The Photochemistry of Cellulose. Effects of Water Vapor and Oxygen in the Far and Near Ultraviolet Regions

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In a current study of the photochemistry of cellulose it was observed that water vapor strongly inhibits photochemical changes in cellulose in the far ultraviolet at 254 millimicrons. Very dry cotton or wood celluloses were found to undergo greater changes in color, cuprammonium degree of polymerization and alpha cellulose than the same celluloses with normal moisture content. This result indicates that at least some of the water molecules are held by cellulose in a fundamental chemical combination, as contrasted with physical phenomena, such as condensation.

It was also observed that gaseous oxygen has no effect upon the rate of change in the far ultraviolet. These results are in strong contrast with those observed by the writers[1a] for the near ultraviolet, and with those observed by Stillings and Van Nostrand[2] in heterogeneous ultraviolet, and permit some new theories regarding the photochemical processes of the cellulose chain molecule.

Experimental

Methods of Analysis.—Values for alpha cellulose and cuprammonium degree of polymerization of the celluloses were determined before, and within one to four hours after, irradiation, using standard methods.[3]

The degree of polymerization was calculated from viscosity, using the expression derived by Battista,[4] DP = 2160 [log (relative viscosity +1) − 0.267]. The values for DP, plotted against log (time of flow), give an almost straight line from DP = 50 to DP = 3000. Cuprammonium dispersions, 0.50% by weight in cellulose, exclusive of other substances present, were used for measurement. The writers use the concept of cuprammonium DP as a convenient comparison of extent of cellulose change at various levels, rather than as fundamental constants capable of rigorous proof.

Diffuse reflectance of the sheets was measured using a Beckman UV spectrophotometer, standardized against freshly smoked magnesium oxide.

Samples Studied.—Widely differing types of cellulose, derived from cotton and wood, in the form of specially made papers, were studied. The use of cellulose in sheet form permitted adequate temperature control during irradiation, and allowed accurate measurement of reflectance.

The papers were made in the paper mill at the National Bureau of Standards, and are described in Table I, in terms of origins of the fibers, added materials, and chemical characteristics. Further details are given elsewhere,[5]

the cellulose sample number corresponding to that of the original paper.

TABLE I

CHARACTERISTICS OF CELLULOSES STUDIED

Cellulose	Fiber origin, and other sheet components	Alpha cellulose content, %	Cuprammonium degree of polymerization (DP)
1372	Unused, unbleached cotton from cloth. No alum, rosin or clay	96.6	1660
1178	Unused, bleached cotton from cloth. Alum and clay	92.4	695
1193	Used, bleached cotton from cloth. Alum and clay	87.7	575
1380	Purified sulfite wood pulp. No rosin, alum or clay. Known commercially as alpha pulp	91.8	1195
885	Ordinary sulfite wood pulp. No rosin, alum or clay. No connection with No. 1380	77.2	645

Apparatus.—The apparatus consisted of special equipment, some of which has been previously described,[1,6] in which celluloses in paper sheet form were irradiated, with several light sources, without heat effects, in atmospheres of air or nitrogen of various moisture contents. Air was passed over anhydrous magnesium perchlorate, or over saturated solutions of lithium chloride or sodium bromide, producing relative humidities of 0.01,[6] 11 and 56%,[7] respectively. Nitrogen was passed over hot copper at 500° to remove oxygen, and was either dried by anhydrous magnesium perchlorate or moistened by alkaline pyrogallol solution. The desired atmospheres were continuously circulated at 5 liters/min. through these systems one and one-half hours before, and during, the irradiation. An electrically heated copper mirror,[8] and a weighed amount of magnesium perchlorate, present in the gas stream during irradiation, served as checks on oxygen and moisture contents when desirable.

During irradiation in the near ultraviolet, usually 92 hours, the sheets were held within 1–2° of 30° by sucking them against a thermostated metal backing, and by elimi-

(1) Now at Western Regional Research Laboratory, United States Department of Agriculture, Albany, California.

(1a) Herbert F. Launer and W. K. Wilson, *J. Research Natl. Bur. Standards*, **30**, 55 (Jan. 1943), (RP 1517).

(2) R. A. Stillings and R. J. Van Nostrand, THIS JOURNAL, **66**, 753 (1944).

