release by alkyl in the excited positive ion. Other physical measurements (study, *e.g.*, ref. 1), while tending to show a definite release effect by alkyl, have not unequivocally demonstrated the C–H hyperconjugative *order* of release.[4]

We suggest that at least part of the apparent contradiction between spectral and ionization potential data and rate data (for reactions in which there is a large demand for electron release in the transition state) may be explained by steric hindrance to solvation. This effect has been invoked by C. C. Price to account for reactivity orders in the saponification of *m*- and *p*-substituted alkyl benzoates.[7a,b] Price also suggested this factor may explain the similar rates of bromination of *t*-butyl- and neopentylbenzene.[11c] In the S_N1 reaction of benzhydryl chlorides,[8] solvation of the intermediate "ion" at the partially positive sites in the neighborhood of the alkyl group would be hindered more by *t*-Bu than Me and this solvation factor should contribute to increasing E_A *and* $\Delta S^{\ddagger}$ values in the order Me < *t*-Bu (compare Table II). The rate data of Baddeley[9] can be accounted for by either steric inhibition to C–H hyperconjugation or solvation. The significant $\Delta S^{\ddagger}$ changes are consistent with the latter. Arnold's *k* data on similar systems[10] fit either explanation, but there is no clear trend in E_A and $\Delta S^{\ddagger}$. The solvation factor also could play a role in the rate differences found in the bromination of C_6H_5R[11,12] and $C_6H_5CH_2R$.[11]

TABLE II

HYDROLYSIS OF *p*-$RC_6H_4CHCl\phi$ IN 80% AQUEOUS ACETONE[8]

R =	H	Me	Et	*i*-Pr	*t*-Bu
$10^6\ k_1$ (0°)	2.82	83.5	62.6	46.95	35.9
E_A (kcal.)	21.0	18.9	19.4	19.8	20.05
$\Delta S^{\ddagger}$	−8.9	−9.8	−8.6	−7.7	−5.6

In light absorption, excitation occurs too rapidly to allow reorientation of solvent molecules.[13] Solvation of the ground state of the neutral molecules of Table I should be important only around the functional group and hence play a very minor role in determining differences in excitation energy. In the conjugate acids, appreciable positive charge is relayed to the ring, hence steric hindrance of solvation may contribute to the larger spread in λ_{max} values.

The evidence presented indicates other modes of interaction, particularly C–C hyperconjugation, or perhaps induction and internal dispersion forces,[14] may be more important than C–H hyperconjugation even when alkyl is attached to an electron demanding system.

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[4] Changes in the low intensity B-band spectra (excitation to homopolar forms) of alkylbenzenes attributed to a C–H hyperconjugative order of electron release (F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Reviews*, **41**, 273 (1947)) have been given a different interpretation by several authors.[2,5,6]

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[CONTRIBUTION FROM COTTON FIBER SECTION, U. S. DEPT. OF AGRICULTURE, SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

The Effect of Aqueous Hydrochloric Acid on the Cotton Cellulose III Lattice and Its Implications Concerning the Determinations of Crystallinity and Leveling-off Degree of Polymerization[2]

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RECEIVED MARCH 1, 1954

Cotton cellulose III, prepared by treating cotton in anhydrous ethylamine and decomposing the resulting amine–cellulose complex by removing the amine by evaporation, was subjected to the action of hydochloric acid of various concentrations at high and low temperatures. X-Ray diffraction patterns of the resulting hydrocelluloses showed that reversion of cotton cellulose III to cellulose I, which takes place readily in boiling water, is almost completely prevented upon heating in acid when the concentration is 6 *N*, and takes place only to a slight and essentially equal extent in hot 4 and 2 *N* acid. Very dilute acid (0.1 *N*) does not prevent reversion. These observations indicate that two methods employing hot strong acid for evaluating fine-structure characteristics of cellulosic materials may be applied with reasonable confidence to cotton cellulose III. Some interesting results of application of hot hydrochloric acid to an experimental material containing both cellulose I and cellulose III are described.

Introduction

Davis and co-workers[3] have shown by X-ray diffraction studies that when cellulose is treated with anhydrous ethylamine, an ethylamine–cellulose addition compound is formed. Removal of the amine by evaporation causes a decomposition of the amine–cellulose complex, and as Segal and co-workers[4] have shown using cotton cellulose and ethylamine, this gives the cellulose III crystal modification. Segal and co-workers[4] found that immersion of

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(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at the Regional Conclave of the American Chemical Society, New Orleans, La., December 10–12, 1953.

