nard). The trap C leads into glacial acetic acid, in which manner diazomethane becomes a reagent which can safely be used without other special precautions.

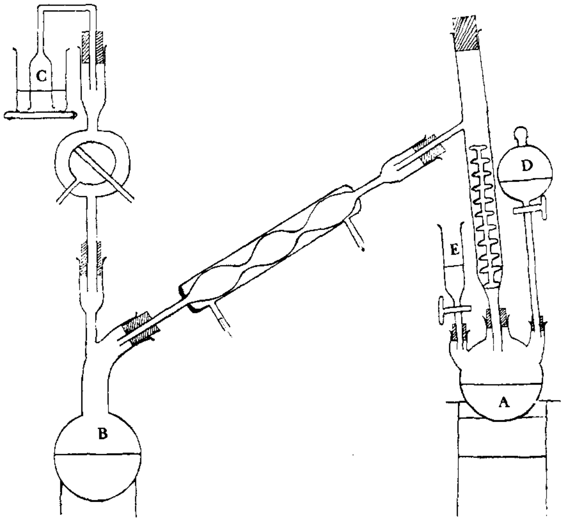

Fig. 1.

Summary

It is shown that the interaction of diazomethane with aromatic acyl chlorides proceeds on the same lines as the Schlotterbeck reaction, and requires no special interpretation, as suggested by Robinson.

BRISTOL, ENGLAND

[COMMUNICATION NO. 397 FROM THE KODAK RESEARCH LABORATORIES]

OPTICAL ROTATION OF CELLULOSIC MATERIALS. I. THE OPTICAL ROTATION OF SOLUBLE CELLULOSE IN ALKALI[1]

BY T. F. MURRAY, JR., C. J. STAUD AND H. LEB. GRAY

RECEIVED JULY 9, 1929 PUBLISHED APRIL 7, 1930

It appeared to the writers that a study of the optical rotation of the alkali-soluble portion of cellulose might help in determining the nature of the material dissolved and possibly the degradation which the cellulose has undergone.

Perhaps no reaction in cellulose chemistry has been more studied than the solubility of cellulose in alkali, almost continuously since the time of John Mercer.[2] A résumé has been published recently by G. Blanco.[3]

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[1] Presented before the Division of Cellulose Chemistry of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] John Mercer, English Patent 13,296 (1850).

[3] G. Blanco, *Ind. Eng. Chem.*, **20**, 926 (1928).

The optical properties of alkaline solutions of cellulose appear to have received but little attention. Hess and Messmer,[4] in 1922, determined the optical rotation of the material regenerated from cuprammonium solutions and in 1923 Hess, Weltzien and Messmer[5] gave the results of three additional observations.

Apparently the interest was to show that the material from cuprammonium solution did not give in alkali a specific rotation comparable with that in Schweizer's reagent.

Experimental

The cellulose employed was a high grade long fiber cotton known as "Eastman Filtration Cotton." It had the following analysis

α-Cellulose	98.9%[6]	Moisture	3.7%[9]
Copper number	0.064[7]	Ash	0.072%
Cuprammonium viscosity 5522 centipoises[8]			

The optical rotation was determined in a Hilger triple field polarimeter accurate to 0.01° angular rotation. The light source was a mercury vapor arc, passed through a Corning Novial glass and Didymium filter (W. and W. No. 77), giving monochromatic green light of wave length 546.1mμ. Readings were made at 25°.

Action of Acids

Three acids were used, orthophosphoric, sulfuric and hydrochloric at concentrations of 3 N. The equivalent of 16.20 g. of dry cotton (0.10 mole of $C_6H_{10}O_5$) was immersed in 600 cc. of acid solution and allowed to stand at 54° (with occasional shaking) for twenty-four and forty-eight hours in a jacketed air-bath heated by boiling acetone.

After the acid treatment, the liquid was filtered by suction, the cellulose forming its own mat with repeated filtration. The filtrate was held for determination of its optical rotation. The residue was washed until neutral to brom thymol blue, dried at 105°, weighed to the nearest centigram and the amount dissolved in the acid thus determined.

The optical rotations of the acid filtrates were determined using 2-dm. polarimeter tubes, and the specific rotations were calculated according to the usual equation.

Two samples weighing 4.05 g. (1/40 mole of $C_6H_{10}O_5$) each of the oven dry residues from the acid hydrolysis were extracted, using with each

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[4] Hess and Messmer, *Ber.*, **55**, 2436 (1922).

