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**THE ACTION
OF ULTRAVIOLET LIGHT
ON CELLULOSE**

A thesis submitted by

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**in partial fulfillment of the re-
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TABLE OF CONTENTS

INTRODUCTION	1
HISTORICAL REVIEW	3
PHOTOLYSIS OF COMPOUNDS RELATED TO CELLULOSE	3
Alcohols	3
Carbohydrates	5
PHOTOLYSIS OF CELLULOSE AND ITS DERIVATIVES	7
Absorption Spectrum of Cellulose	7
Photochemical Threshold	8
Physical and Chemical Changes	10
Effect of Extraneous Materials	12
Atmosphere	12
Moisture	15
Catalysts	16
Kinetics and Mechanism of the Reaction	18
PRESENTATION OF THE PROBLEM	22
APPARATUS, MATERIALS, AND METHODS	23
IRRADIATION APPARATUS	23
MATERIALS FOR EXPOSURE	36
Cellulose	36
Beta-D-Glucose	37
Cellebiose	37
Nitrogen	37
Oxygen	38
OPTICAL MEASUREMENTS	38
Spectral Reflectance	38

TABLE OF CONTENTS

Ultraviolet Absorption	38
Specific Rotation	39
ANALYTICAL METHODS	39
PRESENTATION AND DISCUSSION OF DATA	41
STANDARDIZATION AND CALIBRATION	41
Efficiency of Mixing of Cellulose	41
Blank Determinations	42
Analysis of Known Gas Mixture	43
Rate of Sweeping Out of Chamber	45
Standard Conditions	45
SUMMARY OF EFFECTS NOTED	46
THE EFFECT OF OXYGEN	47
THE EFFECT OF WATER	55
COLOR CHANGES	57
KINETICS AND MECHANISM OF THE REACTION IN NITROGEN	60
Theoretical Considerations	60
Rate of Reaction	62
Decrease in Chain Length	62
Increase in Copper Number	69
Formation of Gaseous Products	69
Effect on Glucose and Cellobiose in Nitrogen	71
Instability of Exposed Samples	75

TABLE OF CONTENTS

Miscellaneous Analyses	78
Volatile Products	78
Ozone	79
Pentosans	79
Acidity	80
Ultraviolet Absorption of Cellulose	80
Reaction Mechanism	83
SUMMARY AND CONCLUSIONS	88
LITERATURE CITED	91

INTRODUCTION

The effect of ultraviolet light on cellulose is of great practical importance in the textile and paper fields and, for this reason, most of the investigations have been made from a more or less practical standpoint, the degradation being followed by strength changes and chemical tests of an empirical nature. While such an approach is satisfactory for some purposes, it is incapable of shedding much light on the mechanism of the reaction, especially when only a single property is evaluated.

It is unfortunate that differences in apparatus, materials, conditions, and methods make it impossible to correlate the results obtained by various observers, because in most cases the effect of these differences on the reactions has not been satisfactorily demonstrated. These differences are responsible, at least to some degree, for the many discrepancies found in the literature.

All investigators agree that, in the presence of oxygen, cellulose is degraded by ultraviolet light whether it be from the sun or an artificial source, such as a mercury vapor lamp. There is no general agreement, however, on whether or not any action takes place when oxygen is completely excluded. Little is known about the kinetics and almost nothing about the mechanism of the reaction.

According to the present concepts of the chemical structure of cellulose, there are two secondary alcohol groups, one primary alcohol group, and one glucosidic linkage per anhydroglucose unit. At one end of the cellulose molecule there is a hemiacetal group and at the other end there is an anhydroglucose unit having three secondary alcohol groups. Considerable work has been done on the photolysis of simple alcohols and the results are useful in predicting what might be expected from cellulose. Glucosidic linkages in the presence of water have been shown to be hydrolysed when irradiated by ultraviolet light, but their behavior in the absence of water is not known. The photolysis of hemiacetal groups has not been studied.

Although considerable work has been done on simple sugars the primary reaction has not been determined. Since the sugars were exposed in water solution the results do not necessarily apply to photolysis in the solid state. No investigations on cellobiose except in its methylated form have been reported.

It is clear that there is much to be learned about the effects of ultraviolet light on carbohydrates in general and cellulose in particular.

HISTORICAL REVIEW

PHOTOLYSIS OF COMPOUNDS RELATED TO CELLULOSE

A consideration of the effect of ultraviolet light on simple compounds structurally related to cellulose might be expected to give some indication of what happens to cellulose itself. In this connection alcohols and certain relevant carbohydrates will be considered.

Alcohols

Methyl and ethyl alcohols are transparent in the near ultraviolet but at about 200 mμ a continuous absorption band begins (1). In agreement with this Berthelot and Gaudeshon (2) found that alcohols are stable to ultraviolet light unless the wavelengths are shorter than about 200 mμ. Farkas and Hirschberg (3) showed that below 200 mμ methyl, ethyl, and propyl alcohols were decomposed according to the following equation.



Since the aldehyde formed by the primary reaction is decomposed, carbon monoxide and hydrocarbons may also be found among the reaction products. Isopropyl alcohol forms hydrogen and acetone as the primary products of decomposition.

Cantieni (4) found that, in the presence of molecular oxygen and ultraviolet light, a number of alcohols formed small

amounts of oxidizing substances, which were determined colorimetrically with titanium sulfate. Since his experiments ruled out the formation of hydrogen peroxide, he postulated the formation of a peroxide of the alcohol, $RO-O-OH$, which, under the influence of ultraviolet light, reacted with the alcohol to form the corresponding aldehyde. In the case of methyl alcohol traces of formaldehyde were found.

The rate of peroxide formation decreased with increasing water content. Using the full light of a mercury arc the rate of formation decreased with increasing number of carbon atoms in the normal alcohols but increased with increasing number of carbon atoms in the isoalcohols. Using only the ultraviolet radiation transmitted by a glass filter the rate of peroxide formation increased with increasing number of carbon atoms for both normal and isoalcohols. For example isocamyl alcohol formed the peroxide four times as fast as did methyl alcohol when using the unfiltered radiation. The ratio of the rate in unfiltered light to the rate in light filtered through a glass plate was 120 for methyl alcohol, 7.8 for butyl alcohol, and 2.3 for isobutyl alcohol.

Simple alcohols in the gaseous state or in water solution appear to be stable to ultraviolet light of wavelength greater than 200 mμ. In the presence of molecular

oxygen, however, they are subject to oxidation when irradiated by light of much longer wavelength. Cantieni did not give the spectral transmittance of the glass filter he used, but, unless made of a special glass, it probably did not transmit appreciably below 340 mμ.

Carbohydrates

Henri and Schou (5) found that, with specially purified glucose, an absorption continuum sets in at about 220 mμ. They found no absorption maximum in the neighborhood of 280 mμ as reported by earlier investigators and concluded that this maximum was due to impurities. Steurer (6) determined the absorption spectrum of pentamethylglucose, which showed the beginning of a continuum at about 280 mμ, and of octamethylcellobiose, which showed a considerably higher absorption extending to longer wavelengths.

Berthelot and Gaudichon (7) divided simple sugars into four classes according to their photochemical activity. The longest wavelength which affects ketoses is above 300 mμ; aldoses, 300 mμ; straight chain polyhydric alcohols, 250 mμ; and ring polyhydric alcohols, 200 mμ. They state that aldoses are practically unaffected by exposure to sunlight. Salley (8), however, found that aqueous solutions of mannitol showed no reaction when exposed to the complete

spectrum of a quartz mercury arc for 30 minutes in the presence of oxygen.

Various investigators (9) have reported the formation of acid, carbon monoxide, carbon dioxide, hydrogen, and methane as the products of the photolysis of glucose. The results are in poor agreement both quantitatively and qualitatively, probably due to differences in the purity of the glucose and the conditions of irradiation. It seems probable, in view of the complexity of the glucose molecule, that several primary photochemical reactions are possible when the complete radiation of a mercury vapor lamp is used. With wavelengths below 200 mμ, the energy is almost certainly sufficient to cause decomposition of any of the alcohol groups and also of the hemiacetal group.

Water solutions of glucosides are hydrolysed under the influence of ultraviolet light. Starch, sucrose, maltose, glycogen, and some other naturally occurring glucosides have been investigated. Apparently no attempt was made to determine the minimum energy necessary to split the glucosidic linkages in these compounds. Practically all of the studies were made in aqueous solutions, and no mechanism for the splitting of a glucosidic linkage in the absence of water has been proposed.

PHOTOLYSIS OF CELLULOSE AND ITS DERIVATIVES

Absorption Spectrum of Cellulose

The ultraviolet absorption spectrum of purified cellulose of high average molecular weight has not been reported. This seems strange in view of the numerous photochemical studies that have been made, but can probably be accounted for by the experimental difficulties involved. Oguri (10) and Hodgman (11) have reported determinations of the spectral transmission of cellophane, presumably commercial samples. Their results are in very poor agreement, perhaps due to impurities such as hemi-cellulose and plasticizers. Marchlewski and Skulmowski (12) investigated the absorption spectrum of hydrocellulose in 2 N sodium hydroxide. Freshly prepared solutions showed no selective absorption, indicating no free aldehyde groups. After standing three hours a band appeared with a maximum at 317 $m\mu$ which became more intense and shifted to 280 $m\mu$ at the end of 22 hours. The significance of the data is doubtful in view of the extremely complex changes which carbohydrates undergo in the presence of alkali.

Steurer (8) determined the absorption spectrum of methylcellulose before and after exposure to ultraviolet light. The absorption before exposure was appreciable at 340 $m\mu$ (the highest wavelength reported) and increased

continuously with decreasing wavelength. Methylcellulose absorbed considerably more than octamethylcellobiose, and exposure to ultraviolet light decreased the absorption somewhat over most of the range. The fact that the ultraviolet absorption of the methyl derivatives of glucose, cellobiose, cellobiose, and cellulose increased regularly in that order can be explained most simply by assuming that the number of glucosidic linkages is responsible for the differences. These linkages appear to absorb quite strongly in the ultraviolet and most of the absorption above 280 mμ is probably due to them. This at once suggests that they are the points at which the primary reaction occurs when cellulose is irradiated by ultraviolet light, especially in the longer wavelengths.

Photochemical Threshold

There is good agreement among the various investigators as to the photochemical threshold, the longest wavelength which is capable of degrading cellulose. Kauffmann (13), experimenting with a mercury vapor lamp with and without glass plates, concluded that only radiation of wavelength less than 350 mμ caused photochemical changes in the cellulose. Barr and Hadfield (14) found that the rate of deterioration of cotton fabric exposed to sunlight was the same in quartz tubes as in glass tubes, transparent

respectively down to about 180 and 330 mμ. They interpreted this to mean that wavelengths less than 330 mμ are unimportant in the deterioration of cotton, but it seems more probable that, under their conditions, the sunlight contained an insignificant amount of energy in this range. Turner (15) reported that wavelengths greater than 360 mμ have no destructive effect, but there is apparently no limit on the short wavelength side. Linen threads were exposed to the spectrum, produced by a Hilger quartz spectrograph, of a Westinghouse Cooper-Hewitt quartz mercury arc lamp and were tested for breaking in the region of exposure. Hirschkind, Pye, and Thompson (16) stated that radiation of wavelength less than 300 mμ has a detrimental effect on cellulose and that the absorption of light by cellulose begins at a wavelength of about 350 mμ. Experimental evidence for these statements is not given. Oguri and Takei (17) irradiated quantitative filter paper one hour with the radiation of a mercury vapor lamp with and without filters. Their results show that only light of wavelength less than 360 mμ has a significant effect upon the copper number of cellulose. Steurer (8), working with methylcellulose in dioxane solution, found the photochemical threshold to be at 325 mμ.

A wavelength of 350 mμ corresponds to an activation energy of about 3.5 electron-volts or 82 kilogram-calories per mole. This is approximately the value commonly given for the strength of the C-O bond.

Physical and Chemical Changes

The most obvious effects of ultraviolet light on cellulose are the loss of strength and change in color which occur when cellulosic materials are exposed to sunlight. Boharwin and Pakschwer (17) reported that samples of cloth sealed in glass in an oxygen atmosphere and irradiated for 30 hours with a quartz mercury arc showed considerable strength loss. Exposure of cotton fabric to sunlight for five weeks was found by Barr and Hadfield (14) to result in an appreciable loss in tensile strength. Turner (15) exposed linen threads in sealed quartz tubes with a similar result. Cotton hairs, yarn, and cloth were irradiated under a variety of conditions by Ounliffe and Farrow (18). They found that hairs lost strength at a constant rate until 40 per cent of the original value was lost, after which the rate fell off slowly. Yarn and cloth lost strength at a slower rate; the bleached material was more rapidly affected than the unbleached. It must be remembered that, in the case of any sample of finite thickness, the intensity of light of wavelengths which are absorbed decreases progressively with increasing distance into the sample. Thicker samples will thus show less change in their overall properties than thin samples under the same conditions. Henk (19), in contrast to other observers, has claimed that short action of ultraviolet light results in an increase in strength due to polymerization. The copper number and the alkali solubility were said to be decreased.

The chemical changes which occur when cellulose is irradiated by ultraviolet light have been studied by use of the common tests. Barr and Hadfield (14) found that exposure to sunlight caused a decrease in cuprammonium viscosity, an increase in copper number and silver number, and little change in the Methylene blue adsorption. Ounliffe and Farrow (18) reported that the copper number increased but the Methylene blue adsorption was little affected when cotton was exposed to the radiation of a quartz mercury arc. Three rag pulps and one alpha pulp were exposed to the light of a carbon-arc "Fade-Ometer" by Foote (20). In all cases he observed a decrease in viscosity and alpha-cellulose content, an increase in copper number and one per cent alkali solubility, and no change in pentosan content. Lewis (21) reported that exposure of the same pulps to the light of a quartz mercury vapor lamp also resulted in a lowering of the viscosity in all cases. Increase in copper number was found by Mason and Rosevear (22) when ramie was exposed to the light of a quartz mercury vapor lamp and by Oguri and coworkers (19) when a variety of cellulosic materials were exposed to radiation from the same type of source.

Montana (23) found that light of wavelength below 290 mμ caused considerable drop in the viscosities of solutions of cellulose in cuprammonium hydroxide and of cellulose acetate and nitrate in various solvents. No

other chemical changes were observable. Exposure of solutions of cellulose acetate, cellulose nitrate, and ethylcellulose was reported by Clément, Rivière, and Beck (24) to result in decreased viscosities. In the solid state cellulose nitrate was affected but not ethylcellulose. There was no decrease in the viscosity of benzylcellulose when exposed in solution. Steurer (8) found that the viscosity of methylcellulose in dioxane solution was decreased by exposure to the radiation of a quartz mercury vapor lamp.

The formation of carbon dioxide has been noted by Scharwin and Pakschwer (17), Barr and Hadfield (14), and Henk (19). Carbon monoxide and an aldehydic odor were also reported by Barr and Hadfield, and Henk observed the formation of water. Kauffmann (13), however, could detect no loss in weight.

Effect of Extraneous Materials

Atmosphere

There is an outstanding lack of agreement among the various investigators on the effect of the composition of the atmosphere surrounding the sample during the irradiation. Results are especially divergent with respect to oxygen. Kauffmann (13) states that the presence of oxygen

is not required in the photochemical action of light on cellulose, as the action takes place in hydrogen to the same extent as in air. Conversely, Barr and Hadfield (14) claim that loss of strength occurs most rapidly in oxygen, less rapidly in air, and to an almost negligible extent in a vacuum, hydrogen, or carbon dioxide. In contrast to this, Gunliffe and Farrow (18) observed that, compared with the loss of strength in dry air, the loss of strength in dry hydrogen was only 13 per cent less, in dry carbon dioxide 17 per cent less, in dry nitrogen 40 per cent less, and in dry oxygen 82 per cent more. Oguri and Yamaguchi (19), who continuously passed various mixtures of oxygen and nitrogen over qualitative filter paper irradiated for one hour with a quartz mercury vapor lamp, found that the copper number increased more rapidly with increasing amounts of oxygen in the gas. Compared with air, the rise in copper number in nitrogen (1.3 per cent oxygen) was 31 per cent less; in pure oxygen it was 10 per cent more. In another series of experiments these investigators found that there was no apparent relationship between the oxygen content of different gases and the rise in copper number of filter paper exposed in these gases. In contrast to the results of Barr and Hadfield, the greatest increase in copper number was observed in the case of hydrogen (0.8 per cent oxygen); carbon dioxide (2.7 per cent oxygen) was second, closely followed by air. It must be remembered, however, that Barr and

Hadfield based their conclusions on tensile strength determinations, whereas Oguri and Yamaguchi determined only the copper number. Moreover the latter authors based their conclusions on very small differences. Turner (15) found that replacing air by hydrogen reduced the strength loss from 20 per cent to 6 per cent, and in another experiment the loss in strength in air was 34 per cent, whereas that in a vacuum was 10 per cent. Mason and Rosevear (22) allowed their samples to stand two days over sodium wire to remove oxygen, water, and carbon dioxide. Exposure resulted in increased copper number.

The effect of oxygen on the reaction might conceivably be due to ozone formed under the influence of ultraviolet radiation. Ellis, Wells, and Heyroth (9) have given a review of the literature on the oxygen-ozone transformation. Under special conditions wavelengths as long as 253 mμ are capable of causing the formation of ozone, but in general this reaction is caused by wavelengths below 200 mμ while there is a decomposition of ozone between 185 and 300 mμ. This agrees with the fact that ozone has an absorption maximum near 255 mμ.

