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OPTICAL ROTATION OF CELLULOSIC MATERIALS. II. THE OPTICAL ROTATION OF TWO FRACTIONS OF ALKALI-SOLUBLE OXIDIZED CELLULOSE

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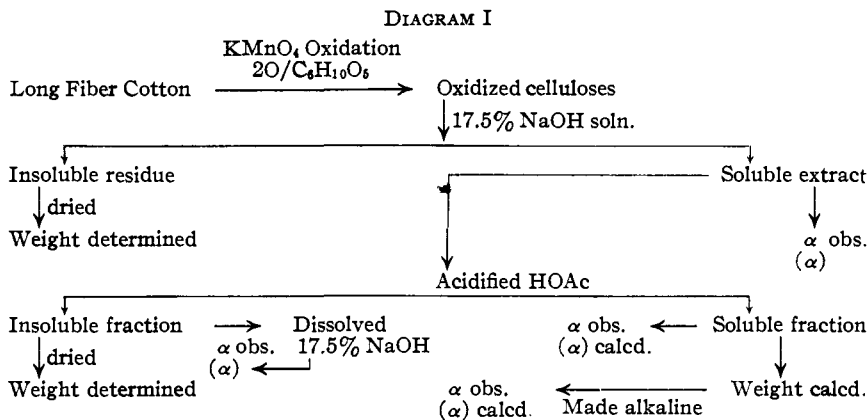
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Introduction

The optical rotations of the alkali-soluble portions of several oxidized celluloses with respect to the severity of the oxidizing conditions were given in the first paper of this series.¹ The present paper deals with the fraction of the alkali-soluble oxidized cellulose, which is precipitated by neutralizing the alkali, *i. e.*, the β -oxycellulose² and the optical rotation of the material remaining in solution after neutralization, the γ -oxycellulose.²

It was thought of interest to determine the relative optical activity of these two fractions.

The general plan of the work is indicated in Diagram I.



Experimental

Oxidation Experiments.—The oxidation experiments were made on samples from the same lot of long-fibered cotton cellulose which was used in experiments recorded in the first paper of this series. The moisture content, owing to atmospheric conditions, was found to have increased from 3.7 to 4.1%.

In this study oxidations were made using only potassium permanganate

¹ Murray, Staud and Gray, *THIS JOURNAL*, 52, 1508 (1930).

² The terms β - and γ -oxycellulose have been used to designate the materials obtained from oxidized cellulose, since there is a possibility that future work may show these substances to be different from the so-called β - and γ -celluloses.

at a concentration of two oxygen equivalents per mole of $C_6H_{10}O_5$ in *N* phosphoric acid. The volume of solution was 600 cc. of the composition indicated in the previous paper. The cotton and the solutions were heated before mixing. The temperature was $53 \pm 1^\circ$. Separate oxidations were made for each sample that was used in optical rotation measurements. The samples were oxidized for one, two, four, six and eight hours. Two such series of oxidations were made.

In the first series the oxidized celluloses were isolated by filtering through a cloth filter, followed by treatment with acidified sodium bisulfite solution, after which they were washed until the wash water gave no test for acidity after standing for sixteen hours. They were then dehydrated with ethyl alcohol, followed by ether and the latter was removed by drying in an air cabinet maintained at 50 to 60° .

In the second series of oxidations the oxidized celluloses were isolated by filtering on cloth as in series one, after which they were treated with acidified sodium bisulfite solution to remove the manganese dioxide present. They were then transferred to centrifuge tubes, where the products were washed to neutrality, as indicated above, dehydrated and dried without removal from the centrifuge tubes.

The products from the first series of oxidations after drying were weighed and the loss due to oxidation determined. In the second series the centrifuge tubes containing the oxidized celluloses were weighed after drying at 50 to 60° . The products were then removed, the tubes weighed again and the loss in weight determined by difference. The filtrates from the oxidation experiments were cleared, when necessary, with a few crystals of sodium bisulfite, and the optical rotations of these solutions were determined in a 2-dm. tube, using light of wave length $546.1 m\mu$ with the same polarimetric equipment as described in the first paper.