[5] Hess, Weltzien and Messmer, *Ann.*, **435**, 139 (1924).

[6] Tentative method proposed by the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem., Anal. Edition*, **1**, 52 (1929).

[7] Staud and Gray, *Ind. Eng. Chem.*, **17**, 741 (1925).

[8] Standard method proposed by the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem., Anal. Edition*, **1**, 49 (1929).

[9] Determined by drying for twelve hours at 105°.

Table I

Experimental Results

3 *N* acid	Phosphoric		Sulfuric		Hydrochloric	
Treatment, hours	24	48	24	48	24	48
Loss of wt., g.	0.06	0	0.11	0.20	0.42	0.73
°α	0.0	..	+0.02	+0.03	+0.05	+0.08
[α]	0.0	..	+54.5	+45.0	+35.7	+33.0

sample 40.5 cc. of 17.5% sodium hydroxide (grams per 100 g. of solution) for twenty-four hours at room temperature, 23–25° with occasional agitation. The material was then filtered by suction on a tared Gooch crucible, the cellulose forming its own mat with repeated filtration. The filtrate was held for polarimetric examination and the residue washed as in the α-cellulose determination.[6] This method was used for the sulfuric and phosphoric acid treated materials.

The hydrochloric acid product was too highly degraded to use the above method. It was separated by centrifuging and washed in the cups with water, 10% acetic acid, and again with water until neutral to litmus. The material was then dehydrated by 95% alcohol and finally ether.

All residues were dried at 105° and weighed. The weight differences were used in calculating the specific rotations. The amounts of material dissolved and the rotations of the alkaline extracts are given in Table II. The alkali extract of the sample hydrolyzed for twenty-four hours with hydrochloric acid was too hazy to read as obtained. It was diluted with two volumes of 17.5% sodium hydroxide and the rotation multiplied by three.

Table II

Experimental Data

Acid used for hydrolysis	Time of acid treatment, hours	Material extracted by 40.5 cc. of 17.5% NaOH, g.	Dissolved in 17.5% NaOH, %	Length of tube, dm.	α	[α]
H_3PO_4	24	0.13	3.2	2	−0.08°	−12.5°
	24	.10	2.5	2	− .08°	−16.2°
				0.5	− .02°	−16.2°
	48	.12	3.0	2	− .08°	−13.5°
				0.5	− .03°	−20.2°
	48	.11	2.7	2	− .08°	−14.7°
				0.5	− .02°	−14.7°
H_2SO_4	24	.30	7.4	2	− .14°	− 9.5°
	24	.25	6.2	2	− .14°	−11.4°
	48	.42	10.4	2	− .25°	− 9.1°
	48	.42	10.4	0.5	− .05°	− 7.3°
HCl	24	1.37	33.8	0.5	− .21°	−12.4°
	24	..		0.5	− .18°	.....
	48	..		0.5	− .21°	.....
	48	1.94	48.0	0.5	− .23°	− 9.6°

Action of Oxidants

Potassium permanganate and potassium dichromate were used as oxidants. All oxidations were conducted in *N* orthophosphoric acid. Concentrations of 0.5 and 2 available oxygen atoms per unit of $C_6H_{10}O_5$ were used. Oxidations were at room temperature, 23–25° and at 54° for two and six hours at each temperature.

As a control phosphoric acid was used alone under the same conditions, the product being filtered by suction, washed until neutral to brom thymol blue and dried at 105°. The differences in weights between the untreated material and the phosphoric acid products varied from 0.01 to 0.08 gram, which was disregarded since the maximum loss is less than $^1/_2\%$.

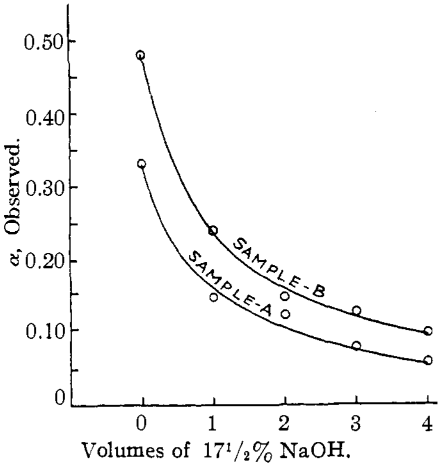


Fig. 1.—Relation between optical rotation and dilution of alkaline extracts of oxidized cellulose.