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cotton cellulose III in boiling water for two hours caused a reversion of its lattice to that of cellulose I. They also showed that this reversion is influenced by temperature, being only slight at 26 to 55°, but quite evident at 80° and apparently complete at 100°.

Consideration of these findings has suggested that "acid-hydrolysis crystallinity" and "leveling-off D.P.," two of the techniques currently in use at this Laboratory for evaluating changes in cellulose fine structure, might be seriously misleading if applied to cellulose III. These methods employ hot aqueous acid as the principal reagent and this, like hot water, could conceivably convert cellulose III to cellulose I. "Acid-hydrolysis crystallinity" is based on the kinetics of cellulose hydrolysis at 100° in 6 N hydrochloric acid.[5,6] "Leveling-off D.P.", abbreviated L.O.D.P., employs 2.5 N hydrochloric acid at 80° to produce the hydrocellulose whose degree of polymerization is used as an index of crystallite length.[7] The larger unit cell dimensions and greater interplanar spacings of cellulose III indicate that the crystallite is of a more expanded structure than that of native cellulose I. This and the rotation of the glucose rings in the crystallite suggest that cellulose III should be more reactive than cellulose I. If cellulose III is attacked by hot acid more rapidly than cellulose I and at the same time is converted to the more compact and less reactive cellulose I, then obviously data obtained by application of these methods to cellulose III would be ambiguous: the rate of hydrolysis would be affected by the rate of reversion. It became important, accordingly, to examine the effect of hot aqueous acid on the cotton cellulose III lattice. The present paper reports the results of these studies.

Experimental

Two types of sample material were used. Most of the experiments were performed on a kiered 20/1 cotton yarn. Cotton cellulose III was prepared from it in the manner described by Segal[4]: the yarn was immersed for 4 hours at ice-bath temperature in anhydrous ethylamine which was then removed by distillation. Transformation of cellulose I to cellulose III was confirmed by X-ray examination.

A few experiments were performed on a quantity of cotton card sliver that was treated with ethylamine and subsequently extracted with hexane in a pilot plant operation. The X-ray tracing of this material indicated extensive decrystallization of the cellulose I and suggested the presence of some cellulose III.

Radial tracings of X-ray diffraction intensities were obtained with a recording X-ray diffraction spectrometer equipped with Soller slits and a Geiger-Müller counter tube in the manner previously described by Segal and co-workers.[8] All fibrous samples were ground in a Wiley mill to pass a 20-mesh sieve, except the powdery hydrocelluloses which did not require grinding.

The degree of polymerization was determined viscometrically by methods in use at this Laboratory.[9-11] The intrinsic viscosity of the 0.5 g./dl. dispersion in cuprammonium hydroxide, given by the formula

$$[\eta] = 1.70\,(\eta_{sp})^{0.694} - 0.160$$

was multiplied by the factor 260 to obtain the degree of polymerization.

In general, the hydrocelluloses were prepared by placing a weighed quantity (usually 2 g.) of cotton in a 250-ml. glass-stoppered erlenmeyer flask, suspended in a constant-temperature bath. Acid of the desired concentration was preheated to bath temperature and added to the sample, which was then shaken or stirred to ensure complete "wetting-out." At the end of 2 hours (or, in several instances, the appropriate longer times) the sample was separated from the acid by filtration on a medium-porosity, sintered-glass filtering crucible, then washed with very dilute ammonium hydroxide, and finally with 4 or 5 changes of hot distilled water. In some experiments the hydrocelluloses were washed with acetone after the last water wash to prevent hornification. The residue was dried in a vacuum oven at 60°. When treating samples with 6 N hydrochloric acid at 100°, a partial exchange of acid solution was effected after about an hour by withdrawing some of the solution through a fritted-glass filter stick and replacing it with fresh, hot acid. This was necessary because the soluble products of cellulose hydrolysis (presumably principally glucose) undergo further reaction in the presence of hot, strong acid giving insoluble, dark brown substances which contaminate the hydrocellulose.[5,6]