(3) The methods were essentially those of the Technical Association of the Pulp and Paper Industry, 370 Lexington Ave., New York, N. Y. A minor difference lay in the use of 240 instead of 200 g. of ammonia per liter, in the cuprammonium test.

(4) O. A. Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351 (1944).

(5) Merle B. Shaw and Martin J. O'Leary, *et al.*, *J. Research Natl. Bur. Standards*, **21**, 671 (1938); **11**, 7 (1933), (RP 1149), (RP 574).

(6) Herbert F. Launer, *J. Research Natl. Bur. Standards*, **24**, 567 (1940), RP 1300.

(7) Institute of Paper Chemistry, Instrumentation Report No. 40 (Feb. 15, 1945).

(8) This consisted of pure sheet copper folded around a nichrome heater, fed by a Variac (a variable transformer), and included a thermojunction in contact with the copper. Oxygen concentration in a gas stream was determined by measuring the temperature at which the interference bluishness of the oxide was observable in five minutes, the instrument being standardized against gases of known oxygen content. The device appeared useful down to concentrations of oxygen near 0.01%; below that, the hydrogen, used to regenerate the copper, was apparently dissolved by the latter in sufficient amounts to render oxide formation erratic. This and other complications, such as the rate being dependent upon the nature of the carrier gas, discouraged further development of the device.

nating the infrared from a Fadeometer carbon arc, used as the light source, with a liquid filter, which also limited the spectrum to the region 330 to 750 millimicrons,[6] with the principal maximum at 388 and a minor one at 359 millimicrons.

For irradiation in the far ultraviolet, usually one-half hour, a General Electric 15-watt Germicidal mercury vapor lamp, operated at regulated 115 volts, was used. This type of lamp is a very convenient source of almost monochromatic ultraviolet at 254 millimicrons, thus avoiding the uncertainties introduced by other wave lengths. The energy output (manufacturers' data) consists of 55% ultraviolet, 2% visible and 43% heat, and of the ultraviolet, 97% is at 254 millimicrons. Since this type of lamp has a very low intensity it was found convenient to wrap the sheets tightly on its glass surface for irradiation. The lamp, which is a tube 15″ × 1″, was then slipped into a glass tube of 2-mm. greater diameter, maintained at 30°, so that the gases passed between the two tubes. The rubber stopper carrying the four lamp leads out of the system was located at the gas-exit end, so that the apparatus, from the conditioning tubes to the paper, was all-glass. Because of the small space between the tubes, the gases previously brought to 30°, streamed past the sheets at high velocity, thus removing considerable heat. By measurement with a thermojunction imbedded in a sheet of paper by a technique previously described,[6] the temperature inside the sheet during irradiation was found to be 40°.

The change in intensity of the lamp with use, and the uniformity of intensity along the central 12-inch portion was studied with light-sensitive paper.[9] The variation in uniformity of four 3-in. portions was found to be less than 3%.

Results

The effects of gases upon the rates of photochemical change in cellulose varied greatly with the spectral energy distribution of the sources used and are presented accordingly. The types of cellulose, test methods, apparatus, gases, and significance of the terms used to differentiate the ultraviolet regions are described in the preceding sections.

Effects of Water Vapor and Oxygen in the Far Ultraviolet.—The effects of water vapor and oxygen in the far ultraviolet, shown in Table II, differed radically from any reported heretofore.[1,2] The effect of water vapor appeared to be decisive whereas that of oxygen, negligible.

TABLE II

EFFECT OF WATER VAPOR AND OXYGEN DURING IRRADIATION IN THE *Far* ULTRAVIOLET[a]

Decrease[b] in alpha cellulose percentage and DP (in parentheses) during irradiation in various atmospheres.

Cellulose no. and type	Moist air	Dry air	Moist N₂	Dry N₂
1372 Cotton	1.0 (325)	5.0 (415)	1.3 (325)	5.7 (440)
1380 Wood	2.3 (200)	6.4 (260)	2.3 (225)	7.0 (260)
885 Wood	2.5 (50)	6.2 (65)	2.4	4.5
1178 Cotton	2.3 (80)	6.8 (85)	4.3	6.6

[a] Irradiation for one-half hour at 254 millimicrons.
[b] Initial values of alpha cellulose and DP are given in Table I.

(9) Herbert F. Launer, *J. Research Natl. Bur. Standards*, **41**, 169 (1948), RP 1916.