In all oxidations the equivalent of 16.20 g. of oven-dried cellulose was used; 600 cc. of oxidizing solutions were prepared by dissolving 3.2 g. and 12.7 g. of potassium permanganate, and 9.8 g. and 39.2 g. of potassium dichromate, respectively, in 600 cc. portions of *N* phosphoric acid. In runs at 54° the cotton and solution were each heated to that temperature before mixing.

The products from potassium dichromate were filtered with suction and washed with water. The residual dichromate was removed as indicated by lead acetate and dried at 105°. The loss in weight was from 0.01 to 0.06 g., or less than 0.4%.

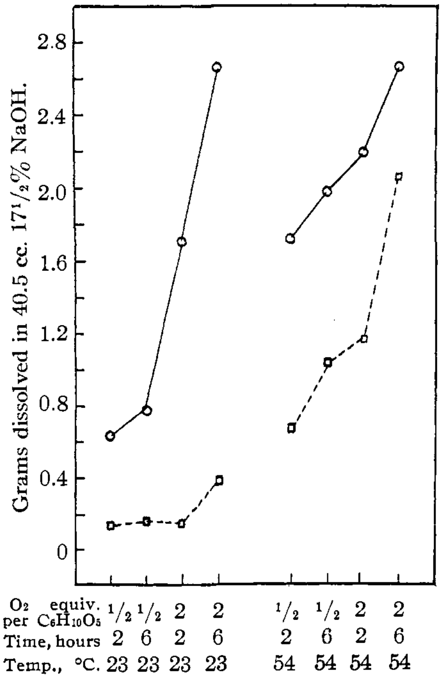
The products from potassium permanganate were filtered by suction, except those oxidized at the higher concentration, which were separated by centrifuging. The excess permanganate, if any, was removed by wash-

Table III

Loss in Weight of Cellulose Due to Oxidation with Potassium Permanganate

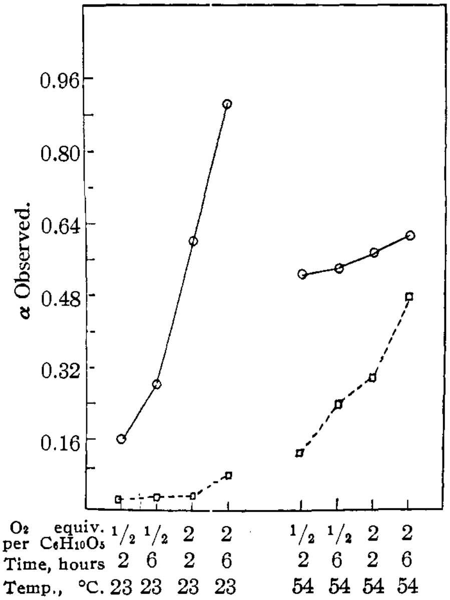
Available oxygen atoms per $C_6H_{10}O_5$	Time of oxidation, hours	Temp., °C.	Loss in weight, g.	Loss, %
0.5	2	23	0.09	0.56
0.5	6	23	0.13	0.80
2	2	23	0.28	1.7
2	6	23	1.38	8.5
0.5	2	54	0.72	4.5
0.5	6	54	0.93	5.7
2	2	54	4.01	24.8
2	6	54	4.11	25.4

ing with water and the manganese dioxide dissolved using dilute sodium bisulfite containing a little hydrochloric acid. The product was washed with water until neutral to brom thymol blue and dried at 105°. The losses in weight are given in Table III.



Oxidants: ———, $KMnO_4$; – – –, $K_2Cr_2O_7$.

Fig. 2.—Relation between oxidizing conditions and weight dissolved in 17.5% NaOH.

