

## Kinetics of Heterogeneous Cellulose Reactions. II. Reaction with Propionyl Chloride

PRONOY K. CHATTERJEE\* and CARL M. CONRAD, *Plant Fibers  
Pioneering Research Laboratory, Southern Utilization Research and  
Development Division, Agriculture Research Service,  
U. S. Department of Agriculture, New Orleans, Louisiana 70119*

### Synopsis

A heterogeneous cellulose reaction was studied by reacting cotton fiber in pyridine medium with propionyl chloride at different initial molar concentrations and at different temperatures. It has been observed that the kinetics of reaction does not follow Sakurada's diffusion equation closely, and the deviation is more noticeable at lower initial concentrations of the reagent and at lower temperatures. A non-uniform reaction rate is also evident from the time-substitution curve. The rate of substitution changes twice during the reaction, the latter change being associated with the loss of cellulose I crystal structure. In an attempt to treat the data according to simple chemical kinetics, the order has been found to decrease continuously from the beginning, suggesting thereby an autocatalytic type of behavior. However, at the final stages of the reaction, when the cellulose I structure was completely lost, the reaction behaved as a pseudo first-order type. The x-ray diffractograms of the reacted samples indicate that cellulose I crystallinity decreases from the beginning of the reaction and that a new crystalline lattice develops gradually. The formation of this new crystal lattice is hindered in the cellulose crystalline region due to the lack of freedom of the chains. The diffusion equation has been modified by substituting a crystallinity index for the rate of diffusion of solvent in a solvent-gel system and thus extending Sakurada's equation. A new mechanism has been proposed considering the simultaneous reactions in the amorphous and crystalline regions. This mechanism can explain the deviation of Sakurada's equation. The kinetics expressions are derived, based on the proposed mechanism. The kinetics of decrystallization of cellulose I is also presented. A satisfactory theoretical explanation is given for the fact that the fall of reaction rate occurs at the conclusion of decrystallization of the cellulose I structure.

### INTRODUCTION

Many controversial theories of the cellulose heterogeneous reactions have been put forward in the past.<sup>1</sup> Some of these have been briefly discussed in our previous communication.<sup>2</sup> However, none of the theories could explain the difference in the kinetic behavior of the reactions under different conditions and environment. Because of faulty understanding of the morphology of the cellulose in the fiber, no sound mechanism could be developed, and consequently very little attempt has been made heretofore at a mathematical treatment of the reactivity. Sakurada<sup>3</sup> in 1934 pro-

\* Postdoctoral Resident Research Associate, 1963-65.

posed a general mechanism for all types of heterogeneous reactions. Experimentally, his equations were found to be valid in certain conditions<sup>4,5</sup> over a major portion of the reaction but not necessarily the same at all conditions.<sup>1,6-8</sup> Conrad, Harbrink, and Murphy<sup>4</sup> noticed that Sakurada's plot of the data gives two intersecting straight lines and that the point of intersection is associated with the complete decrystallization of the cellulose I structure. Later the present authors investigated the phenomenon more thoroughly by studying the cyanoethylation of fibers<sup>2</sup> and discussed the limitations of Sakurada's equation. However, the cyanoethylation reaction has certain limitations due, largely, to side reactions.<sup>9</sup> In order to avoid such difficulties, various other cellulose reactions were explored. But most of the reaction products at higher degrees of substitution either dissolved in the reaction media or gave highly colored products,<sup>10</sup> indicating side reactions. In many cases it was difficult to reach any substantial substitution of the hydroxyl groups.

During preliminary investigation, the reaction of cellulose with propionyl chloride appeared to be very promising. It was noticed that nearly complete substitution can be rapidly achieved, the ester content can be readily determined, and no noticeable side reactions interfered with the main reaction. Therefore, this reaction was studied. Based on these findings and those reported in the literature, a new mechanism has been proposed, and the kinetic equations are derived. The limitation of Sakurada's equation and the relation between the rate of reaction and crystallinity has been deduced and also experimentally verified.

## EXPERIMENTAL

### Sample

Commercial pharmaceutical absorbent cotton, containing highly purified fibers, was used in the present study. Viscosity measurements indicated a DP of 1925. It was cut to pass through a 20-mesh sieve of a Wiley mill.

### Reaction Technique

Pyridine in 30-ml. portions was taken in each test tube which was fitted with a condenser. The required amount of propionyl chloride to make a definite reactant ratio was added dropwise into the pyridine, which was heated to the reaction temperature prior to the addition of the chloride. A yellow precipitate formed on addition of each drop and then immediately dissolved to give a brown colored solution. The test tube was shaken well to make a homogeneous solution, and then 1 g. of the fibers was added. During the latter stages of reaction with propionyl chloride (DS about 2.8) a minute portion of the fibers seemed to dissolve, or to be dispersed into the media. After the required time of reaction, the whole mixture of the reactants and products was mixed with acetone (containing about 5% water to hydrolyze the excess propionyl chloride present) and shaken well in order to

disperse the fibers in the media. Then the fibers, together with any dissolved or dispersed part, were recovered by addition of a large amount of a mixture of methanol-water (1:1), a good antiswelling reagent for the propionates. The product was filtered, washed, and dried. Under these conditions a uniform degree of substitution throughout the sample was obtained. The degree of substitution was determined with 0.25*N* alcoholic sodium hydroxide solution by the method of Genung and Mallatt.<sup>11</sup>

### X-Ray Diffractograms

The fibers were cut to pass a 20-mesh screen, pressed into a thin plate at 25,000 psi, and irradiated with an x-ray beam from a Philips Electronics, Inc. high-precision diffractometer, using a copper target, a pulse height discriminator, and a potentiometer recorder. The technique was that previously described by Conrad and others.<sup>12</sup> Crystallinity indices were computed for loss of crystallinity by plotting  $R = I_{22.6}/I_{19.0}$  and for gain of new crystal lattices by plotting  $R' = I_{7.4}/I_{11.4}$ , where  $I$  is the diffraction intensity and numerical subscripts are the angles at  $2\theta$ .

## RESULTS AND DISCUSSION

### Chemical Substitution and Rate

The extent of reaction of propionyl chloride with cellulose in pyridine at 75°C. was found to be influenced by the concentration of the reagent, the theoretical amount of the reaction product not being realized. A substitution of  $DS = 3$  could be attained only at initial concentrations of the reagent of two or more times the concentration of the cellulose hydroxyl groups. However, at a very high concentration the reaction was impeded by the by-products, resulting in a yellow color of the fibers. Therefore, the reactions were studied with the maximum concentration of the reagent at only twice the concentration of the hydroxyl groups.

