

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

**The Molecular Size of Methylated Cellulose<sup>1</sup>**BY M. L. WOLFROM, JOHN C. SOWDEN<sup>2</sup> AND E. N. LASSETTRE

In previous publications from this Laboratory<sup>3</sup> we have reported studies of the hydrolysis of cellulose (high viscosity cotton linters) made by mercaptalating at various time intervals. Sulfur analyses on the resulting mercaptalated hydrolyzed celluloses then gave an estimate of average molecular size. We wish now to report on an extension of this procedure to the type of methylated cellulose (OMe, 43–44%) obtained by the methylation of commercial acetone-soluble cellulose acetate. Such material represents a somewhat degraded cellulose, as the cellulose has been subjected to acidity during the production of the acetone-soluble cellulose acetate.

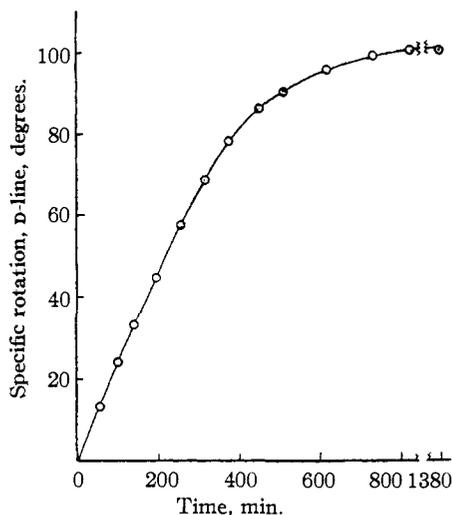


Fig. 1.—Mutarotation of methylated cellulose (OMe, 43.5;  $c$  2.6) in fuming hydrochloric acid ( $d_{44}^20$ , 1.202) at 24°.

In our present work we were interested only in the early stages of hydrolysis and accordingly the methylated cellulose was hydrolyzed at 0° with fuming hydrochloric acid under continuous mercaptalation, as described previously<sup>3c</sup> for cotton linters. Concurrent polarimetric data could not be obtained due to a slight opacity which cleared

(1) The experimental data herein reported were presented before the Division of Organic Chemistry at the 96th Meeting of the American Chemical Society, Milwaukee, Wisconsin, September 8, 1938.

(2) Du Pont Cellulose Research Fellow.

(3) (a) M. L. Wolfrom and L. W. Georges, *THIS JOURNAL*, **59**, 282 (1937); (b) M. L. Wolfrom, L. W. Georges and J. C. Sowden, *ibid.*, **60**, 1026 (1938); (c) M. L. Wolfrom and J. C. Sowden, *ibid.*, **60**, 3009 (1938).

readily when the solution was warmed to 15° but which persisted at 0°. Figure 1 records the polarization changes taking place under comparable conditions but at a temperature of 24°. It is seen that a continuous, smooth curve is obtained. The final rotation is in good agreement with that obtained for an equivalent concentration of 2,3,6-trimethyl-*d*-glucose, thus indicating a substantially complete hydrolysis to this substance. Wolfrom and Georges<sup>4</sup> previously had subjected the same type of methylated cellulose to complete hydrolysis with fuming hydrochloric acid at low temperatures and had obtained 2,3,6-trimethyl-*d*-glucose as its diethyl mercaptal in good yield.

The rotations in benzene solution of several of the hydrolyzed and mercaptalated products were determined and are recorded in Table I. They do not differ greatly from the specific rotation of  $-18.5^\circ$  recorded by Hess and Pichlmayr<sup>5</sup> for trimethylcellulose in benzene solution.

The sulfur analyses obtained on the mercaptalated hydrolyzed products are tabulated in Table I. These products entrained less sodium chloride than was the case in the cotton linters. *d*-Glucose forms a well-defined sodium chloride compound and it is probable that similar compound formation occurs with the unsubstituted hydrolyzed celluloses but not with the methylated hydrolyzed products. From the sulfur analytical data the average degree of polymerization (D. P.) was calculated from the following approximation.

$$\text{D. P.} = \frac{100 \times 2S}{\% S \times C_6H_{10}O_5} = \frac{31.4}{\% S} \quad (1)$$

The above equation represents a very close approximation with material of relatively high molecular weight, such as we are dealing with in the present case. The average degrees of polymerization are tabulated in Table I and are plotted against time in Fig. 2. A smooth line of definite curvature may be drawn through the points. The initial time of hydrolysis was taken as the time of addition of the acid to the methylated cellulose, as this undoubtedly represents the beginning of the solution process, which proceeds

(4) M. L. Wolfrom and L. W. Georges, *ibid.*, **59**, 601 (1937).

