tion coefficient between oil phase and micelles, as a function of oil phase composition. It is found that $K_m$ is not constant, but taking an average value (for the monomer ratios used) as 0.7, and considering these "equilibrium" micelles as the locus of reaction, we should find

$$r_1' = r_1 K_m = 0.50 \times 0.07 = 0.35$$
$$r_2' = r_2/K_m = 0.44/0.7 = 0.63$$

Since these values are likewise significantly different from the experimental values, it would appear that the equilibrium micelles are not important reaction loci.

From the point of view of monomer reactivity ratios, it would appear from the above results that the oil phase would be the principal reaction locus for the system studied. According to Harkins,[9] however, the reaction starts in the soap micelles, but as soon as some polymer forms, monomer will dissolve in the polymer, and the reaction will continue in the resulting monomer polymer particles. Since the composition of the monomer dissolved in the monomer–polymer particles can reasonably be expected to be nearly the same as that of the oil phase, it is easily seen why the polymerization would appear to take place in the "oil phase" as far as monomer reactivity ratios are concerned.

At extremely low conversions, however, the copolymer composition should approach that predicted from micelle compositions. To test this idea, we carried out six additional experiments with conversions ranging from 0.24 to 9.0%. In performing these experiments, especially those for the lowest conversions, extreme precautions had to be taken to remove oxygen from the system. This was necessary since the initial polymer formed would otherwise have been contaminated with oxygen, for it is used up in the induction period as if it were a comonomer.

These experiments, which will not be described in detail, did show composition shifts in the direction predicted by assuming the micelles to be the reaction locus. However, the copolymer compositions never reached the theoretical limit expected for micellar reactions, and were always closer to the oil phase values. Nevertheless, considering the experimental difficulties encountered, there seems to be general compatibility with Harkins' views[9] with respect to the changing nature of the reaction locus.

## Summary

Copolymerization and solubility studies have been carried out on styrene and methyl methacrylate for the purpose of learning more about the mechanism of emulsion polymerization. The copolymerizations were carried out both in solution and in emulsion for three different monomer ratios and the compositions of the resulting copolymers determined. In addition the solubility distribution coefficients for the monomers between oil, water, and soap micelles were measured. These results have been correlated and are in substantial agreement with Harkins' theory of the locus of an emulsion polymerization, namely, that most of the polymerization occurs in the swollen polymer-monomer particles after the initial reaction in the micelles.

URBANA, ILLINOIS RECEIVED MARCH 30, 1950

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY][1]

# The Heterogeneous Methanolysis of Native and Mercerized Cotton Cellulose[2]

BY RICHARD E. REEVES, LAURENCE W. MAZZENO, JR., AND CARROLL L. HOFFPAUIR

In continuing studies on the acid-catalyzed heterogeneous-methanolysis of cotton cellulose[3,4] two effects have been observed which are capable of quantitative evaluation; first, the introduction of acid-labile methoxyl groups into the insoluble cellulose, and second, the dissolution of a portion of the cellulose into the methanolysis reagent. Methanolysis is here regarded as the sum of these two effects.

In the present investigation purified native cotton cellulose and mercerized cotton cellulose have been subjected to methanolyses at different temperatures and the reactions have been followed in the region when 0.1 to 5% of the total glucose units have become involved in reaction. Throughout this region a constant temperature coefficient was found for the rate of methanolysis of native fiber; for mercerized fiber the temperature coefficient was essentially constant, but clearly smaller than that observed for the former substrate. This difference between native and mercerized celluloses extends from the earliest observations to the last.

At equal extents of reaction differences in rate with temperature constitute the temperature coefficient and through this are related to the apparent energy of activation of the rate controlling step of the reaction. For the methanolysis of native cotton cellulose the apparent energy of activation is 24 kilocalories per mole;

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Some of the data in this manuscript were presented before the Cellulose Division at the 114th meeting of the American Chemical Society, Portland, Oregon, September 1948, in a paper entitled "The Methanolysis of Cotton Cellulose."

