup will be converted to *m*-saccharinic acid and remain attached to the cellulose chain; P_{cr} = probability that the reducing endgroup will become inaccessible to the alkali. The sum of these probabilities must equal to unity. If they are

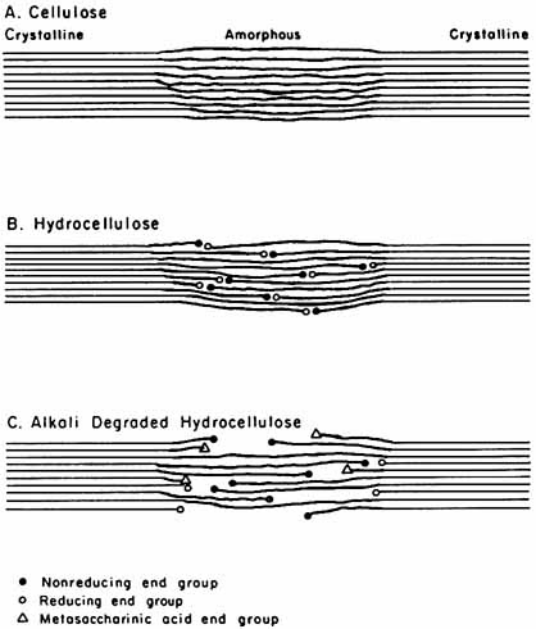

Fig. 2. Schematic representation of cellulose degradation.

considered to be constants then the ratio P_e/P_{msa} must be the same as the ratio of the rate constants of the corresponding reactions. Because of the random distribution of the distance of the reducing endgroups from the crystalline region of the cellulose, the termination process occurring at the crystalline–amorphous transition region may be assumed to proceed at a rate analogous to a first-order chemical reaction. Although no chemical reaction is involved, a formal rate constant k_{cr} may be assigned to this termination process. In practice some error will be introduced by this assumption since the degradation is not abruptly stopped. There is probably a gradual transition from amorphous to crystalline region rather than a distinct interface and these transition regions could be more accessible at some conditions than at others.

With the additional condition that the liquor to cellulose ratio is large enough so that the sodium hydroxide concentration remains practically constant throughout the reaction, three differential equations can be written:

Degradative chain propagation:

$$d[G_e]/dt = k_1[G_r] = dL/dt \tag{1}$$

Chain termination:

$$d[MSA]/dt = k_2[G_r] \tag{2}$$

$$d[G_t]/dt = k_{cr}[G_r] \tag{3}$$

where the terms are defined as: $[G_e]$ = mole fraction of glucose units eliminated by the propagation reaction which equals the weight fraction of alkali loss L; $[G_r]$ = mole fraction of reducing endgroups that are available for reaction; [MSA] = mole fraction of *m*-saccharinic acid formed by the termination reaction; $[G_t]$ = mole fraction of reducing endgroups which are not available for reaction; k_1,k_2,k_{cr} = rate constants of propagation, of termination by conversion to *m*-saccharinic acid and of termination caused by inaccessibility, respectively. $[G_r]$ remains unaffected by the propagation reaction so we can also write

$$-\frac{d[G_r]}{dt} = k_2[G_r] + k_{cr}[G_r] = k_t[G_r] \tag{4}$$

where k_t is the total rate constant for the chain termination. At

$$t = 0,\ [G_r] = [G_r]_0$$

where $[G_r]_0$ is the initial reducing endgroup content.

Equation (4) is integrated to give

$$[G_r] = [G_r]_0 e^{-k_t t} \tag{5}$$

On substituting eq. (5) into eq. (1) we have

$$dL/dt = d[G_e]/dt = k_1[G_r]_0 e^{-k_t t}$$

At $t = 0$, $L = 0$, this equation is integrated to give

$$L = (k_1/k_t)[G_r]_0(1 - e^{-k_t t})$$

Hence,

$$\ln \{1 - (k_t L/k_1[G_r]_0)\} = -k_t t \tag{6}$$

and at infinite time

$$L_\infty = (k_1/k_t)[G_r]_0 \tag{7}$$

On substituting L_∞ into eq. (6) we have:

$$k_t t = \ln [L_\infty/(L_\infty - L)] \tag{8}$$

which can be used to obtain k_t and then k_1 by inserting the value of k_t into eq. (7).