The rate of reaction of the fibers under varying conditions is shown by Figure 1. Curves 1, 3, and 4 represent the reaction with different molar concentrations of propionyl chloride at constant temperature (75°C.). Curve 2 represents the dried fibers at the same molar concentrations as curve 3. Therefore, curve 2 can be compared with curve 3 where all the reaction conditions except the moisture contents of the samples were the same. Curves 1A and 1B represent the results of the reaction at 70°C. and 61°C., respectively, with the original fibers at the same molar concentration as in curve 1. In the subsequent figures also the experimental conditions are characterized by the same curve numbers. Further, curve 3 (Fig. 1) representing two sets of measurements, shows thereby, the good reproducibility of the results. From these curves it is evident that the reaction rate is not uniform, and though moisture retards the rate, it does not change the essential shape of the curve. During the reaction, particularly at lower reagent concentrations and at lower temperatures (61°C.),

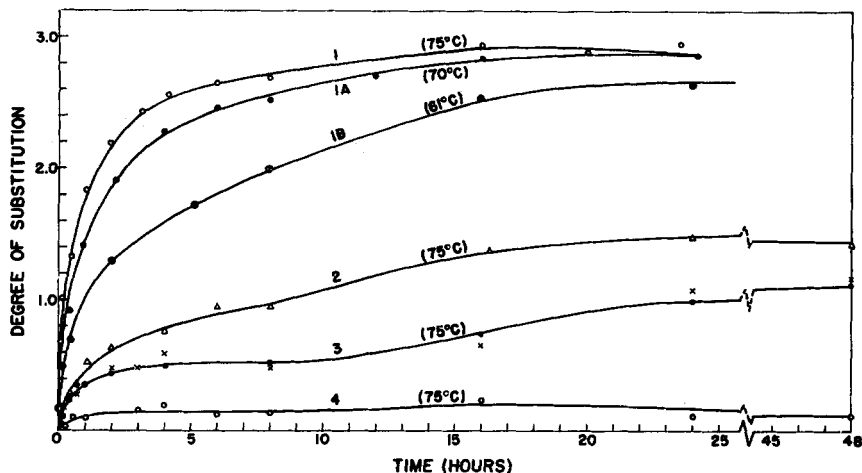


Fig. 1. Effect of concentration of reagent, temperature, and the presence of moisture on the rate of propionylation of cellulose fibers: (1) 2 moles of propionyl chloride per mole of cellulose hydroxyls at 75°C.; (2) dried, 1 mole of propionyl chloride per mole of cellulose hydroxyls at 75°C.; (3) 1 mole of propionyl chloride per mole of cellulose hydroxyls at 75°C.; (4) 2/3 mole of propionyl chloride per mole of cellulose hydroxyls at 75°C.; (1A) 2 moles of propionyl chloride per mole of cellulose hydroxyls at 70°C.; (1B) 2 moles of propionyl chloride per mole of cellulose hydroxyls at 61°C.

initially a rapid increase of the degree of substitution (DS) is observed, followed by a nearly constant DS and then a further slow increase of rate which finally reaches a saturation value. The second rise of rate after a constant DS value apparently indicates an autocatalytic type of behavior.<sup>13</sup> At 61°C. the two phases of the reaction overlap somewhat, and the region of constant DS value is not well pronounced. The effect is less evident at the higher concentration of the reagent and at higher temperatures of the reaction.

On further lowering of the temperature (below 61°C.), as the reaction advances, brown colored crystals form in the reaction mixture and impart a yellow color to the ester. This color could not be removed by washing. Above 75°C. the reaction could not be performed, since the boiling point of propionyl chloride is 80°C., and too much reagent would evaporate during the initial addition of propionyl chloride to the hot pyridine.

The plot of the data in Figure 2 according to Sakurada's equation<sup>3</sup> ( $DS = kt^m$ , where  $t$  is time and  $m$  and  $k$  are constants) shows noticeable deviations of the curves from linearity at the lower reagent concentrations. At higher concentrations (2 moles of propionyl chloride per mole of cellulose hydroxyls, curves 1, 1A, and 1B), the deviations are somewhat minimized, but not completely removed. Above a substitution of  $DS = 1.35$ , the plots could be roughly fitted to two straight lines, intersecting at  $DS = 2.5$ . Therefore, it is evident that Sakurada's equation is not closely obeyed by the present reaction. However, the change of rate at  $DS = 2.5$  could be observed if the data are fitted to two straight lines (curve 1) as found in

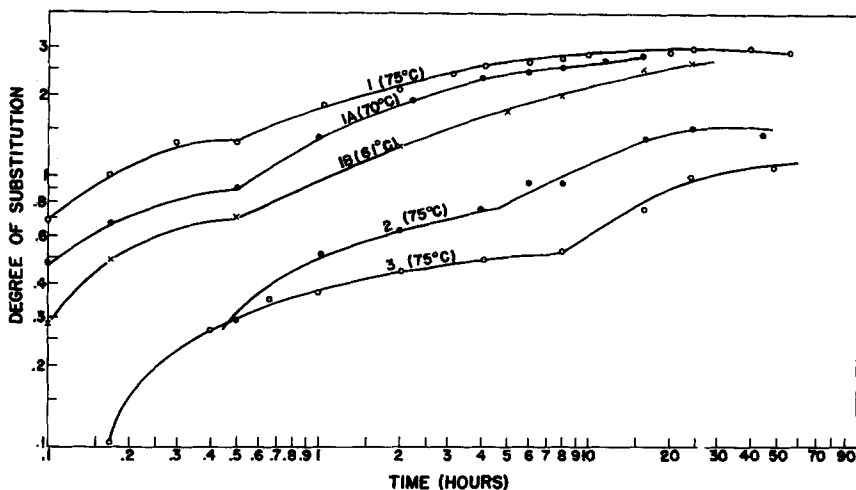


Fig. 2. Sakurada plot of the data of Fig. 1.

the case of cyanoethylation.<sup>2</sup> As discussed later in this paper, the crystallinity of cellulose I is completely lost at this value of substitution. From the deviation at the early stage of the reaction it may be concluded that at least two simultaneous reactions take place during the esterification. When the first reaction approaches completion, the second type starts; alternatively, the second reaction may proceed concurrently with the first, and when the first reaction is complete then only the second reaction continues. If the former is the true situation, then also a sufficient amount of overlapping of two reactions would be expected. A similar type of change at the initial stage of the reaction has been noticed during cyanoethylation<sup>2</sup> and assumed to be due to superimposition of the reaction of the amorphous region on the crystalline region. Evidently the same assumptions can be made in the present case. This is further supported by the x-ray study, discussed below.

An attempt was also made to treat the data according to a first-order reaction system, as was done by Frith,<sup>3</sup> with acid-catalyzed acetylation. But a first-order plot did not show linearity in this case.

