

The Conductance of the Iodate Ion.—McDougall and Davies⁹ using the data of Kraus and Parker, gave 40.93 as the conductance of the iodate ion on the Kohlrausch and Maltby standard, or about 40.89 on the Jones and Bradshaw standard.¹⁰ More recently, however, Davies¹¹ has pointed out that from the data of Kraus and Parker on the conductance of iodic acid, and of Longworth¹² on the mobility of the hydrogen ion, the figure 41.00 is obtained for the iodate ion. On the other hand, Kraus and Parker themselves reported 39.59 (Jones and Bradshaw standard) on the basis of their own measurements of iodic acid

(9) McDougall and Davies, *J. Chem. Soc.*, 1417 (1935).

(10) Jones and Bradshaw, *THIS JOURNAL*, **55**, 1780 (1933); Davies, *J. Chem. Soc.*, 1326 (1937).

(11) Davies, private communication.

(12) Longworth, *THIS JOURNAL*, **54**, 2741 (1932).

and some rather incomplete measurements of potassium iodate.

If we accept the value $\Lambda_{0KIO_3} = 114.00 \pm 0.05$ and make use of the data of Shedlovsky¹³ for $\Lambda_{0KCl} = 149.86$ and $\lambda_{Cl^-} = 76.34$ (all on Jones and Bradshaw standard) then $\lambda_{IO_3^-} = 40.48 \pm 0.05$.

Summary

1. The conductance of potassium iodate has been measured over the range 0.0001 to 0.1 molar in water at 25°.

2. The mobility of the iodate ion at infinite dilution has been calculated from the conductance of potassium iodate and potassium chloride and the mobility of the chloride ion.

(13) Shedlovsky, *ibid.*, **54**, 1405 (1932).

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New Methods for Investigating the Distribution of Ethoxyl Groups in a Technical Ethylcellulose¹

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Although the average degree of substitution and the average molecular weight of partly alkylated cellulose chains can be determined with considerable certainty, the exact mode of distribution of the substituent within the cellulose molecule remains largely unknown. The means of separating and analyzing the mixtures of partly alkylated glucoses obtained by degradation are not yet accurate enough to determine the average distribution within the glucose residues and are only of very slight value in estimating distribution along the chain. Much valuable and semi-quantitative work, however, has been done on this subject and a few of the literature references are appended.^{3-7a} The fractionation of partly alkylated celluloses has provided little information beyond the fact that the more soluble, shorter

chain length fractions tend to be rather more highly substituted than the original material.^{5,8-14} Studies on the course of alkylation,^{4,15} on the mathematical analysis of the kinetics of the reaction¹⁶ and on correlations between physical properties and the extent and mode of distribution^{17,18} have accordingly been hampered by a lack of quantitative data. The present article and the succeeding one attempt to mitigate this deficiency.

In the case of simple glycosides, heating the *p*-toluenesulfonyl (tosyl) esters of primary alcohol groups with sodium iodide in acetone gives a quantitative yield of the corresponding iodoglycoside whereas esters of secondary alcohol groups are unaffected.^{19,7b} This method of estimating primary in the presence of secondary hydroxyl groups was successfully used to differen-

(8) Denham, *J. Chem. Soc.*, 119, 77 (1921).

(9) Heuser and Heimer, *Z. Elektrochem.*, **32**, 47 (1926).

(10) Okamura, *Cellulosechem.*, **14**, 135 (1933).

(11) Ubbelohde, *ibid.*, **14**, 169 (1934).

(12) Lee and Sakurada, *J. Soc. Chem. Ind. Japan*, **38**, Supp. Binding, 436 (1935); *C. A.*, **29**, 8323 (1935).

(13) Signer and Liechti, *Helv. Chim. Acta*, **21**, 530 (1938).

(14) Staudinger and Reinecke, *Ann.*, **535**, 47 (1938).

(15) Lorand and Georgi, *THIS JOURNAL*, **59**, 1166 (1937).

(16) Spurlin, *ibid.*, **61**, 2222 (1939).

(17) Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).

(18) Ott, *ibid.*, **32**, 1641 (1940).

(19) Oldham and Rutherford, *THIS JOURNAL*, **54**, 366 (1932).

(1) Presented before the Division of Cellulose Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Abstracted from a thesis submitted by J. F. Mahoney to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941. Present address: Merck and Company, Rahway, New Jersey.