(3) Hoffpauir and Reeves, *Anal. Chem.*, **21**, 815 (1949).

(4) Reeves, Schwartz and Giddens, THIS JOURNAL, **68**, 1383 (1946).

mercerized, approximately 20 kilocalories per mole of reaction. Temperature coefficients and energies of activation of such magnitude are clearly greater than those expected of a diffusion-controlled type of reaction, hence, it is quite certain that the rate of methanolysis is controlled by reaction, and not by diffusion of the reagent into the fiber.

A search of the literature has failed to reveal any instance in which the apparent energy of activation on heterogeneous *hydrolysis* has been compared for native and mercerized cellulose, although values ranging from 27.8 to 43.1 kilocalories per mole[5,6,7] have been reported for the hydrolysis of native cotton and wood celluloses. In one instance equal values of approximately 35 kilocalories are recorded for the energy of activation on hydrolysis of native cotton cellulose and a regenerated cellulose.[8]

TABLE I

THE CUPRAMMONIUM FLUIDITY OF UNDISSOLVED CELLULOSE AND THE AMOUNT OF GLUCOSE IN SOLUTION AFTER EXPOSURE FOR 240 HOURS AT 30° TO METHANOL CONTAINING VARIOUS AMOUNTS OF ANHYDROUS HYDROCHLORIC ACID

| HCl concentration, mole/liter | Fluidity, rhes | Glucose in solution after hydrolysis,[a] milligrams |
|---|---|---|
| 0.01 | 23.8 | 8.6 |
| .05 | 38.4 | 20.2 |
| .185[b] | 47.9 | 37.2 |
| .44[b] | 51.1 | 81.6 |

[a] From 10 g. of air-dried fiber. [b] Average acid concentration during experiment.

TABLE II

THE METHANOLYSIS OF PURIFIED NATIVE COTTON CELLULOSE IN THE PRESENCE OF 0.5 *N* HCl AT 15 AND 30°

| Duration, hours | Amount of reaction per 162 g. of anhydrous cellulose: Insoluble phase —$OCH_3$, millimoles | Glucose in solution after hydrolysis, millimoles | Total reaction, millimoles |
|---|---|---|---|
| | | (At 15°) | |
| 1 | 0.50 | 0.53 | 1.03 |
| 2 | 0.95 | .53 | 1.48 |
| 5 | 1.50 | .72 | 2.22 |
| 17 | 2.01 | .43 | 2.44 |
| 25 | 2.90 | .67 | 3.57 |
| 50 | 3.62 | .63 | 4.25 |
| 240 | 8.19 | 2.32 | 10.51 |
| 599 | 11.66 | 5.89 | 17.55 |
| 810 | 12.36 | 2.90 | 15.26 |
| 1000 | 13.97 | 5.36 | 19.33 |
| 1200 | 15.05 | 5.55 | 20.60 |
| 1506 | 12.33 | 5.89 | 18.22 |
| 2040 | 13.17 | 6.57 | 19.74 |
| | | (At 30°) | |
| 1 | 1.53 | 0.78 | 2.31 |
| 2 | 1.92 | 0.78 | 2.70 |
| 5 | 3.46 | 0.91 | 4.37 |
| 16 | 5.43 | 1.54 | 6.97 |
| 25 | 7.04 | 2.22 | 9.26 |
| 50 | 9.94 | 1.69 | 11.63 |
| 74 | 9.60 | 2.65 | 12.25 |
| 97 | 9.13 | 6.81 | 15.94 |
| 240 | 14.19 | 10.04 | 24.23 |
| 450 | 13.78 | 16.50 | 30.28 |
| 600 | 15.28 | 23.46 | 38.74 |
| 810 | 13.83 | 25.33 | 39.16 |
| 1200 | 14.73 | 24.37 | 39.10 |
| 2010 | 15.84 | 38.36 | 54.20 |

## Discussion of Experimental Results

**The Influence of Acid Concentration on the Methanolysis of Cotton Cellulose.**—The data presented in Table I illustrate the influence of acid concentration on the methanolysis reaction, the substrate material for this experiment being purified native Empire cotton. Samples were methanolyzed for 240 hours at 30° in the presence of various concentrations of hydrochloric acid. Increasing acid concentrations produced higher cuprammonium fluidities in the undissolved portions and increases in the solution of material, these results showing that the rate controlling process in methanolysis is at least partly dependent upon an acid catalyzed step.