For all types of celluloses studies, the drop in alpha cellulose was considerably greater in dry air and dry nitrogen, than in moist air and moist nitrogen, but practically the same in dry air and dry nitrogen or in moist air and moist nitrogen. These results are in agreement with those for DP when measured: for materials of low DP the test is insensitive and was not applied in all cases.

This effect of water vapor was not the result of absorption of ultraviolet by water vapor at this wave length. It can be calculated that even a 1-mm. thickness of liquid water will absorb only 0.1% at 254 millimicrons.[10]

The effect of water vapor was studied for intermediate values of relative humidity and for longer periods of irradiation, using cellulose 1372. The curves, given in Fig. 1, show that intermediate moisture content of the atmosphere during irradiation had an intermediate effect on the rate of decrease of alpha cellulose and DP. The curves in Fig. 1 also show that the effect of water vapor upon the rate persists until the cellulose has undergone considerable change (alpha cellulose = 85%, DP = 1150), after which the effect disappears, as seen from the fact that the curves tend to approach each other or become parallel, showing
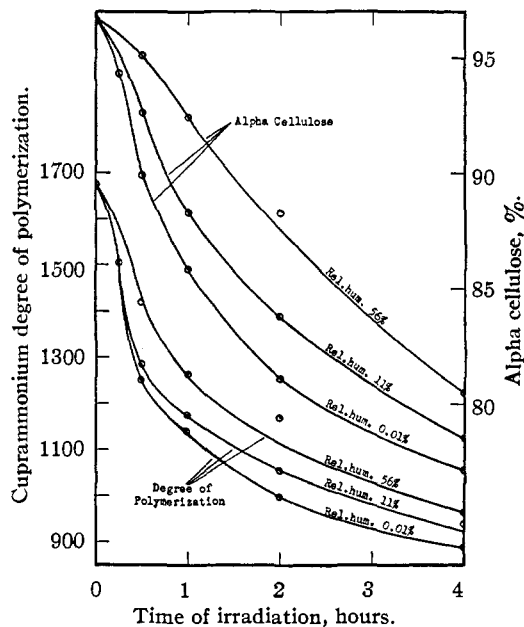

Fig. 1.—Effect of water vapor upon the rate of decrease of alpha cellulose percentage and degree of polymerization of cotton cellulose 1372 during irradiation in the far ultraviolet. The concentration of water vapor in each atmosphere is given in terms of per cent. relative humidity inscribed on each curve. Although the gases were at 30° the cellulose was at 40°. Using typical desorption isotherms, the calculated values for moisture content of the cellulose under the three conditions was 5.0, 2.0 and 0.002%.

(10) L. H. Dawson and E. O. Hulburt, *J. Optical Soc. Am.*, **24**, 175 (1934).

that the slopes and, therefore, the rates, reach common values.

The effect of oxygen was subjected to a similar detailed study for periods up to two hours of irradiation but no difference could be found between the rates in dry air and dry nitrogen. Experiments in pure, dry oxygen showed that DP, but not alpha cellulose values, were somewhat lower, by some 100 glucose units, after irradiation in pure oxygen than in air. Considering the small effect of the enormous differences in concentration, the role of oxygen, during irradiation in the far ultraviolet, can only be a minor one in the pure gas, and probably negligible in air.

The chemical results were borne out by reflectance measurements. The far ultraviolet was found to cause noticeable yellowing, the degree depending mainly upon water-vapor content. The yellowing was greater for dry air and dry nitrogen than for moist air and moist nitrogen. The reflectance curves over the region 360 to 500 millimicrons are shown in Fig. 2 for the typical example of cellulose 1380. The somewhat greater yellowing in dry and moist nitrogen than in dry and moist air is not believed to be due to an inhibitory effect of oxygen, but rather to a slight bleaching effect of ozone, the possibility of which must be considered when using lamps of this type in the presence

of oxygen. Although the chemical results show no effect of ozone (with the possible exception of the results in pure oxygen, for which ozone might be held responsible), ozone being present only in the oxygen-containing atmospheres, it is not unreasonable to assume partial oxidation of the more readily oxidizable color bodies. Even so, such bleaching was not enough to reverse the curves for moist nitrogen and dry air.

The yellowing caused by far ultraviolet is of interest when compared to the effect of near ultraviolet, which the writers found bleaches cellulose.[1] It was shown that yellowing during irradiation in the near ultraviolet is the result of a thermal reaction which can be eliminated by control of cellulose temperatures.