(5) K. Hess and H. Pichlmayr, *Ann.*, **450**, 29 (1926).

heterogeneously for several hours until swelling and complete solution takes place.

It was of interest to attempt an extrapolation to zero time of the data plotted in Fig. 2. This

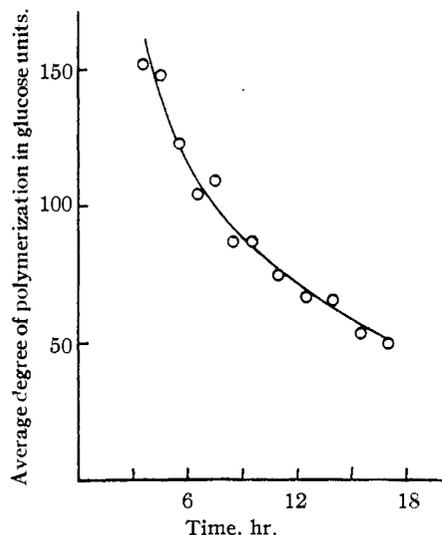


Fig. 2.—Rate of change of average degree of polymerization of methylated cellulose ( $c$  2.3%) in fuming hydrochloric acid ( $d^{16}$ , 1.202) at  $0^\circ$ , as calculated from sulfur content of mercaptalated products.

would then result in an estimate of the average degree of polymerization of the original methylated cellulose. The curvature obtained in Fig. 2 is such that an accurate extrapolation to zero time could not be made. The data were then subjected to a mathematical analysis following the lines laid down by Werner Kuhn. This analysis follows.

In order to find the degree of polymerization at zero time, we assume that in its initial stages the hydrolysis is first order. Let  $Z$  designate the total number of unhydrolyzed linkages at time  $t$ . Since the rate of hydrolysis of linkages is proportional to the number unhydrolyzed we have

$$dZ/dt = -kZ \text{ or } Z = Z_0 e^{-kt} \quad (2)$$

where  $k$  is the specific rate constant and  $Z_0$  is the number of unhydrolyzed linkages at time  $t_0$ . The assumptions made above have been explicitly stated and thoroughly examined by W. Kuhn and have been tested experimentally by Freudenberg, Kuhn, *et al.*<sup>6</sup> It should be emphasized that in view of the results of these workers the above hypotheses can only be valid when the average degree of polymerization is large.

The experimental values of  $d$  used in this paper

(6) W. Kuhn, *Ber.*, **63**, 1503 (1930); K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz and G. Steinbrunn, *ibid.*, **63**, 1510 (1930); K. Freudenberg, *Trans. Faraday Soc.*, **32**, 74 (1936).

are obtained by dividing the number of glucose units by the number of free reducing groups. If we designate the number of glucose units by  $N$  and the degree of polymerization by  $d$ , a simple calculation shows that the number of free reducing groups is  $N - Z$ , and hence

$$d = N/(N - Z) \quad (3)$$

This is sometimes called a number average degree of polymerization. Solving (3) for  $Z$  and substituting in (2), we obtain

$$\frac{d - 1}{d} = \frac{d_0 - 1}{d_0} e^{-kt} \quad (4)$$

where  $d_0$  is the value of  $d$  when  $t = 0$ .

When equation (4) is satisfied a plot of  $\ln_e(d - 1)/d$  against  $t$  will give a straight line the slope of which is  $-k$  and from the intercept of which  $d_0$  can be calculated. The experimental results are shown graphically in Fig. 3. A straight line is obtained and the closely approximate validity of equation (4) is accordingly confirmed. The value of the specific rate constant  $k$  (hours<sup>-1</sup>) at  $0^\circ$ , as estimated from the slope of the line, is  $1.02 \times 10^{-3}$ . The average degree of polymerization,  $d_0$ , for the original methylated cellulose as determined from the intercept, is  $400 \pm 70$ , the uncertainty being estimated graphically.

