

deviations are within the error of the temperature determinations.

Harteck's results are included in Fig. 4 and are in satisfactory agreement with the present results. Harteck obtains an average value for ΔE_0° of $81,807 \pm 300$, which is a little higher than our value of $80,709 \pm 600$. This latter value is in agreement with the one value ($\Delta E_0^\circ = 81,529$) obtained by Fischer and Grieger. It should be pointed out that Harteck's results were obtained from the rate of effusion of saturated vapor through an aperture of known size so that the accommodation coefficient is not involved. The two values of ΔE_0° obtained by Jones, Langmuir and Mackay give an average of $82,966$ cal. per gram atom, which is considerably higher than the values of three investigations which are in agreement. The other values of ΔE_0° in Table III are uniformly low and probably result from uncertainties in the emissivity corrections for copper.

It should be noted that a systematic trend occurs in the present values of ΔE_0° for copper. The values for solid copper lead to a mean ΔE_0° of $81,244$ cal. per gram atom while the values at the

melting point and above give a mean ΔE_0° of $79,853$ cal. per gram atom. This trend indicates a systematic error in the results which we are unable to explain and makes impossible an accurate calculation of the small heat of fusion of copper. In the present case a value of $81,240$ cal. per gram probably represents the "best" value for ΔE_0° , which is also the value Kelley¹² derives from Harteck's results.

Conclusion

The rates of evaporation of iron and copper have been used to determine the vapor pressures of iron and copper. The accommodation coefficient for these two metals appears to be unity, which apparently establishes the validity of the Langmuir method. Direct determinations of the emissivities of iron and copper have been made in conjunction with the vapor pressure study. The values of ΔE_0° for iron and copper are $96,033$ and $81,240$ cal. per gram atom, respectively. These values are shown to be in agreement with previous reliable determinations.

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RECEIVED APRIL 7, 1937

[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

The Mechanism of Cellulose Benzoylation

BY E. J. LORAND AND E. A. GEORGI

The more or less general acceptance of the primary valence chain theory of cellulose constitution has shifted interest to (1) the finer physical or morphological structure of cellulose fibers, and (2) problems of reaction kinetics. That both fields are inter-related is obvious. Any progress made in one will make possible important conclusions in the other. The importance of certain structural elements, such as growth rings, fibrils and especially the "skin system" (cuticle, primary cell wall, etc.), often has been emphasized,^{1,2} while the function of the recently described ellipsoid particles³ in the native fiber awaits interpretation. One of the most important questions related to the mechanism of cellulose reactions is the existence and size of submicroscopic structural units (micelles or crystallites). It has been

claimed that *all* cellulose reactions are of the so-called "micellar-heterogeneous" type.⁴ However, there is evidence^{5,6} to support the view that cellulose reactions do not follow a single pattern, and that the *type* varies, depending on the reaction partner, its concentration, the reaction medium, temperature, etc. It is quite probable that *all* the reaction models, worked out for microheterogeneous systems, such as surface reactions, topochemical macroheterogeneous reactions, permutoid or quasi-homogeneous reactions, as well as the previously mentioned micellar heterogeneous reactions, may apply to cellulose in one case or another, depending on circumstances.

These various reaction types are differentiated by the ratio of reaction velocity and internal dif-

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(1) K. Hess and B. Rabinowitsch, *Kolloid Z.*, **64**, 257-268 (1933).

(2) K. Hess and L. Akim, *Cellulosechem.*, **12**, 95-103 (1931).

(3) W. K. Farr and S. H. Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 189-203, 309-313 (1934).

fusion, *i. e.*, the speed of transport of the mobile reactant from the surface to the internal reaction zone. When this ratio is infinitely large, only surface reactions can take place. Large finite values (relatively slow diffusion) are characteristic of the topochemical-macroheterogeneous type, which permits the reaction to proceed only from layer to layer, while the speed of propagation depends on the rate of diffusion. Low values for the ratio (relatively high diffusion rates), are indicative of permutoid or quasi-homogeneous reactions, characterized by an equal attack on all cellulose chains involved. The concept of micellar heterogeneous reaction presupposes, besides the existence of small structural elements in the cellulose fiber, a relatively high rate of diffusion in the inter-micellar spaces and a relatively low diffusion rate through the surface of each micelle, so that complete conversion of the total internal surface may take place before the chains inside the micelles are attacked.