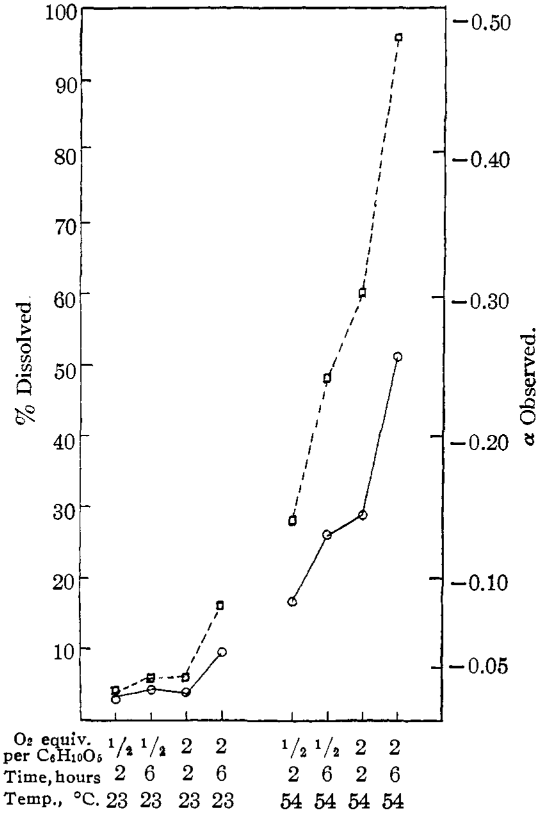


Oxidants: ———, $KMnO_4$; – – –, $K_2Cr_2O_7$.

Fig. 3.—Relation between oxidizing conditions and the observed rotation of the alkaline extracts.

When the cellulose was treated at 54° with 0.5 and 2 oxygen equivalents for six hours, the color of the potassium permanganate had entirely disappeared after approximately three hours, but manganese dioxide was present even at the close of the six-hour period.

The filtrates from the solutions with two oxygen equivalents of permanganate in the two and six hour treatments at 54°, after decolorizing by the addition of a minute quantity of sodium bisulfite crystals, were read. The two-hour sample showed no optical activity and the six gave $-0.03°$ in a 2-dm. tube, corresponding to a specific rotation of about $-2°$.



——, % Dissolved in 17½% NaOH; - - -, observed rotation.

Fig. 4.—Oxidation with potassium dichromate. Effect of conditions on amount dissolved in alkali and observed rotation.

Four and five-hundredths grams ($^1/_{40}$ mole of $C_6H_{10}O_5$) of each of the oxidized materials were extracted for twenty-four hours at room temperature, 23–25°, with 40.5 cc. of 17.5% sodium hydroxide, treated as described under the alkaline extraction of hydrocellulose, filtered where practicable and centrifuged when necessary.

TABLE IV

EXPERIMENTAL RESULTS

Oxidant	Available oxygen atoms per $C_6H_{10}O_5$	Time of treatment, hours	Temp., °C.	Grams dissolved in 17.5% NaOH	Dissolved in 17.5% NaOH	α	$[\alpha]$	Dilution, volumes of 17.5% NaOH added
$KMnO_4$	0.5	2	23	0.58	14.3	−0.14	−19.6	1
				0.69	17.0	− .18	−21.1	2
	0.5	6	23	0.75	18.5	− .28	−30.4	1
				0.80	19.8	− .28	−28.4	2
	2	2	23	1.53	37.8	− .60	−31.8	0
				1.89	46.6	− .51	−21.9	2
	2	6	23	2.66	65.8	− .90		2
						− .90	−27.4	4
	0.5	2	54	1.72	42.5	− .51	−21.3	2
						− .54		2
	0.5	6	54	1.98	49.0	− .54		2
						− .54	−22.2	2
	2	2	54	2.19	54.1	− .63	−23.4	2
						− .51		2
	2	6	54	2.67	66.0	− .57		2
						− .65	−17.3	4
$K_2Cr_2O_7$	0.5	2	23	0.14	3.5	− .02	−11.6	0
						− .01		0
	0.5	6	23	0.17	4.2	− .03	−14.3	0
						− .02		0
	2	2	23	0.15	3.7	− .03	−16.2	0
						− .03		0
	2	6	23	0.39	9.4	− .08	−16.6	0
						− .07		0
	0.5	2	54	0.67	16.5	− .15	−17.9	0
						− .12		2
	0.5	6	54	1.04	25.7	− .24	−18.7	2
						− .24		2
	2	2	54	1.17	28.9	− .27	−18.7	2
						− .33		2
	2	6	54	2.14	52.9	− .45	−17.0	2
				1.99	49.1	− .51	−20.7	2
Controls, H_3PO_4, no oxidant, original cotton	...	2	23	0.09	2.2	− .01	− 9.0	0
	...	6	23	0.08	2.0	− .02	−20.4	0
	...	2	54	0.07	1.7	− .02	−23.2	0
	...	6	54	0.06	1.5	− .02	−27.0	0
	...	.	..	0.09	2.2	− .02	−18.0	0