It should be pointed out that almost all of the previous investigations were carried out by sealing the cellulose sample in glass or quartz tubes. Unless the amount of gas in these tubes was large as compared with the

amount of cellulose, it is probable that the composition of the gas changed considerably during the period of irradiation, because it has been demonstrated that gaseous products are formed in the course of the reaction. It is also quite possible that certain gases, particularly oxygen, are consumed. Therefore, it is obvious that most of the investigations were not carried out in a medium of constant composition, but rather in an atmosphere which varied continuously during the experiment, the magnitude of the variation depending upon the conditions employed.

Moisture

Moisture appears to have little effect on the reaction. Kauffmann (13) stated that the action takes place on dried cotton in dried hydrogen. Turner reported that the presence or absence of moisture does not seem to have much effect. Moisture was found by Gualiffe and Farrow (18) to favor somewhat the loss of strength in air, nitrogen, and oxygen. Oguri (19) obtained results showing that moisture content less than 20 per cent had no effect; above this amount, there was a small increase in the action. The effect of water was somewhat greater in nitrogen than in oxygen.

Catalysts

The influence of certain foreign materials on the photolysis of cellulose has been studied. It is probable that the action of some of these is not truly catalytic, the material merely acting as a light filter or else being itself used up in the reaction. In the following brief summary no attempt will be made to distinguish between these different actions.

Again the results are conflicting. Barr and Hadfield (14), working with strips of cotton fabric sealed in oxygen and exposed to sunlight, reported that the presence of ferric hydroxide resulted in a much more rapid rise in copper number but only a slight increase in the rate of carbon dioxide formation. They hypothesize that iron is a photocatalyst in a reaction which produces less carbon dioxide. The gas evolved contained carbon monoxide, and possibly also hydrogen, to the extent of about 10 per cent of the weight of the carbon dioxide. To determine whether the iron in the ash of cotton was responsible for the effect of sunlight, a piece of cotton was soaked in 0.1 N hydrochloric acid, thoroughly washed, and exposed. It was less affected. Fabric which had been impregnated with 0.01 N sulfuric acid showed a greater rise in copper number and a greater production of carbon dioxide.

Cunliffe and Farrow (18), using a quartz mercury arc, found ferric oxide to have a slight protective influence on cotton cloth as judged by strength tests. Chromium green (chromic oxide) has a great protective effect, prolonging the life as much as five or six times, and a mixture of chromic and ferric oxides was as good as the former alone. The rate of strength loss of samples exposed in moist air was increased somewhat in the presence of ammonia and very much in the presence of sulfur dioxide. Some organic dyes accelerated the reaction, some had a protective effect. Tannic acid gave protection against the light of a carbon arc, but was only slightly effective when the fabric was exposed to the weather.

Henk (19) distinguished between direct catalysts and substances which become catalysts under the influence of light. In the first class he placed oxides and peroxides of heavy metals; in the second class he included certain vat dyes which, although themselves fast to light, act as sensitizers, and certain other dyes which are decomposed by light to form products which affect the cellulose. Specific examples are uranium compounds, Indanthrene Red, and several indigoid vat dyes in the yellow to red range. Basic dyes are said to cause the greatest strength loss, whereas the action of sulfur dyes is erratic, some of them exerting protection as do the vat dyes of the anthraquinone

series and the direct dyes, particularly those of the diazo series.

Oguri (10) found less rise in copper number of tissue paper when moistened with 5 to 10 per cent sodium hydroxide than when exposed dry or moistened with water. He concludes that the presence of sodium hydroxide retards the formation of reducing products, but it seems more probable that the strong alkali removed part of the reducing products formed.

Turner (15) reported that airplane fabrics were covered with lead chromate to cut off light of short wavelengths, and that later a pigment varnish (P.G. 10) was developed which practically prevented deterioration. In the discussion of Turner's paper it was pointed out by Knecht that a mixture of ferric oxide and lampblack had been found to be the best protective medium.

Scharwin and Pakschwer (17) found that dyed cellulose evolved more carbon dioxide than did undyed.

Kinetics and Mechanism of the Reaction

Little attention has been paid to the chemical kinetics of the reactions of cellulose brought about by exposure to ultraviolet light. This is unfortunate since such an approach is usually of value in studying the

mechanism of a reaction. It is regrettable that so many investigators have been content to explain the reaction as the formation of "oxycellulose". Although many authors speak of "oxycellulose" as though it were a chemical individual, it is really only a general term customarily applied to the intermediate products of unknown composition resulting from the partial oxidation of cellulose. To say that "oxycellulose" is formed is just another way of saying that oxidation takes place.

Steurer (6) followed the rate of decrease of chain length of methylcellulose in dioxane solution when irradiated by a quartz mercury vapor lamp. Precautions were taken to exclude oxygen and water. Except for the early stages, the rate of degradation could be expressed fairly well by the equation of Ekenstam for the hydrolysis of cellulose by phosphoric acid. He observed no gas formation in the case of methylcellulose, but methylcellobiose yielded methane and carbon monoxide and showed a loss in weight. From a determination of the photochemical threshold he found that the minimum energy required to split the methylcellulose chains was 88 kilogram-calories per mole, compared with 84 for the aliphatic C-O bond. Since the decrease in chain length determined by the viscosity method was greater than the decrease in chain length calculated from ^e end group determinations, he concluded that there are

cross linkings between the cellulose chains and that these, as well as glucosidic linkings, are split by the action of ultraviolet light.

Barr and Hadfield (14) stated that the reaction is essentially one of oxidation. They believed that two reactions occurred, one resulting in the formation of reducing groups and the other in the formation of carbon dioxide. Henk (19) claimed that two types of oxycellulose are formed. At first alkali-insoluble oxycellulose results, accompanied by the evolution of carbon dioxide and water, the latter resulting from the oxidation of hydrogen of the cellulose. On further exposure, carbon dioxide liberation ceases and alkali-soluble oxycellulose containing reducing groups is formed. Scherwin and Pakschwer (17) considered two possibilities: the formation of oxycellulose which then breaks down to yield carbon dioxide, or the simultaneous formation of carbon dioxide and oxycellulose due to the oxidation of the cellulose. Oguri (10) concluded that aldehydic substances are formed in the presence of a small amount of oxygen. If more oxygen is present, there is a simultaneous formation of aldehydic substances and oxidation of these to carboxylic acids, the rates of the two reactions being about the same. By extrapolation, aldehydic substances are formed in the absence of oxygen. Gunliffe and Farrow (18) found that cotton hairs lost strength at a constant rate until the loss amounted to about 40 per cent, the rate then decreasing.

Fauffman (13) ascribed the action of light to the formation of a compound he called "photocellulose". He stated that this product does not result from oxidation either by oxygen or by the splitting off of hydrogen, and that it is isomeric with cellulose.

Mason and Rosevear (22) made the interesting observation that when ramie was exposed to polarized ultraviolet light vibrating crosswise to the fiber, the increase in copper number was 25 per cent greater than when the light was vibrating lengthwise to the fiber. In other words, the effect is greatest when the vibration is in the direction in which the chains are more deformable.

PRESENTATION OF THE PROBLEM

The aim of this investigation was first to definitely establish whether or not cellulose is degraded by ultraviolet light in the absence of oxygen. Although much has been published on this point, there is no general agreement, and a thorough investigation might be expected not only to answer the question posed but to bring out some of the reasons for the discrepancies found in the literature.

A further goal was to throw some light on the mechanism of the degradation. Previous investigators have had little to say on this score, generally confining themselves to statements that oxycellulose is formed. Even if this is true, it is not very enlightening. It was hoped that a study of the kinetics of the reaction would yield some information about the mechanism.

APPARATUS, MATERIALS, AND METHODS

IRRADIATION APPARATUS

The experimental setup used for exposing materials to ultraviolet light is shown schematically in Figure 1 (and photographically in Figure 2.) Essentially the apparatus consists of a gas purification train, an exposure chamber with magnetic stirring and capable of being evacuated, a mercury vapor lamp, and a gas analysis train with provision for the quantitative estimation of water, carbon dioxide, formaldehyde, hydrogen, carbon monoxide, and organic combustibles.

The gas being used as the atmosphere surrounding the sample during the experiment passes first through a calibrated flowmeter of the orifice type (shown schematically in Figure 3. The difference in level ($h_2 - h_1$) gives the volume rate of gas flow upon reference to the calibration chart; ($h_0 - h_1$) and ($h_0 - h_2$), respectively, give the pressures of the inlet and outlet gas with respect to atmospheric pressure. In addition, the actual gas flow can be calculated from

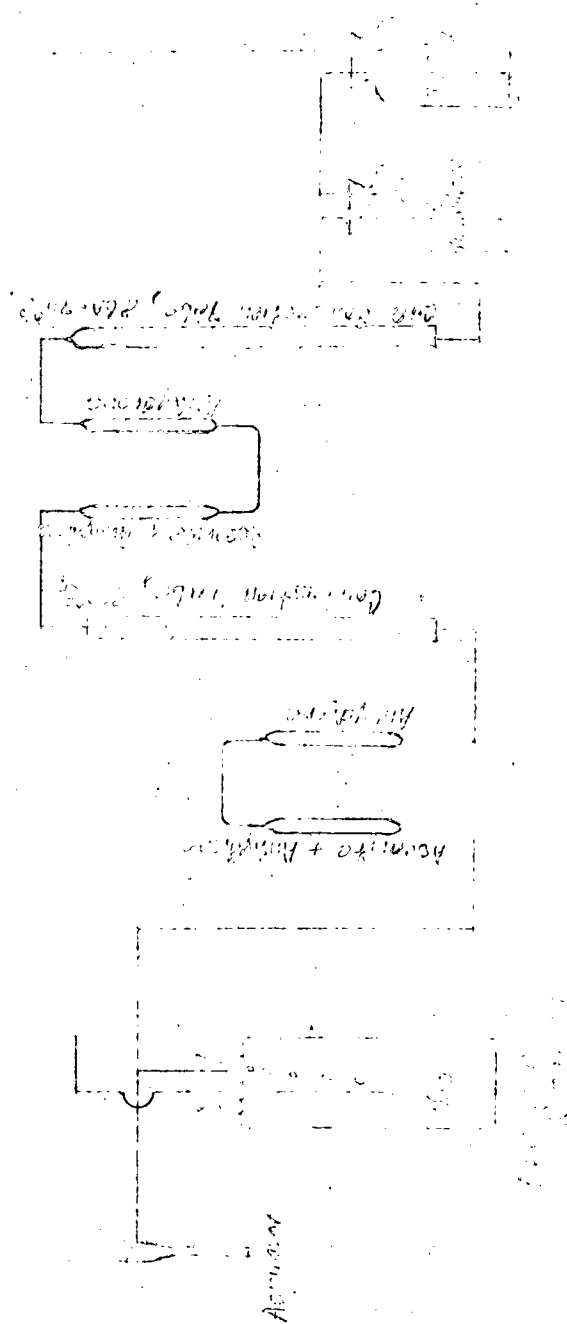
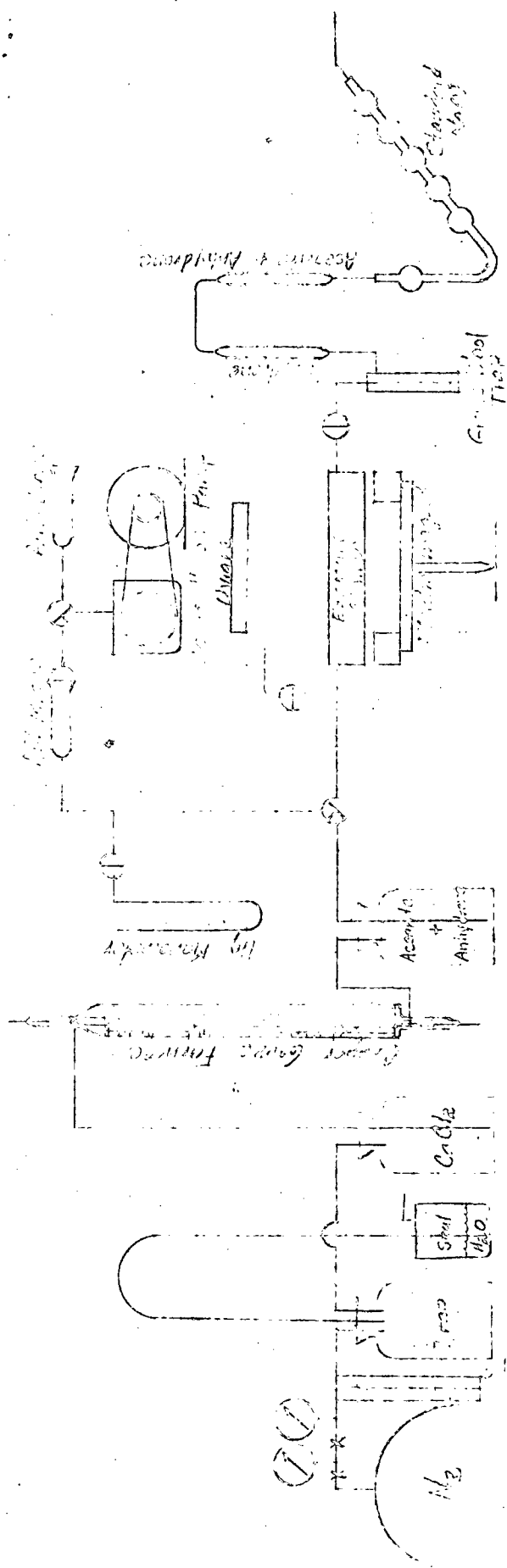
cont. p. 27

$$n = \frac{PV}{RT},$$

where

n = rate of gas flow in millimoles per minute,

P = pressure of exit gas = barometric pressure (inches of water) + ($h_0 - h_2$).]



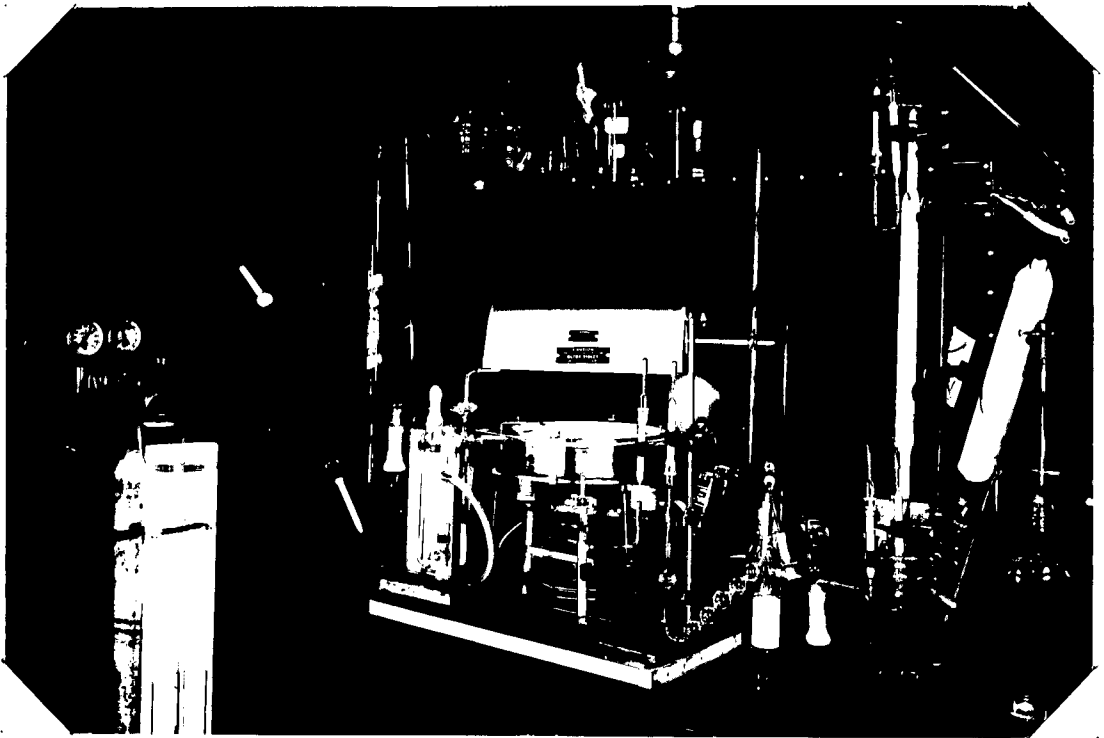
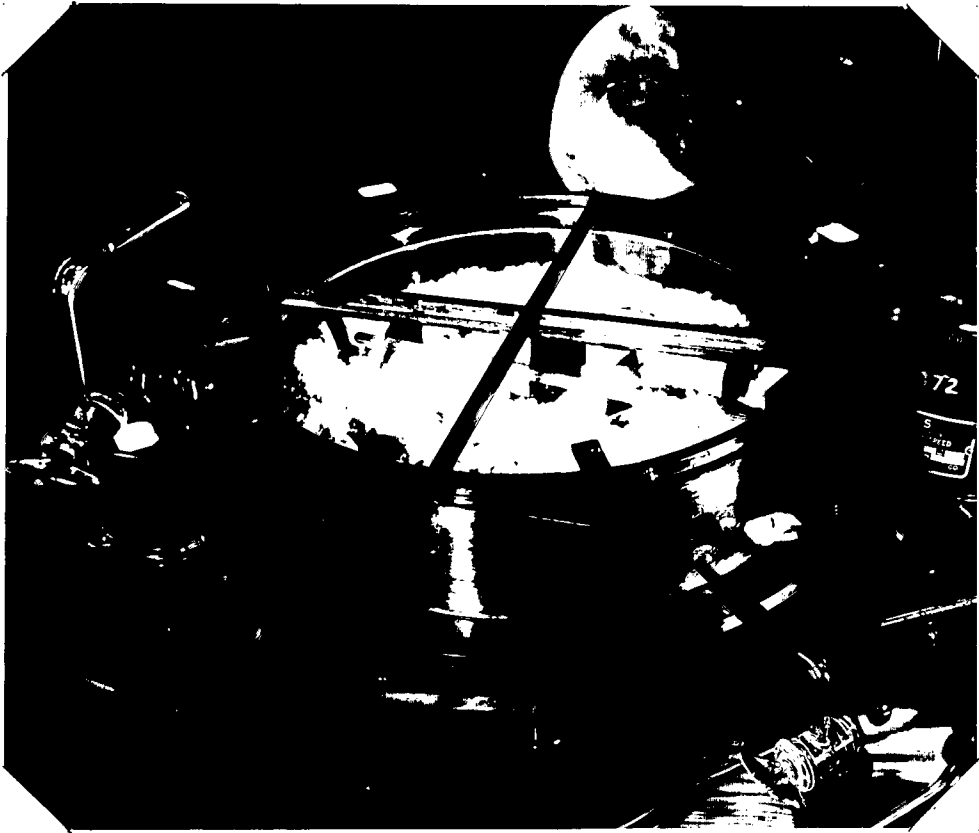