In order to see whether the kinetic data could be fitted to any chemical order at all, the change of the rate of reaction during the kinetic process was determined by measuring the tangents at successive points on the curves in Figure 1. The fraction of the unreacted cellulose hydroxyl groups was also noted at the corresponding points. Now if the reaction follows a single chemical order, then the rate can be expressed as

$$dx/dt = -kx^n$$

where  $x$  is the concentration of unreacted hydroxyl groups. Hence, if  $\log(dx/dt)$  is plotted against  $\log x$ , it should give a straight line<sup>13</sup> whose slope is the order of the reaction with respect to cellulose. Such plots at lower

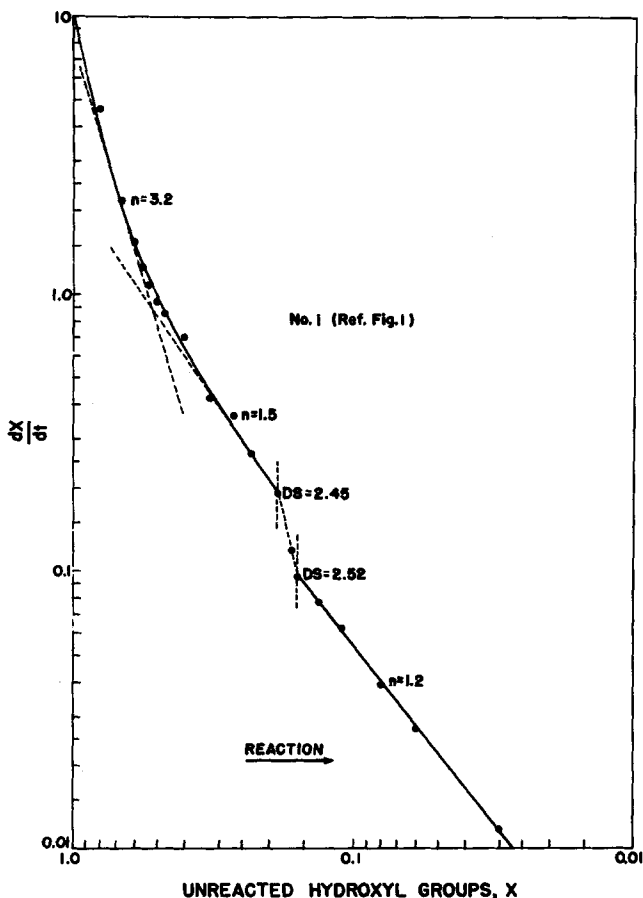


Fig. 3. Relation of  $\log dx/dt$  to  $\log x$ ; ( $x$  = per cent unreacted hydroxyl groups) 2 moles of propionyl chloride per mole of cellulose hydroxyls at  $75^{\circ}\text{C}$ .

concentration of reagent gave complex curves which could not be used for determining the general order of reaction. At higher concentrations of the reagent (Cell—OH: propionyl chloride = 1:2) (curve 1, Fig. 1), the treatment seemed to be somewhat more successful (Fig. 3) than at the lower.

A curvature is evident to about 18% hydroxyl (DS = 2.45), thereby indicating a complex chemical rate curve. The deviation from linearity is due possibly to two consecutive phenomena: (1) diffusion, and (2) chemical reaction. From x-ray diffraction, which is discussed below and also in connection with the cyanoethylation mechanism,<sup>2</sup> it has been concluded that the diffusion velocity of the reagent (present in excess) and solvent effectively come to an equilibrium condition due to the attainment of swelling equilibrium when the crystallinity of the original cellulose is completely lost; during the present reaction this is the case at about 17% hydroxyl (DS = 2.5). A pure chemical reaction was, therefore, expected at about 17% hydroxyl. The plot in Figure 3 shows a break of the curve

between 18 and 16% (DS = 2.45 and 2.52), followed by a straight line having a slope of 1.2, and indicating a homogeneous chemical reaction of the pseudo first-order type. Hence, it could be concluded that a partial diffusion-controlled reaction is followed by a pseudo first-order chemical reaction after the loss of the original crystalline structure. The curvature of the plot up to DS = 2.45 is concave toward the abscissa, which indicates that the order of reaction,  $n$ , decreases continuously as the reaction progresses. If further approximate analysis is made with this portion of the plot by drawing tangents at both ends, then it can be observed that the initial slope of 3.2 decreases to 1.5 during the latter stage. Thus, during the first part of the reaction the overall reaction order changes from 3.2 to 1.5. The third-order initial reaction is obviously higher than could be expected theoretically. Interference of some other factors could, therefore, be assumed under these circumstances which must affect the actual sub-

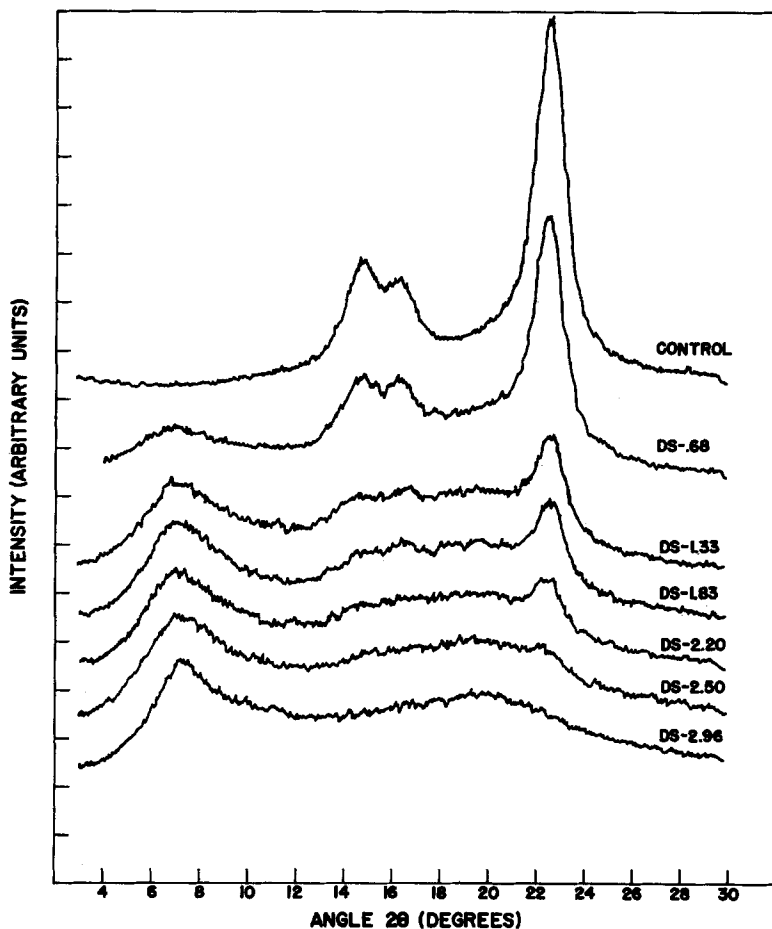


Fig. 4. Diffractograms of cellulose propionate prepared with 2 moles of propionyl chloride per mole of cellulose hydroxyls at 75°C.

stitution reaction. But such a "change" in order, initially, from a higher (3.2) to a lower one (1.6), is an indication of the acceleration of the rate of reaction.

### X-Ray Diffractograms

Figure 4 shows the diffractograms of the samples of cellulose propionate, prepared with 2 moles of propionyl chloride per mole of cellulose hydroxyls and reacted at 75°C. to complete substitution. During the reaction the original crystallinity of the cellulose fiber decreased, and a new crystalline modification gradually developed. Conrad et al.<sup>4</sup> observed a similar change of crystal structure in cellulose acetate.