TABLE V

OPTICAL ROTATION OF DILUTED ALKALINE EXTRACTS

Volumes of 17.5% NaOH added	Sample A		Sample B	
	Obs. α	Calcd. α	Obs. α	Calcd. α
0	−0.33	α −0.33	−0.48	α −0.48
1	− .15	2α − .30	− .24	2α − .48
2	− .12	3α − .36	− .15	3α − .45
3	− .08	4α − .32	− .13	4α − .52
4	− .06	5α − .30	− .10	5α − .50

The alkaline extracts were read and the results are given in Table IV. When too dark in color or too hazy the solutions were diluted with 17.5% sodium hydroxide. The dilutions are indicated in the table and the values under α are equal to the observed rotation multiplied by [1 + (the dilution factor)].

The validity of diluting with 17.5% sodium hydroxide was established as follows. Two samples of cellulose of high alkali solubility were extracted and clear initial solutions obtained. Portions were diluted with 0, 1, 2, 3 and 4 volumes of 17.5% alkali and readings made. The results are given in Table V and shown graphically in Fig. 1.

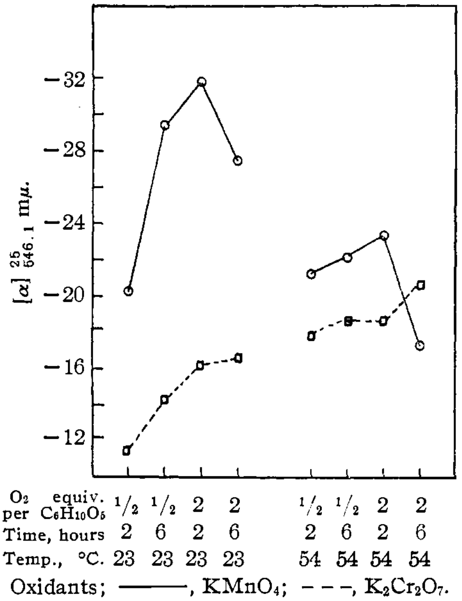


Fig. 5.—Effect of oxidizing conditions on the apparent specific rotation of the alkaline extracts.

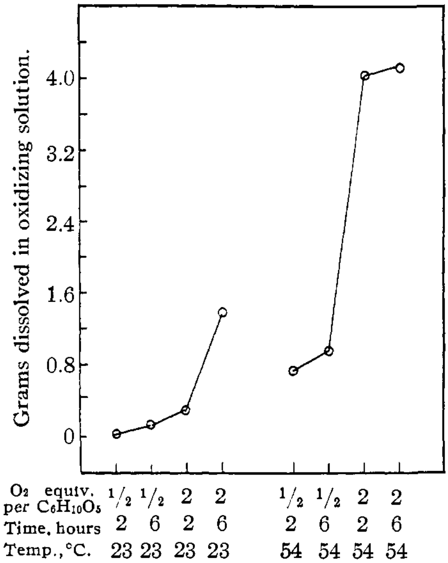


Fig. 6.—Relation between oxidizing conditions using $KMnO_4$ and weight dissolved in oxidizing solution.