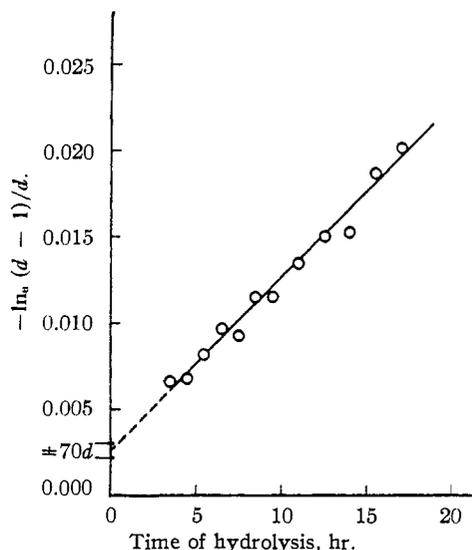


Fig. 3.—Methylated cellulose in fuming hydrochloric acid at  $0^\circ$ .

The hypotheses leading to equation (4) assume explicitly that all of the saccharide linkages are accessible for hydrolysis and that the rate constant  $k$  is independent of the time. It is well known<sup>6</sup> that the value of  $k$  changes in the final stages of hydrolysis of cellulose and it should be

pointed out that at least two other factors affect the hydrolysis in the present case. The first factor arises because the reaction mixture is continuously mercaptalated. The introduction of mercaptyl groups into the molecule probably will change the rate at which adjacent saccharide linkages are hydrolyzed. This effect is expected to become more prominent as the hydrolysis proceeds, since more mercaptyl groups are introduced. The agreement with experiment lends support to the belief that the presence of ethyl mercaptan in the reaction mixture does not invalidate the use of equation (4) in the early stages of hydrolysis. The second factor arises because of the previously mentioned slow rate of solution of solid methylated cellulose. During the process of swelling, it is probable that not all of the saccharide linkages are accessible for hydrolysis, and, hence, that equation (4) is not applicable. If, (a) the swelling process is completed by the time the first experimental data are taken and, (b) swelling affects the rate only by rendering some of the linkages inaccessible, the extrapolated degree of polymerization (*i. e.*, 400) will be too high. Since the experimental data show no systematic tendency to deviate from a straight line, the most reasonable extrapolation which can be made at present consists in extending the straight line to zero time.

The degree of polymerization given by the sulfur analytical data constitutes a number average value. If the material under examination is substantially homogeneous or if it possesses a heterogeneity that does not extend over a wide range, the number average value for the degree of polymerization becomes approximately equal to the weight average value.<sup>7</sup>

The average degree of polymerization of our methylated cellulose should be not greater than that of the acetone-soluble cellulose acetate from which it was prepared by one methylation with methyl sulfate and an excess of alkali, according to the general procedure of Haworth and co-workers.<sup>8</sup> Kraemer<sup>9</sup> has related the degree of polymerization of cellulose acetate to the viscosity of acetone solutions containing low concentrations of cellulose acetate. Kraemer has followed the lines laid down by Staudinger in his extensive

studies of the relation between viscosity and molecular size with the significant difference that the empirical constant in the Staudinger equation has been evaluated by Kraemer through molecular weight determinations by the Svedberg ultracentrifuge sedimentation-equilibrium method. It was then of interest to determine the average degree of polymerization of the acetone-soluble cellulose acetate used in our work by use of the Kraemer<sup>9</sup> equation

$$D. P. = 230 N \quad (5)$$

$N$  = intrinsic viscosity =  $\ln_e Nr/C$ .  $Nr$  = relative viscosity,  $C$  = concentration in g. per 100 cc.

$$D. P. = 230 \left( \ln_e \frac{71.2}{61.6} \right) / 0.096 = 350 \approx 35$$

The uncertainty is based upon the uncertainty in the evaluation of the constant of equation (5) and is approximately  $\pm 10\%$ . It is seen that this weight-average value is in agreement with the number-average value obtained from the mercaptalation data.

