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

The Heterogeneous Hydrolysis of Highly Methylated Cotton Cellulose

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Upon heterogeneous hydrolysis highly methylated cotton celluloses decrease sharply in viscosity (in chloroform solution); pass through minimum values: and, upon prolonged hydrolysis, show increases in viscosity. Different minimum viscosities for different batches of methyl cellulose are attributed to different crystallite dimensions produced during the methylation procedure; this explanation is supported by the X-ray diffraction patterns of the methyl celluloses. The initial viscosity decreases are regarded as due to chain scission; the later increases are regarded as due to the more rapid destruction of the lowest viscosity material.

Well-defined limiting, or leveling-off, viscosities are observed when the progress of heterogeneous hydrolysis of cellulosic materials, such as purified native and mercerized cotton fibers and rayon, is studied by observing the viscosity produced by dissolving portions of the material in an appropriate solvent.[2,3,4] After the leveling-off viscosity has been reached continuation of hydrolysis in the same medium produces either no appreciable change in viscosity or a very slight rate of decrease in viscosity. There is reason to believe that these leveling-off viscosities bear some direct relation to an average crystallite dimension in the material submitted to hydrolysis.

In their study of the heterogeneous hydrolysis of highly methylated cotton cellulose, Steele and Pacsu[5] claimed to observe a limiting viscosity of about 0.64 dl. per g. which corresponded to a degree of polymerization of sixty glucose units. They interpreted this as indicating the distance between periodic weak linkages (acetal cross bonds) in the cellulose structure. The possibility that limiting viscosity in highly methylated cellulose might be related to a crystallite dimension was rejected by these authors with the argument that substitution of methyl groups on the hydroxyls removes the possibility of hydrogen bonding and causes the intermolecular forces to be much more nearly alike throughout the fiber. They state, "A heterogeneous mild-acid hydrolysis should therefore be expected to be little influenced by crystallinity differences. . ."

During work on the methylation of cotton fiber a number of batches of highly methylated cellulose had been prepared under standard conditions of temperature, alkali concentration, and exclusion of atmospheric oxygen. Five batches having essentially the same methoxyl content after two methylation treatments were selected for the study of viscosity changes and weight losses during hydrolysis. Crystallinity, as evidenced by X-ray diffraction patterns, was studied in four of these batches and in two, crystallinity changes were investigated at different stages during hydrolysis.

Experimental

Purified cotton cellulose was prepared by a standard procedure employed in this Laboratory.[6] Empire cotton sliver was extracted in a large Soxhlet extractor with ten passes of hot alcohol, and subsequently boiled, with exclusion of air, for 2 hours with 1% sodium hydroxide (alkali replaced with fresh solution, in the absence of air, every half-hour).

Five different batches of highly methylated cotton fiber were prepared from a single lot of the purified fiber. Each batch was given two methylations; the methoxyl contents after the first and second treatments are given in Table I.

TABLE I

THE METHOXYL CONTENT OF FIVE DIFFERENT BATCHES OF METHYL CELLULOSE

Batch	Methoxyl, % 1st methylation	2nd methylation
A	42.6	44.0
B	42.7	44.2
C	34.4	44.5
D	23.9	43.7
E	9.8	44.5

The methylation procedure was based upon that of Neumann and Hess.[7] The following example describes the first methylation of batch B. Twenty grams of purified Empire cotton (air-dried), ground to 20-mesh in a Wiley mill, was placed in a 3-liter, 3-necked flask through which nitrogen (or, in some later cases, natural gas) was swept for 2 hours. Two liters of 45% sodium hydroxide solution, through which gas had been bubbled for 2 hours, was added and the flask was arranged to permit blowing the blanketing gas over the reaction mixture throughout the entire time of reaction. The flask was set in a water-bath at 55°, and the mixture stirred with a stirrer of the type described by Reid and Buras[8] operating at approximately 1700 r.p.m. Rapid and vigorous stirring is essential to produce highly methylated material in one operation. When the inner flask temperature reached that of the bath, addition of methyl sulfate was begun. Twenty ml. of reagent was added at 15-minute intervals until 200 ml. had been used. An hour of reaction time was allowed after the last addition; then the temperature was raised to 100°. In order to minimize the action of atmospheric oxygen on the methyl cellulose while it was still in contact with alkali the following method of filtering the product was adopted. A glass tube was inserted to the bottom of the flask (the product floats on the surface) and the solution was withdrawn by suction through a sintered glass funnel. Before being poured onto the funnel, the product was washed four times in the reaction flask with changes of boiling distilled water, the current of blanketing gas being maintained throughout. It was then washed with 8 liters of boiling water, twice with acetone, and dried in the air. The yield was 23.07 g. of methyl cellulose from 18.74 g. of purified cotton cellulose (anhydrous basis). Its methoxyl content was 42.7%.