Unfortunately, the experimental methods which can be applied to the determination of the reaction type in a given case are rather limited. One of these methods is based on the analysis of time-conversion curves, obtained by taking samples at regular intervals, determining the chemical change (*e. g.*, the amount of substituent taken up), and plotting the results against the time. These curves do not satisfy simple kinetic formulas, although correlations are improved when allowance is made for the influence of diffusion.⁴ Attempts to apply W. Ostwald's diffusion formula (for gels) to cellulose reactions,⁷ however, have met with strong opposition.⁶ The drawback of the general method is that the conclusions are dependent on interpretation. Similar is the case with the application of X-ray analysis to this problem in spite of numerous attempts to follow reactions closely by taking diagrams at regular intervals. One gains the impression that even the combination of the two methods has not been sufficient to give a picture of the reaction mechanism free from unproved assumptions.⁶ The desirability of other experimental approaches is evident.

In the specific case of cellulose benzylation, we have chosen one of the most obvious approaches, that of microscopic observation. It is true that, in general, this direct method, even under high magnification, is too crude. However, in the present instance, because of conditions peculiar to

etherification and especially to benzylation of cellulose, we found that the microscope supplies direct indications on the progress and mechanism of the reaction.

Benzylation is a typical example of cellulose etherification, and has the advantage that it can be studied under atmospheric pressure, because of the high boiling point of benzyl chloride, used as the benzylating agent. The reaction is carried out in the presence of an alkali (sodium hydroxide), which is incorporated into cellulose as an aqueous solution.⁸⁻¹¹ To assure a uniform attack on all the cellulose fibers, it is best to prepare "alkali cellulose" in a way similar to that used in the production of viscose rayon, *i. e.*, by immersing cellulose in sodium hydroxide solution for a certain length of time, and then pressing out the excess lye. The cake is suitably shredded to increase the surface. Alkali cellulose, thus obtained, contains, in addition to sodium hydroxide, a large proportion of water, despite the dry appearance of the fibers. The presence of this water is not incidental, as its removal greatly retards and even partly inhibits the reaction. It acts as a swelling agent, and it is not necessary to emphasize the importance of swelling in cellulose reactions. However, there is some evidence, as will be shown elsewhere, that swelling (as an aid to diffusion) is not the only function of water in cellulose benzylation.

The immiscibility of water with benzyl chloride further accentuates the heterogeneity of the system, which thus consists of a solid phase (cellulose) and two immiscible liquid phases (aqueous alkali and benzyl chloride). As the alkali cellulose is wet with water, it is to be expected that the penetration of the mobile reactant (benzyl chloride) into the fiber structure will be difficult. This is, in fact, the case, although the surface of the fiber does not repel the benzyl chloride and a considerable amount of benzyl chloride is taken up by imbibition in the spaces between the individual fibers.

The progress of the reaction in the single fibers can be observed best under certain conditions such as the proper composition of the alkali cellu-

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(10) K. Brandt, "Ueber Gewinnung und Eigenschaften von Benzylcellulose," Dissertation, Buchdruckerei Ludwig Begach, Berlin, 1933.

(11) K. Mienes, "Celluloseester und Celluloseäther, etc.," Chemisch-technischer Verlag Dr. Bodenbender, Berlin-Steglitz, 1934.

(7) I. Sakurada, *Cellulosechem.*, **18**, 3-8 (1934).

lose, a certain benzyl chloride-alkali cellulose ratio, avoidance of any vigorous agitation, and moderate reaction temperature. The composition of the alkali cellulose depends on the concentration of the sodium hydroxide used for immersion (it should be 18-30%, preferably 25%) and on the degree of pressing, *i. e.*, the removal of the excess caustic solution. One part of cotton linters should yield 3-5 parts, preferably about 4 parts, of alkali cellulose. This gives a water-cellulose ratio of 2:1 or higher, which is necessary for adequate swelling. The sodium hydroxide-cellulose ratio is less important; it depends on (1) the degree of pressing and (2) the concentration of the solution used for immersion. The amount of benzyl chloride should be about 150% of the alkali cellulose. A reaction temperature of 60° was found best in taking observations.

The only purpose of agitation is to ensure a uniform distribution of the excess benzyl chloride. As this tends to collect at the bottom, it could cause differences between the upper and lower portions of the reaction batch. Vigorous agitation, on the other hand, gradually destroys the fiber structure, and must, therefore, be avoided. The set-up described in the experimental part satisfies the requirements.