Substituting eq. (5) into eq. (2) yields:

$$d[\mathrm{MSA}]/dt = k_2[\mathrm{G_r}]_0 e^{-k_t t}$$

At $t = 0$, MSA = 0 so this equation is integrated to give:

$$[\mathrm{MSA}] = (k_1/k_t)[\mathrm{G_r}]_0(1 - e^{-k_t t})$$

After infinite time

$$[\mathrm{MSA}]_\infty = (k_2/k_t)[\mathrm{G_r}]_0 \tag{9}$$

from which k_2 can be calculated. Finally,

$$k_{cr} = k_t - k_2 \tag{10}$$

To obtain the rate constants for the propagation and termination reaction, k_1 and k_2, the values of $[\mathrm{MSA}]_\infty$ and $[\mathrm{G_r}]_0$ must be known in addition to the weight loss as a function of time.

As in other chain reactions, the ratio k_1/k_t equals the average length of degradable chain in glucose units. For cellulose in solution, the termination is due to *m*-saccharinic acid formation only, and the ratio k_1/k_2 would give the length of degradable chain $\bar{x}_n$. For hydrocellulose k_1/k_{cr} gives the average distance $\bar{x}_d$ of reducing endgroups from the crystalline region in glucose units. Since the breakdown of amorphous chain occurs at random in the hydrocellulose formation, $\bar{x}_d$ is one-half of the total amorphous chain length in the original cellulose:

$$\bar{x}_{\text{amorphous}} = 2\bar{x}_d \tag{11}$$

RESULTS AND DISCUSSION

Determination of k_t

The alkali solubility in 5% sodium hydroxide as a function of time was determined for two different hydrocelluloses. These results are shown in Table I. By use of eq. (8) the values of k_t can be determined at various temperatures. This is done by plotting $L_\infty/(L_\infty - L)$ versus time. It was found that a better fit of the data was obtained if a lower value was used for L_∞ than was obtained by extrapolation. This is attributed to the fact that the degradation is not abruptly stopped when the crystalline region is reached but rather greatly retarded. This degradation into the crystalline region would have a very small effect at the beginning of the reaction when most of the data were taken. The effect would be much more noticeable in the later stages of the reaction, hence a too high value would be obtained for the maximum solubility. The actual values used are shown in Table II. These were determined by trial and error to obtain the best fit with straight lines as shown in Figures 3 and 4. The value used for the maximum solubility has little effect on the location of the first two or

three points on the kinetic plots and the approximation procedure is therefore considered adequate. As would be expected, the rate plots for the two different hydrocelluloses both fall on the same line. At 132°C. it was found

TABLE I
Kinetic Data for Hydrocellulose Degradation

Temperature, °C.	Time, hr.	Loss, %	
		Hydrocellulose I	Hydrocellulose II
65	4	12.0	3.8
	9		6.3
	12	20.5	9.0
	18		9.5
	24	30.7	11.1
	37	34.6	13.4
	48	37.4	14.1
	80	41.6	16.9
	130		18.7
	165	43.4	19.8
78	0.75	10.1	4.3
	2	18.3	9.0
	3		9.5
	4	27.4	11.8
	6	34.7	13.2
	9	37.2	17.5
	12	38.4	16.7
	18		19.0
	30	44.2	21.7
87	0.25	9.2	4.0
	0.75	18.1	7.6
	1		8.1
	1.5	27.8	10.6
	2		11.6
	2.25	33.0	13.6
	3	36.2	14.9
	4.5	39.8	14.2
	6		18.9
	12	44.3	18.0
100	1/12	8.0	2.7
	0.25	18.8	7.2
	0.5	28.3	11.0
	0.75		11.9
	1	36.7	15.4
	1.5	40.2	15.5
	2	41.2	18.0
	3	42.8	18.8
132	1/30	8.2	3.9
	1/15	27.0	12.2
	1/10	35.9	14.8
	2/15		16.6
	1/6	40.9	19.1
	0.25	43.3	20.4
	0.5	45.9	19.7
	1.0	45.2	22.6

