*On the Oxidation of Cellulose. II. On Celluronic Acid Prepared by a Simple Method**

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During the course of chemical research of natural polyuronides[1], it became desirable to obtain celluronic acid[2] for purposes of comparison.

Pigman[3] oxidized cellulose by concentrated nitric acid added with sodium nitrite. The authors[4], using his method, obtained an oxidized cellulose containing one glucuronic residue per five glucose residues. But the mean degree of polymerisation of the oxidized cellulose was about one-fourth of the original cellulose and its copper value was very high.

The present paper presents the results obtained in the oxidation of cellulose by phosphoric acid added with sodium nitrite.

Experimental Results and Discussion

In 150 cc. of 90% phosphoric acid, 5 g. of pulp cellulose was placed and a definite quantity of solid sodium nitrite was added. The suspension was stirred and kept at constant temperature for a definite time. The suspension was then diluted with 50 cc. of water and filtered. The oxidized cellulose was suspended in 500 cc. of water, stirred, kept at least 12 hrs., and filtered. The washing was repeated in the same manner until the acidity of the filtrate vanished. The oxidized cellulose was then washed several

TABLE I

Sample Number	Reaction time (hr.)	Reaction temp. (°C)	$NaNo_2$ (g.)	Carboxyl content (%)	Glucuronic content (%)	Glucurono lacton / Glucose
1	1	10	0	0.08	0.31	1/311
2	1	10	2	2.09	8.17	1/12
3	1	10	5	2.30	9.00	1/12
4	1	15	10	7.90	30.90	1/4
5	1	20	15	16.07	62.85	3/5
6	1	20	20	18.32	71.65	2/3
7	1	20	2	4.17	16.31	1/7
8	1	25	5	11.92	46.62	1/2
9	1	20	10	9.75	38.13	1/3

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1) Reviewed in "A Summary of Chemical Studies on Polyuronides", *Bulletin of the Faculty of Textile Fibres, Kyoto University of Industrial Arts and Textile Fibres*, **1**, 116 (1954) (in English).

2) W. O. Kenyon et al., *J. Am. Chem. Soc.*, **64**, 121, 127 (1942); **69**, 342, 349, 355 (1947); **70**, 270 (1948).

3) W. W. Pigman et al., *J. Am. Chem. Soc.*, **71**, 2200 (1949).

4) S. Machida, N. Uchino and M. Inano, *J. Chem. Soc. Japan*, **74**, 204 (1953).

times with acetone and finally with ether and dried in a vacuum desiccator.

The oxidized cellulose thus obtained was a white powder, and the yield was about 90%. Carboxyl group contents determined by the calcium acetate method and the calculated theoretical glucuronic residue contents of the oxidized cellulose obtained in various reaction conditions are shown in Table I.

As is shown in the table, the highest value of the carboxyl content is 18.32%, which means that one uronic residue is present per 1.5 glucose residue in the chain molecule. The presence of the uronic group in the oxidized cellulose was confirmed by the naphthoresorcinol test. Its content was actually determined by heating the sample with 12% hydrochloric acid and estimating the furfural liberated from it. For example, Sample No. 9, was found to contain 36.5% glucurono lactone in this actual determination. The theoretical uronic residue content calculated for the same sample is 38.13%, assuming that the 9.75% value of carboxyl content is wholly due to uronic groups. Therefore, it is found that carboxyl groups of this substance are largely of the glucuronic type and only a few of them are of other types, such as the aldonic.

The mean degree of polymerisation of the oxidized cellulose was determined by the viscosity measurement of acetone solution of its nitric ester. The results obtained are shown in Fig. 1.

The solubilities of the oxidized cellulose in 1% caustic soda solution at 20°C and 100°C were determined, and are shown in Fig. 2.

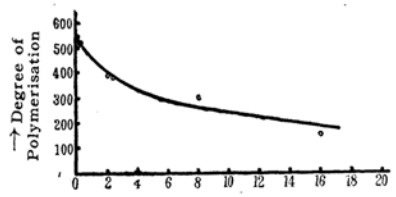

Fig. 1. Degree of polymerisation of the celluronic acids.

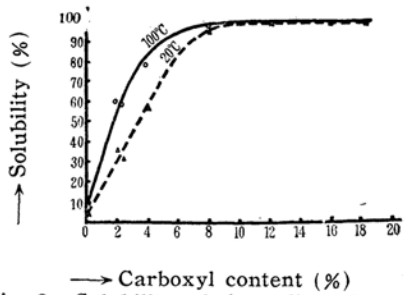

Fig. 2. Solubility of the celluronic acids in 1% caustic soda solution.

As is shown in Fig. 2, the oxidized cellulose, whose carboxyl content was more than 8%, is almost entirely soluble; and, by referring to Fig. 1, it is found that the mean degree of polymerisation of such oxidized cellulose is 322, which is nearly two-thirds that of the untreated cellulose.

These facts indicate that the oxidation of cellulose by concentrated phosphoric acid added with sodium nitrite is much more convenient; that is, the cellulose is not apt to be hydrolyzed heavily and the oxidation proceeds smoothly. The reason, perhaps, is that phosphoric acid as compared with nitric acid has weak acidity and strong ability to make cellulose swell. As the phosphoric acid group was not detected in the oxidized cellulose, it could not be considered that the phosphoric acid group combined chemically with the oxidized cellulose enhanced its solubility.

The alkaline solution of the oxidized cellulose was fluid. Furthermore it was coagulated by adding salts of alkali earth or heavy metal or a large volume of alcohol or acetone. By neutralization with acid, about 85% of the oxidized cellulose was recovered from the alkaline solution. The recovered oxidized cellulose had almost the same carboxyl group content as the original oxidized cellulose and still indicated the color reaction with naphthoresorcinol. However, it can easily be imagined that the molecules must have disintegrated.

Summary

Cellulose was conveniently oxidized by concentrated phosphoric acid added with sodium nitrite; that is, the cellulose was not apt to be hydrolyzed heavily and the oxidation proceeded smoothly.

It was found that carboxyl groups of the oxidized cellulose were largely of the glucuronic type.

The oxidized cellulose, whose carboxyl content was more than 8%, was almost soluble in dilute caustic soda solution; and the mean degree of polymerisation of such oxidized cellulose was nearly two-thirds of that of the untreated cellulose.

Some properties of the alkaline solution of the oxidized cellulose were investigated.

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