TABLE I
DATA CONCERNING OXIDATION OF CELLULOSE WITH POTASSIUM PERMANGANATE

Time of oxidation, hours	Residue, g.	Loss in weight, g.	Loss, %	α obs. filtrate	Apparent $(\alpha)_{546.1 m\mu}^{25}$
First Series					
1	12.9	3.3	20.40	-0.04	-3.65
2	13.0	3.2	19.75	- .04	-3.70
4	13.4	2.8	17.30	- .07	-7.40
6	12.7	3.5	21.60	- .06	-5.20
8	12.6	3.6	22.20	- .04	-3.35
Second Series					
1	13.7	2.5	15.40	- .03	-3.75
2	13.1	3.1	19.15	- .03	-2.90
4	13.1	3.1	19.15	- .06	-5.80
6	12.8	3.4	21.00	- .06	-5.40
8	12.6	3.6	22.20	- .06	-5.00

The loss of weight due to oxidation and the observed and apparent specific rotations³ of the filtrates from these oxidations are given in Table I.

Extraction Experiments.—Extractions with 17.5% sodium hydroxide were carried out on 4.05-g. samples as described in the previous paper except that all of the products were isolated by centrifuging and the residues were washed in the centrifuge cups. The washing, 10% acetic acid treatment, subsequent washing with water, dehydration and drying at 105° were conducted as described under the section "The Action of Acids" in the earlier paper.¹ The weight of the alkali-soluble portion in each case was determined by the difference between the weight of the original material and the weight of the residue obtained.

This residue is usually called α -cellulose. The alkali extracts were obtained by decanting the alkaline supernatant liquid from the oxidized cellulose after centrifuging. Five cubic centimeter portions of the alkaline extracts were diluted with 10 cc. of 17.5% sodium hydroxide in each case and the optical rotations were determined.

The weight of the residues from the 17.5% sodium hydroxide extractions, weight dissolved by the alkali, the observed and specific rotations⁴ of the alkaline extracts, are given in Table II. The values given for the observed rotations are the actual observed rotations multiplied by three to correct for the dilution.

TABLE II
DATA CONCERNING EXTRACTION OF OXIDIZED CELLULOSE WITH 17.5% SODIUM HYDROXIDE SOLUTION

Time of oxidation, hours	Residue, g.	Weight dissolved, g.	Dissolved, %	α obs. $\times 3$	$(\alpha)_{416.1}^{25}$ m μ
First Series					
1	2.06	1.99	49.1	-0.63	-25.6
2	2.08	1.97	48.6	- .54	-22.2
4	2.14	1.91	47.0	- .54	-22.9
6	2.12	1.93	47.5	- .54	-22.65
8	2.10	1.95	48.0	- .48	-20.0
Second Series					
1	2.00	2.05	50.6	-0.57	-22.55
2	1.98	2.07	51.2	- .57	-22.3
4	1.96	2.09	51.6	- .57	-22.1
6	1.99	2.06	50.9	- .57	-22.4
8	2.01	2.04	50.4	- .57	-22.7

Fractionation of the Alkali-Soluble Oxidized Celluloses.—To 5 cc. of each of the undiluted alkaline extracts was added 5 cc. of 41.92% by weight

³ The apparent specific rotation is calculated on the loss in weight of the cellulose due to oxidation, not on a known weight of optically active material in solution.