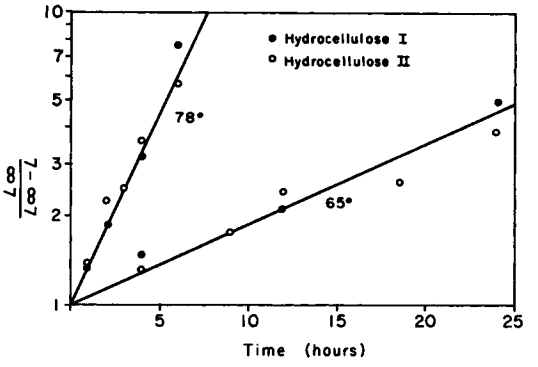

Fig. 3. Rate plot for determination of k_t at 65 and 78°C.

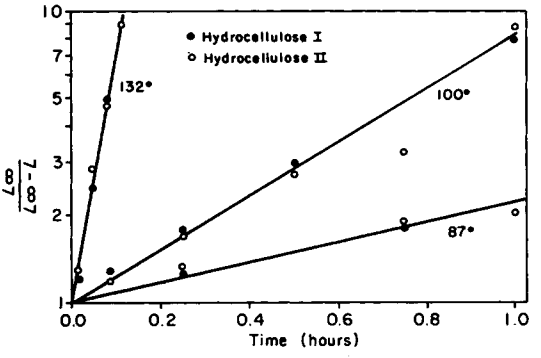

Fig. 4. Rate plot for determination of k_t at 87, 100, and 132°C.

necessary to select the zero time at a point at which the autoclaves had reached this temperature.

TABLE II
Maximum Solubilities Used in Determination of k_t

Temperature, °C.	Solubility, %	
	Hydrocellulose I	Hydrocellulose II
65	38.8	15.0
78	40.0	16.2
87	40.8	16.7
100	42.1	17.4
132	45.0	18.7

Determination of $[MSA]_\infty$

The value of $[MSA]_\infty$ is conveniently measured from the increase in the carboxyl content of the hydrocellulose after it has been degraded for an extended period of time in sodium hydroxide. These data are shown in Table III.

TABLE III
Carboxyl Contents of Degraded Hydrocelluloses

Degradation liquor	Temperature, °C.	Time of degradation, hr.	Weight loss L, %	Carboxyl content, meq./100 g.	$[MSA]_\infty$ mole fraction $\times 10^3$
Hydrocellulose I[a]					
1M $Sr(OH)_2$	100	10	9.8	4.72	6.25[b]
5% NaOH	78	30	44.3	2.04	1.20
5% NaOH	100	4	45.0	2.44	1.54
5% NaOH	132	0.5	46.6	2.91	1.88
15% NaOH	100	2	59.6	2.53	—
Hydrocellulose II[c]					
1M $Sr(OH)_2$	100	10	3.8	2.49	2.98[b]
5% NaOH	65	165	19.6	0.84	0.20
5% NaOH	78	30	17.9	0.90	0.31
5% NaOH	87	12	18.7	0.97	0.39
5% NaOH	100	4	20.8	1.25	0.71
5% NaOH	132	0.5	23.2	1.41	1.04
15% NaOH	100	2	28.7	1.25	—
0.25M Na_2CO_3	132	20	22.3	1.69	1.41

[a] Initial carboxyl = 0.39 meq./100 g.
[b] Assumed to be equal to $[G_r]_0$
[c] Initial carboxyl = 0.55 meq./100 g.