FIGURE 2

GAS FLOWMETER

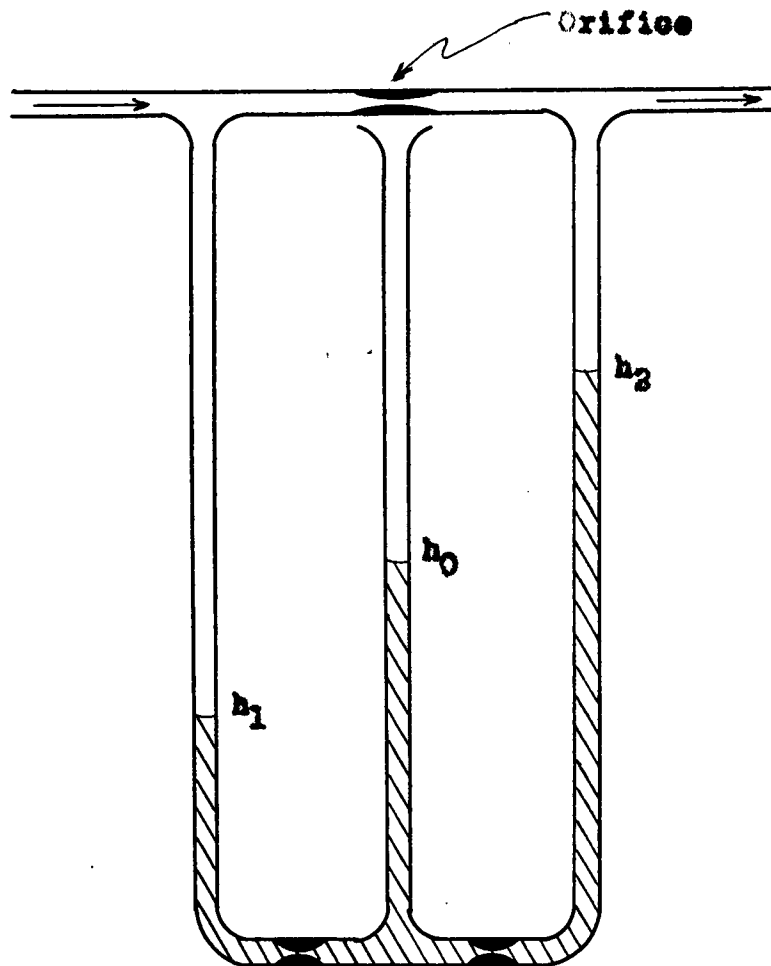


FIGURE 3

[\underline{V} = gas flow in ml. per minute obtained from calibration chart of \underline{V} vs. $(h_2 - h_1)$,]

\underline{T} = temperature of exit gas (assumed to be room temperature) in degrees Kelvin, and

\underline{R} = gas constant = 33.27 ml. inches.

The rate of flow in millimoles per minute can thus be found from h_1 , h_0 , h_2 , barometric pressure, and room temperature.]

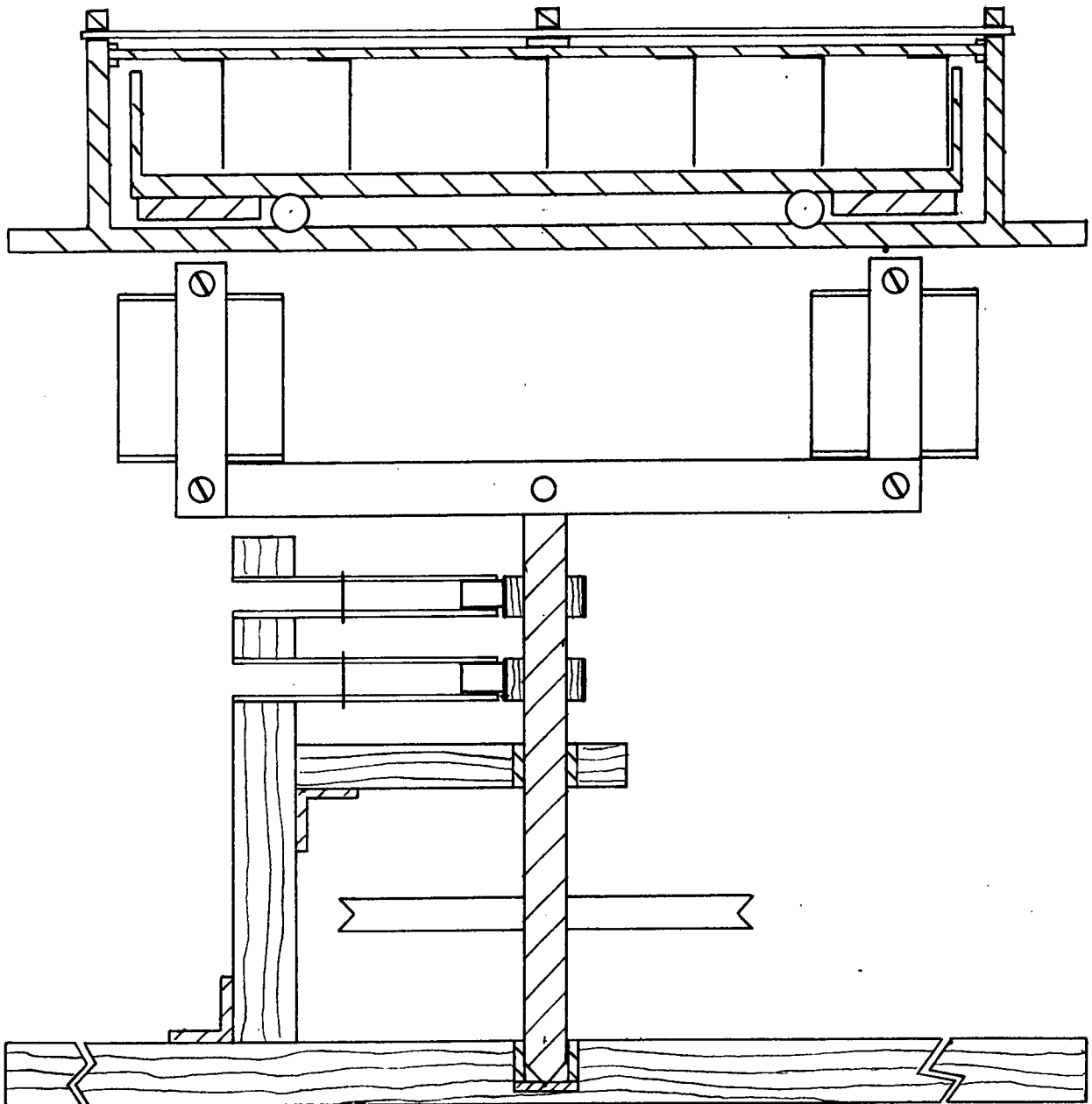
The gas line leading from the flowmeter has a side connection leading to a bubbler, in which the water level is maintained about two inches above the gas outlet. This side tube serves as a safety valve, never permitting the gas pressure in the exposure chamber to rise above two inches of water. From the flowmeter the gas passes through a calcium chloride tower to remove water vapor, a copper gauze furnace to remove oxygen, an Ascarite-Anhydrous bottle to remove carbon dioxide and the last traces of water vapor, and finally through the three-way stopcock into the exposure chamber. The copper gauze furnace is of the type described by Savage and Ordal (25), consisting of 40-mesh copper wire gauze wound on a "Calrod" heating element (General Electric Company), the assembly being encased in a tight-fitting Pyrex tube. When oxygen was being used in the gaseous atmosphere, the furnace was turned off; otherwise the gas received the same purification treatment.

Figure 4 is a scale drawing of the exposure chamber and agitator. The outer shell is an open-top

*To the effect
chamber
covered*

Overlaid

FIGURE 4



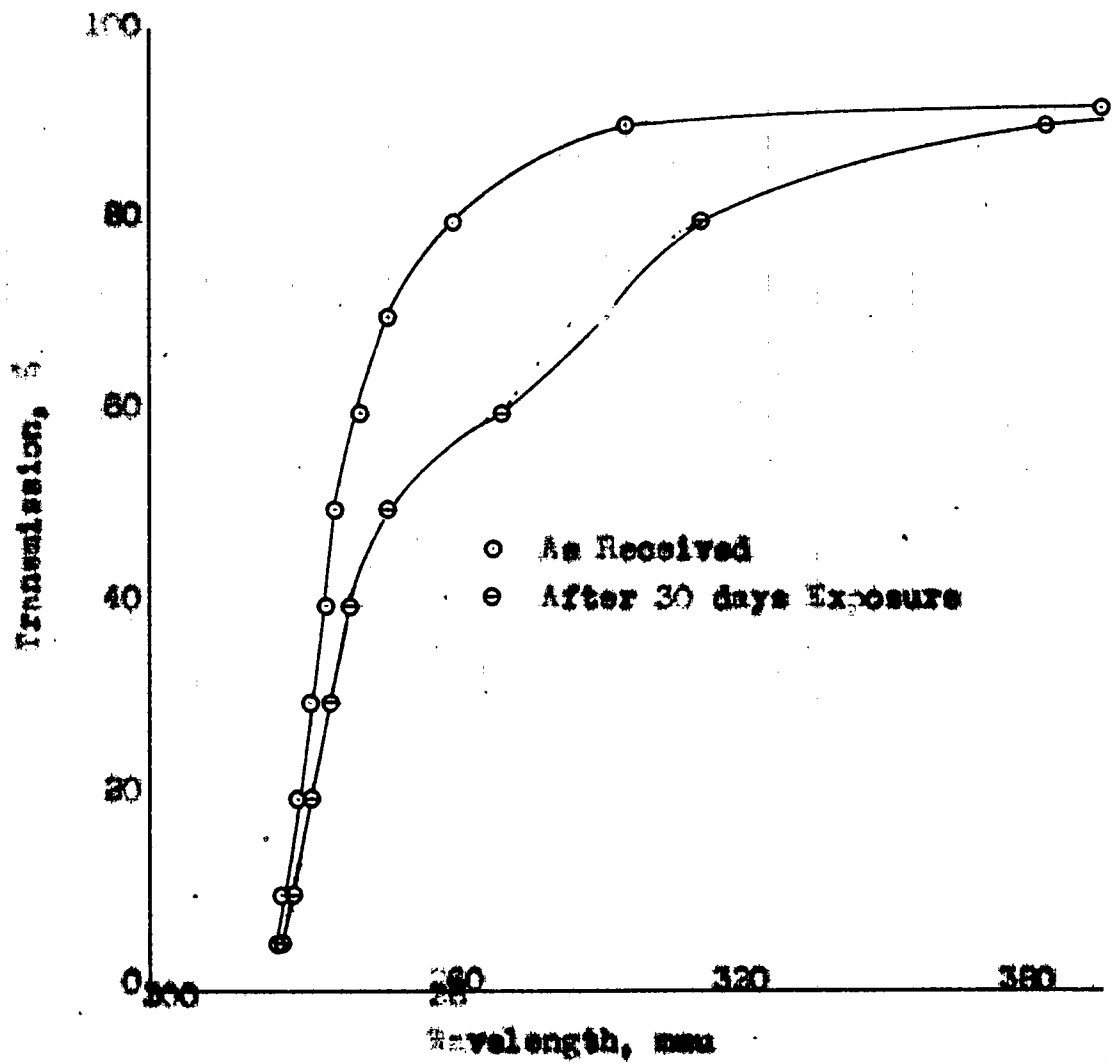
EXPOSURE CHAMBER AND STIRRING MECHANISM

Scale: One-Half Actual Size

brass cylinder, inside of which is a concentric rotatable, brass cylinder supported on ball bearings. Two pieces of iron ^{were} are fastened to the bottom of the inner cylinder so that it can be turned by the motor-driven, rotating electro-magnet below the outer shell. Direct current ^{was} is fed to the coils of the magnet by means of simple slip-rings, about 50 watts being required for satisfactory operation of the agitator. The material to be irradiated ^{was} is placed in the inner cylinder, and, when this rotates, the material is ^{then} mixed by stationary plows attached to the outer shell. As the plow-holder ^{was} is held in place by bayonet clamps it ^{could} can be removed easily, thus allowing the inner cylinder to be taken out. A conventional mercury-in-glass thermometer ^{was} is attached to the plow-holder. To keep the temperature down during irradiation a fan blows ^{and} air over the exposure chamber.

The cover consists ^{of} of four pieces, each $5 \frac{5}{8}$ inches square, of "Vycor" high silicon ultraviolet-transmitting glass (Corning Glass Works). [The spectral transmission of this glass in the two mm. thickness used is shown in Figure 5, both as received and after 30 days' exposure to the mercury vapor lamp at a distance of four inches. It was necessary to use four pieces because a single plate of sufficient size could not be obtained. The components were not permanently cemented together, but were] sealed in place with beeswax-rosin mixture at the start of each experiment.

FIGURE 5
ULTRAVIOLET TRANSMISSION OF "VYCOR" GLASS



[Since the glass window could not withstand much pressure,] an auxiliary cover consisting of a vacuum desiccator lid was placed on top of the Vycor glass during evacuation, [both the inside of the exposure chamber and the space between the two covers being simultaneously evacuated. The ultra-violet-transmitting plates were placed directly on the top of the brass shell which had been ground flat, but a greased rubber gasket the same size and shape as the rim of the shell was used between the two covers to take up any inequalities.] A Genco Hyvac pump was used for evacuation, the pressure being indicated by a closed tube mercury manometer opening into the evacuation line, which also contained an Anhydrene tube to absorb water vapor.

A General Electric Portable Ultraviolet outfit consisting of the UA-26A2 quartz tubular, A.C. Ultraviolet in a matte aluminum reflector was used as the source of radiation. Technical data for this 360-watt discharge tube have been given by Johnson and Webster ⁽²⁾ [26]. In all of the experiments the distance from the discharge tube to the glass cover of the chamber was eight inches, the shortest distance which could be used and still have the whole sample area uniformly illuminated. A 250-watt General Electric infrared drying lamp in a gold-plated reflector was used in some of the experiments to heat the sample before exposure for the purpose of drying it.

(2) Johnson and Webster, Rev. Sci. Instruments, 10, 1, 1938, 938.

The gas emerging from the exposure chamber passes through a glass wool trap to remove any entrained particles of cellulose, through an Anhydrene tube for the estimation of water, an Ascarite-Anhydrene tube for the estimation of carbon dioxide and an alkaline solution of standard iodine for the estimation of formaldehyde or other easily oxidizable substances. At this point, oxygen ^{if necessary, to maintain the pressure} may be introduced to aid in the subsequent combustions. The mixture of gases then passes through a calcium chloride bottle to remove water, an Ascarite-Anhydrene bottle to remove any carbon dioxide and the last traces of water, and into the first cupric-oxide-filled combustion tube. This tube is maintained at 260-270° C. for the combustion of carbon monoxide to carbon dioxide and hydrogen to water. The water and carbon dioxide ^{are} are estimated by absorption in Anhydrene and Ascarite-Anhydrene tubes, and the gas passed on into the second cupric-oxide-filled tube. This tube is maintained at about 800° C. for the combustion of organic matter to carbon dioxide and water, which ^{were} are then estimated as before. The pressure drop through the gas analysis train is compensated by a pressure regulator connected to the end of the train, thus maintaining the pressure in the exposure chamber at the desired value.

All connecting tubes in the gas purification and analysis trains were of glass. The junctions were made

[with rubber pressure tubing which had been caustic extracted and impregnated with molten paraffin as specified by Pregl (27). The connections were made so as to expose a minimum amount of rubber to the gas. The six absorption tubes for estimating water and carbon dioxide were of the type specified by Pregl, and were constructed from 13 x 14 mm. standard taper flask length ground Pyrex joints. The ground joints in these and the other absorption bottles were sealed with Krönig's cement; stopcocks were made tight with "Lubri-Seal".