There remains to be considered the value obtained by Haworth and Machemer<sup>10</sup> for the methylated cellulose obtained by the one-step alkaline methylation of acetone-soluble cellulose acetate prepared by these workers under controlled conditions. Haworth evaluated the degree of polymerization or chain length by the end-group assay method performed by determining the amount of tetramethylglucopyranose present in the products of complete hydrolysis. The amount of tetramethylglucopyranose found was 0.6% of the hydrolysis product and this leads to a chain length of 100–200 glucose units. This value is somewhat lower than that determined by us for a high-grade commercial sample of cellulose acetate. Unfortunately Haworth and co-workers record no viscosity characteristics for the acetone-soluble cellulose acetate prepared by them. As Kraemer has shown that commercial samples of acetone-soluble cellulose acetate vary from an average degree of polymerization of 175 to 360 glucose units, it is seen that the Haworth end-group assay value falls within this range but a direct comparison with our value is not possible.

## Experimental

**Preparation and Purification of Methylated Cellulose.**—Commercial acetone-soluble cellulose acetate<sup>11</sup> was methyl-

(7) For definition of number and weight averages, *cf.* Ref. 9a.

(8) W. N. Haworth, E. L. Hirst and H. A. Thomas, *J. Chem. Soc.*, 821 (1931).

(9) (a) E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 164 (1935); (b) E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

(10) W. N. Haworth and H. Machemer, *J. Chem. Soc.*, 2270 (1932).

(11) Furnished through the courtesy of the du Pont Rayon Company, Waynesboro, Va.;  $\text{CH}_3\text{CO}$ , 39.6%; relative viscosity at 25  $\approx$  0.01 $^\circ$ , in acetone solution ( $c$ , 0.0962), 1.156.

ated approximately to the trimethylcellulose stage with methyl sulfate and sodium hydroxide in acetone solution.<sup>8</sup> The crude product was purified either by precipitation from its dioxane solution with low-boiling petroleum ether, or by precipitation from benzene solution with low-boiling petroleum ether.<sup>5</sup> In this manner the product was obtained in the form of a fine white powder; OMe, 43-44%; viscosity at 25° in 1% dioxane soln., 5.77 centipoises; sp. rot. -18° (32°, D-line, *C* 2, C<sub>6</sub>H<sub>6</sub>). Hess and Pichlmayr<sup>6</sup> record a specific rotation of -18.5° (20°, D-line, C<sub>6</sub>H<sub>6</sub>) for trimethylcellulose of 45.4% methoxyl content.

#### Hydrolysis and Mercaptalation of Methylated Cellulose.

—The methylated cellulose (43.87 g., moisture content 0.93%) contained in a 2-liter, 3-necked flask at 0°, equipped for rapid mechanical stirring and for rapid removal of samples through a delivery tube, was treated with fuming hydrochloric acid (1550 cc.;  $d_{4}^{16}$ , 1.202;  $d_{4}^{20}$ , 1.212) previously cooled to 0°. The density of the resulting solution was found to be essentially unchanged from that of the original solvent and the concentration of the methylated cellulose (moisture-free basis) was thus 2.804 g. per 100 cc. of solution or 2.282% by weight.

The mixture was maintained at 0° with rapid mechanical stirring. After two and one-half hours, the homogeneous mixture was treated with well-purified ethyl mercaptan (100 g.) previously cooled to 0° and the rapid stirring continued. Continuous mercaptalation was thus provided for the degradation products as the hydrolysis progressed. Samples of 120 cc. were withdrawn after the time intervals recorded in Table I, and immediately poured, with stirring, into mixtures of sodium bicarbonate (135 g.) and water (450 cc.). The precipitated products were collected on the filter pump, using raw silk cloth as a filter. Concurrent polarimetric data could not be obtained due to a slight opacity which cleared readily when

TABLE I  
MERCAPTALATED PRODUCTS FROM METHYLATED CELLULOSE (2.3%) IN FUMING HYDROCHLORIC ACID ( $d_{4}^{16}$ , 1.202) AT 0°