Determination of $[G_r]_0$

Obtaining the value of $[G_r]_0$ is not as straightforward, since there is not a reliable standard method by which the reducing endgroup content can be accurately measured. After some experimentation, it was found that copper number values were not reliable enough for the determination. An alternative method for determining $[G_r]_0$ was developed based on the results of Colbran and Davidson.[6] They found that practically all the degrading chains terminate to *m*-saccharinic acid units when the degradation is carried out in concentrated strontium hydroxide solution. Consequently, the new carboxyl groups generated in prolonged treatment of hydrocellulose by strontium hydroxide provide a measure for the original reducing endgroup content. The value measured in this way is probably slightly low. Values of $[G_r]_0$ have been calculated by using the carboxyl values given in Table III. The mole fraction $[G_r]_0$ is 6.25×10^{-3} for hydrocellulose I and 2.98×10^{-3} for hydrocellulose II. These reducing endgroup measurements correspond to degrees of polymerization of 160 and 336 for hydrocelluloses I and II, respectively. These values are in a reasonable range for acid-hydrolyzed celluloses as determined by viscometric methods.

Calculation of Rate Constants

With the values of $[G_r]_0$ and $[MSA]_\infty$ which can be obtained from the carboxyl contents. the rate constants can be calculated by using k_t values

obtained from rate plots in Figures 2 and 3 and by applying eqs. (7), (9), and 10. The values of k_1, k_2, k_t, and k_{cr} are shown in Table IV. Since the k_2 values determined at 132°C. are probably low, a sample was degraded in $0.25M$ sodium carbonate and the ratio k_1/k_2 was obtained from these data. This can be done since the ratios of rate constants can be expected to be unaffected by the hydroxyl ion concentration, although the constants themselves are subject to substantial variation.

TABLE IV
Calculated Values of Rate Constants

Temperature, °C.	k_t	Hydrocellulose I			Hydrocellulose II		
		k_1	k_2	k_{cr}	k_1	k_2	k_{cr}
65	0.061				4.0	0.0041	0.057
78	0.294	20.8	0.056	0.238	17.8	0.031	0.263
87	0.74				46.3	0.097	0.64
100	2.1	151	0.518	1.58	147	0.50	1.60
132	20	1490	6.02	14.0	1550	6.98	13.0
132[a]					1500	9.86	10.1

[a] Rate constants calculated using k_1/k_2 values determined in $0.25M$ sodium carbonate.

Activation Energy Relationships

Arrhenius plots for the propagation and termination reactions are shown in Figures 5 and 6. The activation energy of the propagation reaction is

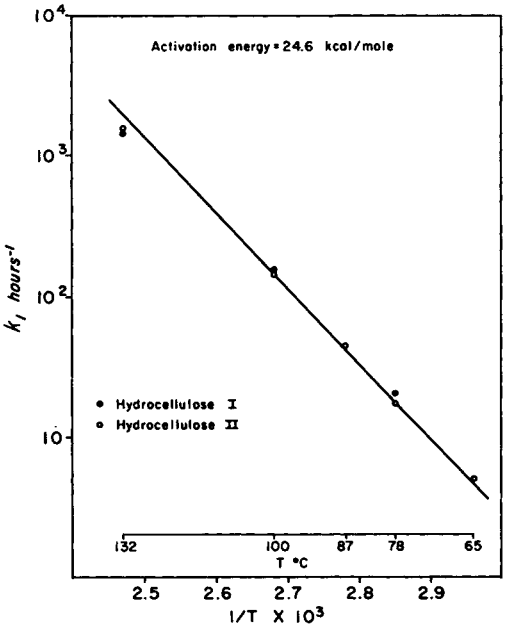

Fig. 5. Arrhenius plot for propagation reaction.