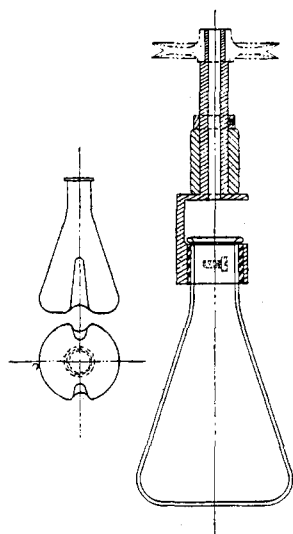


Fig. 1.

Experimental Part

The essential part of the apparatus is an Erlenmeyer flask (Fig. 1) with two deep indentations serving as baffles to prevent slipping of the mass on the glass wall. The neck of the flask is held in a special clamping device with an attached hollow shaft which turns in a bearing and carries a drive pulley. The flask, in an inclined position, is

partially submerged in a constant temperature oil-bath, and revolves at 10 r. p. m. or less.

A typical benzylation mixture, which gave characteristic photomicrographs, was prepared in the following way: 16 g. of high viscosity cotton linters was steeped in 200 cc. of 25% sodium hydroxide. After two hours, the excess caustic solution was removed by draining and pressing, so that 65 g. of alkali cellulose was obtained. The cake was disintegrated by vigorous shaking in the flask, and its alkali content was determined by adding to a small sample an excess of 0.5 *N* hydrochloric acid and back-titrating with 0.5 *N* sodium hydroxide. The alkali cellulose contained 13.9 g. of sodium hydroxide and 35.1 g. of water (estimated by difference).

Discussion

The changes taking place in the fibers with the progress of the reaction are shown by the photomicrographs, selected from a series of pictures taken at regular intervals. The first (Fig. 2) shows the alkali cellulose alone; the second (Fig. 3) in the presence of benzyl chloride. The first sign of a change in the system is the appearance of small droplets of water (or lye) on the surface of the fibers and in the medium (benzyl chloride) surrounding the fibers (Fig. 4). This lye (an aqueous solution of sodium hydroxide and sodium chloride) had been squeezed from the fibers by the penetration of benzyl chloride into the alkali cellulose and by its chemical action on the latter.¹² The more hydroxyl hydrogens are substituted by benzyl groups, the less *hydrophilic* the attacked fiber elements become, and thus more and more lye is displaced. On the other hand, with the increasing number of benzyl groups attached, the outer layers of the fibers turn increasingly *organophilic*, so that benzyl chloride penetrates more readily and acts as a swelling agent. This, in turn, furthers the reaction of additional hydroxyls in the same zone, as well as the propagation of the reaction to new zones (Figs. 5-7).

This progress of the reaction is made visible by the continuing separation of lye droplets which collect in the spaces between the growth rings of the cotton fibers. (Figure 8 is a cross-sectional view, Figure 9 is a longitudinal view of the fiber in the course of benzylation. Especially in the latter, the growth rings are readily discernible. Magnification = $\times 500$, as against $\times 125$ for the previous figures.) At first, the droplets are able to escape in the radial direction. However, very soon their exit is clogged by highly hydrophobic,

(12) Without taking any definite stand as regards the actual constitution of the cellulose-sodium hydroxide complex, the benzylation reaction may be represented by the equation

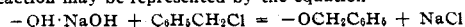




Fig. 2.

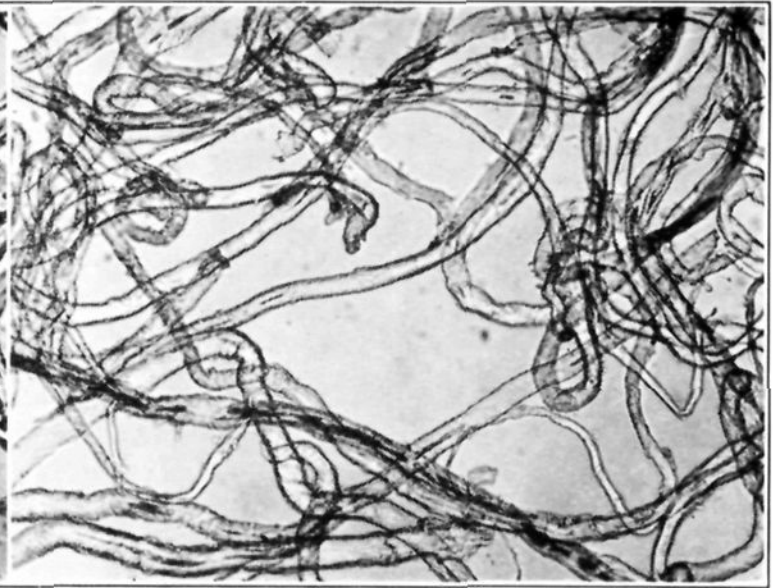


Fig. 3.