**The Kinetics of the Methanolysis of Cellulose.**—Tables II and III show for native and mercerized cotton, respectively, the amounts of glycosidic methoxyl in the insoluble cellulose and the amounts of glucose dissolved by the methanolysis reagent for successive periods of time under standard conditions. Throughout these experiments the

TABLE III

THE METHANOLYSIS OF PURIFIED MERCERIZED COTTON CELLULOSE IN THE PRESENCE OF 0.5 *N* HCl AT 15 AND 30°

| Duration, hours | Amount of reaction per 162 g. of anhydrous cellulose: Insoluble phase —$OCH_3$, millimoles | Glucose in solution after hydrolysis, millimoles | Total reaction, millimoles |
|---|---|---|---|
| | | (At 15°) | |
| 1 | 0.73 | 0.29 | 1.02 |
| 3 | 0.89 | .31 | 1.20 |
| 5 | 1.15 | .34 | 1.49 |
| 16 | 2.51 | .39 | 2.90 |
| 25 | 4.01 | .18 | 4.19 |
| 50 | 4.00 | .55 | 4.55 |
| 97 | 5.08 | .87 | 5.95 |
| 210 | 10.02 | 1.31 | 11.33 |
| 304 | 13.07 | 2.46 | 15.53 |
| 497 | 15.27 | 3.61 | 18.88 |
| 760 | 12.83 | 2.93 | 15.76 |
| 940 | 14.97 | 3.77 | 18.74 |
| | | (At 30°) | |
| 1 | 1.36 | 0.34 | 1.70 |
| 3 | 2.46 | 0.34 | 2.80 |
| 5 | 3.14 | 0.47 | 3.61 |
| 16 | 6.25 | 0.94 | 7.19 |
| 27 | 8.37 | 1.39 | 9.76 |
| 50 | 9.30 | 1.91 | 11.21 |
| 94 | 12.44 | 3.92 | 16.36 |
| 210 | 16.97 | 11.44 | 28.41 |
| 306 | 17.90 | 13.59 | 31.49 |
| 499 | 19.04 | 21.77 | 40.81 |
| 760 | 18.25 | 24.29 | 42.54 |
| 1000 | 19.60 | 27.57 | 47.17 |

(5) A. Meller, *J. Polymer Sci.*, **4**, 619 (1949).
(6) J. F. Saeman, *Ind. Eng. Chem.*, **37**, 43 (1945).
(7) O. Eisenhut and E. Schwartz, *Die Chemie*, **55**, 380 (1942).
(8) H. J. Philipp, M. L. Nelson and H. M. Ziifle, *Textile Research J.*, **17**, 585-596 (1947).

acid concentration was maintained at 0.5 *N*, and runs were made at two different temperatures, 15 and 30°.

By analogy with the known behavior of carbohydrates, there is ample reason for believing that each acid-labile (glycosidic) methoxyl group introduced into the insoluble cellulosic material represents cleavage of a single glucose–glucose bond of the original cellulose. Likewise each fragment dissolved in the methanolysis reagent must represent cleavage of a bond of the original cellulose. The possibility of a single reaction both introducing glycosidic methoxyl and causing solution of a fragment is limited to a maximum of one per original molecule, or since cellulose of a high degree of polymerization (> 3000) was employed as starting material the uncertainty due to this occurrence could not exceed about 0.33 mole per thousand glucose units.

The uncertainty introduced by regarding each dissolved glucose unit as a fragment is unavoidable with the present experimental techniques. Experiments designed to study the molecular size of the dissolved material indicate that the average size of the fragments in solution after 500 hours is 1.3 glucose units. The error introduced by regarding each glucose unit as a separate fragment is probably systematic and of insufficient magnitude to alter the conclusions.