The relatively low methoxyl content of batch C was obtained inadvertently (it is believed that the stirring was not sufficiently vigorous in this case). In the first methylation of batches D and E the amounts of methyl sulfate were reduced to 60 and 40 ml., respectively, in order to produce lower methoxyl contents at the end of the first step.

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[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] G. F. Davidson, *J. Textile Inst.*, **34**, T87 (1943).

[3] M. Brissaud, *Mém. Poudres*, **25**, 476 (1932–1933).

[4] O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).

[5] R. Steele and E. Pacsu, *Textile Res. J.*, **19**, 771 (1949).

[6] J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **14**, 432 (1942).

[7] F. Neumann and K. Hess, *Ber.*, **70**, 721 (1937).

[8] J. D. Reid and E. M. Buras, *Science*, **104**, 326 (1946).

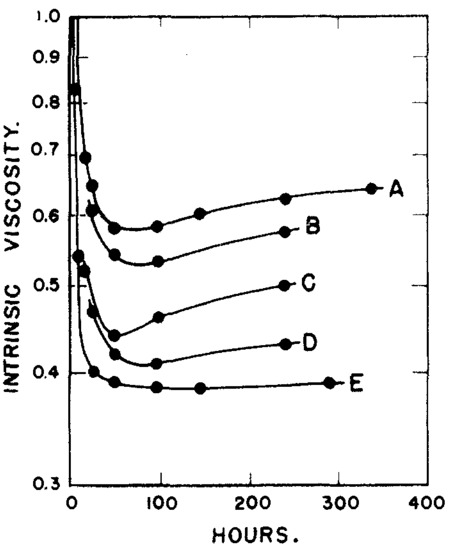

Fig. 1.—Intrinsic viscosity changes during the hydrolysis of the five different batches of methyl cellulose listed in Table 1.

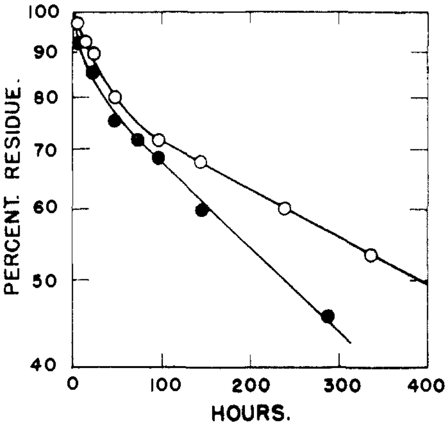

Fig. 2.—The per cent. residue remaining during the hydrolysis of methyl celluloses: upper curve, batch A; lower curve, batch E.

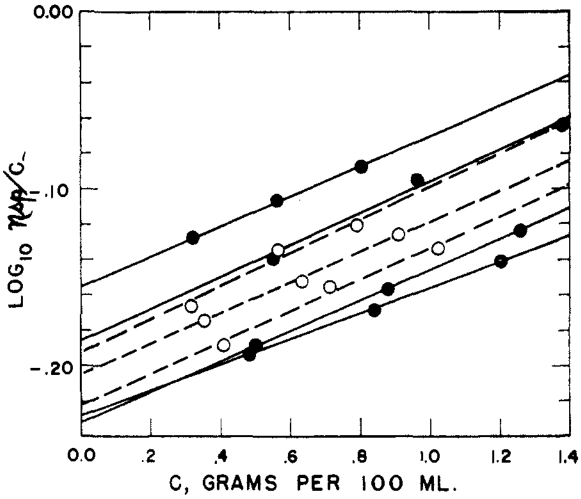

Fig. 3.—The intrinsic viscosity extrapolations for methyl cellulose, batch A, after hydrolysis for various periods of time at 80° with N hydrochloric acid containing 0.10% Aerosol OS. Proceeding downward the solid lines represent hydrolysis times of 16, 24, 48 and 96 hours, respectively. Proceeding upward the dashed lines represent 144, 240 and 336 hours, respectively.

Methoxyl analyses were made by the Zeisel procedure[9] modified by the omission of phenol. The hydriodic acid was refluxed for a brief period before introduction of initial charges of methyl cellulose as recommended by Steele and Pacsu.[5] Not more than three analyses were run with a single charge of hydriodic acid. The analyses reported in the table are average values and are believed to be reliable to about ±0.5%.