The decrease of cellulose I crystallinity during substitution was determined by plotting the ratio of intensities of diffraction from the cellulose 002 lattice at  $2\theta = 22.6^\circ$  to that at  $2\theta = 19^\circ$  against degree of substitution. The growth of new crystallinity in the sample was determined in a similar way by plotting the ratio of intensities of diffraction at  $2\theta = 7.4^\circ$  to that at  $2\theta = 11.4^\circ$ . Diffractograms (not shown) were also obtained with the samples prepared with one mole of propionyl chloride per mole of cellulose hydroxyls and the same intensity ratios calculated. Since a partial substitution occurred in this case, only a partial decrease of the cellulose I crystallinity was found. From the results of both series it is evident that as the original crystallinity of the cellulose decreases with degree of substitution, the new crystalline lattice increases. However, in either case the ratios follow an exponential relationship with degree of substitution and thus give straight lines on plotting the logarithmic values against the degree of substitution, as shown in Figure 5. It was thought, based on one of the possibilities assumed earlier, that the amorphous portion of the fibers reacts first and that the reaction would approach completion before the crystalline portion would show noticeable reaction but the figure reveals that the crystalline portion also begins to react from the initial stage of the reaction. This observation is at variance with the conclusions of Warwicker and Spedding,<sup>14</sup> who studied the acetylation of cellulose II. However, their plot of x-ray equatorial scans for acetylated sheet cellulose (Fig. 5 of ref. 14) shows a noticeable decrease of peak height even at a very low degree of substitution (DS = 0.42). Of course, they did not present any plot of the decrease of cellulose I crystallinity against the degree of substitution.

The new crystalline lattice increases with the degree of substitution (Fig. 5) up to about the lower transition point of the rate of substitution (see Fig. 2), that is, about DS = 0.8, and then becomes essentially constant. Thus, new crystallinity is formed principally during the reaction of the amorphous regions. It is believed that the randomized chains in the amorphous regions are able to orient themselves during the reaction to form a new crystalline lattice. But such reorientation of the molecules in the cellulose ordered regions is restricted due to lack of freedom of rotation of the chains. Therefore, the reaction of cellulose crystalline regions does not contribute to the development of the particular new crystalline lattice.



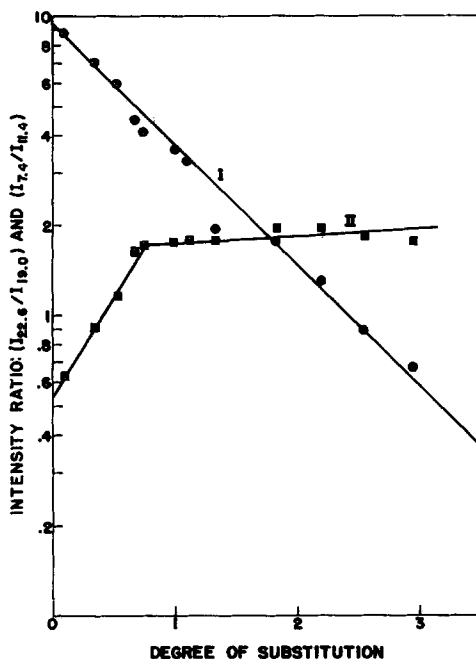


Fig. 5. Logarithmic plot of the decrease of original crystallinity and the formation of new crystalline lattice with the degree of substitution: (I) decrease of cellulose I ( $\otimes$ ) during partial substitution and ( $\bullet$ ) during the complete substitution; (II) increase of cellulose ester ( $\boxtimes$ ) during partial substitution and ( $\blacksquare$ ) during complete substitution.

### Application of a Diffusion Equation to the Decrease of Cellulose Crystallinity

The equation of ordinary diffusion of solvent into a gel,

$$dL/dt = k(1/L) \quad (1)$$

where  $L$  is the length of capillary,  $t$  is time, and  $k$  is a constant, could be applied for determining the rate of diffusion.<sup>15</sup> If we assume that the whole fiber is composed of intermolecular chains interpenetrated by fine capillaries and these capillary cross-sections, of the dimension of intermolecular space are strongly hydrogen-bonded in the crystalline region and less so in the amorphous region, then the eq. (1) could be applied to the present case with certain modifications, as

$$dL/dt = k(1/L^n) \quad (2)$$

where  $n$  is dependent upon the nature of the hydrogen bond.<sup>2</sup> Now Sakurada<sup>3</sup> supposed that  $L$  could be taken as the amount of substitution at any time  $t$ . It has been discussed earlier<sup>2</sup> that this assumption may be true only under certain specific conditions. In the present case it has been seen that Sakurada's equation is not applicable within the range of temperature here studied.

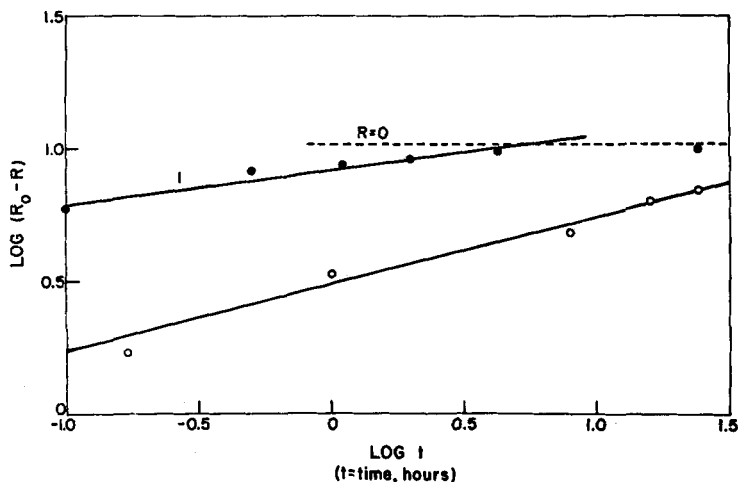


Fig. 6. Logarithmic relation of the decrease of crystallinity index to time of reaction (●) during complete esterification (○) during partial esterification.

According to Miles<sup>16</sup> and Mathieu,<sup>17</sup> as the reaction at the surface of the crystalline region takes place, the chains are first dilated and thus the reaction penetrates into the crystalline region. Therefore, it is to be expected that in the diffusion equation if the amount of loss of the crystallinity of the cellulose I structure is substituted for  $L$  in the diffusion equation then the resulting equation could be applied to all types of reaction. This would be true provided the original crystallinity of the cellulose is not affected by any additional factors such as catalysts or solvent media or any intermediate reaction product. Accordingly, the degree of substitution in Sakurada's equation ( $DS = kt^m$ ) was replaced by the amount of decrease of the cellulose I crystallinity index<sup>18</sup> and the equation was thus transformed as:

$$R_0 - R = kt^m \quad (3)$$

where  $R$  is the intensity ratio ( $I_{22.6}/I_{19.0}$ ) of the sample and  $R_0$  is the same intensity ratio of the control. The logarithmic form of eq. (3) is plotted in Figure 6. The plot shows fairly good straight lines with the data from both concentration series. Possibly, the scattering of a few points may be due to the experimental error inherent in the determination of the crystallinity index. Otherwise, the equation appears to fit fairly well in the present reaction.