It is not possible at present to state definitely that yellowing during irradiation in the far ultraviolet is a true photochemical reaction, although interior sheet temperatures during irradiation did not exceed 40°. Experiments were also conducted at 10, 20 and 30°, but no evidence of a temperature coefficient of yellowing was found. On the other hand, previously irradiated sheets yellowed extensively during storage in the dark, showing that yellowing does occur in the absence of light and must, therefore, be a thermal reaction. Such yellowing may, of course, be the result of another process. It is noteworthy that the yellowing during irradiation does not appear to be influenced by oxygen.

Effects of Water Vapor and Oxygen in the Near Ultraviolet.—The results for this region of the spectrum, given in Table III, confirm the
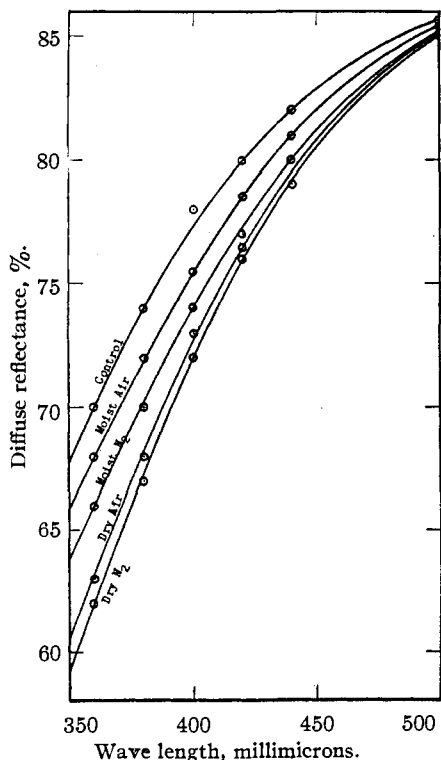

Fig. 2.—Effect of atmosphere upon the yellowing of wood cellulose no. 1380 during irradiation in the far ultraviolet for half an hour. The reflectances of sheets irradiated in the atmospheres as inscribed upon the curves are compared with the unexposed control.

TABLE III

EFFECT OF OXYGEN AND WATER VAPOR DURING IRRADIATION IN THE Near ULTRAVIOLET[a]

Decreases in alpha cellulose percentage and DP (in parentheses) during irradiation in various atmospheres.

Cellulose no. and type	Moist air	Dry air	Moist N₂	Dry N₂
1372	0.4	1.1	0.0	0.2
Cotton	(445)	(230)	(130)	(95)
1380	4.0	2.8	0.8	1.1
Wood	(385)	(250)	(115)	(120)
885	5.9	4.5	1.5	1.4
Wood	(110)	(55)	(50)	(40)
1178	1.2	3.3	0.0	0.3
Cotton	(65)	(20)	(0)	(0)
1193	6.1	9.6	4.0	2.8
Cotton	(75)	(75)	(0)	(0)

[a] Irradiation for ninety-two hours with carbon arc.

writers' previous findings[1] for the effects of oxygen and water vapor, and those of others[2] for oxygen. The drop in alpha cellulose and in DP are considerably greater in the presence of oxygen than in its absence, for the various types of cellulose. In the presence of oxygen, water vapor promotes certain reactions and hinders others: the drop in DP of all of the celluloses is usually definitely greater in the presence of water vapor than in its

absence, whereas the drop in alpha cellulose is greater in wood cellulose, and smaller in cotton cellulose, in the presence of water vapor, than in its absence. This confirms the previously found, more pronounced results[1] indicating a difference between wood and cotton celluloses. The results also illustrate that alpha cellulose and cuprammonium tests do not always coincide.

Discussion

The lack of effect of oxygen and the inhibitory effect of water vapor show that oxidation and hydrolysis, the expected reactions, do not play a predominant part in the photochemical reactions of cellulose in the far ultraviolet. In the near ultraviolet, however, these reactions do play a dominant role.[1] When a light source including both of these regions is used, it is reasonable to expect a mixture of effects. This may explain why Stillings and Van Nostrand,[2] using a G.E. quartz Uviarc, model UA 26A2, which has about equal output in the near, middle and far ultraviolet regions,[11] did not observe the effects peculiar to each region. Upon decreasing the oxygen content in steps from 100 to 0.002% (the latter being the oxygen content of their purified nitrogen) they observed considerable decreases in the rate of change of cellulose. This apparently corresponded to the near ultraviolet portion of their spectrum, whereas some or all of the changes that persisted in purified nitrogen corresponded to the far ultraviolet, in which oxygen is without effect.