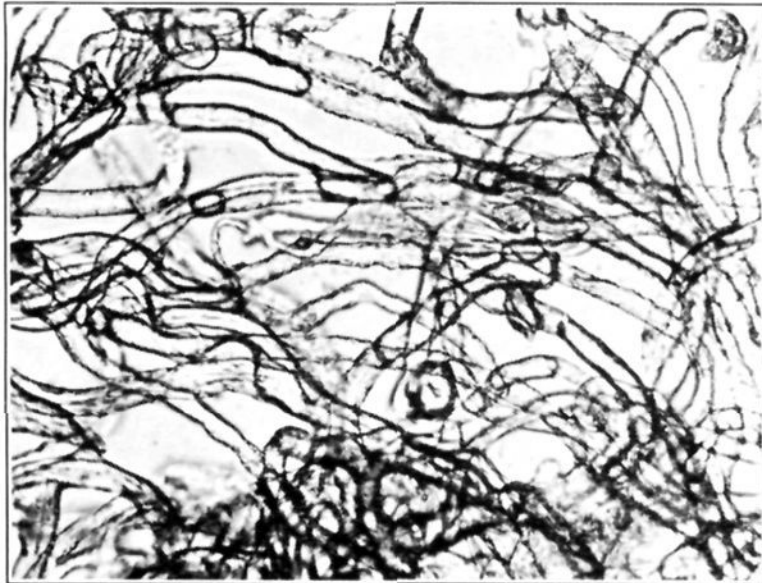


Fig. 4.



Fig. 5.



Fig. 6.

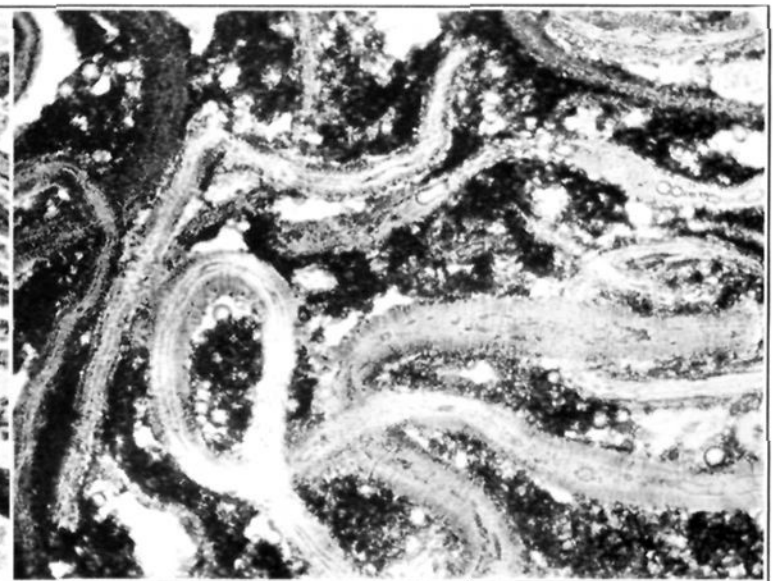


Fig. 7.