The combustion tubes were heated by suitable windings of Nichrome wire, layers of asbestos paper being used for external insulation. The low temperature tube was of ordinary Pyrex tubing, but the high temperature tube was a special combustion type made of Vycor glass. A mercury-in-glass thermometer was included in the former, and the temperature was adjusted by means of a variable resistance in series with the heating wire. As the temperature of the second tube did not have to be closely controlled, it was adjusted once and for all at the beginning of the work, a thermocouple being used as the measuring instrument.

The procedure followed in making a run on cellulose was as follows: the sample, which had been dried at room temperature in a vacuum desiccator over Anhydron, was weighed and introduced into the exposure chamber. The clean ultraviolet-transmitting cover was then put in place

[and all of the joints sealed with a 1:1 beeswax-rosin mixture applied smoking hot from a medicine dropper. After cooling, the excess sealing material was shaved off the top of the glass with a razor blade. The auxiliary cover with its freshly greased gasket was then put in place, connected to the vacuum line, and evacuation started with the stop-cocks so adjusted that both the inside of the chamber and the space between the two covers were simultaneously evacuated.] *The auxiliary cover was sealed with a gasket.* By means of a small electric hotplate beneath the exposure chamber, *(200 W. or more)* the temperature of the cellulose was raised to 35-40° C., and evacuation was continued until no more water vapor was being removed, as judged by the Anhydrene tube coming to constant weight. Cellulose dried in this manner was found to retain about 0.2 per cent moisture as determined by oven drying. An alternative drying procedure, which was found to be more effective, was to heat the sample to about 60° C. *(60°)* by radiation from an infrared drying lamp while passing through the chamber a current of air or nitrogen dried over Anhydrene. *The first method permitted drying to 0.2 and the latter to 0.02.* [By this method] the cellulose *to 0.2 and* [could be dried] to less than 0.02 per cent moisture as determined by oven drying. [In the first method, the maximum temperature was limited by the softening of the beeswax-rosin sealing material; in the second, the seals could be kept cool by blowing a current of air over the outside of the chamber.]

When the exposure was to be made in the absence of oxygen, the drying period was followed by repeated evacuation to a pressure less than 0.1 mm. of mercury and admission of purified nitrogen to a pressure of about 200 mm. of mercury. Calculation shows that seven of these cycles are sufficient to remove all oxygen which can be removed by the procedure. After the seventh evacuation, nitrogen was admitted to atmospheric pressure, the stop-cock in the line leading to the auxiliary cover was closed, and this cover was disconnected and removed. A brass support was then clamped over the Vycor top to protect the sealing material from direct radiation and to keep the glass from bulging upward due to the small excess of pressure in the chamber.]

NOT The entire system, including the gas analysis train, was then swept out by passing ^{purified nitrogen} gas through it for about five hours at a rate of 50 ml. per minute, which is equivalent to about 2.0 millimoles per minute under the conditions obtaining. The absorption tubes were then removed, wiped, weighed, replaced, and the gas flow continued for a sufficient time to determine any blank changes in weight of the tubes. In most cases the infrared lamp was used during the blank to maintain the cellulose temperature at the value which prevailed during the actual exposure. At the conclusion of the blank, the infrared lamp was

replaced by the mercury arc and the gas flow was continued at 50 ml. per minute throughout the exposure except when the absorption tubes were being weighed. [The agitator was run at a speed of 30 r.p.m.; higher speeds produced too violent an action. Finally, a second blank was run in most cases. The cover was then removed, two moisture samples immediately taken in tared weighing bottles, and the rest of the material transferred to a tared aluminum can. After weighing the latter, its contents were stored in a screw-top bottle until needed for analysis. It was not found possible to determine the yield with sufficient accuracy to measure the small loss in weight which probably occurred as a result of the evolution of volatile products. The material in its dry condition easily picked up a static charge which made quantitative transfers impossible.]

MATERIALS FOR EXPOSURE

Cellulose

The cellulose used in all cases consisted of cotton linter pulp (Hercules Powder Company) which had been cut to a powder-like state by the Clairemont Waste Manufacturing Company. Microscopic examination showed the fiber lengths to range from 0.01 mm. to 0.6 mm., with most of the fibers in the neighborhood of 0.4 mm. The chemical analysis of this cellulose is given in Table III.

Beta-d-Glucose

The beta-d-glucose was prepared from commercial dextrose by the method of Hudson and Dale (28). The specific rotation of the purified product was

$$(\alpha)_D^{20} = 20.0^\circ \text{ (water, } g = 5.02)$$

three minutes after the start of solution, and the molecular extinction coefficient is plotted as a function of wavelength in Figure 11.]

Cellobiose

Sample
The cellobiose was an accumulation of student preparations. It was purified by dissolving in a minimum amount of hot water, filtering, and precipitating with acetone. The specific rotation of the purified product was

$$(\alpha)_D^{20} = 35.8^\circ \text{ (water, } g = 3.82),$$

[and the molecular extinction coefficient is plotted as a function of wavelength in Figure 12.]

Nitrogen

Tank nitrogen of 99.7 per cent purity was used. After passing through the copper gauze furnace it contained about 0.002 per cent by volume of oxygen as determined by the starch-iodine complex in a manner similar to that given by Snell (29).

Sample

[Oxygen

Tank oxygen of 99.7 per cent purity was used.

[OPTICAL MEASUREMENTS

Spectral Reflectance

Measurements of spectral reflectance in the visible range were made by the General Electric recording spectrophotometer. The samples were placed in an open glass cup, the open side being turned to the sample opening of the instrument. To prevent contamination of the integrating sphere, a sheet of "Ethofoil" was used in front of both sample and standard.

Ultraviolet Absorption

The absorption of ultraviolet light by the glucose and cellobiose in water solution was determined by means of a Bausch and Lomb medium quartz spectrograph equipped with the multistep sector photometer developed at the Institute. The solution and solvent were contained in a divided quartz cell having an inside thickness of one cm. The source of illumination was an iron arc, the slit width was 0.15 mm., and the sector frequency was 40 per second. Molecular extinction coefficients were calculated from the formula

$$E = (1/2x)(\log_{10} 1/I).$$

where

E = molecular extinction coefficient,

C = concentration expressed as molarity,

L = length of path in the solution expressed in cm., and

T = transmittance of the solution.

Specific Rotation

A Bausch and Lomb saccharimeter with a tungsten light source and a yellow filter was used to measure the rotation of the glucose and cellobiose in water solution. In the case of the beta-d-glucose the sample was dissolved in water at 0° C. and the rotation taken as quickly as possible to minimize the mutarotation effect. The specific rotation was calculated from the formula

$$[\alpha]_D = 34.86 \frac{a}{cL}$$

where

a = scale reading of the instrument,

c = concentration of the solution in g./100 ml., and

L = length of the path in the solution in decimeters.

ANALYTICAL METHODS

Copper number, alpha-cellulose, and ash determinations were run in duplicate by Institute Methods 609, 421, and 422, respectively. Uronic acid content was estimated according

[to Institute Tentative Method 25 by distillation with 12 per cent hydrochloric acid and measurement of the carbon dioxide evolved. In determining pentosans, the distillation was carried out according to Institute Method 424, exactly 250 ml. of distillate being collected.] The ^{and} furfural in a 20 ml. aliquot of this was determined colorimetrically by the method of Stillings and Browning (30). With the remaining 230 ml., the standard precipitation by means of phloroglucinol was used, *these determinations were also carried out by the method of*

(For determinations of acidity, a conductimetric titration procedure was used. A one-gram sample of cellulose was covered with 25 ml. of distilled water and allowed to stand about 15 hours. It was then rinsed into the titrating beaker with 15 ml. of distilled water and titrated with 0.01 N sodium hydroxide. A constant voltage was applied across the electrodes and a reading of the current was taken after each addition of caustic, *and a curve was plotted.*

The reducing power of the glucose and cellobiose was determined by the method of Auerbach and Bodländer (31) ³⁾ using 0.1 N iodine buffered to a pH of 10.1-10.2 with a carbonate-bicarbonate mixture. The samples were allowed to stand in the dark for two hours at room temperature before acidification and back-titration of the excess iodine.

Staudinger's viscosity method was used to determine the chain length of the cellulose, employing the apparatus

(3) *Auerbach and Bodländer, Z. phys. Chem. 20 (1927) 100.*

and procedure described by Heuser and Green ⁴⁾ [(32)]. In calculating the degree of polymerization, 5×10^{-4} was used as the value of Staudinger's constant. [Recent ultracentrifuge work by Kramer (33) confirms the validity of Staudinger's viscosity equation but indicates that the above value of the constant may be 25 per cent high].

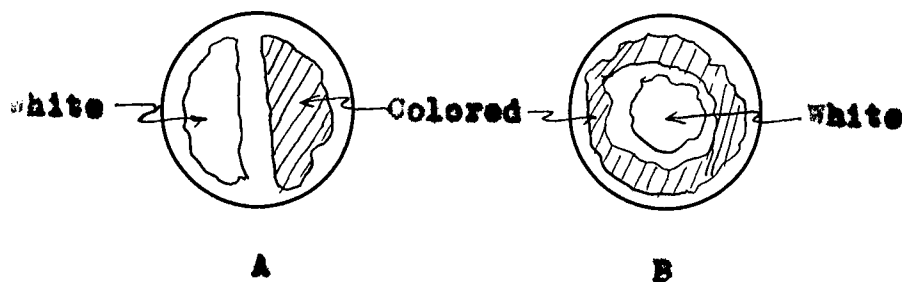
For detailed data see reference #236 (Stillings, p. 70844).

PRESENTATION AND DISCUSSION OF DATA

STANDARDIZATION AND CALIBRATION

Efficiency of Mixing of Cellulose

Thorough mixing is necessary to insure uniform exposure of the material. To test the speed and completeness of mixing, 20 grams of the cellulose to be exposed and 20 grams of colored cotton flocc of similar particle size were placed in the apparatus, the agitator was started, and samples were taken at intervals. The disposition of the two materials is shown in the sketch.



When the two materials were placed as in sketch A, the mixture appeared completely homogeneous after 5 minutes of

(4) Heuser and Green, Ind. Eng. Chem., 22, 858 (1930).

mixing. When started as in B, 40 minutes were required to attain homogeneity. This was considered satisfactory, because the shortest exposure made was for 24 hours.

Blank Determinations

To determine the blank increases of weight of the gas analysis absorption tubes, nitrogen and oxygen were passed through the apparatus under operating conditions. As these blanks were somewhat variable, it was decided to run a blank determination before and after each exposure.

Typical values of the blank increases in weight with nitrogen passing through the apparatus at 50 ml. per minute are given in Table I. The absorption tubes are numbered in the order in which the gas passes through them.

TABLE I
TYPICAL BLANK VALUES

Gain in Weight of Absorption Tubes, mg./hr.

1	2	3	4	5	6
H ₂ O	CO ₂	H ₂ O from H ₂	CO ₂ from CO	H ₂ O from Organic	CO ₂ from Organic
0.02	0.01	0.18	0.02	0.04	0.00

Whether or not the arc was burning made no appreciable difference; from this it can be concluded that the beeswax-rosin mixture used to seal on the Vycor glass

cover introduced no volatile products into the system during irradiation. The hydrogen blank is much higher than any of the others, which may be due to hydrogen given up by the nitrogen purifier (heated copper gauze). Because the copper was reduced with hydrogen, it is probable that some hydrogen was retained by the metal, to be later released as the copper was oxidized by the oxygen present in the nitrogen. This is supported by the fact that in one blank run, in which air instead of nitrogen was accidentally drawn through the system, the blank increase in weight of tube 3 jumped to about 13 mg. per hour.

Although the blank values appear small, they probably affected to some extent the accuracy of the gas analysis results, because the blanks were somewhat variable and of appreciable size compared to the amounts of gases produced.

Analysis of Known Gas Mixture

The results of an analysis of a known mixture of carbon dioxide, carbon monoxide, hydrogen, and methane are shown in Table II.

The pure gases were measured out volumetrically at 20° C. and 738 mm. pressure, and the weights were calculated from the gas law. A blank was run first with the

[

TABLE II
ACCURACY OF GAS ANALYSIS

Gas	Volume Used ml.	Weight Used g.	Weight Found g.	Percentage Error on Weight Used
CO ₂	20.4	0.0363	0.0365	+0.55
H ₂	31.1	0.00253	0.00246	-2.38
CO	22.1	0.0250	0.0248	-0.80
*CH ₄	24.4	0.0158	0.0130 (from H ₂ O)	-17.6
			0.0144 (from CO ₂)	-8.85

* Probably contained some ethane

ultraviolet lamp burning and nitrogen flowing through the system at a rate of 50 ml. per minute. The mixture of gases was then introduced into the exposure chamber and the nitrogen flow resumed for five hours. Finally, a second blank was run under the same conditions. The results given in the table are corrected for the blanks. No oxygen was admitted prior to the combustions, and this perhaps accounts for the low methane values.

In the case of carbon dioxide, hydrogen, and carbon monoxide, the accuracy is considered very satisfactory. The methane analysis could probably have been improved by introducing oxygen, but in view of the non-specificity of the determination it did not seem justified.

It can be concluded further from this run that there was no appreciable interaction of these gases under]

[the conditions obtaining in this and subsequent experiments. Therefore, the volatile products found in these experiments must have been formed as such from the material being irradiated.

Rate of Sweeping Out of Chamber

It can be shown that the time required to sweep out a given fraction of the gas in the exposure chamber is given by the equation:

$$t = (2.3V/F)(\text{colog}_{10} X)$$

where

t = time in minutes,

V = volume of chamber in ml.,

F = rate of gas flow in ml./min., and

X = fraction of original gas remaining.

Instantaneous mixing is assumed in the derivation. Solutions for this apparatus ($V = 2800$ ml.) when the gas flow is 50 ml. per minute are given below.

X	0.5	0.1	0.01	0.001
t	39 min.	129 min.	258 min.	387 min.

Standard Conditions

In all of the experiments on cellulose, the weight of sample used was 38.87 grams on an oven-dry basis. The temperature of the cellulose during exposure was $45 \pm 5^\circ \text{C.}$

the fluctuations being due to variations in room temperature. Except in rare cases the temperature lay between 43° and 46° C. In all experiments except 8, the rate of gas flow through the apparatus was maintained at 50 ml. per minute. A positive pressure of about one inch of water was maintained in the sample chamber during exposure. *continuation p. 46*

[SUMMARY OF EFFECTS NOTED

The brief enumeration at this point of the changes which were found to take place when cellulose was exposed to ultraviolet light may aid the reader's perspective in appraising the more detailed account to follow.]

Exposure both in the presence and absence of oxygen resulted in decreased chain length, increased copper number, and decreased alpha-cellulose content. All three effects took place more rapidly in the presence of oxygen. In nitrogen, no change in uronic acid content could be detected, but in oxygen there appeared to be a very small increase. No change in pentosan content could be detected in either case. There was a slight production of acidity in both atmospheres, the effect being much greater in oxygen. The spectral reflectivity of the material was changed, the exposed samples being more yellow. In this case the effect was greater in the absence of oxygen than when oxygen was present.

(phenomenon that) person in laboratory laboratory

An interesting point brought out by this investigation is that the material was left in an unstable state at the conclusion of the exposure to the mercury vapor lamp. Degradation of the samples continued during storage following the exposure.

THE EFFECT OF OXYGEN

[It has been pointed out that the literature does not give a consistent answer to the question of the role played by oxygen when cellulose is exposed to ultraviolet light. Most investigators regard the effect as an oxidation, but there is some evidence that cellulose is modified even when oxygen is carefully excluded. If the latter is true, it means that the action of light can not be explained as the formation of oxycellulose, even if there is some oxidation in the presence of oxygen.

A series of experiments was made, therefore, to determine whether the cellulose was affected in the absence of oxygen and to what extent the presence of oxygen changed the reaction. The data obtained from these experiments are given in Table III. As the analyses of the samples continued to change for several months after the actual exposure, the data are not directly comparable unless taken after approximately the same storage period. The number of days elapsed between the beginning of each exposure and the

TABLE III

EFFECT OF OXYGEN

Experiment	Atmos.	Length of Exposure Hours	Final H ₂ O %	Copper No.	Alpha- Cellulose %	Uronic Acid % CO ₂	D.P.	Elapsed Time Days	Gases Evolved mmoles CO ₂	CO ₂
5	N ₂	24	0.22	0.42	95.1	0.25	1070	93	0.06	0.08
10	10% O ₂	24	0.00	0.58	92.2	0.29	950	50	0.18	0.17
9	20% O ₂	24	0.02	0.78	90.0	0.31	870	57	0.22	0.22
6	O ₂	24	0.24	1.49	82.9	0.29	740	85	0.39	0.37
4	N ₂	96	0.00	0.65	92.6	0.23	870	84	0.24	0.39
8	N ₂	96	0.30	0.70	91.4	0.27	840	63	0.34	0.44
Blank	O ₂	22	0.28	0.29	-----	-----	-----	---	0.00	0.00
Unexposed			2.62	0.28	98.8	0.24	1400			

D.P. is used to signify degree of polymerization. The values in the column headed "Elapsed Time" indicate the number of days elapsed between the beginning of the exposure and the determination. The ash content of the unexposed material was 0.086 per cent. Where the atmosphere was part oxygen, the rest was nitrogen.