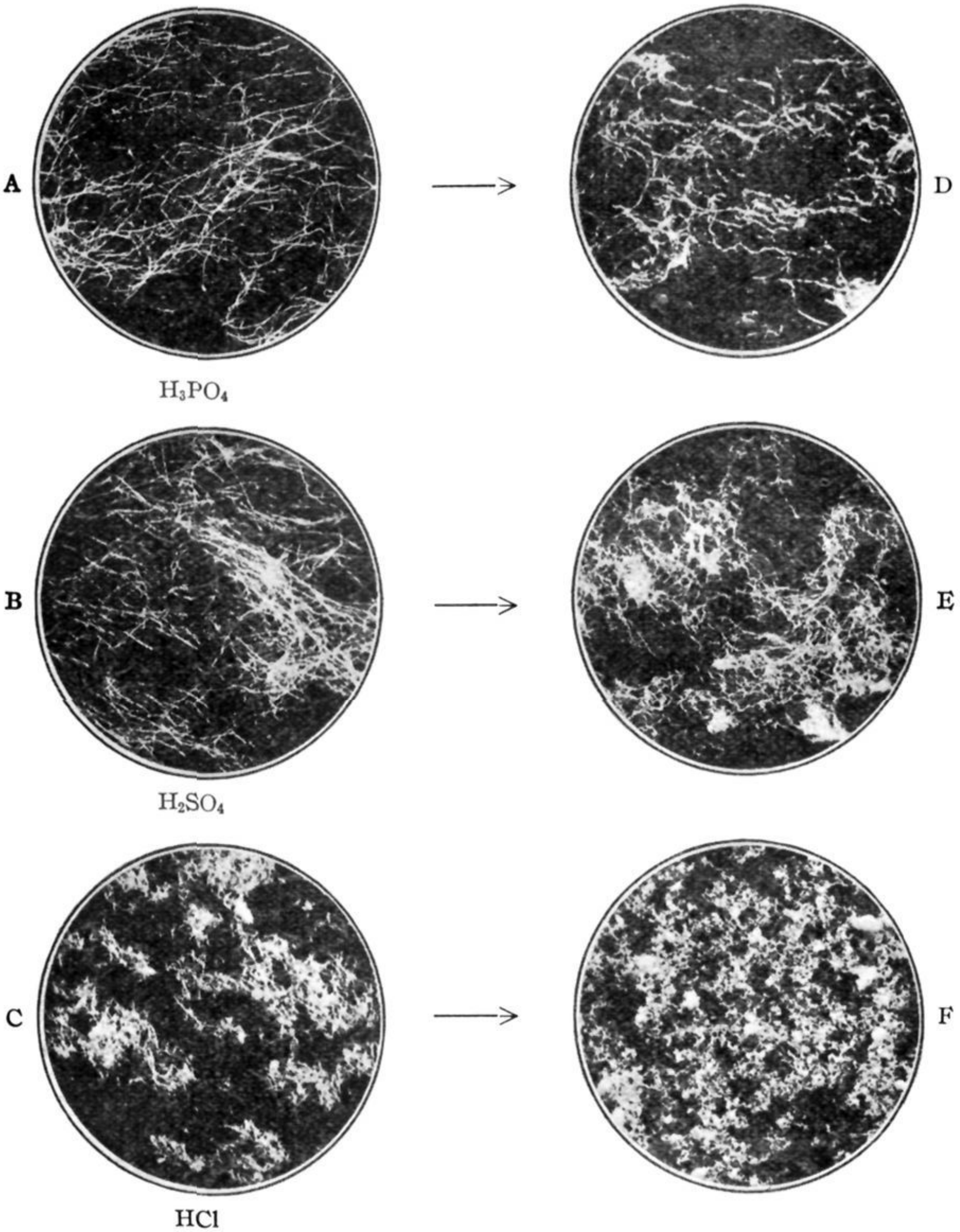
Discussion of Results

Action of Acids.—The activity of the acid solutions, indicated by material dissolved and fiber breakdown (Plate I, A, B and C) increased in the order orthophosphoric, sulfuric and hydrochloric acids.

The acid filtrates were all dextrorotatory, indicating possibly dextrose. Dextrose in the three 3 *N* acids gave specific rotations of +61.0°, +61.0° and +62.0°. The small amounts dissolved during acid hydrolysis render the specific rotations somewhat doubtful.

The alkaline extracts varied from 2.5% for the phosphoric to 48% for the hydrochloric acid hydrocellulose (Table II). All were levorotatory (from −0.02 to −0.23°), confirming the observations of Hess[4,5] and his co-workers on regenerated cellulose.

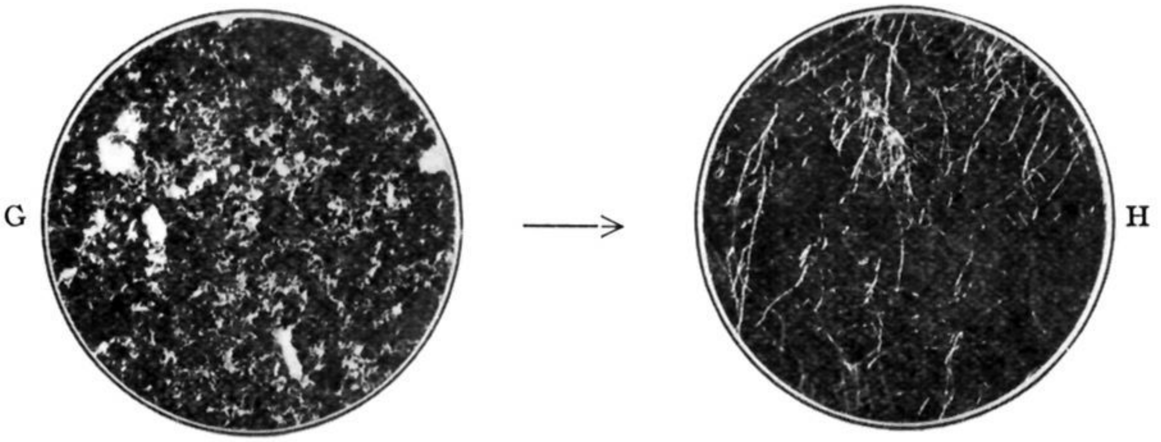
Action of Oxidants.—The loss in weight by potassium dichromate oxidation varied from 0.06 to 0.37% approximating the *N* phosphoric