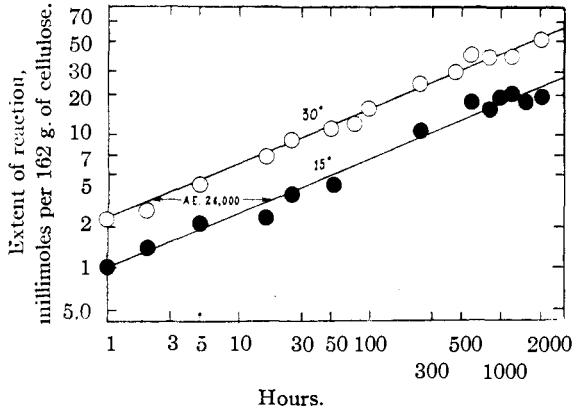


Fig. 1.—The methanolysis of native cotton cellulose.

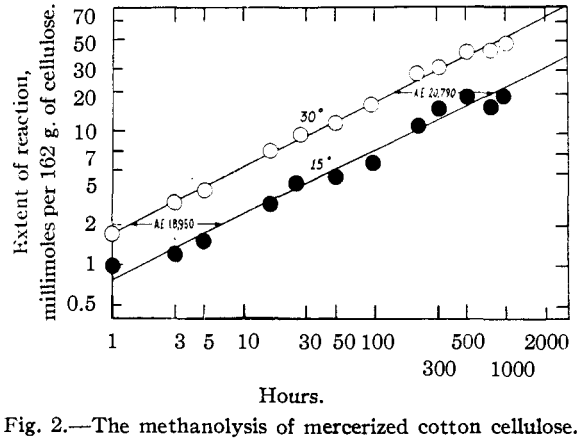


Fig. 2.—The methanolysis of mercerized cotton cellulose.

Figures 1 and 2 show the course of the methanolysis of native and mercerized cotton celluloses at two temperatures. The abscissas represent time of methanolysis; the ordinates, extent of reaction (moles of glycosidic methoxyl in the insoluble cellulose phase plus moles of glucose passing into solution) per thousand moles of glucose anhydride in the original cellulose. Empirically, the data are observed to fit a straight line in double logarithmic coördinates. Equation (1)

$$dy/dt = ay^b \quad (1)$$

describes the rate of the reaction at any instant in terms of extent of reaction. $t$ represents time in hours; $y$, extent of reaction; $a$ and $b$ are constants characteristic of each reaction. The $a$ and $b$ values for each reaction are given in Table IV. By choosing equal extents of reaction (equal $y$ values) for either native or mercerized cellulose at the two temperatures the ratio $(dy/dt)_{30}/(dy/dt)_{15}$ approximates the temperature coefficient of the reaction (15-degree interval) and may be substituted for the ratio of specific reaction rates in the integrated form of the Arrhenius equation for the calculation of apparent activation energies. In the methanolysis of native cotton cellulose the parallel lines in Fig. 1 are a reflection of the situation that a temperature coefficient of 8 (15° interval), and an apparent activation energy of 24,000 cal. per mole, applies through the entire studied range of the reaction. In the methanolysis of mercerized cotton cellulose (Fig. 2) the temperature coefficients and apparent activation energies show slight increases during the investigated portion of the reaction. The values found at the levels of 2 and 20 millimoles of reaction were, respectively: temperature coefficient, 5.15 and 6.04 (15° interval); activation energy, 18,950 and 20,790 cal. per mole. It may be questionable whether or not this trend is real within the limits of accuracy of the experimental method. However, there is little doubt that the temperature coefficient is lower for mercerized than for native cotton cellulose.