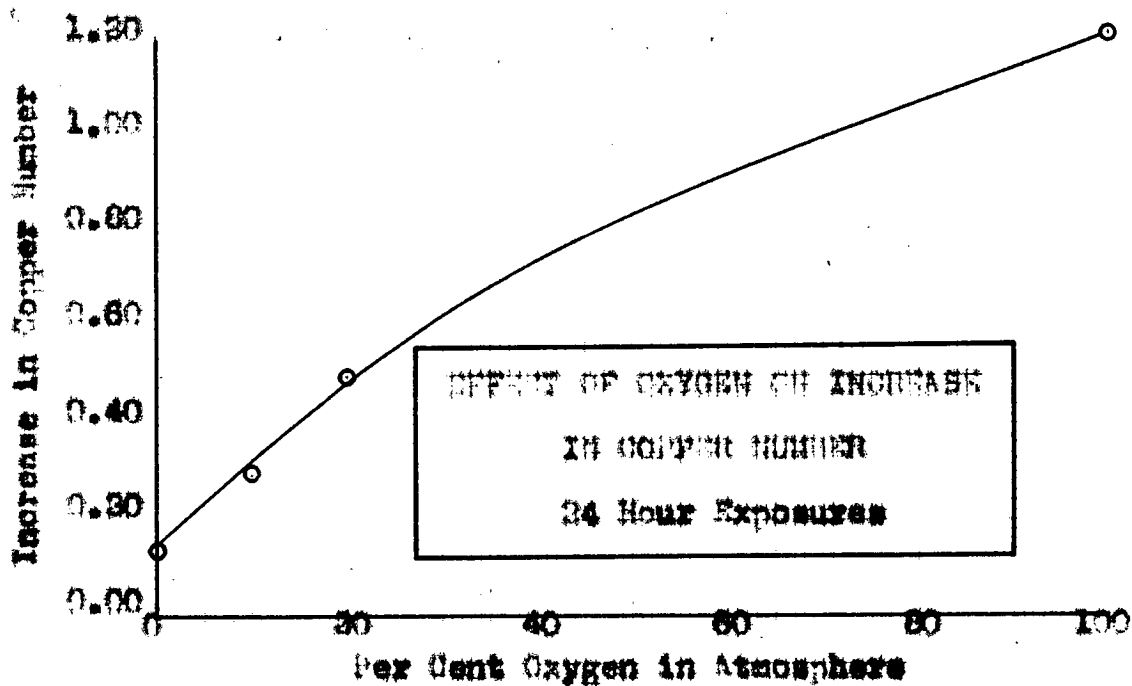
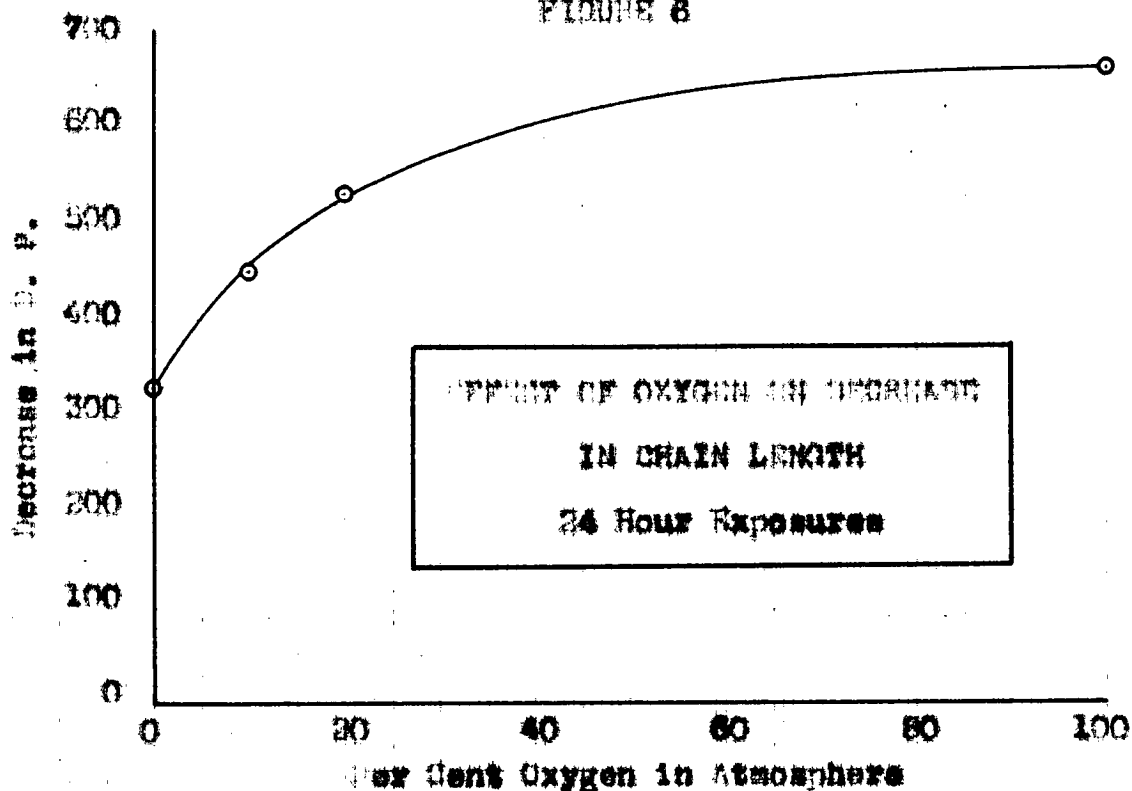
determination of the chain length is given in the table. These values are close to the ultimate values which would be obtained on further storage, because most of the change was found to take place in the first two months. The copper number and alpha-cellulose determinations were made from four to eleven days after the start of the exposure, and are therefore not necessarily the ultimate values which would have been reached. As the changes were small and slow, the figures are directly comparable despite the time differences.

The experiment listed as "blank" was made to determine whether any of the effects noted were due to the elevated temperature ^(43°) used during drying and exposure. [The usual procedure was followed except that, instead of exposing the cellulose to ultraviolet light, the sample was heated to 43° C. by placing an electric hot plate under the chamber.] The material so treated showed no significant increase in copper number, and therefore the effects observed in the other experiments must have been photochemical.

It can be seen from Table III that the samples exposed in nitrogen, with all possible precautions to remove and exclude oxygen, showed considerable degradation. The effect of the oxygen content in the atmosphere surrounding the sample during irradiation on the change in chain length and copper number is shown in Figure 6, and

6-11-50

FIGURE 8



the effect on the amounts of gases formed and the decrease in alpha-cellulose content is shown in Figure 7. The rate of degradation of the cellulose increased with increasing oxygen content over the whole range of oxygen concentrations.

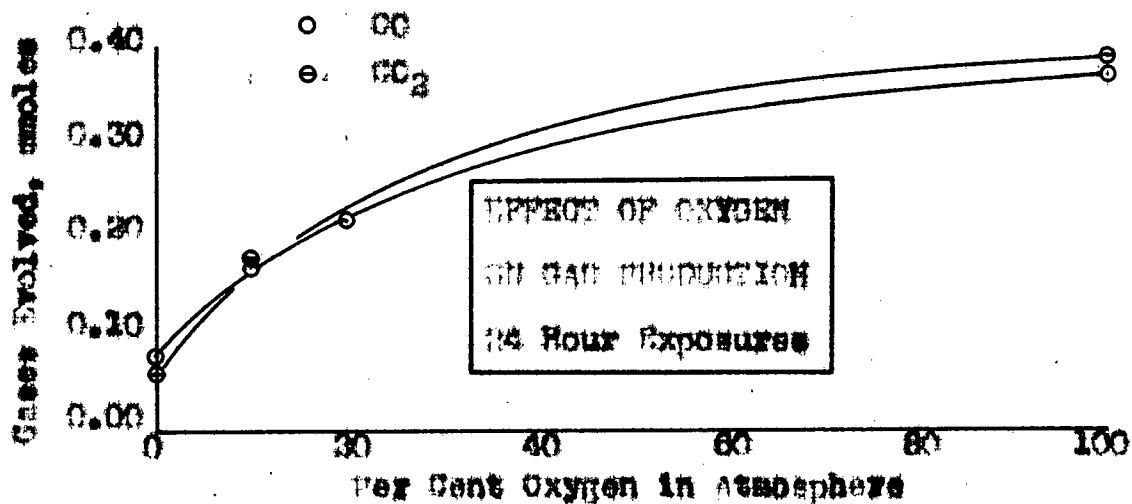
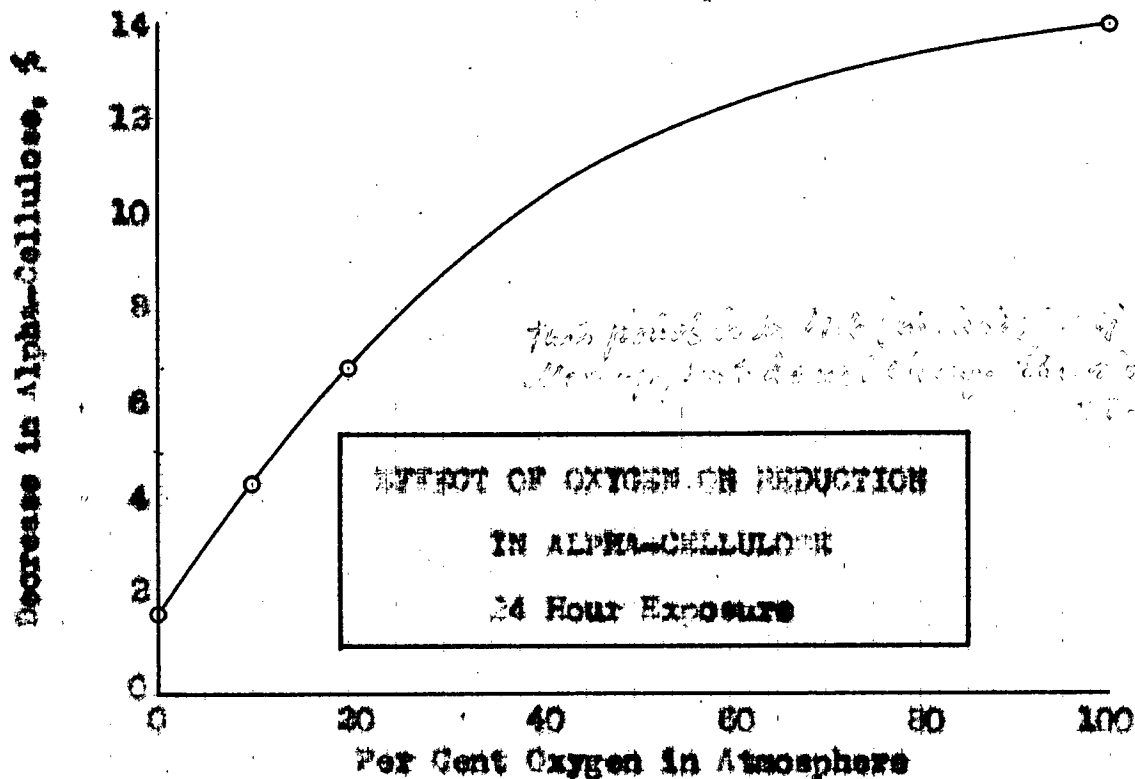
In spite of the precautions taken to remove and exclude oxygen during the exposures conducted in nitrogen, the possibility of oxygen having been present in significant amounts must be considered. [Oxygen might be present in the system at the start of the exposure or it might be introduced during the exposure through a leak in the apparatus or as an impurity in the nitrogen. The following facts indicate that the effects noted upon exposure in nitrogen were not due to the presence of small amounts of oxygen.]

[The system was tested for leaks before each experiment. Only leaks in the exposure chamber itself or in the line leading to it from the copper gauze furnace could admit atmospheric oxygen to the sample being exposed. This portion of the system was always kept under a positive pressure with respect to the atmosphere, so that if a leak were present, nitrogen would flow out but no air would get in.]

Analysis of the nitrogen showed that, after passing through the copper gauze furnace, it still contained a very

425 (2)

FIGURE 7



small amount of oxygen (about 0.002 per cent by volume). A comparison of Experiments 4 and 8 shows that this amount was insignificant. The two exposures were made under the same conditions except that nitrogen was passed continuously through the system at 50 ml. per minute during Experiment 4, whereas during Experiment 8 the nitrogen-filled chamber was sealed off. If the oxygen in the nitrogen were responsible for the degradation, the effect should be much greater in the experiment in which nitrogen was continuously introduced. Reference to Table III shows that this was not the case, as the analyses of the two exposed samples agree within experimental error. The calculated amount of oxygen introduced with the nitrogen in Experiment 8 is 0.024 millimoles or 1.6×10^{-4} per cent based on the cellulose. To prepare an oxycellulose of the same copper number as exposed sample 8 would require about 0.05 per cent oxygen, assuming oxidation was carried out under conditions which give the greatest increase in copper number for a given oxygen consumption. This is 280 times the amount ^{which} actually ^{was} present in the nitrogen filling the chamber in Experiment 8. Furthermore, the shapes of the curves in Figures 6 and 7 leave no doubt that degradation occurs at zero oxygen concentration, as the curves are far from passing through the origin.

In spite of the evacuation, heating, and flushing treatment employed to remove moisture and oxygen, a very

small amount of oxygen was doubtless retained by the cellulose. If this were responsible for the degradation which occurred, the rate of reaction would be expected to be maximum at the beginning and fall off to zero as the oxygen was consumed. Actually, no such effect was observed. Degradation continued to take place over the whole range of exposure time studied. Figure 9 shows the rate of change of copper number and chain length, and Figure 10 shows the rate of evolution of gaseous products. The latter rates actually increased continuously with increasing time of exposure. Thus the degradation occurring in a nitrogen atmosphere can not be accounted for by oxygen retained by the cellulose.

Compared with air, the increase in copper number was 68 per cent less in nitrogen, 148 per cent more in oxygen; the decrease in chain length was 38 per cent less in nitrogen, 25 per cent more in oxygen; the decrease in alpha-cellulose was 75 per cent less in nitrogen, 104 per cent more in oxygen; and the combined amounts of carbon dioxide and carbon monoxide evolved were 68 per cent less in nitrogen, 73 per cent more in oxygen. In a qualitative way, these results confirm those of Cunliffe and Farrow⁵⁾ and ^{and Mitzky} [18], who found that, compared with air, the loss of strength in nitrogen was 40 per cent less, in oxygen 62 per cent more; those of Turner⁶⁾ [15], who found that the loss of strength

(5) Cunliffe, Farrow, and Mitzky, J. Textile Inst. 19, T162 (1928).

(6) Turner, J. Soc. Dyers & Colourists, 36, 165 (1920).

was 70 per cent less in hydrogen or a vacuum; and those of Oguri and Yamaguchi ² [(10)] who found that the rise of the copper number in nitrogen (1.2 per cent oxygen) was 31 per cent less, in oxygen 10 per cent more. The conclusion of Kauffmann ⁸ [(13)] that light degrades cellulose in the absence of oxygen is confirmed, but not his statement that the action takes place to the same extent in the absence of oxygen as in air. ⁹ The results do not confirm those of Barr and Hadfield [(14)] who claimed that, in the absence of oxygen, the action takes place only to a negligible extent.

THE EFFECT OF WATER

No comprehensive study of the effect of the presence of water on the reaction was carried out. One experiment was made in nitrogen at a higher moisture content (4.34 per cent) to determine whether it was necessary to dry the samples prior to exposure. The nitrogen was humidified by bubbling through water before entering the exposure chamber, thus preventing the sample from drying out during the exposure. A comparison of exposure 7 with exposures 2 and 3 (Table V) shows that the presence of a considerable amount of moisture markedly retarded the reaction, the degradation being only about half as great as when the material exposed was dry. However, a comparison of Experiment 2 with 3 and 4 with 8 indicates that the

(7) Oguri and Yamaguchi, J. Soc. Chem. Ind. Japan,
Suppl. Bunkyo, 40, 300B, 356B (1937).

(8) Kauffmann, Cellulose Chem., 7, 617 (1928).

(9) Barr and Hadfield J. Textile Inst., 2, T490 (1921).

effect of the small variations of moisture content which normally occurred was less than the experimental error arising from other sources, as in these cases the samples having the higher moisture contents showed slightly greater degradation.

This retarding effect of moisture does not confirm the results of other observers. Gunliffe and Farrow⁽¹⁵⁾ found that moisture favored somewhat the loss of strength in air, nitrogen, and oxygen; and Turner⁽⁶⁾⁽¹⁵⁾ reported that moisture had little effect. Oguri⁽¹⁰⁾⁽¹⁰⁾ obtained results showing that moisture contents less than 20 per cent had no effect, but above this amount there was a small increase in the action, the effect being greater in nitrogen than in oxygen. The reason for this discrepancy is not clear, but it may be owing to differences in the spectral energy distributions of the radiation incident on the samples. In the three investigations cited, quartz apparatus and mercury arcs were used, so that the short wavelength limit was probably about 180 mμ. In this investigation the lower limit was about 230 mμ. Also, it should be pointed out that the data here presented concerning the effect of moisture are the result of a single experiment and so must be interpreted with caution even though the differences revealed were quite large.

10) Oguri, J. Soc. Chem. Ind., Japan, Seppu, Crystallization, II, 273 (1937).