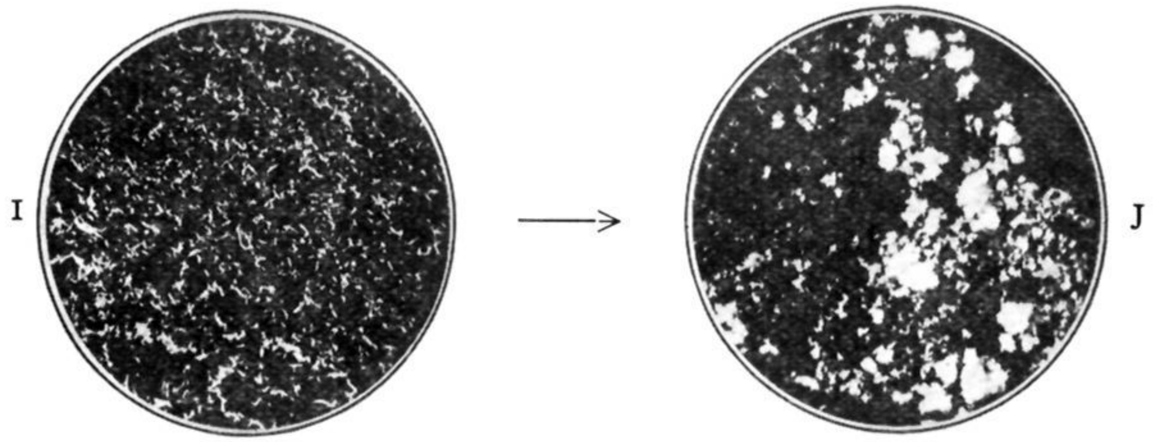
The effect of 3 *N* acids at 54° for forty-eight hours on cellulose.

The effect of $17^1/_2\%$ sodium hydroxide on the corresponding hydrocelluloses.

Plate I.



$K_2Cr_2O_7$



$KMnO_4$

The effect of oxidants on cellulose using 2 oxygen equivalents per $C_6H_{10}O_5$ for six hours at 54°.

The effect of $17^1/_2\%$ sodium hydroxide on the corresponding oxidized celluloses.

Plate II.

acid control. The 17.5% sodium hydroxide soluble was 0.14 to 2.14 g. (Fig. 2 and Table IV), increasing steadily for that treated at 54°. All observed rotations were levorotatory (from -0.02 to $-0.48°$, Fig. 3). The apparent specific rotations were $-11.6°$ to $-20.7°$ (Table IV and Fig. 5). Both the observed and specific rotations increase with more severe oxidation. A parallelism between weight dissolved and observed rotations appears to exist (Fig. 4).

With potassium permanganate from 0.56 to 25.4% dissolved (Table III and Fig. 6), which is a marked difference from the potassium dichromate oxidation. Alkaline extracts contained from 0.58 to 2.67 g. (Table IV and Fig. 2). These values fall into two groups, depending upon the temperature of oxidation, each increasing with increased severity of oxidation. The parallelism of the potassium dichromate series (Fig. 4) is not as marked in this case (Fig. 7). Apparent specific rotations of the alkaline extracts pass through maxima at both temperatures (Fig. 5).

The term "apparent" specific rotation has been used because probably more than one substance is present in the alkaline solution, and the concentrations are based on weight differences. It is assumed that no volatile products were lost.