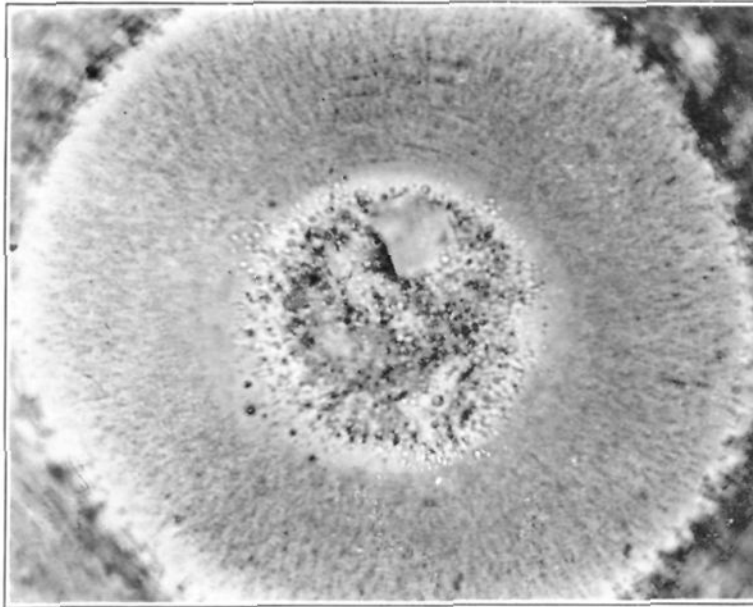


Fig. 8.



Fig. 9.

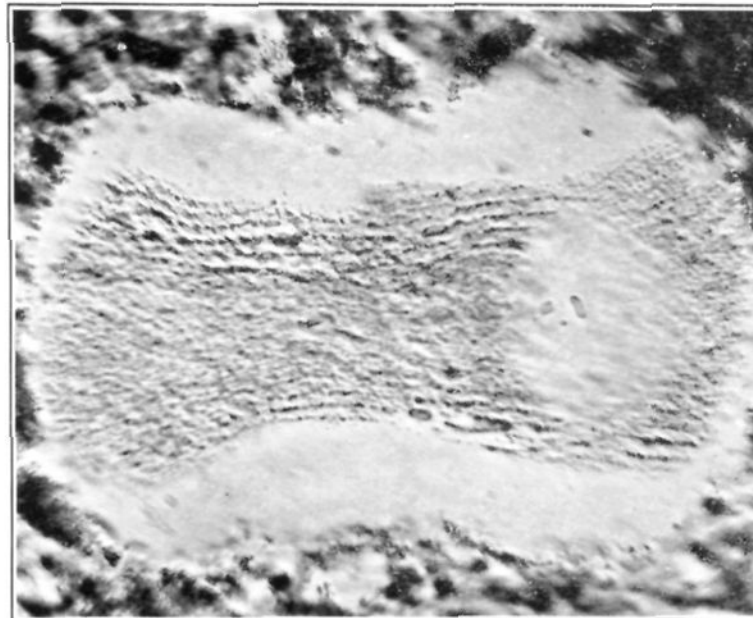


Fig. 10.

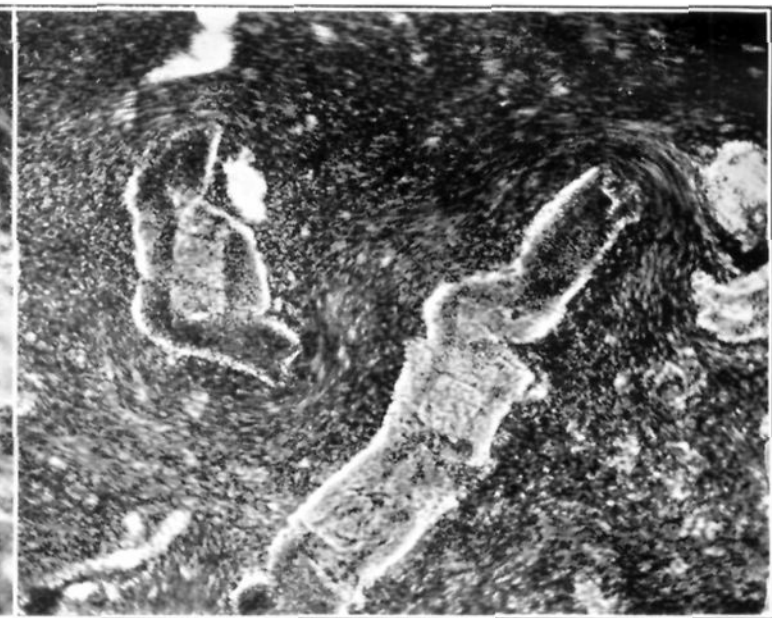


Fig. 11.