COLOR CHANGES

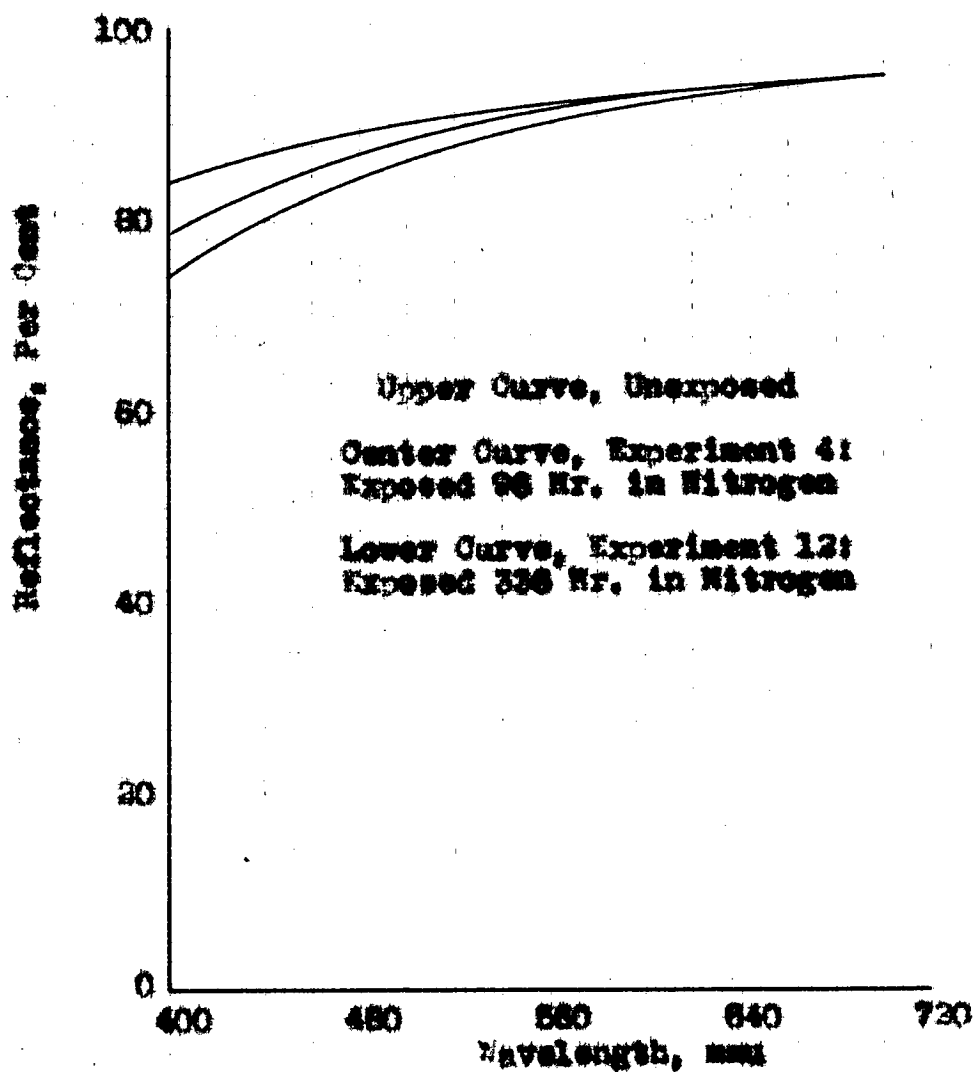
The spectral reflectance curves of the unexposed cellulose and of exposed samples 4 and 12 are given in Figure 8. Due to variations in the preparation of the sample for measurement, the reproducibility was good to only ± 0.5 per cent. To minimize this error, all of the curves were normalized at 700 m μ . This procedure is justified because there was no appreciable change in reflectance above 640 m μ even in the case of sample 12, which showed the greatest change in color.

Figure 8 shows that the samples exposed in nitrogen experienced a pronounced drop in reflectance in the blue—that is, they were definitely yellowed. The samples can thus be conveniently compared by giving their reflectances at some arbitrarily chosen wavelength in the blue region of the spectrum. In Table IV the values at 458 m μ are given. This wavelength was chosen because it is the effective wavelength of the General Electric reflection meter using filter number one. The values given in the table are therefore comparable to "brightness" readings which would be obtained with this instrument.

An interesting point brought out in Table IV is that exposure in 100 per cent oxygen did not result in a drop in reflectance, but exposure in nitrogen did. As

Continued

FIGURE 8
SPECTRAL REFLECTANCE
OF CELLULOSE



Judged by chemical analysis, sample 6 was the most degraded of those listed but it showed no loss in reflectance, whereas sample 12 showed a drop of nearly 5 per cent. Exposure in air gave intermediate results. It is apparent that the color and brightness of cellulose are quite stable to ultra-violet light, especially in the presence of oxygen. With the exception of sample 12, the largest changes which occurred were scarcely perceptible to the eye.

TABLE IV
REFLECTANCE OF SAMPLES AT 456 mμ

Experiment	Atmosphere	Length of Exposure Hr.	Reflectance Per Cent
Unexposed			87.2
Blank	O ₂	22	88.7
5	N ₂	24	85.8
10	10% O ₂	24	86.5
9	20% O ₂	24	86.4
6	O ₂	24	87.1
2	N ₂	48	85.3
3	N ₂	48	86.1
4	N ₂	96	85.5
8	N ₂	96	85.8
12	N ₂	336	82.3
7	H ₂ O, N ₂	48	86.8

KINETICS AND MECHANISM OF THE REACTION IN NITROGEN

In studying the kinetics of the reaction, a separate experiment was made for each time interval rather than taking samples periodically during a single run. [There were several reasons for this. Samples could not be taken without introducing oxygen and moisture, the removal of which would have required a repetition of the procedures used at the beginning of the experiments. Furthermore, the removal of sufficient material for analysis would have appreciably changed the average light intensity to which the remainder was exposed, and this would have necessitated an extra series of experiments to determine the effect of size of sample on rate of reaction. Also, the method used insured an ample amount of material for analysis.]

Theoretical Considerations

Under certain conditions the photolysis of a compound irradiated by light of a constant intensity might be expected to display the overall behavior of a monomolecular reaction. The conditions that would have to be fulfilled are that the products do not enter into side reactions with the original compound and that they absorb light of active wavelengths to the same extent as does the original. If these prerequisites are met, the reaction rate at any time would be expected to be proportional to

the concentration of unreacted material. Consider the case of a sample of cellulose being subjected to a photolytic reaction which results in chain-splitting. If M is the total number of splits possible and x is the number which have occurred at time t , then the rate of splitting at this time is given by $dx/dt = k(M - x)$. During the initial stages of the reaction when x is small compared with M , the rate of splitting is proportional to M and, therefore, is essentially constant.

Sakurada and Okamura ⁽¹¹⁾ recently developed an equation relating the average number of splits per molecule to the change in average degree of polymerisation as determined by the viscosity method. For the early stages of the reaction their equation reduces to the form

$$P/M = (2/x^2)(x - 1 + x^{-2}),$$

where

P = degree of polymerisation after the reaction,

M = original degree of polymerisation, and

x = average number of splits per molecule.

The formula is derived by statistical considerations on the assumption that the probability of being split is the same for each potential point of attack. The authors do not assume chains of infinite length, as has been done by others. Using data obtained by Ekenstam for the hydrolysis of cellulose by concentrated acids, the authors demonstrated the validity of their equation.

(11) Sakurada and Okamura, *Z. phys. Chem.*, A178, 289 (1943).

The relation is useful in examining the data obtained in this investigation. If the photolysis proceeded as a first-order reaction, the rate of splitting should have been constant over the limited range studied. By means of chain length measurements by the viscosity method, and the Sakurada equation, the rate of splitting can be calculated. Whether or not this rate is constant, the \bar{g} value is an important one when considered in conjunction with other measurable changes, because such a comparison is capable of indicating whether these changes are concerned with chain splitting.

Rate of Reaction

The data on the rate of reaction in nitrogen are presented in Table V. The reproducibility of the results is quite good, as can be seen by comparing Experiments 2 and 3. Experiments 4 and 8 are also directly comparable except that, in the latter case, nitrogen was not passed continuously through the chamber during the exposure. The poorest agreement is in the gases evolved. This is probably due, at least in part, to inaccuracy in the determination of the small quantities involved.

Decrease in Chain Length

The fact that the degree of polymerization of the exposed samples decreased markedly during storage after the

TABLE V

KINETICS IN NITROGEN

Experiment	Atmosphere	Length of Ex. Hr.	Final H ₂ O %	Copper No.	Time Days	Alpha-Cellulose %	Time Days	Uronic Acid % CO ₂	D.P.	Time Days	Gases Evolved mmoles CO ₂
Unexposed			2.82	0.28		96.8		0.24	1400		
5	N ₂	24	0.22	0.42 0.44	4 103	95.1	4	0.25	1290 1070	4 93	0.06 0.08
2	N ₂	48	0.19	0.50	8	93.8	8	0.20	1020 970	64 146	0.12 0.15
3	N ₂	48	0.38	0.53 0.66	4 131	93.6	4	0.22	1000 960	71 106	0.21 0.22
7	H ₂ O, N ₂	48	4.34	0.40 0.40	17 95	95.8	17	0.25	1260 1210 1230	11 17 86	0.16 0.11
4	N ₂	96	0.00	0.65 0.80	7 97	92.6 88.6	7 108	0.22	1040 930 870 860	16 35 84 113	0.24 0.39
8	N ₂	96	0.30	0.70	11	91.4	11	0.27	1050 840 860	13 63 88	0.34 0.44
12	N ₂	336	0.09	1.20	20	88.8	20	0.22	860 780 700	19 26 39	0.33 0.88

* The values given in the columns headed "Time" indicate the number of days elapsed between the start of the exposures and the determinations of the values listed in the columns immediately preceding.

irradiation indicates that there was a primary photochemical reaction which did not break the chains, but produced points of weakness which later resulted in chain splitting. For simplicity, however, the kinetics of the reaction will be treated as though the break immediately followed the primary effect, as the extent of this effect is measured by the ultimate decrease in degree of polymerization. Experiment 12 has only a limited usefulness in this connection because at the conclusion of the investigation the degree of polymerization of the product had not reached anything like a constant value.

Figure 9 shows the actual rate of decrease of chain length compared with the theoretical rate calculated on the assumption that the photolysis proceeds^{ed} as a first-order reaction; therefore, that the rate of change of \bar{n} is constant over the limited range studied. The theoretical rate was arbitrarily chosen so that the curves intersect at the two-day mark.

It is apparent that the actual rate deviates considerably from the calculated rate, and, therefore, that the photolysis does not proceed as a monomolecular reaction. Several explanations of this are possible. If an appreciable amount of oxygen were present in the system at the start of the exposure, the chain splitting would proceed faster in the beginning and would come to a constant rate only after

Fig. 1

Only the upper
portion of Fig. 9.

no
left cards
on side & handle in
caption out

Decrease of Polymerization
Degree of Polymerization

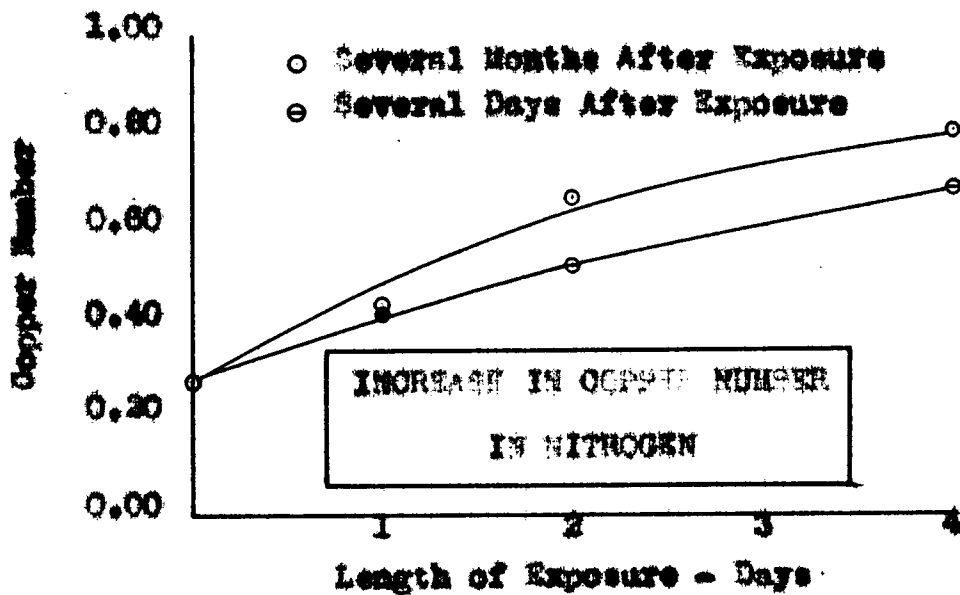
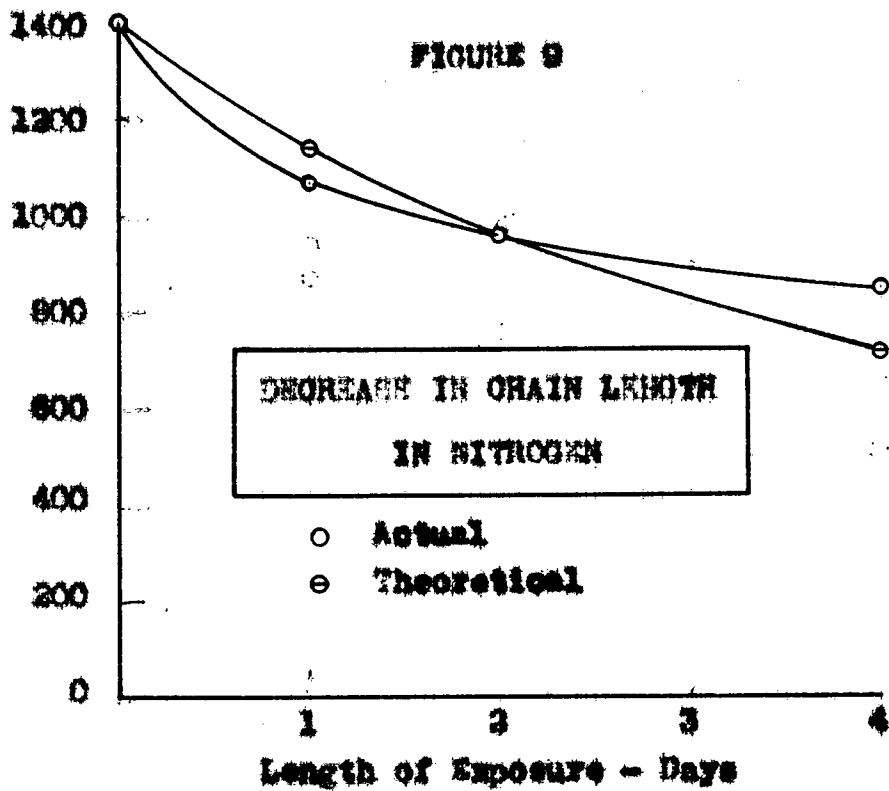
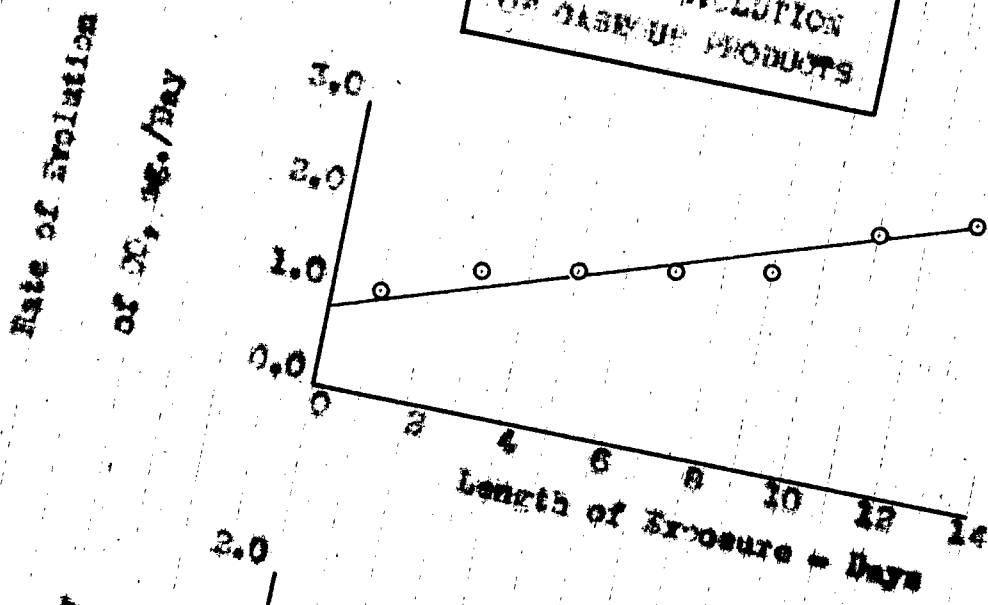


FIGURE 10
 RATES OF EVOLUTION
 OF GASEOUS PRODUCTS



Rate of Evolution
 of CO_2 , mg./Day

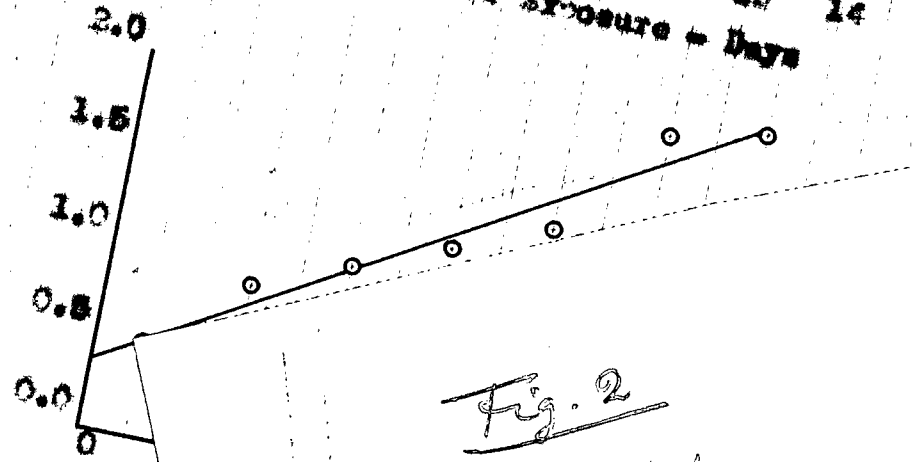
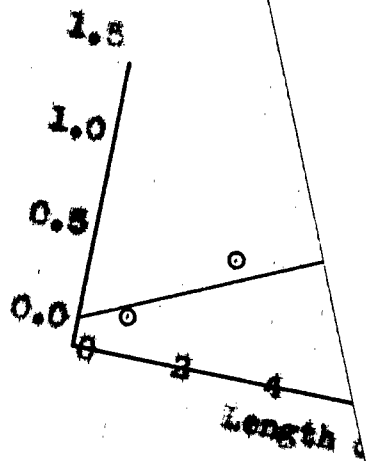


Fig. 2

all of it.