Time of hydrolysis, hrs. <sup>a</sup>	$[\alpha]_{D}^{25}$ (C <sub>6</sub> H <sub>6</sub> ; <i>C</i> 2)	% ash as NaCl	Mercaptalated product from 3.09 g. methylated cellulose, g. <sup>b</sup>	% S	D. P. <sup>d</sup> by S content
3.5		0.73	2.37 <sup>c</sup>	0.210	150
4.5	-18.9°	.21	2.74	.216	145
5.5		.07	2.89	.259	121
6.5		.32	2.94	.308	102
7.5	-18.3°	.15	2.93	.294	107
8.5		.36	2.95	.365	86
9.5		.36	2.80	.366	86
11.0		.38	2.78	.424	74
12.5	-17.3°	.88	2.80	.476	66
14.0		.59	2.90	.480	65
15.5		.82	2.84	.594	53
17.0	-16.6°	.78	2.75	.642	49

<sup>a</sup> Initial time taken as time of addition of the acid to the methylated cellulose. <sup>b</sup> Calculated on vacuum-dried (63°) and sodium chloride free basis. <sup>c</sup> Part of product lost mechanically during neutralization. <sup>d</sup> Average degree of polymerization in glucose units.

the solution was warmed to 15° but which persisted at 0°. Figure 1<sup>2</sup> records the polarization changes taking place under comparable conditions but at a temperature of 24°. The final specific rotation was +100° (+92° on a trimethylglucose basis) which compares with the value of +101° found for 2,3,6-trimethyl-*D*-glucose in fuming hydrochloric acid at the same concentration and temperature.

**Sulfur Analyses.**—The sulfur analyses were performed by the Parr bomb method in the manner described in the previous publications on cotton linters.<sup>3</sup> Total samples of approximately 1 g., on an ash-free, moisture-free basis were employed. The degrees of polymerization were calculated from the sulfur analytical data from the following approximation

$$D. P. = \frac{100 \times 2S}{\%S \times C_6H_{10}O_5} = \frac{31.4}{\%S}$$

The results are recorded in Table I and are diagrammed in Fig. 2.

We are indebted to E. I. du Pont de Nemours and Company, Inc., for a fellowship held by one of us (J. C. S.).

#### Summary

1. Methylated cellulose, from acetone-soluble cellulose acetate, has been hydrolyzed with fuming hydrochloric acid at 0° in the presence of an excess of ethyl mercaptan. The resulting mercaptalated mixtures of hydrolyzed products were isolated at various time intervals during the first seventeen hours of the hydrolysis.

2. Sulfur analytical data indicated that the average degree of polymerization of the mercaptalated products varied from 150 trimethylglucose units after three and one-half hours to 50 trimethylglucose units after seventeen hours.

3. The optical rotation changes in fuming hydrochloric acid have been observed at 24° for a solution of methylated cellulose.

4. An equation (4) is derived which expresses the rate of change of the degree of polymerization as a straight line function.

5. A graphic analysis of the data yields a value of  $1.02 \times 10^{-3}$  for the specific rate constant (hours<sup>-1</sup>) of the rate of change of the degree of polymerization in fuming hydrochloric acid at 0°.

6. By graphic analysis the value  $400 \pm 70$  glucose units is obtained for the initial average degree of polymerization of the methylated cellulose.

(12) Experimental work by Mr. R. D. Koons of this Laboratory.

7. The value  $350 \pm 35$  is obtained for the average degree of polymerization of the corresponding cellulose acetate by application of the

Kraemer equation (5) to the viscosity of the acetone solution of the cellulose acetate.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

## Isomerization of Alkylcyclopentanes

BY HERMAN PINES AND V. N. IPATIEFF

Methylcyclopentane with aluminum chloride undergoes isomerization to cyclohexane.<sup>1</sup> An indirect proof of the isomerization of the cyclopentyl to the cyclohexyl ring was given by Tarazova,<sup>2</sup> who showed that by brominating 1,2-methylethylcyclopentane with bromine, using aluminum bromide as a catalyst, tetrabromo-*p*-xylene is obtained. It has not been shown, however, whether or not it is essential for a methyl group to be attached to the cyclopentyl ring in order to have isomerization.