The differing mechanisms are explainable upon the basis of bond energies. Both the $-C-C-$ and the $-O-C-$ bonds, with dissociation energies near 80 kcal.,[12] are dissociable by a far-ultraviolet photon, corresponding to 112 kcal., without aid. However, the near-ultraviolet photons, in the cyanogen-band group at 388 to 385 millimicrons, corresponding to 73 to 74 kcal., lack the energy for such dissociation, and the deficit must be supplied by the exothermic reaction with oxygen, whose partial pressure thus becomes important in determining the rate in the near ultraviolet. The photons in the considerably weaker cyanogen band at 359 to 358 millimicrons, corresponding to 79 kcal., may barely have enough energy to cause disruption without the help of oxygen, in agreement with the writers' previous results[1] at low concentrations of oxygen, using the same carbon arc source.

The inhibitory effect of water vapor in the far ultraviolet indicates that some water molecules are in a fundamental chemical combination with cellulose. Such a combination is strongly indicated by the high heat of sorption and other departures from simple physical phenomena, as discussed by Valko[13] and is assumed to consist in

bonds of $-H-O-H-$ between proximate $-OH$ groups along two or more molecular chains, producing a lateral, inter-chain "lacing," as discussed by Heuser.[14] These bonds are spontaneously formed, either at the expense of similar $-H-$ bonds, than which they are more stable, as shown by the free energy decrease of water-bond formation, $-\Delta F = 3200$ cal./mole,[15] or they may be formed in addition to the existing $-H-$ bonds with unsaturated $-OH$ groups.[16] In either case it could be expected that the introduction of H_2O molecules into the inter-chain spaces would result in decreased freedom of displacement for those C-atoms in the vicinity of a $-H-O-H-$ bond. Thus, when a far-ultraviolet photon is absorbed, the deformation and disruption of a given glucose unit may be rendered less likely when such bonds exist nearby. The effect of deformability within the cellulose macro-molecule upon photochemical change has been indicated by the results of Mason and Rosevear.[17]

This explanation of the inhibition of the photochemical reaction by water vapor would indicate that the initial disruption occurs in the vicinity of C-atoms 2 or 3, rather than at the glycosidic linkage. This would in turn furnish a reasonable explanation for the instability of previously irradiated cellulose, observed by the writers[1] and confirmed by Heuser and his co-workers, Stillings, Van Nostrand and Chamberlin.[2,18] If, for example, the bond between C-atoms 1 and 2 were disrupted, this would not necessarily cause immediate rupture of the cellulose chain, but C-atom 1, attached now to three electronegative groups, would become sensitive to future thermal oxidation, thus disrupting the chain.

The $-C-O-$ group is usually held responsible for the broad absorption band below 300 millimicrons, but such absorbed energy can migrate rapidly to another part of the molecule, as discussed by Frank and Teller.[19] Such transfer of absorbed energy to a more reactive group occurs even between discrete particles, as in photochemical sensitization.

It is of interest to note that the region of moisture content, 0 to 5%, for the results shown in Fig. 1, are essentially within the region found by Magne, Portas and Wakeham[20] to correspond to hydrogen-bonded water in cotton fibers.

Referring again to Fig. 1, it is of further interest to note that the first addition of water vapor to the dry cellulose has a smaller inhibitory effect upon

(11) L. B. Johnson and S. B. Webster, *Rev. Sci. Inst.*, **9**, 325 (1938).

(12) Kenneth S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

(13) E. I. Valko, "High Polymers V, Cellulose." Emil Ott, Ed., Interscience Publ. Inc., New York, p. 379.

(14) Emil Heuser, "Chemistry of Cellulose," Wiley and Sons, New York, 1944.

(15) Alfred J. Stamm and W. Karl Loughborough, *J. Phys. Chem.*, **39**, 121 (1935).

(16) S. M. Neale and W. A. Stringfellow, *Trans. Faraday Soc.*, **37**, 525 (1941).

(17) C. W. Mason and F. B. Rosevear, THIS JOURNAL, **61**, 2995 (1939).