⁴ The specific rotations were calculated on the difference between the weight of oxidized cellulose taken and the α -cellulose isolated.

acetic acid. This resulted in the precipitation of a part of the alkali-soluble cellulosic materials, the β -oxycellulose, which was separated by centrifuging for approximately one hour. The supernatant liquid containing the unprecipitated fraction of the alkali-soluble oxidized cellulose, *i. e.*, the γ -oxycellulose, was decanted and its optical rotation determined in a 0.5-dm. polarimeter tube without further dilution. The observed rotations were multiplied by two to correct for the volume change due to the addition of the acetic acid solution. These operations yielded the observed rotations of the γ -oxycellulose in slightly acid solution. After determining the optical rotations of these solutions, there were added to 3 cc. of each, 3 cc. of 35% sodium hydroxide solution, from which the observed rotation of the γ -oxycellulose was obtained in 9.0% sodium hydroxide solutions. The observed rotations were multiplied by four to correct for the dilution. In Table III are given the observed and specific rotations of the γ -oxycellulose.

TABLE III
OPTICAL ROTATIONS OF γ -OXYCELLULOSE

Time of oxidation, hours	α obs. slightly acid soln. $\times 2$	$(\alpha)_{446.1}^{25}$ slightly acid soln.	α obs. 9% NaOH soln. $\times 4$	$(\alpha)_{446.1}^{25}$ 9% NaOH soln.
First Series				
1	-0.26	-12.75	-0.54	-26.6
2	-.24	-11.55	-.36	-17.4
4	-.26	-13.65	-.42	-22.1
6	-.26	-12.62	-.48	-23.1
8	-.24	-11.53	-.42	-20.2
Second Series				
1	-0.28	-14.08	-0.44	-22.0
2	-.28	-14.13	-.40	-20.1
4	-.26	-12.69	-.40	-19.9
6	-.28	-14.13	-.40	-20.2
8	-.26	-13.25	-.40	-20.4

The fractions which precipitated upon acidification of the alkaline extract of the oxidized cellulose were washed with two portions of distilled water in the centrifuge tubes. To the moist residues were added 5 cc. of 17.5% sodium hydroxide, in which this material again dissolved. The observed rotations of these solutions, containing the β -oxycelluloses, were determined in a 0.5-dm. polarimeter tube.

Separate portions of 17.5% sodium hydroxide extracts of the oxidized celluloses were acidified with 41.92% acetic acid as described above, and the fractions which precipitated, *i. e.*, the β -oxycellulose, were washed in the centrifuge tubes with distilled water until the washings were neutral to brom thymol blue. They were dehydrated with ethyl alcohol, followed by ether and dried in the centrifuge tubes at 105°. The weights of the γ -oxycellulose in the samples were obtained by difference. The weights thus

obtained were used in calculating the specific rotations of this fraction in 17.5% sodium hydroxide as given with the observed rotations in Table IV.

TABLE IV
OPTICAL ROTATIONS OF β -OXYCELLULOSE

Time of oxidation, hours	α obs. β -oxycellulose in 17.5% NaOH soln.	$(\alpha)_{445.1}^{25}$ β -oxycellulose in 17.5% NaOH soln.
First Series		
1	-0.10	-25.9
2	-.08	-22.2
4	-.10	-21.7
6	-.08	-23.3
8	-.09	-27.4
Second Series		
1	-0.11	-22.7
2	-.12	-21.1
4	-.12	-22.7
6	-.13	-23.3
8	-.13	-23.3

In the first series, the β -oxycellulose, which precipitated upon acidification, was centrifuged within two hours after the addition of acetic acid, whereas in the second series the precipitates were permitted to stand for approximately sixteen hours before centrifuging. In Table V are given the weights of β -oxycellulose obtained from 5 cc. of the 17.5% sodium hydroxide extracts of the oxidized cellulose. There is also given in each case the calculated weight of this material in 40.5 cc. of the extract, the total weight of alkali-soluble oxidized cellulose dissolved in 40.5 cc. of 17.5% sodium hydroxide, and the weights of γ -oxycellulose in 40.5 cc. of 17.5%