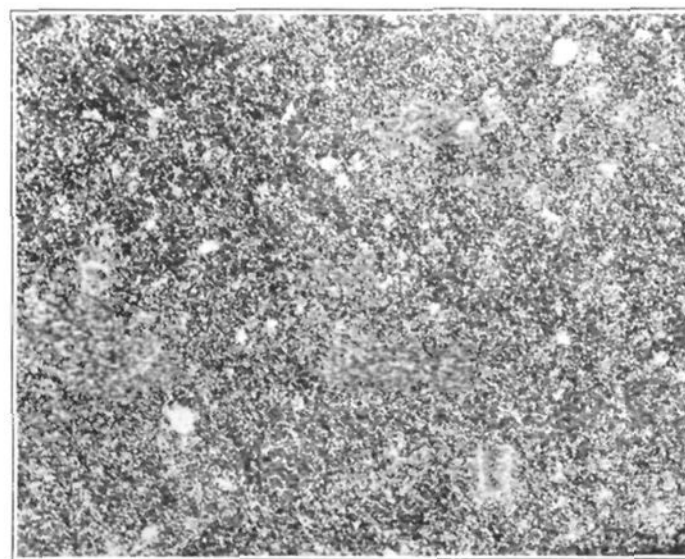


Fig. 12.

gelatinized fiber-layers, formed by increasing substitution and swelling at the periphery. From now on, they wander along the longitudinal channels between the growth rings, or axially toward the wider central canal. However, this latter route may not be open if benzyl chloride has penetrated the canal and has attacked its wall sufficiently to make it impervious to the aqueous lye.

Figure 10 shows a fiber fragment in an advanced stage of benzylation. Inside, rows of droplets indicate growth rings, while the surrounding uniform jelly layer represents an advanced stage of conversion, as shown by the high degree of swelling. In contrast to the inside portions, the jelly has no double refraction, indicating that the orientation of the fiber elements has been destroyed. In spite of the strong swelling, the jelly is not yet soluble in benzyl chloride, but may be dissolved in benzene-alcohol (8:2) or dioxane. Analysis, after purification by reprecipitation, shows that about 50% of the hydroxyl hydrogens have been substituted by a benzyl group.

In this stage, the reaction stops because no more alkali is available. To increase the substitution, it is necessary to break up the jelly with vigorous agitation and to bring it into intimate contact with fresh alkali of sufficient concentration (30% or more). Figure 11 shows fiber fragments resulting from the breaking up of the fibers by agitation. After a slight increase in substitution, the jelly dissolves in benzyl chloride, as shown in Fig. 12, representing the complete dispersion of the fibers.

With the progress of the reaction within the single fibers, as previously described, marked changes, partly discernible with the naked eye, take place outside of the fibers. As benzyl chloride is taken up by the swelling of the fibers, the moist-appearing fibrous mass turns into a white mush, indicating the presence of an emulsion in the spaces between the fibers. As increasing amounts of lye are squeezed out from the fibers, the ratio of the two liquids in the emulsion continuously changes and even reverses. As the emulsion surrounding the fibers is not very stable, the great increase of the aqueous phase leads to partial separation or even to a reversal in the type of the emulsion. However the case may be, lye separates out from the fibrous mass, which, because of its high degree of swelling and the loss of water, becomes doughy.

At this point, the batch consists of three distinct regions. One of these is the separated lye containing a small amount of benzyl chloride dispersed as fine droplets; the second consists of the fibers greatly swollen in benzyl chloride and mostly enclosing a dispersion of aqueous sodium hydroxide and sodium chloride solution between some of the growth rings. Finally, the third region consists of the emulsion surrounding the fibers, as described. This latter contains the greater part of the "free" benzyl chloride, *i. e.*, that part which is not bound by swelling. The relative amount of this "free" benzyl chloride not only influences the consistency of the mix, but also determines the extent of lye separation. Large amounts of benzyl chloride tend to make the dough softer, keep the lye dispersed, and prevent or retard its separation. By decreasing the ratio of benzyl chloride, the free part of it becomes insufficient to hold the lye dispersed; therefore, a large portion of the lye separates out, as described above. Further decrease may eliminate the "free" benzyl chloride, as the total amount would be taken up by swelling. If, finally, the total benzyl chloride is less than that needed for the swelling of the fibers, the reaction is retarded, and lack of uniformity in the attack of the single fibers appears. Batches of such composition have a dry appearance, and fall to crumbs floating in the separated lye.

This picture of the benzylation process shows that the reaction proceeds from layer to layer, probably from growth ring to growth ring. In this way, cellulose benzylation appears to be a topochemical-macroheterogeneous reaction, determined by diffusion difficulties, *i. e.*, the slow penetration of benzyl chloride into the fiber structure. This fact becomes even more evident when the process is studied at temperatures higher than 60°.