### Mechanism and Kinetics of the Heterogeneous Reaction

Cellulose in the wall of the cotton fiber exists in at least two phases, a crystalline and a noncrystalline one. The crystalline phase is inaccessible to most liquids, whereas the noncrystalline, or amorphous phase is generally accessible by a diffusion process. Chemical reactions taking place in the

amorphous regions proceed by two independent rates: the rate of diffusion and the rate of chemical reaction. The slower of the two rates becomes the rate-governing or pace-setting rate.

The chemical reagent cannot diffuse into the crystalline region. It must first react at the chain ends or on the surface of the crystallites. This results in the opening or unzipping of some of the hydrogen-bonded chains of cellulose, thus producing some amorphous cellulose. The reagent then diffuses into this newly produced amorphous portion reacting with the cellulose and simultaneously generating more amorphous cellulose. The phenomenon is therefore extremely complex, and the kinetics cannot be treated either as a simple chemical process or as a simple diffusion process. Both processes are concurrently occurring and they are dependent on each other.

The following discussion, concerning the kinetics of reaction, reveals the extent to which a chemical substitution within the cotton fiber may be modified by the diffusion process in the amorphous and crystalline regions.

In dealing with the kinetics, the fact that the decrystallization occurs from the very beginning of the reaction has been taken into consideration.

If the initial amount of cellulose hydroxyl groups in the crystalline regions is  $C$  and in the amorphous regions is  $A$ , then the total amount of hydroxyl groups,  $S$ , in the fiber is

$$S = A + C \quad (4)$$

The reaction scheme comprises two simultaneous parallel reactions (path I and II) which may be represented by the scheme in Figure 7, where  $A_1$  and  $C_1$  represent the hydroxyl groups which are exposed to the reagent by the diffusion of the reagent into the amorphous and to the sites of the crystal-

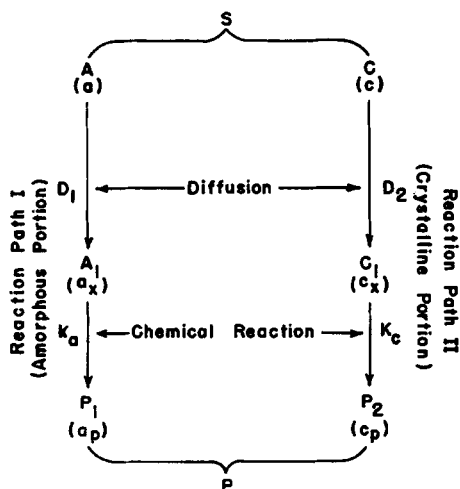


Fig. 7. Combined diffusion-reaction scheme.

line portions of the fiber, respectively.\*  $D_1$  and  $D_2$  represent the rate constants of the diffusion processes and  $k_a$  and  $k_c$  those of the chemical reaction. Since the chemical reaction involves the interaction between the hydroxyl groups and the reagent in both cases under similar conditions  $k_a = k_c$ . Hence  $k$  may be substituted for both  $k_a$  and  $k_c$ .

Let  $c$  be the amount of  $C$  present at any time  $t$ ;  $c_x$ , the amount of  $C_1$  approached by diffusion at time  $t$  and rate constant  $D_2$ ;  $c_p$ , the amount of product  $P_2$  formed at any time  $t$  at rate constant  $k_c$ . Also, let  $a$  be the amount of  $A$  present at any time  $t$ ;  $a_x$  the amount of  $A_1$  approached by diffusion at time  $t$  and rate constant  $D_1$ ; and  $a_p$  the amount of  $P_1$  formed at time  $t$  at reaction rate constant  $k_a$ , where  $P_1$  and  $P_2$  are the substituted groups in the original amorphous and crystalline portions, respectively, and  $P_1$  and  $P_2$  their respective amounts, and where

$$P = P_1 + P_2 \quad (5)$$

and also

$$s = a + c \quad (6)$$

where  $s$  is the total amount of unsubstituted groups in the fiber at any time  $t$ .

**Case I.** In both paths I and II, the rate of diffusion is greater than the rate of chemical reaction. The rate of substitution in the amorphous portion will follow the simple law: the slower process governs the rate.

Therefore,

$$da_p/dt = k_a a = ka \quad (7)$$

The reaction in the crystalline portion is somewhat complex, however, as discussed above.

Considering the substitution in the original crystalline region only,

$$dc_p/dt = k_c(c_x - c_p) = k(c_x - c_p) \quad (8)$$

where  $c_x = f(t)$ .

In order to solve this equation, we must determine  $c_x$  at any time  $t$ . Fick's general law of diffusion is inadequate in this case, since the reagent has no free diffusion path into the crystalline regions, due to the presence of intermolecular hydrogen bonding between the cellulose chains. We, therefore, assume that the reagent diffuses to the crystalline site through the amorphous portion which was created by the initial chemical interaction at the surface of the original crystallite of the fiber. Accordingly, we further assume that the diffusion of reagent proceeds according to the modified form of Ostwald's equation.<sup>15</sup> This was, however, the basic assumption for Sakurada's<sup>3</sup> and Bernoulli's<sup>6</sup> equations. Therefore,

\* The amorphous cellulose formed at the original crystalline region by the chemical interaction, as discussed above, and the surface of the crystallites from all directions, including the ends of the chains of the crystallites are all defined by the sites of the crystalline portions.

$$dL/dt = D_2(1/L^n) \quad (9)$$

where  $L$  is the diffusion path of the reagent and  $D_2$  and  $n$  are constants. The value  $n$  is dependent upon the hydrogen bond-breaking process.<sup>2</sup> Therefore,  $n$  is constant for a given sample and reagent.