Results and Discussion

Effect of Strong Acid at 100°.—A portion of a sample of cotton yarn that had been substantially converted to cellulose III was treated with 6 N hydrochloric acid at 100° for 2 hours. X-Ray spectrometer tracings of the material before and after hydrolysis are shown in the top and bottom curves, respectively, of Fig. 1. It may be seen that after hydrolysis the diffraction peaks of the cellulose III pattern (indicated in Fig. 1 at 2θ = 11.4 and 20.4°) have become much sharper and more intense, while the residual, weak diffraction peaks of cellulose I, found in the original material, at approximately 2θ = 14, 16 and 22° have almost completely disappeared. This result was unexpected inasmuch as boiling water *alone* has been shown to cause a restoration of cellulose I.[4]

The disappearance of the cellulose I peak under such strong hydrolyzing conditions cannot be explained at present. Consideration of the lattice parameters of cellulose III, given in Table I, would lead one to expect the opposite effect. The 25% greater interplanar distance between the 101 planes and the more skewed unit cell of the cellulose III lattice (beta angle = 58°) suggests the likelihood

TABLE I

LATTICE PARAMETERS OF CELLULOSES I AND III

Interplanar spacings (Å.)					
Cellulose I[a]			Cellulose III[b]		
101	10$\bar{1}$	002	101	10$\bar{1}$	002
6.05	5.45	3.92	7.55	4.30	4.30
Unit cell dimensions (Å.)					
a	b	c	a	b	c
8.35	10.3	7.95	7.87	10.31	10.13
Beta angle (degrees)					
84			58		

[a] K. H. Meyer, "Natural and Synthetic High Polymers," Second Ed., Interscience Publishers, Inc., New York, N. Y., 1950, p. 299; S. T. Gross and G. L. Clark, *Z. Krist.*, **A99**, 357 (1938). [b] A. J. Barry, F. C. Peterson and A. J. King, THIS JOURNAL, **58**, 333 (1936).

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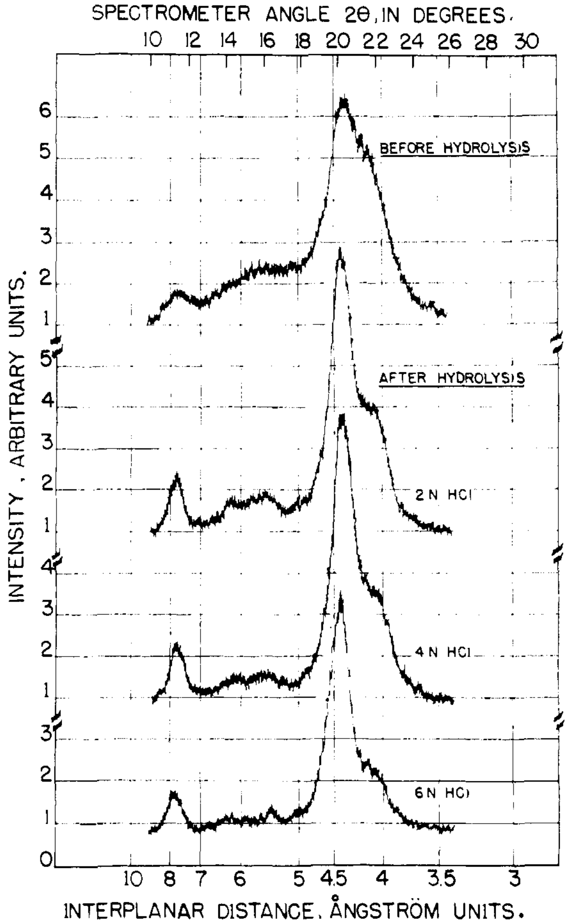

Fig. 1.—Radial X-ray spectrometer tracings showing effect of drastic hydrolysis (2 hours in strong hydrochloric acid at 100°) on cotton cellulose III.

that it would be more extensively penetrated by aqueous acid, and consequently should be more rapidly hydrolyzed than the compact cellulose I lattice.

Since hydrolysis with 6 *N* hydrochloric acid is an extremely drastic treatment, somewhat more moderate conditions were tried, using 2 and 4 *N* hydrochloric acid. X-Ray spectrometer tracings made from the resulting hydrocelluloses are given in Fig. 1. A progressive decrease in intensity of the residual cellulose I peaks (at 2θ = 14.7, 16.3 and 22.6°) accompanies the increase in acid strength. The residue weight remaining after hydrolysis (Table II) indicates the relative severity of treatment. In view of what has been said before, it is surprising that the ratio of cellulose III to cellulose I (on the basis of the X-ray patterns) has apparently actually increased as more material was hydrolyzed to soluble compounds.