Hydrolyses were conducted at 80° ± 0.1° in normal hydrochloric acid in the presence of 0.10% Aerosol OS[10] as wetting agent. The undissolved residues were filtered on weighed sintered-glass disc crucibles, washed free of acid with hot distilled water, and allowed to dry in air. Weight-losses were computed on the air-dry basis, it having been previously established that hydrolysis did not significantly alter the low moisture content of the air-dry material.

That methoxyl is not removed from the highly methylated cellulose by hydrolysis under the conditions employed in this work was indicated by analyses on a composite sample containing material hydrolyzed from 48 to 288 hours. The hydrolyzed samples contained 44.4% unhydrolyzed, 44.5% methoxyl, respectively. These values agree within the limits of accuracy of the analytical method.

Viscosity measurements were made in freshly distilled chloroform solution at 25° with an Ostwald viscometer. After brief hydrolysis the samples were completely soluble in chloroform. Before hydrolysis the methyl celluloses were only partially soluble in chloroform, and for this reason satisfactory intrinsic viscosity measurements could not be made on the unhydrolyzed materials. Table II lists the per cent. solubility in chloroform and the intrinsic viscosities determined on the soluble fractions of batches A, B, D and E. Also included in the table are the minimum intrinsic viscosities observed on each of the five samples during hydrolysis.

The changes in intrinsic viscosity occurring during hydrolysis are shown for each of the five batches in Fig. 1. Figure 2 shows, for A and E, the changes in per cent. residue during hydrolysis. Figure 3 illustrates the actual viscometric measurements of batch A and their extrapolation to zero concentration to obtain intrinsic viscosity. Three different concentrations were employed for each hydrolyzed sample.

X-Ray diffraction patterns of the methyl celluloses were obtained with a recording X-ray diffraction spectrometer employing a Geiger–Mueller counter tube. The specimen consisted of 0.125 g. of methyl cellulose compressed in a half-inch disc to a thickness of approximately 0.9 mm. While making the tracings specimens were maintained in a position so that their surfaces made an angle of θ to the primary beam (the reflecting position). X-Ray diffraction patterns were obtained for batches A, C, D and E. Unfortunately, batch B was consumed in hydrolysis experiments before it was realized that no diffraction pattern was available. The patterns for batches A and E are shown in the upper two curves of Fig. 4. Batch D did not differ

TABLE II

CHARACTERISTICS OF FIVE DIFFERENT BATCHES OF METHYL CELLULOSE AFTER TWO METHYLATIONS

	Before hydrolysis		After hydrolysis
Batch	Solubility in $CHCl_3$, %	Intrinsic viscosity of part soluble in $CHCl_3$, dl./g.	Minimum intrinsic viscosity in $CHCl_3$, dl./g.
A	83	12.0	0.58
B	21	10.8	.53
C	..	..	.44
D	29	10.7	.41
E	22	13.5	.37

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(9) Assoc. Offic. Agr. Chemists, "Official and Tentative Methods of Analysis," 6th ed., 1945, p. 762.

(10) The manufacturer stated that Aerosol OS is sodium isopropylnaphthylsulfonate. The mention of a trade product does not imply its endorsement by the Department of Agriculture over similar products not named.

significantly from E, while C was intermediate between A and E.

X-Ray diffraction studies were also made on batches A and E after various intervals of hydrolysis. The patterns after 24 hours hydrolysis are given in the lower two curves of Fig. 4.

Discussion

In the initial stage of hydrolysis each batch of methyl cellulose became soluble in chloroform and its viscosity in this solvent decreased sharply. These phenomena are satisfactorily explained as the hydrolytic depolymerization of relatively high molecular weight materials. Not immediately apparent, however, are the reasons for the different minimum viscosities exhibited by the different batches when hydrolyzed under standard conditions, nor for the viscosity increases which were observed when the hydrolyses were continued beyond 96 hours.

As shown in Fig. 1 the minimum intrinsic viscosities upon hydrolysis ranged between 0.58 for batch A and 0.37 for batch E. Obviously, the explanation advanced by Steele and Pacsu[5] that the minimum (limiting) viscosity results from a structural feature pre-existing in the cellulose before methylation cannot apply, for if this were the case all five batches would have exhibited the same minimum value.