Let it be assumed that the hydroxyl groups are randomly distributed along the diffusion path. On the average, if  $\alpha$  moles of hydroxyl groups are present in the unit length of the diffusion path, the rate at which these hydroxyl groups will be exposed to the reagent can be expressed as

$$dc_x/dt = D_2(\alpha^n/c_x^n) \quad (10)$$

By integration

$$c_x^{n+1} = (n+1)D_2t\alpha^n + \text{constant}$$

At  $t = 0$ ,  $c_x = 0$ ; therefore the constant = 0. Therefore,

$$c_x^{n+1} = (n+1)D_2t\alpha^n \quad (11)$$

or

$$c_x^m = k_1t \quad (12)$$

where

$$D_2(n+1)\alpha^n = k_1$$

and

$$(n+1) = m$$

Substituting eq. (12) in eq. (8) we get

$$dc_p/dt = k(k_1^{1/m}t^{1/m} - c_p) \quad (13)$$

or

$$dc_p/dt + kc_p = k_2t^{1/m} \quad (14)$$

where

$$k_2 = kk_1^{1/m}$$

Solving the differential equation, eq. (14), we obtain (see Appendix) the expression

$$c_p e^{k_2 t} = [k_2 \int t^{1/m} e^{k_2 t} dt] + k_3 \quad (15)$$

where  $k_3 = \text{constant}$ , or

$$c_p e^{k_2 t} = k_3 + k_2 [(t^{1/m} e^{k_2 t} / k) - (1/mk^2) t^{(1/m-1)} e^{k_2 t} + (1/mk^3) (1/m-1) t^{(1/m-2)} e^{k_2 t} - \dots + \{(-1)^{n+1} (1/mk^n) (1/m-1) (1/m-2) \dots (1/m-(n-2))\} t^{1/m-(n-1)} e^{k_2 t}] \quad (16)$$

Now, by dividing both sides of the eq. (17) by  $e^{kt}$  we get

$$c_p = k_2 t^{1/m} / k \{ [1 - 1/mk](1/t) + 1/mk^2(1/m - 1) (1/t^2) - \dots \} + k_3 e^{-kt} \quad (17)$$

If  $k$  is very small, eq. (17) cannot be solved by any simple method. But, when the value of  $k$  is in the neighborhood of 1 or greater than 1, the terms containing higher degrees of  $t$  can be neglected, since  $t$  and  $m$  both are greater than 1. In a chemical reaction,  $k$  increases with temperature. Therefore, eq. (17) can be approximately reduced to the form of eq. (18) above the temperature at which  $k \rightarrow 1$ .

$$c_p = k_2 t^{1/m} / k [1 - 1/mkt] + k_3 e^{-kt} \quad (18)$$

Substituting the values of  $k_2$  and  $m$  [eqs. (14) and (12)]

$$c_p = \{ D_2(n+1)\alpha^n \}^{1/(n+1)} \{ (1 - 1/[(n+1)kt]) \} t^{1/(n+1)} + k_3 e^{-kt} \quad (19)$$

By combining eq. (19) with the integrated form of eq. (7) for the amorphous regions the total reaction form can be represented, as

$$P = kat + \{ D_2(n+1)\alpha^n \}^{1/(n+1)} \{ 1 - 1/[(n+1)kt] \} t^{1/(n+1)} + k_3 e^{-kt} \quad (20)$$

After the complete reaction of path I, the substitution, however, proceeds according to eq. (19).

### Present Equation as Compared to Sakurada's Equation

Sakurada's<sup>3</sup> equations with the present terminology can be represented as

$$c_p = [D_2(n+1)]^{1/(n+1)} t^{1/(n+1)} \quad (21)$$

or

$$c_p = k_4 t^{m_c}$$

where  $k_4$  and  $m_c$  are constants.

This equation can be compared with eq. (19), since Sakurada did not take into consideration the differences between amorphous and crystalline portions of the cellulose fiber. If  $k$  is very large and if the magnitude of  $t$  is also large, then  $1/t$  and  $1/e^{kt}$  becomes small, and, therefore, the terms  $1/[(n+1)kt]$  and  $k_3 e^{-kt}$  may be neglected, and the relation between  $c_p$  and  $t$  in eq. (19) will take the form of eq. (21) since  $\alpha$  is also a constant. But at earlier stages of the reaction the magnitude of  $t$  is obviously small. Therefore, the deviation must occur at the early stages even if the  $k$  value is large. Therefore, it appears, that Sakurada's equation is an approximate form of eq. (19) and it has a very narrow field for its application. However, Sakurada's equation seems to fit the system, in a more general way, when the reactions fall under cases III or IV (see below).

**Case II.** This is a special form of Case I, where in path II the rate of diffusion is much greater than the rate of chemical reaction. All other conditions being the same, the rate-governing steps in both paths, in this case, would be the chemical reactions only.

Thus,

$$-da/dt = da_p/dt = k_a a \quad (22)$$

and

$$-dc/dt = dc_p/dt = k_c c \quad (23)$$

Therefore

$$ds/dt = -k(a + c) = -ks \quad (24)$$

since

$$k_a = k_c = k$$

and

$$(a + c) = s$$

The overall reaction will, therefore, behave as a chemical first-order type.

**Case III.** If the rate of diffusion is lower than the rate of chemical reaction in both paths I and II, then diffusion will be the rate-governing steps in both paths. Hence, the rate of substitution  $dc_p/dt$  would be equivalent to  $dc_x/dt$  [eq. (10)]. Therefore,  $c_p$  would be expressed as:

$$c_p = k_6 t^{m_c} \quad (25)$$

and similarly

$$a_p = k_6 t^{m_a} \quad (26)$$

For total substitution,

$$P = k_6 t^{m_a} + k_6 t^{m_c} \quad (27)$$

where,  $k_6$ ,  $m_a$ ,  $k_5$ , and  $m_c$  are Sakurada's constants, relative to amorphous and crystalline portions, respectively. Equation (27) is similar to that suggested by Bernoulli et al.<sup>6</sup> as a modification of Sakurada's equation.<sup>3</sup> As soon as the reaction in path I is completed, the substitution will proceed according to Sakurada's equation.

**Case IV.** The rate of diffusion is greater than the rate of chemical reaction in path I, but the rate of diffusion is lower than the rate of chemical reaction in path II.

Hence,

$$a_p = kat \quad (28)$$

and

$$c_p = k_5 t^{m_c} \quad (29)$$

For total substitution

$$P = kat + k_5 t^{m_c} \quad (30)$$

Therefore, the deviation from Sakurada's equation should occur as long as the cellulose hydroxyl groups in the original amorphous portion continues reacting.

Again, as soon as the original amorphous portion is all reacted, the reaction will proceed according to Sakurada's equation.

Since most of the reagent diffuses very fast into the amorphous regions, presumably, case III is a very rare case. On the other hand, case IV seems to occur more frequently than case III. Cases III and IV differ only in the relative rates of diffusion and chemical reaction in path I.

### Apparent Autocatalytic Nature of the Reaction Curve

Earlier it was pointed out that the shape of the propionylation reaction curve suggests an autocatalytic type of reaction. Autocatalysis in a general sense may be defined as the acceleration of the reaction rate during the progress of the reaction without any additive. The mathematical expression for autocatalysis is:  $d^2c_p/dt^2 = +\text{quantity}$ . Now if the reaction system falls under case I, then by differentiating eq. (8) with respect to  $dt$  we get

$$d^2c_p/dt^2 = k(dc_x/dt - dc_p/dt) \quad (31)$$

where  $dc_p/dt$  indicates the rate of chemical substitution and  $dc_x/dt$  the rate at which hydroxyl groups are exposed to the reagent.

Therefore  $dc_x/dt$  is the rate of diffusion of the reagent to the crystalline region.