TABLE V
WEIGHT OF β - AND γ -OXYCELLULOSES EXTRACTED WITH 17.5% SODIUM HYDROXIDE SOLUTIONS

Time of oxidation, hours	Weight of β -oxycellulose from 5 cc. of 17.5% NaOH solution, g.	Calcd. weight of β -oxycellulose in 40.5 cc. of 17.5% NaOH solution, g.	Total weight oxidized cellulose dissolved in 40.5 cc. of 17.5% NaOH solution, g.	Calcd. weight of γ -oxycellulose in 40.5 cc. of 17.5% NaOH solution, g.	%	
First Series						
1	0.0425	0.3440	17.3	1.99	1.646	82.7
2	.0360	.2915	14.9	1.97	1.678	85.1
4	.0460	.3720	19.5	1.91	1.538	80.5
6	.0340	.2750	14.3	1.93	1.655	85.7
8	.0340	.2750	14.0	1.95	1.675	86.0
Second Series						
1	.0485	.3920	19.0	2.05	1.658	81.0
2	.0570	.4610	22.5	2.07	1.609	77.5
4	.0530	.4290	20.5	2.09	1.661	79.5
6	.0560	.4540	22.0	2.06	1.606	78.0
8	.0560	.4540	22.0	2.04	1.586	78.0

sodium hydroxide. The last group of values was obtained by subtraction of the weight of β -oxycellulose from the total weight of oxidized cellulose dissolved in 17.5% NaOH solution.

Effect of Varying Fractionation Conditions.—Theoretically, a 5-cc. portion of 26.25% (weight) acetic acid is sufficient to neutralize 5 cc. of 17.5% sodium hydroxide. It was found, however, that under the conditions obtaining a solution acid to litmus resulted. In the experiments described above, 5 cc. of 41.92% acetic acid was used to precipitate the β -oxycellulose, providing, therefore, a considerable excess of acetic acid.

To determine the effect of this excess of acetic acid on the amount of β -oxycellulose precipitated and on the observed rotation of γ -oxycellulose in slightly acid solution, a group of experiments was made using acetic acid of 26.25% (weight) concentration.

To 5 cc. of the 17.5% sodium hydroxide extracts of the oxidized celluloses, described in the second series, were added 5-cc. portions of 26.25% acetic acid and the solutions containing the precipitates of β -oxycellulose were allowed to stand for approximately sixteen hours before centrifuging. The weights of β -oxycellulose precipitated were determined as described above and are given in Table VI (compare results in Table V).

TABLE VI

WEIGHT OF β -OXYCELLULOSE PRECIPITATED BY 26.25% ACETIC ACID SOLUTION					
Time of oxidation, hours.....	1	2	4	6	8
β -Oxycellulose from 5 cc. of 17.5% NaOH soln., g.....	0.0550	0.0605	0.0610	0.0620	0.0610

The observed rotations of the γ -oxycellulose solutions from which the β -oxycellulose had been separated in the above experiments were determined and multiplied by two to correct for dilution. To 5 cc. of each of the nearly neutral solutions were added 5-cc. portions of 35% sodium hydroxide solution and the observed rotations obtained in a 0.5-dm. tube and multiplied by four to correct for dilution. These values are given in Table VII (compare results in Table III).

TABLE VII

OBSERVED ROTATIONS OF γ -OXYCELLULOSE IN NEUTRAL AND 17.5% SODIUM HYDROXIDE SOLUTIONS

Time of oxidation, hours	α obs. γ -oxycellulose in nearly neutral soln. $\times 2$	α obs γ -oxycellulose in 17.5% NaOH soln. $\times 4$
1	-0.30	-0.40
2	- .30	- .40
4	- .28	- .40
6	- .30	- .40
8	- .28	- .40

Discussion

The results of the oxidation experiments for two and six hours appear to agree, in general, with those given in the previous paper, as regards

loss in weight of cellulose during oxidation, specific rotation of the filtrates from the oxidized celluloses, amount of oxidized cellulose dissolved in 17.5% alkali and the specific rotations of the alkaline extracts.