(18) E. Heuser and George N. Chamberlin, *ibid.*, **68**, 80 (1946).

(19) James Frank and Edw. Teller, *J. Chem. Phys.*, **6**, 861 (1938).

(20) Frank C. Magne, H. J. Portas and Helmut Wakeham, THIS JOURNAL, **69**, 1896 (1947).

the chemical changes than the second addition of water vapor. This does not coincide with the known energy changes of hydration,[15] but a consideration of the molecular processes involved shows that no correlation is to be expected. When a photon is captured by dry, i. e., 0.002%-moisture, cellulose, corresponding to one water-molecule per three cellulose chains of some 1700 glucose units each, the probability that the capture and C–C-bond rupture will occur near a water-bridge is very small. Even if the moisture content were increased 100-fold to 0.2%, corresponding to 30 water-molecules per chain of 1700 glucose units, the probability of a photon rupturing an adjacent C–C-bond is still very small. Thus, the first increments of water cannot be expected to exert much inhibitory effect, and proportionality of effect cannot obtain until a sizable fraction of the glucose units are water-bonded.

The depolymerizing action of water vapor observed during the ninety-two hours of irradiation in the near ultraviolet is a slow reaction which probably occurs to a slight extent in the one-half hour of irradiation in the far-ultraviolet, and which would probably manifest itself upon extensive irradiation in the latter region. This may partially explain the fact that the curves in Fig. 1 approach each other for longer periods. Such an approach would, furthermore, be a result of progressive depolymerization, inasmuch as water bonding probably decreases as the chains shorten and start to lose their high-polymeric character.

The differing effects of water vapor during irradiation in the near ultraviolet upon the alpha cellulose values of wood and cotton celluloses, as seen from Table III, appear to arise from unknown differences between these two types of cellulose.

Finally, it is of interest to attempt a calculation of the quantum efficiency, that is, the frequency with which cellulose chains are ruptured by captured photons at 254 millimicrons.

At this wave length the lamp radiates 2.9 watts (manufacturers' data) or 3.7×10^{18} quanta/sec., over its arc length, 14 in. During one-half hour, one piece of paper, no. 1372, 3 in. wide, wrapped completely around the lamp, absorbs 1.4×10^{21} quanta, assuming practically no loss by transmission through the paper (0.08 mm. thickness). This amount of paper corresponds to 0.5 g. cellulose or 1.9×10^{21} glucose units. Since there are 1660 glucose units in an average chain (i. e., DP = 1660) of this cellulose, there are 1.1×10^{18} chains

before irradiation. From the expression derived by Sakurada and Okamura[21] relating change in DP to the number of scissions, s, per chain

$$\frac{\text{DP final}}{\text{DP initial}} = \frac{2}{s^2}(s - 1 + e^{-s})$$

and from the final DP $= 1245$, after irradiation, in dry air, it may be calculated that, on the average, 0.93 scission per chain molecule, or 1.0×10^{18} scissions occurred. Thus 1.4×10^3 quanta or photons were required per scission, or roughly every thousandth photon encountered conditions favorable for a rupture of a cellulose chain molecule. Actually, the number of successful encounters was probably larger than this, inasmuch as a disproportionately large number of scissions may have occurred in the leading layers of cellulose chains, without greatly affecting the cuprammonium DP values.

Summary

1. Water vapor was found to retard, and oxygen was found to be without effect upon, the decrease in alpha cellulose and the depolymerization, of cotton and wood celluloses, during irradiation in the far ultraviolet. The reverse of both of these effects was confirmed for the near ultraviolet.

2. The contrasting behavior of cellulose in the two spectral regions is ascribed to bond energies in the molecular chain, in relation to the photon energies involved. Far ultraviolet photons have sufficient energy to disrupt the bond, whereas most near ultraviolet photons do not, and require participation of oxygen.

3. The retarding action of water vapor in the far ultraviolet is ascribed to inter-chain water bridging with the hydroxyl group on carbon atoms 2 or 3, thus interfering with the freedom of displacement of the carbon atom. This supports the theory that a part of the moisture in cellulose is in a fundamental chemical combination.

4. It was found that only one photon out of 10^3, at 254 millimicrons, encounters conditions favorable for a rupture of the cellulose molecular chain.

(21) I. Sakurada and S. Okamura, Z. physik. Chem., **A187**, 289 (1940).