According to case I  $dc_x/dt > dc_p/dt$ ; hence  $d^2c_p/dt^2 = +\text{quantity}$ . Therefore, it appears that the apparent autocatalytic nature of the curve is evident as long as the diffusion process under case I is active. In a recent publication of Manjumath and Nanjundayya<sup>19</sup> on benzylation, if DS is plotted versus  $t$ , the curve shows a continuous rise, indicating thereby a behavior similar to that of propionylation.

### Abrupt Fall of Reaction Rate and a First-Order Kinetic Process After the Loss of Cellulose Crystallinity

When the reagent has completely diffused through the system (the crystalline portion has disappeared), no more hydroxyl groups will be left to be exposed and, therefore,  $dc_x/dt = 0$ . Under the above circumstances, according to case I, eq. (31) gives  $d^2c_p/dt^2 = -\text{quantity}$ , which indicates that the rate will fall during the reaction. Again if  $dc_x/dt = 0$ , then  $c_x = a$  constant, say,  $c_e$ .

Substituting this value in eq. (8) we get

$$dc_p/dt = k(c_e - c_p) \quad (32)$$

Equation (32) represents a first-order type of reaction. The experimental data (Fig. 3) with propionylation is in conformity with the above deviation.

The abrupt fall of the reaction rate curves under case III may be explained as follows:



The logarithm of total substitution is given by eq. (27) as a first approximation as

$$\log P = \log k_s + \log k_b + (m_a + m_c) \log t \quad (33)$$

Therefore, in Sakurada's plot of  $\log P$  versus  $\log t$ , the initial slope would be  $(m_a + m_c)$ , since both amorphous and crystalline phases begin to react simultaneously. If the decrystallization proportionality factor,  $g$  [eq. (34), see below] is greater than 1 or, in other words, if the decrystallization precedes the diffusion by some factor then, eventually, the crystalline phase will be exhausted but the diffusion and chemical reaction in the amorphous phase will continue. At this stage, obviously, the slope of the plot would be  $m_a$  and thus it would indicate a decrease of the reaction rate.

In a similar way, the decrease of rate when the reaction comes under case IV may be explained. On the other hand, it may be predicted that no such decrease would be observed in the case of reactions which come under case II.

It is believed that the above phenomenon occurs during the acetylation and cyanoethylation reactions, and explains the change in slope of the Sakurada curves.

### Loss of Cellulose Crystallinity and Its Kinetics

Since the diffusion of the reagent into the crystalline portion results in the loss of cellulose I crystallinity, the decrease of crystallinity in all the cases may be directly proportional to the diffusion. Hence,

$$dL/dt = -gdC_r/dt \quad (34)$$

where  $g$  is the proportionality factor and  $C_r$  is the crystallinity of the fiber at time,  $t$ . Hence, as in eq. (9), we have

$$gdC_r/dt = -D_2(1/C_r^n) \quad (35)$$

Therefore,

$$C_r = -[(D_2/g)(n + 1)]^{1/(n+1)}t^{1/(n+1)} + K \quad (36)$$

When  $t = 0$ ,  $C_r = (C_r)_0$  = original crystallinity of the fiber; therefore  $k = (C_r)_0$

$$(C_r)_0 - C_r = k_7t^m \quad (37)$$

where

$$k_7 = [(D_2/g)(n + 1)]^{1/(n+1)}$$

and

$$1/(n + 1) = m$$

Figure 6 shows the logarithmic plot of eq. (37), where  $R$  and  $R_0$  stand for  $C_r$  and  $(C_r)_0$ , respectively.

## DISCUSSION

The mathematical derivation is based on the assumption that the actual chemical reaction is a pseudo first-order type, the rate being dependent upon the concentration of the free cellulose hydroxyl groups only. This suggests that the kinetic equations, as derived in the present paper, are applicable to the experimental data if the reaction is carried out with large excesses of the reagent. Hence, the experimental condition under which we studied the cyanoethylation of cellulose fiber<sup>2</sup> seems to be an ideal condition for the present requirement. The only problem confronting us in the case of cyanoethylation was the catalyst (NaOH solution) which was only sparingly miscible to the reagent. In the case of propionylation, although no such limitation exists, reaction with a very high concentration of the reagent is not permissible due to the increasing amount of byproducts. However, in the latter case, the results obtained with the permissible highest concentration of the reagent (2 moles to 1 mole of cellulose hydroxyl groups in the initial mixture) has been mostly discussed in the light of the present theory. Because of the fact that in the crystalline regions (which is the major component of the fiber) the free hydroxyl groups are not all exposed at one time, therefore, the concentration of the reagent is always in excess relative to the exposed hydroxyl groups. It is evident that the results obtained from the propionylation reaction correlate well with our postulation on the kinetics of reaction. The mechanism of the reaction and its kinetics, which have been proposed in this paper, are aimed not only at explaining the propionylation reaction but also to cover all types of heterogeneous cellulose reactions which lead to addition or substitution products.

Reese and Eyring<sup>20</sup> and Katz et al.<sup>21</sup> studied the diffusion of chemical reagents into wool and proposed mechanism for the kinetics of the reaction. Their mechanism is not applicable to cellulose fibers, however, for the following reasons.

(1) They derived equations, based on the theory of uniform diffusion through a single-phase structure. In cellulose the reagent diffuses through a two-phase structure, the diffusion in one phase being dependent upon a prechemical reaction.

(2) Since they considered free diffusion of the reagent into the fiber they could apply the Fick's law of diffusion in their treatment. In the case of cellulose, free diffusion is not applicable to the crystalline portion. Consequently, the assumptions and mathematical procedure employed by them are not applicable to the present problem.

The mechanism proposed here is applicable to both one- and two-phase structures. It may be pointed out, however, that the kinetic derivation is not applicable to a bimolecular type of reaction, and as it stands at present it does not take into account the specific reactivity of different hydroxyl groups. Before further modification of the equation to widen its applicability considerable research would be needed about the diffusion phenomenon in such complex systems.

It may be observed that although our approach is entirely different under certain conditions our kinetic equation can be reduced to the form of Sakurada's equation. It may, therefore, be inferred that Sakurada's equation has a more limited applicability than ours.

One of the more important results of our investigation is that it should help to regroup the various types of cellulose heterogeneous reactions under different classes, as illustrated in this paper. This should help to clarify the contradictory results which occur in the literature.

## APPENDIX

### Solution of Equation (14)

$$dc_p/dt + kc_p = kt^{1/m} \quad (14)$$

Multiplying each side by  $e^{kt}$  yields

$$e^{kt}dc_p/dt + kc_pe^{kt} = k_2t^{1/m}e^{kt} \quad (14a)$$

Since

$$e^{kt} = (1/k)(de^{kt}/dt)$$

eq. (14a) can be written as

$$e^{kt}dc_p/dt + c_p(de^{kt}/dt) = k_2t^{1/m}e^{kt} \quad (14b)$$

The left-hand side is now a perfect differential. Therefore,

$$d(c_pe^{kt})/dt = k_2t^{1/m}e^{kt} \quad (14c)$$

Integrating both sides yields

$$c_pe^{kt} = k_3 + k_2 \int t^{1/m}e^{kt}dt \quad (15)$$

where  $k_3$  is a constant.