It has now been found that alkylated cyclopentanes undergo isomerization in the presence of aluminum chloride to yield methylated cyclohexanes. Ethylcyclopentane yielded methylcyclohexane; propyl- and isopropylcyclopentane isomerized to 1,3-dimethylcyclohexane; while *n*-butyl-, *s*-butyl- and *t*-butylcyclopentane yielded 1,3,5-trimethylcyclohexane. The isomerization took place at a temperature of 50° and the yield of isomerized product obtained exceeded 80%. The structure of the isomerized product was determined by dehydrogenating it into the corresponding aromatic hydrocarbon using, as a catalyst, platinumized aluminum oxide. The aromatic hydrocarbons were identified by their bromo or nitro derivatives, which were checked by analysis and mixed melting point. Alkylated cyclopentanes do not undergo dehydrogenation under similar conditions.

It is probable that, analogous to the isomerization of alkylated cyclohexane,<sup>3</sup> the reaction proceeds via the formation of polymethylated cyclopentane which isomerized to methylated cyclohexane.

Ethyl-, *n*-propyl-, and *n*-butylcyclopentane were prepared from cyclopentanone and the corresponding alkylmagnesium bromide according to the method of Chavanne and Becker.<sup>4</sup> Iso-

propyl- and *s*-butylcyclopentane were prepared by hydrogenating dimethyl- and methylethylfulvene. The fulvenes were obtained by condensing cyclopentadiene with acetone and methyl ethyl ketone in the presence of sodium ethoxide.<sup>5</sup> An attempt was also made to prepare isopropylcyclopentane from isopropylmagnesium bromide or chloride and cyclopentanone, but the main product of the reaction was cyclopentenylcyclopentanone. A similar observation was also made by Meerwein.<sup>6</sup> The method of preparation of *t*-butylcyclopentane will be described in a separate paper.<sup>7</sup>

### Experimental Part

**Preparation.** Ethyl-, *n*-propyl- and *n*-butylcyclopentane were prepared from cyclopentanone and ethyl-, *n*-propyl-, and *n*-butylmagnesium halide, respectively, using the procedure described by Chavanne and Becker.<sup>4</sup> The carbinols which were obtained as intermediate products were dehydrated to form the corresponding alkylcyclopentenes. The dehydration was carried out by passing the carbinols over 40 g. of activated alumina with a rate of 40 cc. per hour and a temperature of 345°. The alkylcyclopentenes were hydrogenated to alkylcyclopentanes at 100° in the presence of 10% by weight of nickel catalyst and 100 atmospheres of hydrogen. The yields on dehydration and hydrogenation were almost quantitative.

**Isopropyl- and *s*-Butylcyclopentane.**—Twenty-four grams (*ca.* 1 mole) of sodium was dissolved in 300 cc. of absolute ethanol. To the solution of sodium ethoxide was added a mixture of freshly distilled cyclopentadiene (1 mole) and acetone (1 mole). (For the preparation of *s*-butylbenzene methyl ethyl ketone was used.) The temperature of the flask was kept at 40° by controlling the rate of addition of the reagents, which required one hour. The dimethylfulvene formed was steam distilled; the distillate was of an orange color. It was separated from the water layer and diluted with three volumes of isopentane. During the reaction care was taken to prevent the fulvene from coming in contact with air.

The isopentane solution of the dimethylfulvene was hydrogenated with 18 g. of nickel catalyst (nickel on kieselguhr). The hydrogenation was carried out at the beginning at room temperature and 50 atmospheres pressure.

(1) Nenitzescu and Cantunari, *Ber.*, **66B**, 1097 (1933).

(2) Tarazova, *C. A.*, 8173 (1935); *B. C. A.*, **AII**, 283 (1937).

(3) Grignard and Stratford, *Compt. rend.*, **178**, 2149; *Bull. soc. chim.*, [4] **35**, 931 (1934).

(4) Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927).

(5) Thiele, *Ber.*, **33**, 671 (1900).

(6) Meerwein, *Ann.*, **405**, 155 (1914).

(7) Pines and Ipatieff, abstracts of the Division of Organic Chemistry of the American Chemical Society, Baltimore, April 3-7, 1939.