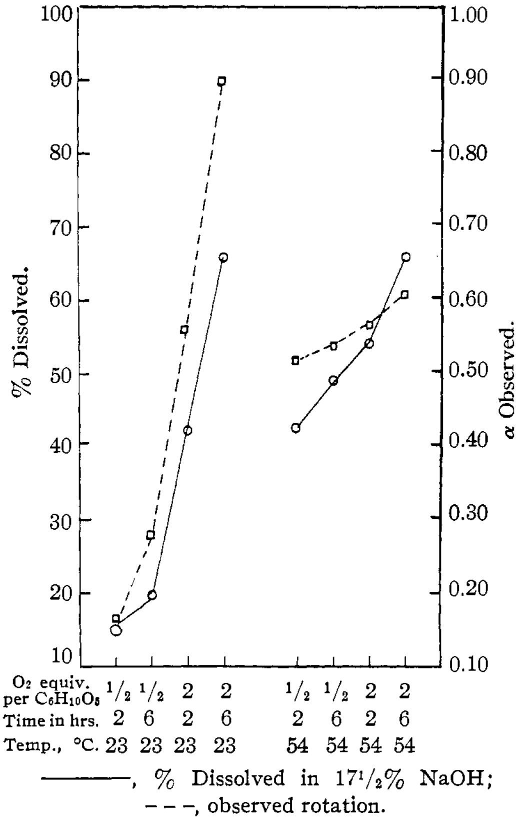


Fig. 7.—Oxidation with potassium permanganate. Effect of oxidizing conditions on amounts dissolved in alkali and observed rotation.

Acknowledgment.—The authors wish to express their gratitude to Mr. A. A. Robson for the preparation of the photomicrographs appearing in this paper.

Summary

1. Hydrocelluloses have been prepared by the action of phosphoric, sulfuric and hydrochloric acids and the specific rotations of the acid filtrates determined.
2. The hydrocelluloses have been extracted with 17.5% of sodium hydroxide and the specific rotations determined.

3. Long fiber cotton has been oxidized with potassium dichromate and potassium permanganate, extracted with 17.5% sodium hydroxide and the optical rotations have been determined.
4. Photomicrographs showing fiber breakdown are given.

Organic Research Laboratory
Eastman Kodak Company
Rochester, New York

[Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, No. 48]

THE ALIPHATIC DIOLEFINS. III. THE BEHAVIOR OF Δ-1,5-HEXADIENE AND Δ-2,4-HEXADIENE TOWARD HYDROCHLORIC ACID

By Frank Cortese[1]

Received July 19, 1929 Published April 7, 1930

In a previous paper from this Laboratory,[2] it was shown that Δ-1,5-hexadiene, when treated with sulfuric acid, gives either esters of hexanediol-2,5 and its internal ether, or polymers, according to the temperature and acid concentration employed. It was shown, further, that the polymers are not formed from the hydrocarbon, but are condensation products of the internal ether. The behavior of this hydrocarbon toward hydrochloric acid is analogous. Mainly a mixture of 5-chloro-1-hexene and 2,5-dichlorohexanes is formed, together with some diallyl oxide and a trace of its condensation products. On the other hand, the conjugated isomer, Δ-2,4-hexadiene, gives a mixture of monochlorohexenes and polymers. No dichlorohexanes are obtained.

Experimental Work

The Action of Hydrochloric Acid on Δ-1,5-Hexadiene.—Wurtz[3] obtained a mixture of 5-chloro-1-hexene, boiling at 130–140°, and 2,5-dichlorohexane, boiling at 170–180°, when he treated Δ-1,5-hexadiene with concentrated hydrochloric acid in sealed tubes. Both were analyzed for chlorine.

In our work 100 cc. of diallyl was shaken with 500 cc. of concentrated hydrochloric acid for 120 hours. A deep green layer of 96 cc. resulted. It was washed with 15%

Table I

Constants Obtained for the Compounds

	5-Chloro-1-hexene		2,5-Dichlorohexane	
Boiling point, °C.	28–30 (13)	43–45 (45)	56–58 (9)	85–87 (38)
(mm.)	64–66 (103)	121–125 (760)	104–106 (84)	176–178 (760)
Density, d_4	$0.9141^{20°}$	$0.8891^{25°}$	$1.0686^{0°}$	$1.0441^{25°}$
Index of refr., n_D	$1.4332^{15°}$ $1.4305^{20°}$	$1.4279^{25°}$	$1.4487^{15°}$	$1.4465^{25°}$
Molecular refr.	Calcd. 34.34	Found 34.31	Calcd. 39.32	Found 39.64

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[1] Research Associate, Massachusetts Institute of Technology, 1926–1928.

[2] Cortese, *Ber.*, **62,** 504 (1929).

[3] Wurtz, *Ann. chim. phys.*, [4] **3,** 155 (1864).