TABLE IV

THE CALCULATED VALUES OF THE CONSTANTS OF EQUATION (1) FOR PARTICULAR NATIVE AND MERCERIZED COTTON CELLULOSE SPECIMENS AT 15 AND 30°

| | $a$ | | $b$ | |
|---|---|---|---|---|
| | 15° | 30° | 15° | 30° |
| Native cotton cellulose | 0.417 | 3.306 | −1.42 | −1.42 |
| Mercerized cotton cellulose | .290 | 1.425 | −1.07 | −1.00 |

**The existence of limiting average minimum chain lengths** on methanolysis of native cotton cellulose is supported by the results in Fig. 3. These curves show glycosidic methoxyl and cuprammonium fluidity as a function of the duration of methanolysis. For native cotton

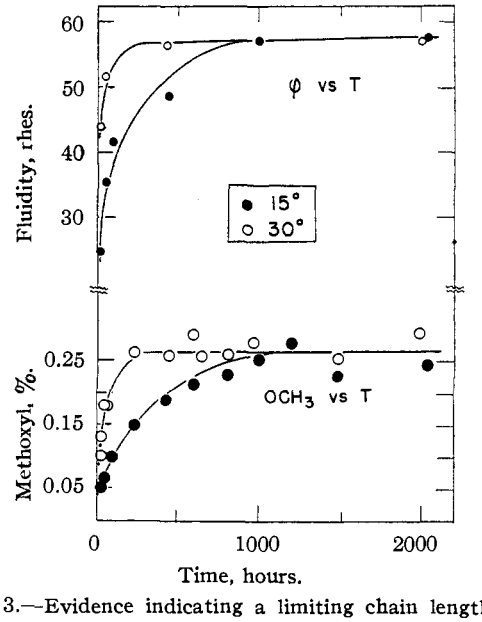


Fig. 3.—Evidence indicating a limiting chain length on methanolysis of native cotton cellulose.

cellulose the fluidities appear to level off at about 57 rhes,[9] and methoxyl values at about 0.26%. The latter show a large spread possibly due in part to the limited accuracy of the analytical method, and in part to unavoidable differences in sample preparation. However, it is noteworthy that maximum values of both properties are reached at about the same time; after 1,000 hours at 15° and 240 hours at 30°.

Both fluidity and glycosidic methoxyl are undoubtedly related to molecular size. The viscometrically determined average degree of polymerization (essentially a weight average) of the most degraded native samples corresponds to 170 glucose units (intrinsic viscosity × 260 = $DP_v$). The number average degree of polymerization, considering one glycosidic methoxyl group per molecule containing 0.26% methoxyl, is 74. Such a great discrepancy between weight average and number average chain lengths is only possible in a sample having a great degree of non-homogeneity. Fractionation experiments in progress appear to confirm this non-homogeneity in methanolyzed cellulose.

**The relationships between glycosidic methoxyl content and cuprammonium fluidity** of native and mercerized cotton cellulose are illustrated in Fig. 4. It may be observed that at equal methoxyl contents the fluidity is slightly higher for mercerized than for native fiber. This may be a result of the fractional removal of short chain cellulose during the mercerization step preceding methanolysis. However mercerized fiber attains higher methoxyl contents and fluidity values than those reached by native fiber.

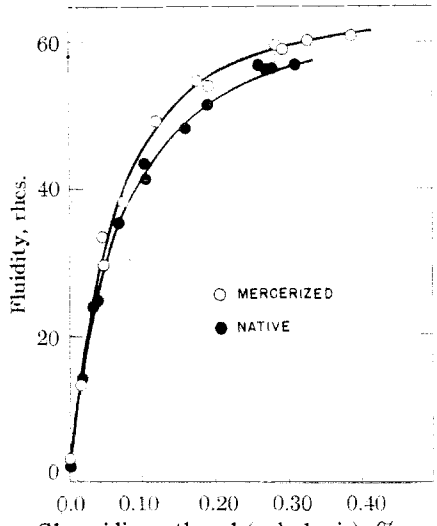


Fig. 4.—The relationship between glycosidic methoxyl content and cuprammonium fluidity.