Rate of Evolution
 of H_2O , mg./Day



No furthering
 of any kind

the oxygen was used up. As each point on the curve was obtained from a separate experiment, such an effect would operate as an additive factor, but the constancy of this factor would depend on whether or not all of the oxygen was consumed in each experiment. Assuming that, because of the presence of some oxygen, the g values need to be decreased by the constant factor 0.45, the values given in Table VI were obtained. The actual corrected degrees of polymerization were calculated from the corrected g values; the theoretical corrected degrees of polymerization are based on a constant rate of splitting equal to the actual corrected rate which prevailed during the first day of exposure.

TABLE VI
HYPOTHETICAL CORRECTION FOR OXYGEN

Length of Exposure	g	$g - 0.45$	Actual Corrected D.P.	Theoretical Corrected D.P.
24	0.86	0.41	1230	1230
48	1.26	0.81	1090	1090
96	1.75	1.30	950	870
336	-----	-----	-----	390

Although this correction brings the actual rate much closer to the calculated one, the 96-hour exposure still shows a deviation large enough to be significant. If the correction

factor were not constant as a result of the hypothetical oxygen not being all consumed during the shorter exposures, then the deviation would be even greater. This means that the failure of the reaction to follow a monomolecular rate can not be explained by the assumption that an appreciable amount of oxygen was present at the start of the exposure. It is possible, however, that oxygen was a contributing factor.

Another possible explanation for the decreasing rate of reaction is that the products absorb light of active wavelengths to a ^{smaller} greater extent than did the original material. [That this actually occurred can be inferred from the spectral reflectance curves given in Figure 8.] ^{Indeed,} The exposed material showed a decreased reflectance in the blue end of the spectrum, and ^{and the curves} the shape of the curves indicates that the difference was even greater in the ultraviolet. Furthermore, ^{it has been found} the absorption of ultraviolet light by glucose and cellobiose was increased by irradiation, as shown in Figures 11 and 12.

A third possibility is that the cellulose chains had a comparatively small number of linkages which reacted at a faster rate than did the predominant type of linkage. If this were true, it would shed some interesting light on the structure of the cellulose molecule, but an accurate evaluation of the first two factors would be a prerequisite to such a study.

(2)
Steurer ⁽⁶⁾ irradiating methycellulose in dioxane solution with precautions to exclude oxygen and water, also found that during the early stages the reaction was not of the monomolecular type. During the later stages of some of his experiments the rate approximated that of a first-order reaction, but his data are not consistent in this respect.

Increase in Copper Number

[It should be pointed out that the copper number determination is an empirical test and bears no exact stoichiometric relationship to any particular group in the cellulose molecule.] It is reasonable to expect, however, that the increase in copper number upon exposure to ultraviolet light is proportional to the increase in reducing groups. If the reaction which formed the reducing groups were of the first-order type, then a straight line should result for the first stages of the reaction when copper number is plotted against time of exposure. Figure 9 shows that this was not the case. The considerations brought out in the preceding section are equally applicable in explaining this deviation.

Formation of Gaseous Products

Although the cellulose being exposed could not conveniently be analysed at intervals during a single run, the rate of evolution of gases could be followed throughout

(12) Steurer, Z. phys. Chem., B, 111, 187 (1924), 201 (1925), and Usterlitz, Ber., 74, 190 (1941).

the exposure. Figure 10 shows that the rates of evolution of carbon monoxide, carbon dioxide, and water all increased continuously during the course of the longest exposure made (Experiment 12). In the case of the first two of these products, the rate of evolution was probably equal to the rate of formation, but this does not hold for the water. As cellulose in the dry state is extremely hygroscopic, the rate of evolution of water would not equal the rate of formation until the moisture content had risen to a certain value determined by the experimental conditions. Unfortunately, this made it impossible to follow, by the procedure used, the rate of formation of water during the irradiation. Furthermore, owing to the variability of the moisture contents of the samples at the start of the exposures, the amount of water formed during a given experiment could not be measured accurately. The data obtained in Experiment 12 definitely show that water was formed during the exposure.

The fact that the carbon monoxide and carbon dioxide were formed at increasing rates during the exposure indicates that they were the products either of secondary reactions or of both a primary reaction and of secondary reactions. As the curves extrapolate to an appreciable rate at zero time, the latter alternative is more probable.

Effect on Glucose and Cellobiose in Nitrogen

[The difference in the proportion of functional groups present in glucose, cellobiose, and an idealized cellulose is shown in Table VII.

TABLE VII

NUMBER OF FUNCTIONAL GROUPS PER GLUCOSE UNIT

Group	Glucose D.P. = 1	Cellobiose D.P. = 2	Cellulose D.P. = 1400
Glucosidic	0	0.5	0.999
Hemiacetal (End Group)	1	0.5	0.0007
Primary Hydroxyl	1	1	1
Secondary Hydroxyls	3	2.5	2]

[In view of these relationships,] The exposure of glucose and cellobiose under the same conditions used for cellulose might be expected to give some information of value. For example, if carbon monoxide resulted only from the photolysis of glucosidic linkings, no carbon monoxide would be expected when glucose was irradiated. Table VIII gives a comparison of the rates of evolution of carbon monoxide and carbon dioxide from glucose, cellobiose, and cellulose. The value for the latter is an average of several experiments.

No change in reducing power of either the glucose or cellobiose could be detected, although the method used

TABLE VIII
RATES OF GAS EVOLUTION

Compound	Length of Exposure Hr.	Rate of Evolution mmoles per Day	
		CO	CO ₂
Glucose	48	0.03	0.04
Cellobiose	108	0.02	0.02
Cellulose	—	0.09	0.07

was reproducible to ± 0.2 per cent. Both compounds after exposure showed an increased light absorption in the ultra-violet, as shown in Figures 11 and 12, but there were no characteristic features about the curves which might indicate the chemical nature of the products.

The results of these experiments give no direct information as to what actually happens to cellulose, but they do eliminate certain possibilities. The gases did not result from the photolysis of hemiacetal groups; if this were the case, the rates of evolution from glucose and cellobiose should have been much greater than from cellulose, because of the much higher proportion of hemiacetal groups in the sugars. The gases were probably not formed as primary products of the decomposition of glucosidic linkings, because they were evolved from glucose to about the same extent as from cellobiose. It should be remembered in this connection that the glucosidic linkage in cellobiose is not exactly equivalent to a glucosidic linkage in cellulose, owing to differences in the surrounding groups.

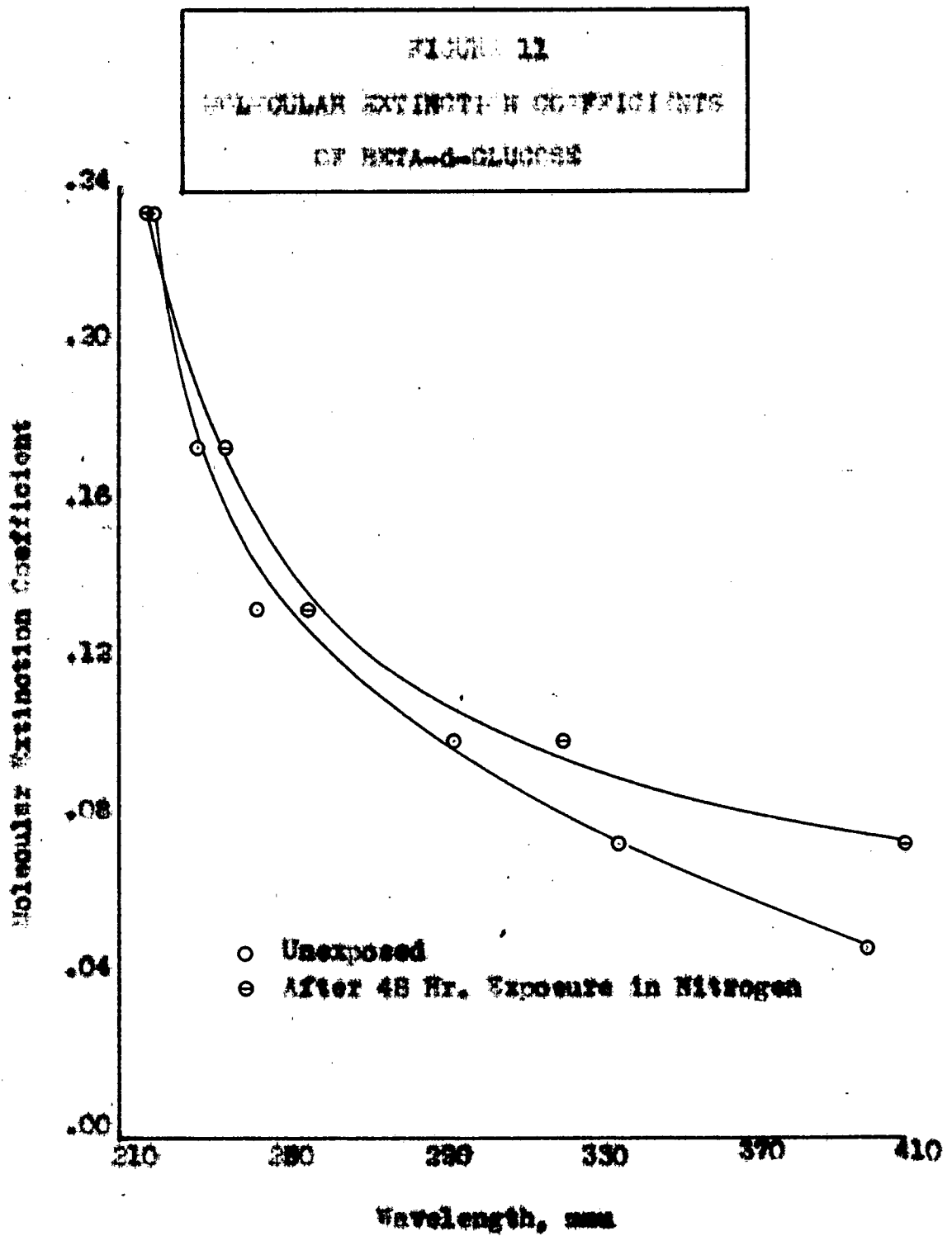
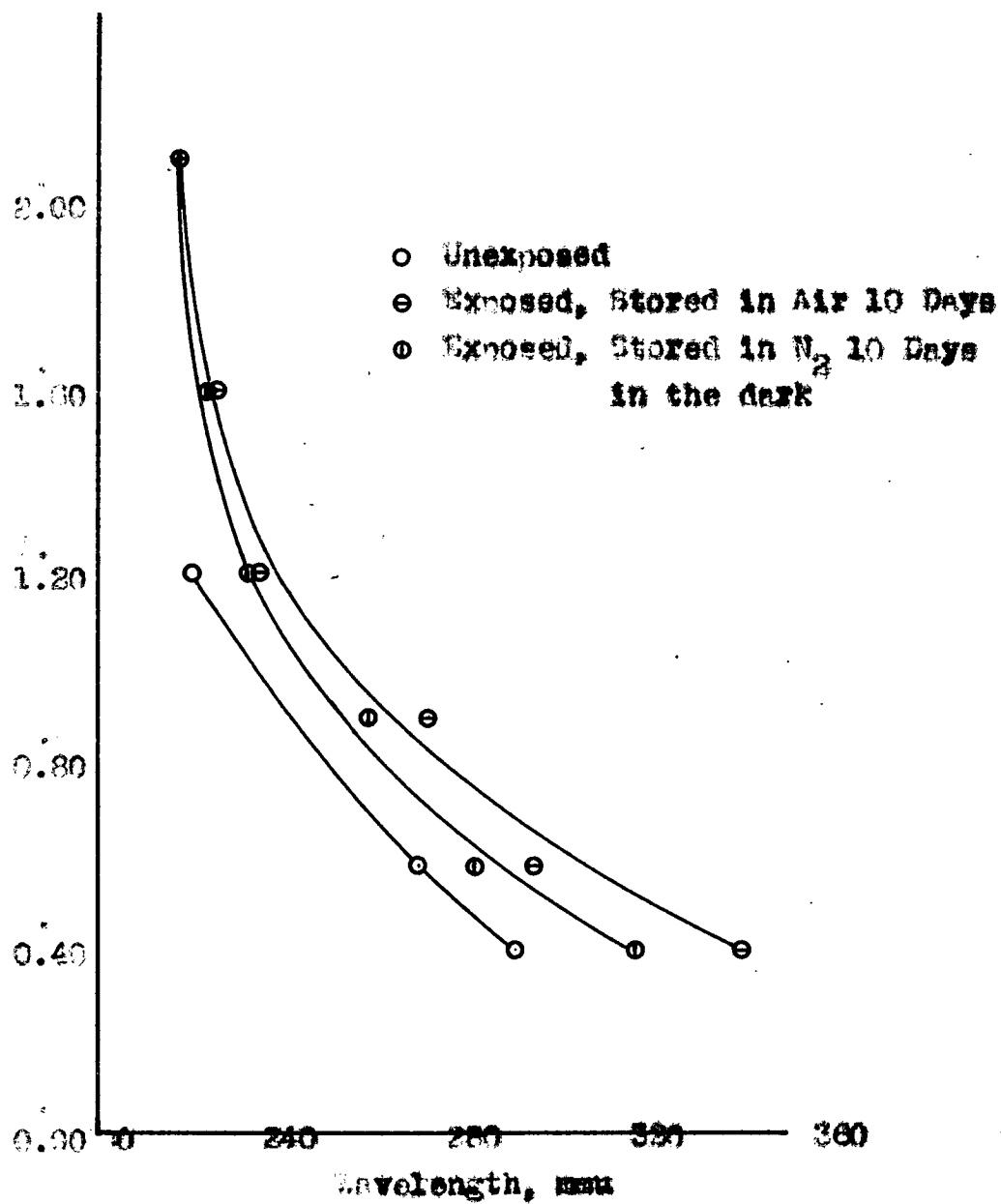


FIGURE 12
MOLECULAR EXTINCTION COEFFICIENTS
OF CELLOBIOSE



Instability of Exposed Samples

As the samples were exposed to light.

Degradation of the exposed samples continued during storage after the conclusion of the actual irradiation. Unfortunately, this effect was not discovered until late in the investigation, with the result that the data are somewhat haphazard and incomplete. The exposed samples were stored in air in screw-top glass bottles on a shelf in a laboratory with windows on the north wall. The samples were thus never exposed to direct sunlight or to elevated temperatures. No degradation occurred in the unexposed material stored under the same conditions during the investigation.

Figure 13 shows the change in degree of polymerization of several samples during storage. In the case of exposed sample 4, about two months were required to reach a constant value. Table V shows that the copper number and alpha-cellulose content also continued to change during storage. The changes were much smaller for the samples exposed in the presence of oxygen.

After exposed sample 12 had been stored in air for a week, a portion of it stored in nitrogen in the dark for the succeeding two weeks showed no decrease in chain length during the latter period. At the same time, the sample stored in air in the light of the laboratory underwent

no degree of polymerization
a drop from 780 to 700. A portion of ^a sample 14, which had been irradiated 48 hours in a nitrogen atmosphere, was stored in nitrogen in the ordinary light of the laboratory immediately at the conclusion of the exposure. The rest of the exposed material was stored in air under the same conditions. At the end of the irradiation, the degree of polymerization was 1280. After six days' storage, the sample in nitrogen had a degree of polymerization of 1310; that of the portion in air had dropped to 1200. These results *seem to show* [definitely establish] that the after effects are due to oxidation by atmospheric oxygen.

decrease in chain length
In an attempt to [determine whether any decrease in chain length actually occurred during the irradiation in a nitrogen atmosphere,] the cuprammonium viscosity of *the sample* [exposed] sample 14 was determined as soon as possible after the end of the irradiation. The material was *exposed to* air for about one hour during the weighing of the samples and filling of the dissolvers. [A decrease in chain length] *had occurred, as the value obtained by this procedure* was 1260 compared with the original degree of polymerization of 1400. On the basis of the data obtained, however, it can not be said definitely that this decrease was caused by the action of light in the absence of oxygen. The decrease could also be explained by ~~the presence of~~ ^{left} a small amount of oxygen in the cellulose at the start of the irradiation

or by the fact that the sample was exposed to air for a short time between the end of the exposure and the start of the viscosity determination.