The D. P. values given in Table II are noteworthy since they are essentially constant within the error of measurement (approximately ±5% for D. P. determined viscometrically) even though weight loss has ranged from 10 to 31%. They agree reasonably well with the L.O.D.P. value of 113 obtained under the conditions routinely employed for this determination. These data confirm previous observations that the D. P. of cotton cellulose levels off after moderate weight loss by acid hydrolysis and remains essentially constant during extensive weight loss. The slightly lower D.P. values of the samples dried from acetone might result from occluded acetone, which is not removed by oven-drying as completely as is water. Occluded acetone would give a false cellulose correction factor in the viscosity measurement.

TABLE II

RESIDUE WEIGHT AND D.P. OF COTTON CELLULOSE III TREATED FOR 2 HOURS AT 100° WITH HYDROCHLORIC ACID OF DIFFERENT CONCENTRATIONS

	Residue,[a] %		Degree of polymerization	
Acid concn., *N*	Dried from acetone	Dried from water	Dried from acetone	Dried from water
2	90	90	104	116
4	81	..	101	..
6	69	65	94	112

[a] Per cent. remaining is based on dry weight of cellulose in the original sample.

Application to Experimental Material.—An opportunity to apply these findings to the evaluation of experimental material was furnished by the card sliver treated in the pilot plant operation. Portions of the sample were treated with hot aqueous acid of 0.1, 2 and 6 *N* concentrations, as well as with boiling water. Figure 2 presents the X-ray tracings obtained from the materials treated in these experiments. The bottom curve is the tracing of the material before treatment with water or acid. The curve representing material after drastic hydrolysis in 6 *N* hydrochloric acid shows the characteristic peaks of cellulose III at 2θ = 11.4 and 20.4°, thus confirming the presence of cellulose III in the original material. In the X-ray spectrometer tracing of the untreated control the poor resolution of the diffraction peaks, resulting from the low degree of crystallinity, made uncertain the detection of cellulose III. Treatment with 2 *N* hydrochloric acid gave an X-ray pattern of good resolution and high peak intensities; the characteristic peaks of cellulose III at 2θ = 11.4 and 20.4° are clearly defined, while those of cellulose I, well resolved but of a slightly lower intensity, are noted at 2θ = 14.7, 16.3 and 22.6°. In comparing the curves for 6 and 2 *N* acid, it may be noted that although the over-all intensity of the curve for 6 *N* acid is somewhat reduced, it is still obvious that the ratio of cellulose III to cellulose I is greater in this material than in the material resulting from treatment with 2 *N* acid.

Treatment with dilute acid (0.1 *N*) at 100° for 2 hours resulted in a tracing of fairly high crystallinity that was predominantly that of cellulose I with only a trace of cellulose III present. Immersion in boiling water for 2 hours caused complete reversion to cellulose I, accompanied by recrystallization to a marked degree.

Microscopical Appearance of Residues.—Microscopical examination of the hydrocelluloses after extensive degradation disclosed that removal of material by hydrolysis is far from being a uniform process. Photomicrographs of hydrocelluloses re-