## Experimental Methods

**Purified Native Cotton Cellulose.**—Combed Empire cotton was extracted in 500-g. lots for 6.5 hours with hot alcohol in a large Soxhlet extractor, squeezed from excess solvent, and air-dried. The material was then kiered for two hours at 120° in a stainless steel container in approximately 70 parts of 1% sodium hydroxide. After cooling, the sample was rinsed at room temperature with 1% sodium hydroxide and washed with running tap water for three hours. It was then given two changes of distilled water, soured with 0.5 *N* acetic acid for 25 minutes, thoroughly rinsed with distilled water and air-dried. This material had a cuprammonium fluidity of 2.52 rhes (reciprocal poise) in 0.5% concentration.

(9) The technique currently employed for the determination of cuprammonium fluidity is somewhat different from the one employed in the earlier communication, see ref. 4.

**Mercerized Cotton Cellulose.**—One kilo of purified native cotton was immersed in 16 liters of 18% sodium hydroxide solution at room temperature for 0.5 hour. The sample was rinsed free of alkali, soured for 20 minutes with dilute acetic acid, thoroughly washed with distilled water, and air-dried. This material had a cuprammonium fluidity of 3.04 rhes in 0.5% concentration.

**Procedure for Methanolysis.**—The weighed cotton sample (usually 10 to 20 g.) was soaked for two hours in anhydrous methanol, filtered on a sintered glass funnel, and dried for one hour in a current of dry air. This material was immediately placed in wide-mouth glass-stoppered bottles containing 0.5 *N* hydrochloric acid in anhydrous methanol, and previously brought to the temperature of the run. Throughout the experiments thermostat temperatures were maintained within ±0.2°. The ratio of grams of cellulose to volume of solution was approximately 1 to 30. At intervals of approximately 100 hours the acid concentration of each reagent solution was checked by titration of a small aliquot. The acid concentration was maintained between 0.46 and 0.52 normal by adding small volumes of concentrated HCl–methanol stock solution as required.

After various lengths of time in the thermostat the residues were filtered, washed with ethanol until free of chloride, rinsed with ether, and dried. These residues were reserved for the determination of glycosidic methoxyl. The combined alcoholic extracts were evaporated to a small volume in a current of air and reserved for the determination of reducing sugar after hydrolysis.

**Glycosidic methoxyl** was determined in the insoluble cellulosic material by the method of Hoffpauir and Reeves.[3] This method covers the range from 0.02 to 0.50% methoxyl with an accuracy estimated to be about ±5%. Unlike the Zeisel method which shows an appreciable "blank" with crystalline D-glucose and purified cellulose, the glycosidic methoxyl procedure gives a zero blank with these materials.

**The glucose passing into the methanolysis reagent** (largely as methyl glucoside) was determined after aqueous hydrolysis to the maximum reducing value. The alcohol was removed by evaporation after addition of water, and the acid concentration was then adjusted to 1 normal. The solution was kept at 100° for four hours in a glycerol-water-bath. Reducing sugar was determined on aliquots by the Hanes modification of the method of Hagedorn-Jensen.[10]

**Cuprammonium fluidities** were adjusted to 0.5% concentration and a gradient of 500 sec.$^{-1}$. The procedure described by Conrad and Tripp[11] was employed. The cuprammonium hydroxide solution contained 30 g. of copper, 165 g. of ammonia and 10 g. of sucrose per liter.

**The average molecular size of material in the methanolysis solution** was studied on a 250-g. (anh. basis) portion of mercerized cotton fiber after 500 hours at 30° in the presence of 0.5 *N* HCl. The solution was separated by filtration and the cellulosic residue was rinsed with ethanol. A portion of the combined filtrate and washings was examined after hydrolysis to maximum reduction and reducing sugar corresponding to 5.26 g. of glucose was observed. The remainder of the solution was neutralized with lead carbonate, filtered from insoluble salts, and concentrated. After deionization the solution, on evaporation to dryness, left a residue amounting to a total of 5.17 g.