The occurrence of these secondary oxidation effects probably helps to explain the many discrepancies in the literature on the relation of oxygen to the photolysis of cellulose. If one investigator performed his analysis immediately after exposure in the absence of oxygen, he probably observed smaller effects than another who stored his exposed samples in air for some time before analysing them. It is believed that this difference would show up not only in chemical analysis, but also in strength determinations, as tensile strength of fibers is closely related to viscosity in cuprammonium hydroxide or chain length.]

Miscellaneous Analyses

Volatile Products

No hydrogen or volatile organic products could be detected in the gas issuing from the sample chamber during any of the exposures. Any easily oxidizable compounds, such as formaldehyde, would have been detected by the sodium hypiodite solution; any other organic material would have been burned in the high temperature combustion tube and detected as carbon dioxide and water.]

Ozone

The formation of ozone could be a factor in the degradation of cellulose by ultraviolet light in the presence of oxygen. During Experiment 9, conducted in air, the gas issuing from the chamber was tested for the presence of ozone by bubbling through a potassium iodide-starch solution. No ozone could be detected by this sensitive test.

Pentosans

Table IX shows that there was no appreciable change in the pentosan content of the cellulose during irradiation in either nitrogen or air. The markedly lower values given by the colorimetric method are probably due to the fact that this method is specific for furfural, whereas the phloroglucinol precipitation is not.

TABLE IX

EFFECT OF EXPOSURE ON PENTOSAN CONTENT

Experiment	Atmos.	Length of Exposure Hr.	Phloroglucinol Pentosans %	Colorimetric Pentosans %
Unexposed			0.75	0.26
12	N ₂	336	0.77	0.26
9	20% O ₂	24	0.73	0.28

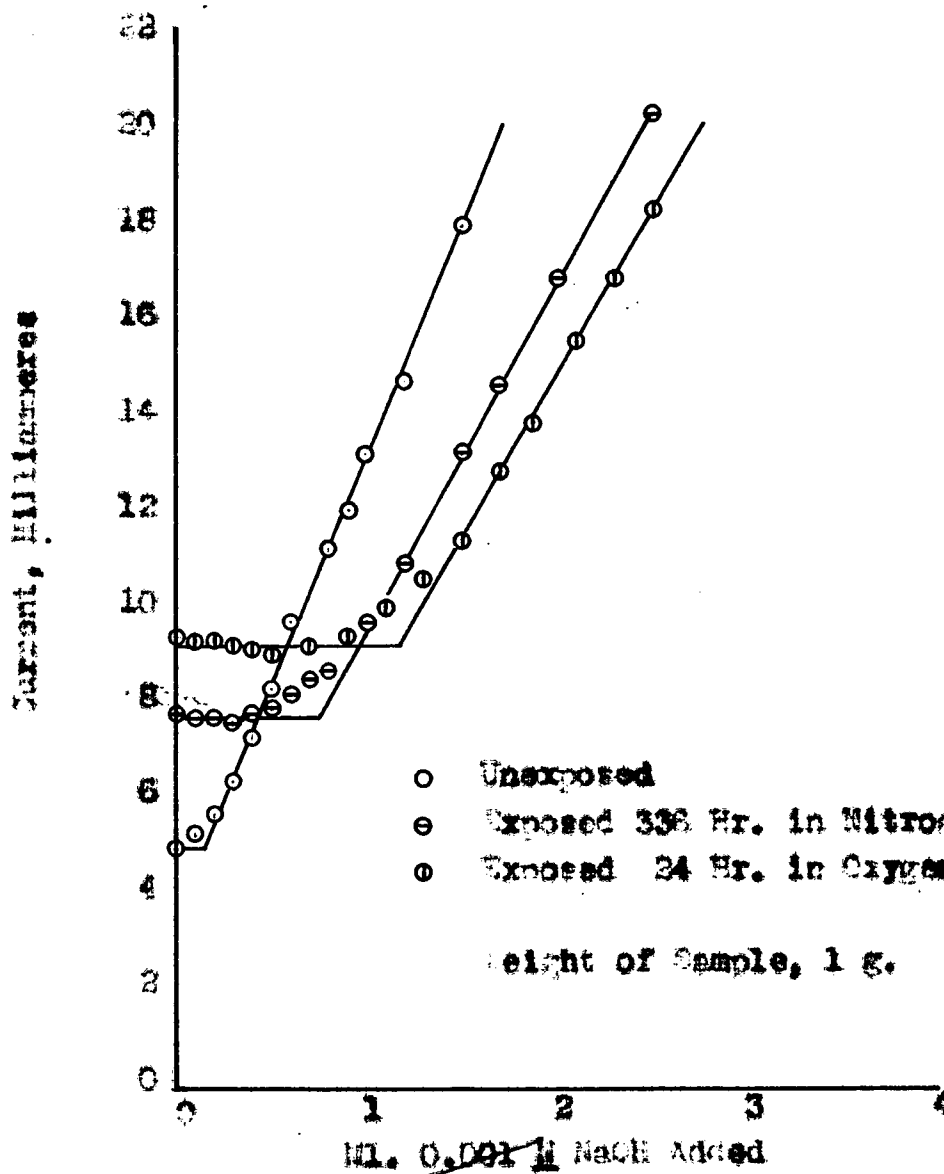
Acidity

Figure 14 shows that minute amounts of a monobasic acid were produced by exposure in both nitrogen and oxygen. This acid could not have been responsible for the degradation of the sample during storage for several reasons. In the first place, any acid formed would be necessarily organic and therefore weak. Exposed sample 6, which showed the largest acid content, suffered less secondary degradation than did most of the other exposed samples. Finally, the action was stopped by excluding atmospheric oxygen, and therefore could not have been caused by acid hydrolysis.

Ultraviolet Absorption of Cellulose

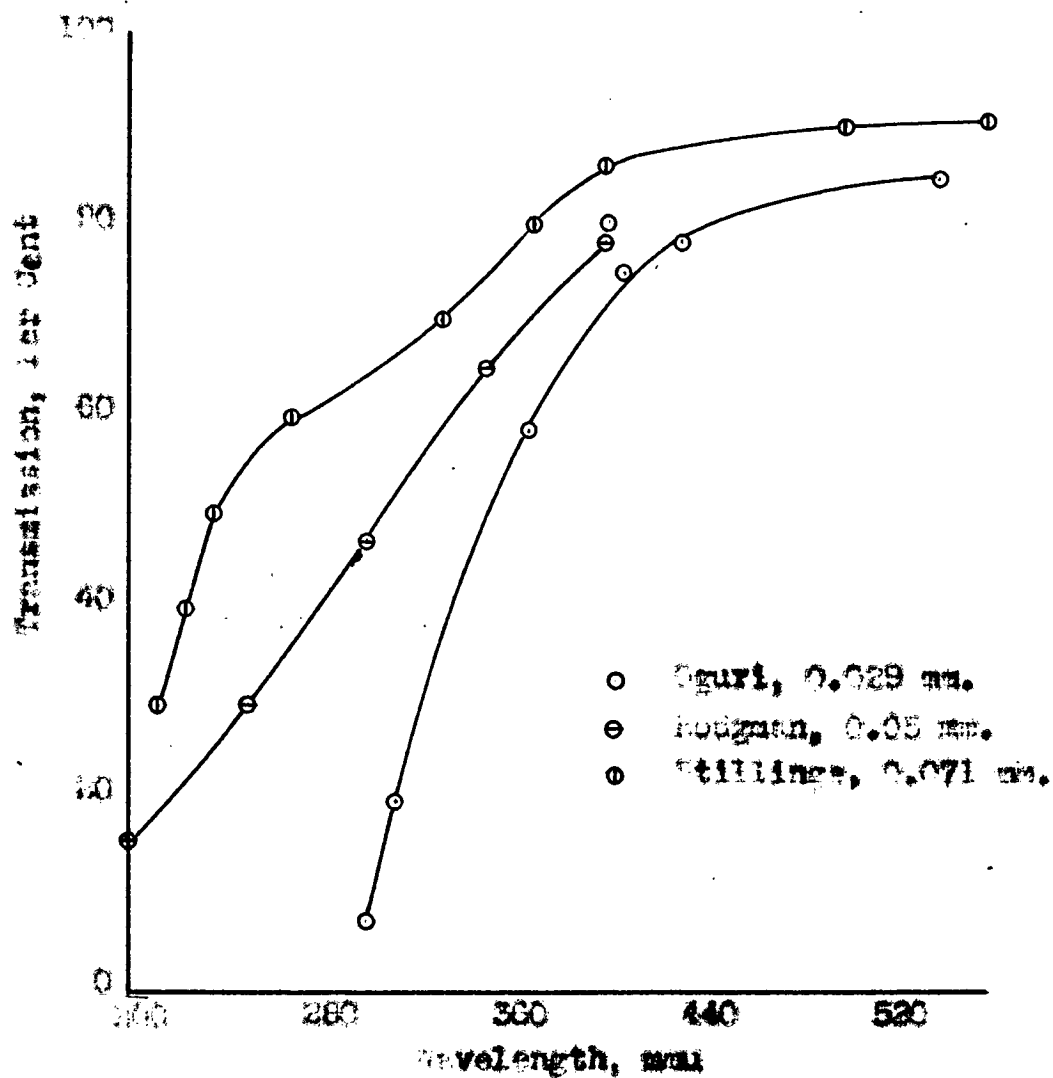
Figure 15 shows the spectral transmission of cellophane as determined by several investigators. Cellophane is not composed wholly of cellulose, but it seems probable that the absorption of light by a relatively pure cellulose would be no greater than that of the most transparent sample of cellophane. The sample measured in this investigation had been water extracted to remove the plasticizer, which perhaps accounts for the higher transmission found. It would have been desirable to express the results as absorption coefficients, but this could not be done because the index of refraction of cellulose in the ultraviolet was not known.

FIGURE 1:
CONDUCTIMETRIC TITRATIONS
OF CELLULOSE



0.01

FIGURE 15
SPECTRAL TRANSMISSION
OF POLYIMIDE



hydrogen was formed during irradiation of the cellulose. Photolysis of simple primary alcohols results in the formation of hydrogen and the corresponding aldehyde; secondary alcohols yield hydrogen and the corresponding ketone.

If the primary action were ^{the} [the splitting] of glucosidic linkages, the chain length would necessarily be decreased during the irradiation. It has been shown that this occurred only to a small extent and could ^{possibly} be explained [equally well] by the presence of a small amount of oxygen in the cellulose at the start of the exposure. ^{It would be possible to} Even if some ^{change} [chain-splitting] did occur as the result of the primary photolysis of glucosidic linkages, this could not have been the only primary reaction. The fact that the chain length ^{had} of the exposed samples ^{were} decreased by air oxidation following the actual irradiation period necessarily means that some other primary reaction took place. This reaction was not directly concerned with chain-splitting, but it ^{obviously} modified the linkages affected so that they were no longer stable to atmospheric oxygen.

The question arises whether the increase in reducing power and the evolution of gases were concerned in the reaction that made the chains subject to ^{decomposition} [splitting] by air oxidation. Some indication can be obtained by comparing the g values calculated by the Sakurada equation with the production of reducing groups and gases expressed as

millimoles per millimole of cellulose. Based on an average chain length of 1400 glucose units or a molecular weight of 227,000, a millimole of cellulose is 227 grams.

Table X is a tabulation of such a comparison for most of the experiments. As the \underline{g} values were calculated from the chain lengths which were reached after oxidation of the exposed samples by air, only those experiments are included in which the chain length had reached a practically constant value. The reducing power was calculated from the increase in copper number. The values of reducing power given for Experiments 2, 5, and 8 are based on copper numbers determined about a week after the start of the exposure, and so are not the ultimate values which would have been attained.

It can be seen that, on the whole, there is a fairly close correspondence between the \underline{g} values and the carbon monoxide and carbon dioxide values. This is a strong indication that the production of these gases was directly associated with the reaction which ultimately led to chain ^{cleavage /}splitting, one molecule of each gas being produced per ^{split}split.

The values for reducing power run about ten times the \underline{g} values. This would correspond to the production of five aldehyde or similar groups per chain split, which seems

Reaction Mechanism

In considering the photolysis of cellulose in the absence of oxygen, several possibilities present themselves.

If only the end reducing groups were involved in the primary reaction, no appreciable decrease in chain length would be expected unless the attack continued progressively along the chain. In such a case, a given reduction in degree of polymerization would be accompanied by the formation of a corresponding amount of low molecular weight compounds. If the chain length were decreased to 60 per cent of its original value by this type of process, a corresponding decrease in alpha-cellulose content would be expected. This was not the case. The fact that the exposure of glucose and cellobiose, which have a very much larger proportion of reducing groups than cellulose, resulted in no measurable change in reducing power is another indication that the reducing groups were not appreciably affected.

A second possible point of attack is an alcohol group. Other investigators have shown that in the absence of oxygen simple alcohols are stable to light of wavelengths above 200 mμ.⁽¹³⁾ As the lower wavelength limit in this investigation was about 230 mμ, analogy indicates that the alcohol groups, especially the primary one, were probably not affected. This was confirmed by the fact that no

(13) Barthelme and Szwarcman, Compt. rend., 156, 68 (1912);
Franks and Plummer, J. Am. Chem. Soc., 59, 2450 (1937).

TABLE X
RELATIONSHIP OF ANALYTICAL RESULTS

Experiment	D.P.	n	*Reducing Power milliequiv.	*CO moles	*CO ₂ moles
5	1070	0.87	5.0	0.47	0.35
2	970	1.22	7.9	0.88	0.70
3	960	1.28	13.6	1.29	1.23
4	960	1.70	18.6	2.28	1.40
8	960	1.70	15.0	2.57	1.99
10	950	1.30	13.5	0.99	1.05
9	870	1.65	17.8	1.29	1.29
6	740	2.31	44.3	2.16	2.28
7	1230	0.40	4.3	0.64	0.94

* Based on one millimole or 227 grams of cellulose

rather improbable. More likely, the reducing groups were formed, at least in part, from some other reaction not ultimately resulting in chain splitting.

The acidity formed during exposure 6 amounted to only 0.23 milliequivalents per millimole of cellulose, and in the other experiments the proportion was even smaller. Thus, the production of acidity was either a secondary reaction or the result of some reaction not resulting in chain splitting.

The fact that carbon dioxide and carbon monoxide were formed necessarily means that anhydroglucose units were being decomposed. This suggests that pentose units might have resulted, but no change in pentosan content could be detected, [confirming the results of Foote (20)]. The possibility remains that desoxy pentoses or carbohydrate units of still fewer carbon atoms were formed, but the amounts corresponding to the quantities of gases produced would be very small.

SUMMARY AND CONCLUSIONS

An apparatus has been developed which is suitable for the ultraviolet irradiation of solids in powder form in various atmospheres. Provision was made for evacuation prior to the exposure, continuous mixing, and continuous analysis of gaseous products.

The influence of oxygen on the photolysis of cellulose has been studied, as have the kinetics of the reaction in nitrogen. Samples of glucose and cellobiose have been irradiated in a nitrogen atmosphere under the same conditions as used for cellulose. The most important results obtained in the investigation may be briefly summarized as follows.

1. The samples irradiated in nitrogen with all possible precautions to remove and exclude oxygen showed considerable degradation, the amount increasing with increasing time of exposure. These changes could not be explained by the presence of oxygen in the nitrogen or retained in the cellulose at the start of the exposure.
2. The rate of degradation increased with increasing oxygen content in the atmosphere.
3. The rate of reaction was smaller for cellulose in the air-dry state than in the oven-dry state.

4. The cellulose was yellowed by irradiation, the effect increasing with increasing time of exposure in nitrogen but decreasing with oxygen content in the atmosphere.

5. The rates of change of chain length and copper number during irradiation in nitrogen did not correspond to the rates calculated on the assumption that the reaction was of the first-order type.

6. Exposure of glucose and cellobiose, ^{glucose} resulted in the production of carbon monoxide and carbon dioxide, but at a considerably slower rate than in the case of cellulose. No change could be detected in the reducing power of these sugars, but exposed samples showed an increased absorption of ultraviolet light.

7. Cellulose irradiated in the absence of oxygen was left in an unstable state at the conclusion of the exposure, ^{- i.e., the changes which the cellulose showed after irradiation continued to occur} ~~oxidation by atmospheric oxygen occurring during~~ ^(continued) ~~storage at room temperature, however, as a special case, the~~ ^{cellulose was found to be stable.}

The following main conclusions can be drawn from the results.

1. The photolysis of cellulose occurs in the ^{presence of} absence of oxygen, but at a slower rate than when oxygen is present.

2. One primary reaction which occurs in the absence of oxygen is a modification of the original linkages without ^{actual rupture} [chain splitting]. Subsequent exposure to atmospheric oxygen at room temperature results in breakage of these modified linkages.

3. There is also some evidence that ^{chain} splitting occurs during irradiation in the absence of oxygen.

4. The production of carbon monoxide and carbon dioxide are probably related in some manner to the primary reaction which results in the ^{formation of the} easily oxidizable linkages.

5. The production of reducing groups is probably independent, at least in part, of this reaction.

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