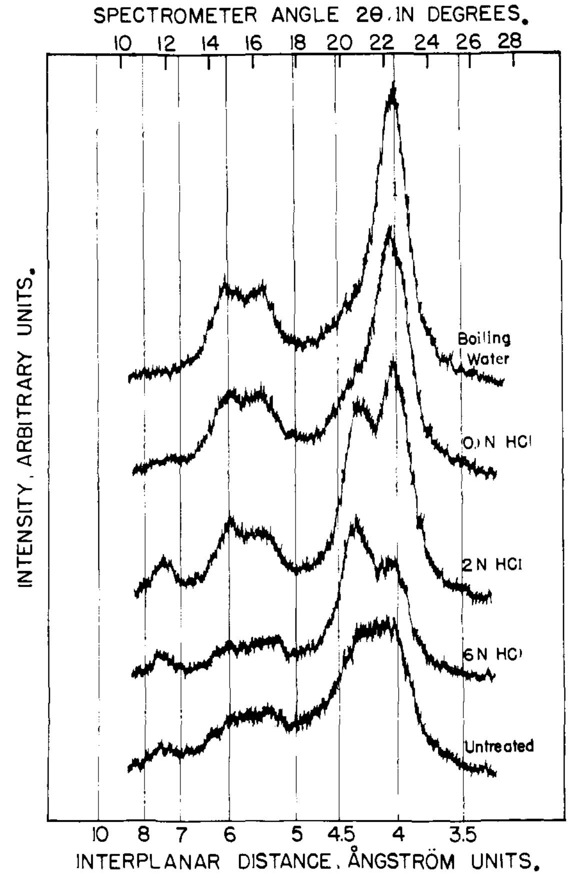

Fig. 2.—Radial X-ray spectrometer tracings showing the effect on a sample containing both cellulose I and cellulose III of treatment at 100° for 2 hours with various strengths of acid and with water.

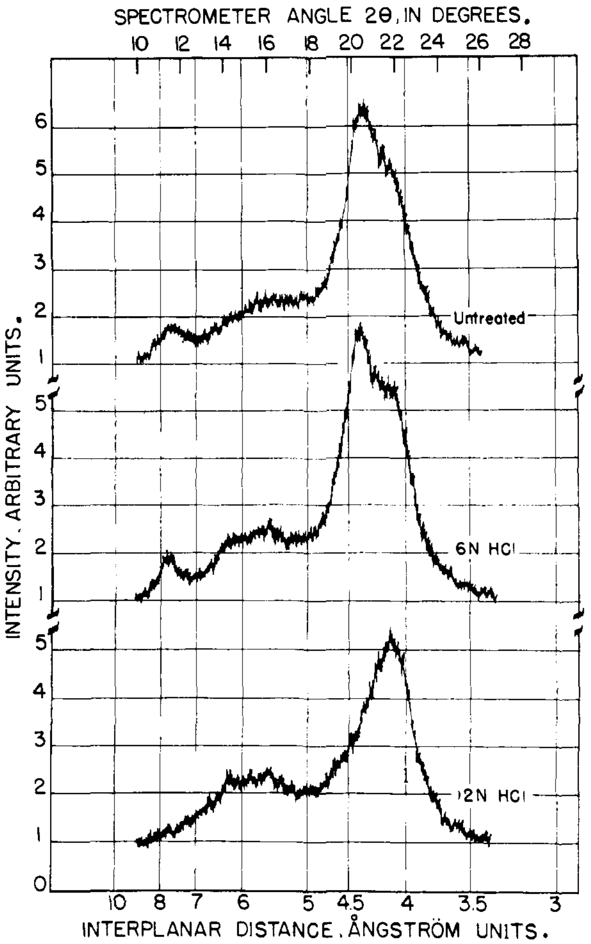

Fig. 3.—Radial X-ray spectrometer tracings of hydrocelluloses prepared from cotton cellulose III by immersion for 2 hours at room temperature in 6 and 12 *N* hydrochloric acid.

maining after treatment of cotton cellulose III with 2 *N* hydrochloric acid show fairly large easily recognizable, fiber fragments. Much smaller fragments, still identifiable as segments of fibers, remain after treatment with 6 *N* hydrochloric acid. Although high weight losses take place during hydrolysis, large sections of the fibers still retain their morphological structure. It is quite possible that these sections are merely the framework of the original fiber, and consist of the more resistant portions which remain after acid attack has dissolved away the more easily hydrolyzable portions. Such details as these, however, are below the resolving power of the optical microscope.

Effect of Strong Acid at Room Temperature.—Since it had been found previously that water at room temperature produced only very slight reversion to cellulose I the effect of strong acid at room temperature was also investigated. Results of the X-ray examination of samples of cotton cellulose III allowed to stand in 6 and 12 *N* hydrochloric acid for 2 hours are shown in Fig. 3, while residue weight and D.P. data are given in Table III. The data show that, although 6 *N* acid hydrolyzed only 1% of the sample, the D.P. was reduced from the original value of 4521 to 697, indicating extensive degradation. Treatment with 12 *N* hydrochloric acid induced marked swelling of the fibers with solution of part of the cellulose which could be reprecipitated upon dilution. The undissolved portion was found to have a D.P. of 189, even though approximately 31% of the material had dissolved. The fact that this D.P. is about 70% greater than the leveling-off D.P. of 113 is not a contradiction of the previous statements as to the constancy of this parameter but is an indication of the great changes brought about in the fine structure by the strong swelling induced by 12 *N* acid.