This residue from the methanolysis solution contained 12.45% methoxyl corresponding to one glycosidic end-group per 1.3 glucose units. This indicates that the number of fragments in the methanolysis solution equals about three-fourths the number of glucose units.

A 40% yield of methyl α-glucoside was obtained by crystallization from the residue dissolved in alcohol. Chromatographic adsorption studies indicated that the uncrystallized portion of the residue was composed of a mixture of methyl glucosides and methyl cellobiosides.

(10) C. S. Hanes, *Biochem. J.*, **23**, 99 (1929).

(11) Conrad and Tripp, *Textile Res. J.*, **16**, 275 (1946).

## Conclusions

The rate measurements are undoubtedly related to the number of glucose–glucose linkages cleaved by the methanolysis reagent and this bond cleavage is clearly an acid catalyzed reaction. Yet if primary valence bond cleavage alone were the rate controlling step, equal energies of activation would be anticipated for both native and mercerized celluloses. If reaction occurred initially in amorphous regions of the fiber equal energies of activation would be anticipated for the reaction of native and mercerized fibers. If highly reactive acid-sensitive linkages were the reason for the high initial rate of reaction then also equal energies of activation would be expected for the native and mercerized fibers. That different values are encountered points to the conclusion that some factor in addition to the cleavage of primary valence linkages controls methanolysis and that the reaction does not involve amorphous cellulose, nor weak linkages.

In speculating as to the nature of the rate controlling step it is recognized that in passing from glucose–glucose units situated in a solid phase to methanolyzed glucose–methyl glycoside units the secondary forces holding the reacting units must be broken as well as the primary valence linkages. Different activation energies are a reflection of different secondary valence forces between the structural units in native and mercerized celluloses. In order that primary valence bonds and secondary valence bonds be involved in the rate controlling step requires that both types of bonds be broken in a single step in the methanolysis reaction.

The rate of methanolysis decelerates too rapidly with too little material dissolved for the change to be attributed solely to dissolution of amorphous material. Also, as was pointed out in the preceding paragraph, there is definite indication that the reaction does not take place in an amorphous region. Some hitherto unrecognized effect must be contributing to the rate decrease. In explanation it is suggested that the initial rapid reaction is due to a large amount of surface exposed by relatively fine crystallites; as reaction progresses these crystallites coalesce forming larger crystalline volumes with less surface. This concept resembles, in certain respects, the crystallization concept advanced to explain the behavior of cellulose upon hydrolysis[12] where amorphous regions are believed to crystallize as mobile chain ends occur during the course of the reaction.

**Acknowledgments.**—The authors are indebted to B. J. Barrett and V. W. Tripp for the cuprammonium fluidity determinations, to L. Loeb and Mary G. Blair for assistance with the soluble material from the large methanolysis experiment, and to Wilhelmina M. Schwartz for the preparation of some of the methanolyzed celluloses.

## Summary

The methanolysis of cotton cellulose produces two measurable results: introduction of acid-labile methoxyl groups into the insoluble phase, and dissolution of a portion of the cellulosic material into the methanolysis reagent. When the total reaction is considered it is found that the rate of methanolysis smoothly decreases in the region where 0.1 to 5% of the glucose units have undergone reaction. Throughout this investigated region the temperature coefficient for native cotton cellulose remained constant; for mercerized, a lower, essentially constant value was observed. It appears that the rate controlling step in methanolysis involves in a single step the rupture of secondary as well as primary valence forces.

Incompatible with either the concept of reaction in an amorphous region or with relatively few acid-sensitive linkages, the present data is explicable in terms of reaction with an initially large crystalline surface, diminishing strongly as the surface is reduced by the coalescence of crystalline areas when internal tensions relax due to reaction within the fiber.

NEW ORLEANS, LOUISIANA RECEIVED MARCH 17, 1950

(12) K. Ward, Jr., *Textile Res. J.* **20**, 363 (1950), has reviewed the recently published evidence indicating that in many cases acid-hydrolysis may be accompanied by the formation of new crystalline areas.