It is conceivable that in addition to regularly spaced weak linkages pre-existing in the cellulose, new labile positions are caused by degradation during the methylation procedure. The minimum viscosities would then be reached upon hydrolysis of both the original and the new weak linkages. One cannot dismiss completely the possibility of degradation during the methylation treatments employed in this work. However, by selecting batches prepared under standard conditions of temperature and alkalinity, and by exclusion of atmospheric oxygen it was hoped to secure materials which were comparable as far as degradation during methylation was concerned. That actual chain scission during methylation was slight is indicated by the incomplete solubility of the products in chloroform and by the high viscosities of those portions which did dissolve. If degradation during methylation is to be considered a factor in determining the minimum viscosity of methyl cellulose during hydrolysis, then the degradation must have been of some type other than chain scission, and must have increased regularly in amount from batches A to E.

The concept of the hydrolysis of weak linkages to produce the minimum viscosity does not appear to rest on any well-established experimental observations. It does not provide a ready explanation of the increases in viscosity observed upon long continued hydrolysis of methyl cellulose, nor of the fact that, by the time the minimum viscosity is reached, approximately 20 to 30% of the material has dissolved. For these reasons we are inclined to look to crystallinity differences as a possible explanation of the results.

X-Ray diffraction patterns indicate a very appreciable enhancement of crystalline diffraction during the initial stage of the hydrolysis of methyl cellulose. The highest crystalline diffraction is reached at about the same time that the minimum viscosity occurs. This suggests that in methyl cellulose, as in cellulose itself, the aqueous acid is unable to penetrate the interior of the crystalline regions and that as a consequence, hydrolysis proceeds first in the poorly crystalline regions, then upon the surfaces of the crystallites.

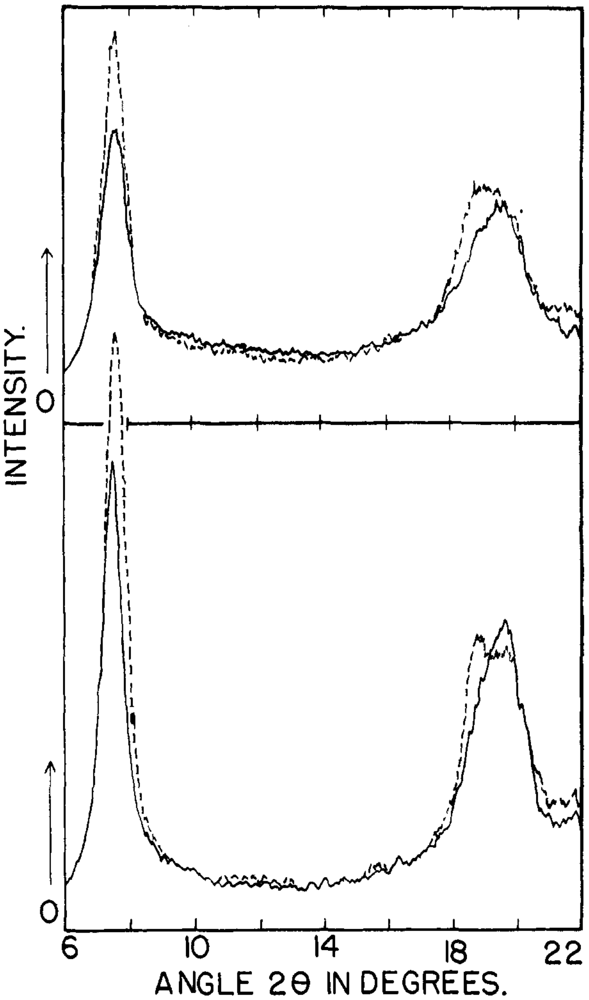

Fig. 4.—X-Ray diffraction patterns of methyl celluloses A (dashed lines) and E (solid lines) are shown by the two upper curves. The two lower curves represent the same materials after 24 hours of hydrolysis.

Crystallinity differences were readily apparent in the four batches of methyl cellulose which were examined by X-ray methods. Batch A with the highest minimum viscosity gave the most intense crystalline diffraction pattern; batches D and E gave the least intense diffraction. In addition to having the most intense peak at 7.6°, A showed a peak at 18.6° which was not resolved in the pattern of E. After hydrolysis some of the differences in the two materials were accentuated; E showed more intense diffraction at 19.6°.

It was noted that material from batch E dissolved more rapidly upon hydrolysis than did that from batch A. This was to be expected since the former has the lower minimum viscosity—hence the shorter average chain length—and the attractive forces between chains must diminish with decreasing length.