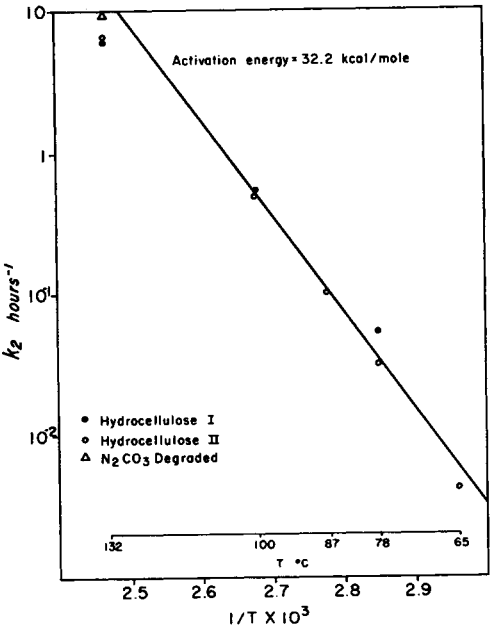

Fig. 6. Arrhenius plot for termination reaction.

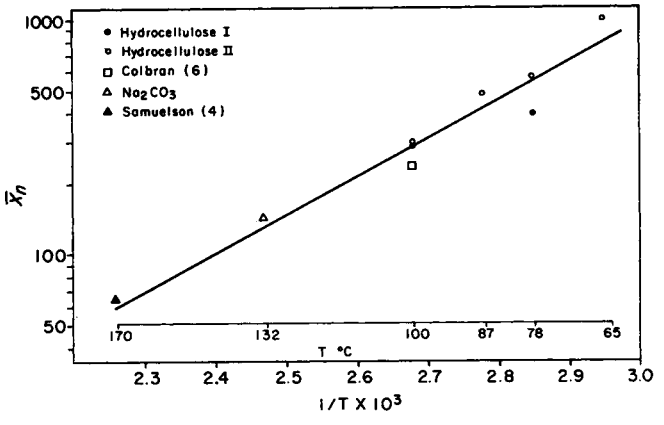

Fig. 7. Arrhenius plot for degradative chain length.

24.6 kcal./mole. The termination reaction has an activation energy of 32.2 kcal./mole. As pointed out earlier, k_1/k_2 equals the average degradable chain length $\bar{x}_n$. An Arrhenius plot for $\bar{x}_n$ is shown in Figure 7 and illustrates that the degradable chain length of dissolved cellulose is highly temperature dependent varying from 60 to 1000 in a 100°C. temperature range. An activation energy of −7.8 kcal./mole is obtained which is the difference between the activation energies of the propagation and termination reactions. A point which was calculated from the data of Colbran and Davidson[6] is included in the figure. The plot has also been extrap-

olated to 170°C. to check agreement with Samuelson's value for $\bar{x}_n$ at that temperature. In both cases good agreement is obtained.

Length of Amorphous Regions

The ratio k_1/k_{cr} is the length of one-half the intercrystalline segment in glucose units [eq. (11)]. The values of $\bar{x}_d$ are shown in Table V. The results show that the accessibility of the cellulose increases with temperature. The lowest value of 140 glucose units for the amorphous chain length is obtained at 65°C. under the swelling action of 5% sodium hydroxide. According to the hypothesis advanced by Manley[10] there is not

TABLE V
Average Length of Degradable Amorphous Chain $\bar{x}_d$

	$\bar{x}_d$	
Temperature, °C.	Hydrocellulose I	Hydrocellulose II
65		70
78	88	75
87		72
100	95	92
132	106	119
132[a]		150

[a] Rate constant ratios determined in 0.25*M* sodium carbonate.

a separate amorphous phase in the cellulose fibrils. Rather, a continuous cellulose chain is folded to segments roughly 10 glucose units or less in length. The amorphous region would have to be located at or near sharp bends in the cellulose chains and would be contained as a part of the crystalline structure itself. For the present results to conform with the Manley hypothesis requires, however, an additional assumption of irregularities in the folded structure allowing approximately seven folds to disentangle in the alkaline degradation. On the other hand, the data obtained here will fit into the fringe micellar theory of cellulose structure without any additional assumptions.