Apparently the oxidation reaction, under the conditions employed, reaches completion in one hour or less as indicated by the weight of oxidized cellulose recovered (Table I), the amounts dissolved in 17.5% alkali (Table II), and the specific rotations of the latter (Table II). This is further indicated by the uniformity in the ratio of β - to γ -oxycellulose (Table V). This ratio is approximately 1:4 and shows that the oxidation procedure employed results in the production of alkali-soluble oxidized cellulose in which γ -oxycellulose predominates, as determined by fractionation experiments.

In fractionation it has been found that removal of the β -oxycellulose approximately two hours after acidification of the 17.5% alkaline extract results in somewhat lower values than are obtained when a fifteen-hour interval is allowed for complete precipitation (Table V), the average values being about 0.3 g. from 40.5 cc. of 17.5% alkali in the former instance and approximately 0.45 g. in the latter. It seems desirable to allow sixteen hours or longer to elapse between acidification and centrifuging.

In this same connection it has also been observed that when an amount of acetic acid calculated to neutralize the sodium hydroxide present is employed, the results are approximately the same as when a considerable excess of acetic acid is used (Tables V and VI). The values for β -oxycellulose are approximately 0.06 g. from 5 cc. of the 17.5% alkaline extract when 26.25% acetic acid is used as compared with approximately 0.055 g. when 41.92% acetic acid is employed.

As regards specific rotations, it is seen that the specific rotations of the γ -oxycellulose in neutral solution are approximately one-half to two-thirds of the values obtained when dissolved in 9.0% sodium hydroxide (Table III).

The specific rotations of β - and γ -oxycelluloses appear to be equal in the sodium hydroxide solutions used within experimental error, and the observed rotations of γ -oxycellulose do not appear to be affected by changes of acetic acid concentration amounting to about 15% (Table III, second series, and Table VII). Also changes in concentration of sodium hydroxide and sodium acetate within the ranges studied do not appear to result in appreciable changes in observed rotation of γ -oxycellulose (Tables III and VII).

Summary

Long fiber cotton has been oxidized with two available oxygen equivalents per $C_6H_{10}O_5$ group, using potassium permanganate in normal phosphoric acid at 53°.

The oxidized celluloses obtained have been extracted with 18.5% sodium hydroxide and the optical rotations determined.

The alkaline extract has been separated into fractions soluble and in soluble in dilute acetic acid.

The optical rotations of insoluble portions were determined in 17.5% sodium hydroxide.

The optical rotations of the soluble portions were determined in dilute acetic acid and in alkaline solutions.

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CONDENSATIONS BY SODIUM INSTEAD OF BY THE GRIGNARD REACTION. III. TERTIARY CARBINOLS AND ACIDS

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In previous papers¹ we have emphasized the fact that sodium will bring about the same condensations as are normally brought about by the Grignard reaction with the advantages that with sodium one may use aryl chlorides and solvents other than ether. In addition, the reaction can be carried out in one step rather than through the intermediate formation of the Grignard reagent. These advantages are of considerable laboratory and practical value since the metal, the halide and the solvent are far cheaper than for the corresponding materials with the Grignard reaction. The importance of this has led us to further studies and in this paper we shall report some preparations which show the possibilities of this synthesis.

Tribiphenylcarbinol was prepared by Schlenk and Weickel² by a round-about method involving the initial preparation of iodobiphenyl and parphenylbenzoic acid. The preparation of these intermediates is in itself a laborious process. We have succeeded in preparing tribiphenylcarbinol from chlorobiphenyl, diethyl carbonate and sodium in benzene solution in one step with a yield of 46% crude material, from which we obtained pure material amounting to 23% of the theoretical. This simplification in preparation and cost makes available this interesting and somewhat rare compound.

In further studies on chlorobenzene which is unreactive to a large number of reagents, we have been able to bring about its reaction with diethyl carbonate, forming triphenylcarbinol in benzene solution with a yield of 66% of crude material. With benzoyl chloride and benzophenone the yields were 79 and 98%, respectively.

¹ Morton and Stevens, *THIS JOURNAL*, **53**, 2244, 2769 (1931).

² Schlenk and Weickel, *Ann.*, **368**, 295 (1909).