The experimental observations appear to be in accord with the following explanation of the changes occurring upon hydrolysis of methyl cellulose. In the initial stage the long chains which may pass through several crystalline and intercrystalline regions are broken and hydrolyzed to the boundaries of the crystalline regions. In the later stage the crystalline regions undergo attack from the surface and those crystallites having short dimensions in the direction of the primary valence bonds are hydrolyzed more rapidly than the longer ones. Through the selective removal of the shorter-chain material the average length of what remains is increased, an increase in viscosity resulting when the material is brought into solution.

It is likely that the introduction of small amounts of methoxyl during the first methylation (batches D and E) disturbed the crystalline pattern of the cellulose more effectively than occurred when essentially all the methoxyl was introduced by the first treatment (batches A and B). Upon hydrolysis the former produced more short-chain crystallites, lower viscosity in chloroform solution, and was more readily attacked by aqueous acid.

An increase in average chain length through selective removal of the shorter material seems to be the most likely explanation of the later-stage viscosity increases. Alternative explanations considered, but regarded as much less satisfactory, include the following: the increases may be due to the partial hydrolysis of methoxyl from the methyl cellulose; or to an altered distribution of the unsubstituted hydroxyl positions as hydrolysis progresses; or to a repolymerization of the hydrolyzed fragments. The first of these explanations seems to be contradicted by analyses indicating no detectable loss of methoxyl due to hydrolysis. The second seems unlikely because the amount of unsubstituted positions is very small. The possibility of repolymerization, the third alternative explanation, seems remote since the only reaction capable of recombining the smaller molecules would involve a reducing end-group forming a glycosidic or acetal structure. In dilute aqueous acid the equilibrium for such a reaction would be expected to favor hydrolysis rather than condensation.

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NEW ORLEANS 19, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY]

The Reaction of 1,1-Diarylethylenes with Thionyl Chloride. II. Preparation of 2,2-Diarylethene-1-sulfinic Acids and Some N-Aryl-2,2-diphenylethene-1-sulfinamides

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A number of new 2,2-diarylethene-1-sulfinic acids were prepared by the reaction of 1,1-diarylethylenes with thionyl chloride. The primary product present in the reaction mixture, 2,2-diphenylethene-1-sulfinyl chloride was also used, without isolation, for the preparation of several aryl amides. A polar mechanism is proposed for the reaction. The reaction velocity and the stability of the resulting sulfinyl chlorides and sulfinic acids is shown to be influenced by the various substituents in the para position of the aryl groups.

In a previous communication[1] we reported the preparation of 2,2-diphenylethene-1-sulfinic acid from 1,1-diphenylethylene and thionyl chloride. The main product of this reaction and the only identified product of other 1,1-diarylethylenes with thionyl chloride was the corresponding 1,1-diarylvinyl-2-chloride.

The object of the present work was to elucidate the mechanism of the reaction and to determine whether under more carefully controlled conditions the yield of the 2,2-diphenylethene-1-sulfinic acid could be improved; and on the basis of the information so gained, to prepare other 2,2-diarylethene-1-sulfinic acids and some derivatives of these.

Several experiments were made under different light conditions: in ultraviolet light, in diffuse sunlight and in total darkness, without having any effect on the reaction. The presence of benzoyl chloride in the reaction mixture lowered the yield of the sulfinic acid. Accordingly, the reaction probably proceeds through a polar mechanism, in the manner proposed by Kharasch[2] for the carboxylation of 1,1-diphenylethylene by oxalyl chloride.

Two phases of the reaction could be distinguished by direct observation of the reaction mixture: On addition of thionyl chloride to an ether solution of a diarylethylene, a green color developed immediately, without any other signs of the reaction being perceptible. This color is probably due to the formation of a carbonium ion by the addition of thionyl chloride to the polarized double bond of the ethylene.[3] After a shorter or longer period, depending on the reactants used and on the reaction temperature, the second stage of the reaction becomes evident by the evolution of hydrochloric acid from the reaction mixture, which changes its color from green to yellow or brown. The end of this stage, as indicated by the slowing down of the gas evolution, coincides with the greatest attainable concentration of the 2,2-diarylethene-1-sulfinyl chloride in the reaction mixture. Any further delay in the working up of the reaction

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(1) S. Patai and F. Bergmann, THIS JOURNAL, **72**, 1034 (1950).

(2) M. S. Kharasch, *et al.*, *ibid.*, **64**, 333 (1942).

(3) A similar green color was observed on the addition of arsenious chloride to 1,1-diphenylethylene (S. Patai, *et al.*, *ibid.*, **72**, 923 (1950)) and also on the addition of stannic chloride to 1,1-diphenylethylene.