TABLE III

RESIDUE WEIGHT AND D.P. DATA FOR COTTON CELLULOSE III TREATED WITH STRONG HYDROCHLORIC ACID AT ROOM TEMPERATURE FOR 2 HOURS

Acid concn., *N*	Residue, %	Degree of polymerization
None	100	4521
6	99	697
12	*ca.* 69	189

A state of high disorder is indicated by the X-ray pattern since the crystalline diffraction is much reduced. The two broad diffraction bands observed correspond to cellulose I; all traces of the cellulose III pattern have disappeared.

When the cotton card sliver with mixed lattice types was treated with 6 *N* acid at room temperature (25°) for 25 hours and at 40° for 4 hours, the results obtained were similar to those described for treatment at 100°. Figure 4 shows X-ray spectrometer curves for the untreated control and for samples treated at 100° for 2 hours, at 40° for 4 hours, and at 25° for 25 hours. Except for a greater over-all intensity, the curves for material treated at 40° and 25° are very similar to the curve for material treated at 100°. All three show mixed patterns with considerable cellulose III. From the similarity of these curves it may be concluded that the observed effects are more dependent on acid concentration than on temperature.

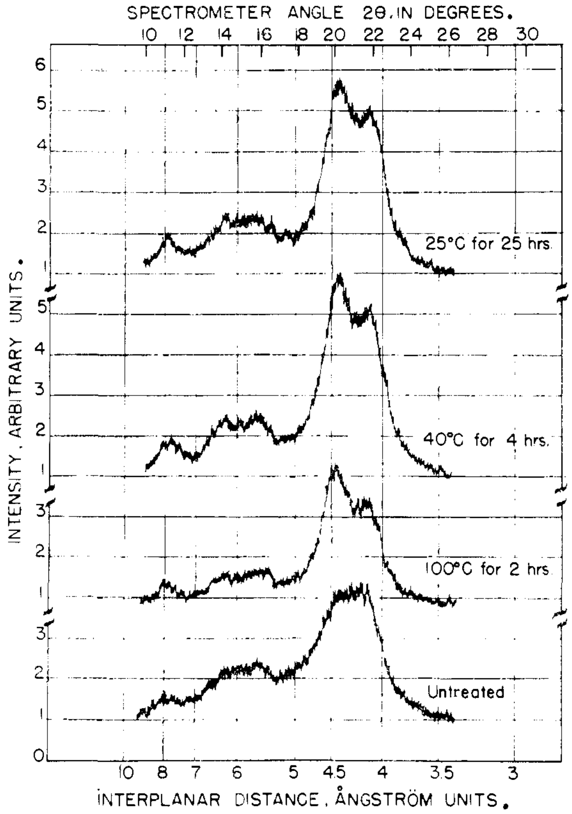

Fig. 4.—Radial X-ray spectrometer tracings showing the effect of hydrolysis of a sample containing cellulose I and III with 6 *N* hydrochloric acid at different temperatures for different periods.

Conclusions

These experiments show (1) that aqueous hydrochloric acid of 6 *N* concentration at 100° almost completely blocks reversion of cotton cellulose III to cellulose I, in contrast to the complete reversion brought about by boiling water; (2) that hydrochloric acid of somewhat lower concentrations (4 and 2 *N*) is slightly less effective in preventing reversion, but still yields hydrocelluloses containing predominantly the cellulose III lattice; and (3) that very dilute hydrochloric acid (0.1 *N*) is essentially without effect in preventing reversion to cellulose I.

Since the acid used in both the acid-hydrolysis crystallinity method and the L.O.D.P. determination is of such strength as to almost completely prevent reversion of lattice type, this effect does not enter into considerations of the hydrolysis rates of crystalline celluloses. The results of these analytical methods, therefore, may be considered valid in assessing the fine structure of cellulosic materials containing the cellulose III lattice.

The mechanism whereby strong hydrochloric acid prevents reversion of cotton cellulose III to cellulose I is unknown at present.

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