The mention of manufacturers or trade names is not to be considered as an endorsement by the U. S. Department of Agriculture over equivalent products of other companies.

## References

1. T. Timell, *Studies on Cellulose Reactions*, Stockholm, 1950, pp. 68-91.
2. P. K. Chatterjee and C. M. Conrad, *J. Polymer Sci. A-1*, **4**, 459 (1966).
3. I. Sakurada, *Cellulose Chem.*, **15**, 3 (1934).
4. C. M. Conrad, P. Harbrink, and A. L. Murphy, *Textile Res. J.*, **33**, 784 (1963).
5. I. Kido and H. Kitojima, *J. Soc. Textile Cellulose Ind. Japan*, **8**, 228 (1952).
6. A. L. Bernoulli, M. Schenk, and F. Rohner, *Helv. Chim. Acta*, **17**, 897 (1934).
7. K. Asada, *J. Soc. Textile Cellulose Ind. Japan*, **8**, 134 (1952).
8. W. C. Frith, *Tappi*, **46**, 739 (1963).
9. P. K. Chatterjee and C. M. Conrad, *J. Polymer Sci. A-1*, **4**, 233 (1966).
10. P. K. Chatterjee and D. J. Stanonis, *J. Polymer Sci. A-1*, **4**, 434 (1966).
11. L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).
12. C. M. Conrad, D. J. Stanonis, P. Harbrink, and J. J. Creely, *Textile Res. J.*, **30**, 339 (1960).

13. K. J. Laidler, *Chemical Kinetics*, McGraw-Hill, New York, 1950, p. 15.
14. J. O. Warwicker and H. Spedding, *J. Appl. Polymer Sci.*, **9**, 1913 (1965).
15. W. Ostwald, *Kolloid-Z. Suppl. II*, **20**, (1908).
16. F. D. Miles, *Trans. Faraday Soc.*, **29**, 7, 110 (1933).
17. M. Mathieu, *Compt. Rend.*, **198**, 1434; *ibid.*, **199**, 55 (1934); *ibid.*, **200**, 143 (1935).
18. L. Segal, J. J. Creely, A. E. Martin, Jr., and C. M. Conrad, *Textile Res. J.*, **29**, 786 (1959).
19. B. R. Manjunath and C. Nanjundayya, *Textile Res. J.*, **35**, 1020 (1965).
20. C. E. Reese and H. Eyring, *Textile Res. J.*, **20**, 743 (1950).
21. S. M. Katz, E. T. Kubu, and J. H. Wakelin, *Textile Res. J.*, **20**, 754 (1950).

### Résumé

Une réaction hétérogène sur la cellulose a été étudiée en faisant réagir la fibre de coton en milieu pyridinique avec le chlorure de propionyle à concentrations molaires initiales différentes et à différentes températures. On a observé que les cinétiques de la réaction ne suivent pas l'équation de Sakurada et que la déviation à cette équation est plus notable à des concentrations initiales du réactif basses et à des températures également plus basses. Les courbes temps-substitution indiquent également une vitesse de réaction non-uniforme. La vitesse de substitution change deux fois en cours de réaction, le dernier changement étant associé avec la perte de la structure cristalline de la cellulose I. Dans un essai de traitement des résultats conformément à la cinétique chimique ordinaire, l'ordre de la réaction diminue continuellement depuis le début suggérant ainsi un type autocatalytique de comportement. Toutefois, aux époques finales de la réaction, lorsque la structure de la cellulose I a complètement disparu, la réaction se comporte suivant un type pseudo premier ordre. Les diffractogrammes aux rayons-X d'échantillons qui ont réagi indiquent que la cristallinité de la cellulose I décroît depuis le début de la réaction et qu'un nouveau réseau cristallin se développera graduellement. La formation de ce nouveau réseau cristallin est empêchée dans la région cristalline de la cellulose par suite du manque de degré de liberté des chaînes. L'équation de diffusion a été modifiée en substituant l'indice de cristallinité à la vitesse de diffusion du solvant dans le système solvant-gel et ainsi en généralisant l'équation de Sakurada. Un nouveau mécanisme a été proposé qui considère les réactions simultanées dans les régions amorphes et cristallines. Ce mécanisme peut expliquer les déviations au départ de l'équation de Sakurada. Les expressions cinétiques sont déduites basées sur les mécanismes proposés. La cinétique de décristallisation de la cellulose I est également présentée. Une explication théorique satisfaisante est donnée pour le fait que la diminution de la vitesse de réaction se passe à la fin de la décristallisation de la structure de la cellulose I.

### Zusammenfassung

Die heterogene Reaktion von Cellulose bei der Einwirkung von Propionylchlorid auf Baumwollfasern in Pyridin wurde bei verschiedenen Ausgangskonzentrationen und bei verschiedenen Temperaturen untersucht. Die Kinetik der Reaktion befolgt die Diffusionsgleichung von Sakurada nicht streng und die Abweichung ist grösser bei niedrigerer Ausgangskonzentration des Reagens und bei niedrigerer Temperatur. Eine uneinheitliche Reaktionsgeschwindigkeit ergibt sich auch aus der Kurve für die Zeitabhängigkeit der Substitution. Die Substitutionsgeschwindigkeit ändert sich während der Reaktion zweimal, wobei die zweite Änderung mit dem Verlust der Cellulose-I-Kristallstruktur verknüpft ist. Bei einer einfachen kinetischen Behandlung der Daten ergibt sich vom Beginn an eine kontinuierliche Abnahme der Ordnung, was für ein autocatalytisches Verhalten spricht. Im Endstadium der Reaktion jedoch, sobald die Cellulose-I-Struktur völlig verschwunden ist, besteht eine pseudo-erste Ordnung. Die Röntgendiagramme der umgesetzten Proben zeigen, dass die Cellulose-I-Kristallinität vom Beginn der Reaktion an abnimmt und dass sich allmählich ein neues Kristallgitter entwickelt. Die

Bildung dieses neuen Kristallgitters wird im kristallinen Cellulosebereich durch die mangelnde Freiheit der Ketten behindert. Die Diffusionsgleichung wurde durch Substitution eines Kristallinitätsindex für die Diffusionsgeschwindigkeit des Lösungsmittels in einem Lösungsmittel-Gelsystem unter Erweiterung der Sakurada-Gleichung modifiziert. Ein neuer Mechanismus mit Berücksichtigung der gleichzeitigen Reaktion in den amorphen und kristallinen Bereichen wurde vorgeschlagen. Dieser Mechanismus kann die Abweichung von der Sakurada-Gleichung erklären; auf seiner Grundlage werden die kinetischen Ausdrücke abgeleitet. Die Dekristallisationskinetik von Cellulose-I wird ebenfalls entwickelt. Für den Abfall der Reaktionsgeschwindigkeit beim Abschluss der Dekristallisation der Cellulose-I-Struktur wird eine befriedigende theoretische Erklärung gegeben.

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