On raising the temperature, the initial speed of the reaction increases. Nevertheless, it is more difficult to complete the benzylation even with agitation and further increase of the temperature than is the case with a batch started at 60°. At 70°, this difference becomes noticeable, and is quite marked at 80°. The explanation is simple if we keep in mind the above reaction mechanism and distinguish between the *velocity of benzylation* (of the single hydroxyls) and the *speed of propagation* (advance of the reaction zone from layer to layer). The latter mainly depends on the speed of diffusion. At 60°, the velocity of benzylation

and the diffusion of benzyl chloride into the fiber body are of the same magnitude, so that diffusion and reaction go hand in hand. At higher temperatures, however, this is not the case. Because of the increase in the velocity of benzylation the outer layers of the fibers are rapidly benzylated. As the penetration (diffusion) of benzyl chloride is not increased appreciably, the outer layers have time to take up a larger number of benzyl groups before the next layer is attacked. The strongly organophilic higher substituted fiber portions gelatinize and thus insulate, in increasing degree, the remainder of the fibers. The lye set free by the originally hydrophilic layers, which have been converted into a hydrophobic condition, cannot escape radially, and is compelled to migrate toward the unattacked regions, diluting there the sodium hydroxide, and thus lowering the reactivity of those unattacked portions. In the meantime, the substitution of the outer layers, because of the higher reaction velocity, has increased to a point where solubility in benzyl chloride sets in. In this state, these layers can be dispersed readily by pressure (*e. g.*, on the cover glass under the microscope), or by agitation (in the batch). The remaining fiber fragments seem hardly attacked at all (as shown by their intense double refraction) and, what is worse, are in a rather inactive state because of the loss of their alkali content by what might be called "demercerization." It is difficult to introduce fresh alkali from without because of the presence of hydrophobic films, so that it takes a very long time to complete the benzylation.

Summary

Alkali cellulose prepared from cotton linters has been benzylated under conditions favorable to the preservation of the fiber structure.

A microscopic study of the changes within the fibers in the course of benzylation shows that the reaction is greatly influenced by the presence of two immiscible liquid phases (water and benzyl chloride), which causes diffusion difficulties. As alkali cellulose reacts with benzyl chloride, the originally hydrophilic system becomes hydrophobic, whereby aqueous lye is expelled and a dispersion is formed. This and the swelling of the increasingly organophilic system in benzyl chloride facilitate microscopic observation of the reaction.

The progress of the chemical conversion depends on the ratio between the reaction velocity and the speed of diffusion. At about 60°, the two are of the same magnitude; as a result, the reaction zone progresses continuously toward the center of the fiber. Even under these favorable conditions, the reaction is of the topochemical macroheterogeneous type, *i. e.*, starting at the surface of the fiber, it is propagated from layer to layer.

With rising temperature, the reaction velocity increases more rapidly than the rate of diffusion. In this way, differences in the degree of benzylation of the fiber layers arise. The highly substituted outer layers form an insulating jelly shell around the unreacted region, thus preventing diffusion, and the reaction comes to a stop unless the shell is mechanically broken.

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RECEIVED MARCH 11, 1937

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE, AND NO. 151 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Analysis of Fructoside Mixtures by Means of Invertase. VI. Methylated and Acetylated Derivatives of Crystalline β -Benzylfructopyranoside¹

BY C. B. PURVES AND C. S. HUDSON

When α -methylfructofuranoside was dissolved in benzyl alcohol containing hydrogen chloride the optical rotation of the solution first diminished very rapidly and subsequently much more slowly. A previous article^{2a} described the data used in plotting this decrease against a new time scale (Fig. 1, curve AA₁) and showed that the sub-

stances present in solution at the break in the curve (region A) were mainly benzylfuranosides.

On the present occasion, when neutralization of the hydrogen chloride was delayed until the end of the slow, secondary optical change (region A₁), only 14% of the fructose remained as the benzyl derivative hydrolyzed by invertase. The bulk of the product comprised a sirup of a non-carbohydrate nature which was not investigated (up to 40%) and a new, crystalline glycoside, β -benzyl-

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Purves and Hudson, *THIS JOURNAL*, (a) **59**, 49 (1937); (b) **56**, 702 (1934); (c) **56**, 708 (1934).