Alkaline Degradation with Additives

Some experiments of preliminary nature were carried out to determine the stabilizing action of certain additives. The results of this are shown in Figure 8. It may be noted that the stabilizing effect of hydroxylamine is better than that of sodium borohydride at 100°C. However, when the temperature of degradation was increased, most of the stabilizing effect was lost due to the decomposition of hydroxylamine at higher temperature. The stabilizing action of hydroxylamine is considerably reduced by conversion of acetone oxime. These observations are in good agreement with recent results by Clayton and Marracini.[11] Jayme[12] has made observations indicating that dithionites may exert stabilizing action. The

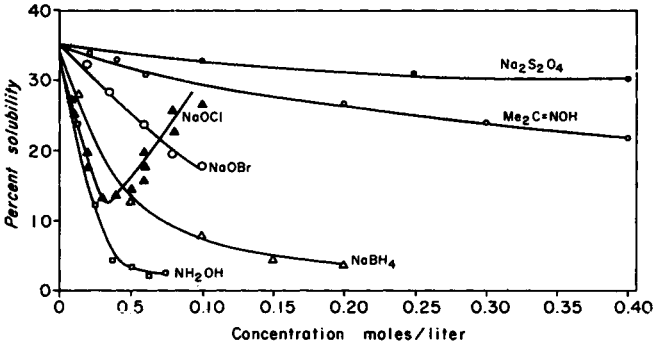

Fig. 8. Effect of additives on hot alkali solubility at 100°C.

effect of dithionite was found to be very small, however, probably because it decomposes rapidly in solution and large amounts are required for any significant stabilization. When complexing agents were added in attempts to stabilize the dithionite, only slight improvements were recorded. Hypohalites can achieve some stabilization, but the oxidation reaction is nonspecific and competing reactions occur. At higher concentrations the oxidation continues, forming new carbonyl groups which cause the cellulose to again become alkali-degradable.

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Résumé

On a étudié la cinétique de dégradation alcaline de l'hydrocellulose de coton dans la soude caustique à 5% à différentes températures. On a déterminé une énergie d'activation de 24 kcal/mole pour la réaction de dégradation terminale tandis qu'on a mesuré une énergie d'activation de 32 kcal/mole pour la réaction de terminaison via un groupement d'acide *m*-saccharinique stable. Par conséquent, le degré de polymérisation ($\overline{DP}_n$) de la chaîne dégradable dépend fortement de la température de réaction, celui-ci est égal à 1000 à 65°C et à 140 à 132°C. Aux températures plus basses, la majorité des chaînes en dégradation se terminent par un groupement réduit normal situé dans la zone de transition entre la phase cristalline et la phase amorphe. A partir de ces données, on a calculé que le degré de polymérisation ($\overline{DP}_n$) des segments de chaînes de cellulose intégrés dans les régions amorphes de la fibre de coton

initiale, doit être égal à 140. Ces résultats confirment plutôt une structure classique en forme de fibrile micellaire qu'une structure repliée telle ye le propose Manley.

Zusammenfassung

Die Kinetik des alkalischen Abbaus von Baumwollhydrocellulose wurde in 5% NaOH bei mehreren Temperaturen untersucht. Für den Abbau vom Kettenende wurde eine Aktivierungsenergie von 24 Kcal/Mol gefunden, während diejenige der Stabilisierung zu einer meta-Saccharinsäureendgruppe 32 Kcal/Mol beträgt. Folglich ist der DP_n der abbaufäigen Kettenlänge stark von der Reaktionstemperatur abhängig, er beträgt 1000 bei 65°C und 140 bei 132°C. Bei niedrigeren Temperaturen stabilisiert sich die Mehrzahl der abspaltenden Ketten zu einer normalen reduzierenden Endgruppe im kirtallin–amorph Ubergangsbereich. Aus den Daten wurde der $\overline{DP}_n$ der an den amorphen Bereichen der ursprünglichen Baumwollfibrille beteiligten Cellulosekettensegmente zu 140 berechnet. Dieses Ergebnis bildet eine starke Stütze für die klassische micellare Fibrillenstruktur gegen dem von Manley vorgeschlagenen Faltungsmodell.

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