(3) Denham and Woodhouse, *J. Chem. Soc.*, **111**, 244 (1917).

(4) Hess, Trogus, Evekling and Garthe, *Ann.*, **506**, 260 (1933).

(5) Hess, *ibid.*, **506**, 295 (1933).

(6) Heddle and Percival, *J. Chem. Soc.*, 249 (1939). This article gives other references.

(7) Compton, *THIS JOURNAL*, (a) **60**, 2823, (b) 1203 (1938).

tiate between unsubstituted groups in the primary, or sixth, position and those in the second and third positions of two acetone-soluble cellulose acetates.²⁰ The same principle has now been applied to a high grade technical ethylcellulose of the type used in plastics.²¹ The specimen examined dissolved completely in most organic solvents to give clear, colorless solutions of relatively low viscosity and the ethoxyl content of 48.5% corresponded to an average substitution of 2.48.

Rate of Esterification with Excess *p*-Toluenesulfonyl Chloride in Pyridine.—The acid chloride used was a colorless product with the correct melting point of 69°. Refined, colorless pyridine was dried by refluxing over barium oxide, was stored over fresh barium oxide and was redistilled when required.

Forty grams of the ethylcellulose (0.0896 mole unsubstituted hydroxyl groups) and 212 g. of *p*-toluenesulfonyl chloride (tosyl chloride, 1.11 moles) were separately dissolved in 480 and 230 ml. of pyridine, respectively, and the two solutions were mixed and kept at 20°. These conditions were the same as those adopted for acetone-soluble cellulose acetate.²⁰ In the first few minutes, the entire mixture changed to a highly elastic, very tough rubbery gel which remained stable and homogeneous during the entire reaction period of three months. Dilution of the pyridine with various organic solvents did not prevent gel formation and markedly decreased the speed of the reaction. Portions of the gel were cut out at various times and were triturated with ice cold, 10% aqueous acetone for twenty minutes to hydrolyze the excess tosyl chloride. As none of the tosylated specimens dissolved in common organic solvents, although all swelled, precipitation methods of purification were replaced by macerations in acetone until the extracts were neutral and free from chloride ions. The samples were thoroughly dried *in vacuo* over phosphorus pentoxide and the first twelve (Table I) were white and fibrous. The next nine were white and horny but the last specimen tenaciously retained a slight brown color derived from the highly discolored mother liquor. The specimens contained no chlorine or nitrogen. Alkoxy estimations were carried out by a standard method,²² with the recent modification of the mode of heating,²³ and sulfur analyses by a convenient and accurate semi-micro technique.²⁴

If x , y and z represented the substitution of ethoxyl, tosyl and iodine (see below), respectively, the molecular weight of the average substituted glucose residue was $111 + 45x + 171y + 127z + 17(3-x-y-z)$ and its content of ethoxyl, sulfur and iodine was $45x$, $32y$ and $127z$, respectively. The analytical data were easily related to these quantities by simultaneous equations which led

(20) Cramer and Purves, *THIS JOURNAL*, **61**, 3458 (1939).

(21) Presented by the Hercules Powder Company through the courtesy of Dr. H. M. Spurlin.

(22) Clark, *J. Assoc. Off. Agr. Chem.*, **15**, 136 (1932).

(23) Arndt and Neumann, *Ber.*, **70B**, 1835 (1937).

(24) Mahoney and Michell, *Ind. Eng. Chem., Anal. Ed.*, **14**, Jan. (1942).

to solutions for x , y and z . Iodine was absent in the present case and z was zero in the calculations leading to the molar amount of tosylation after various times (Table I, column 6). The sulfur content was also calculated from the assumption that the ethoxyl substitution remained constant throughout, and the fall in per cent. ethoxyl was entirely due to the increase in molecular weight caused by tosylation. With few exceptions, these calculated values (column 5) checked the observed ones within 3% and thereby eliminated the possibility that adventitious impurities had seriously interfered with the data.

Iodination of Tosylated Ethylcelluloses.—One gram of dry sodium iodide and 0.6 g. of the tosylated ether were mixed with 50 ml. of acetylacetone which had been dried over calcium chloride and redistilled at atmospheric pressure just before use. The mixture was kept at 115° for two hours with occasional shaking, then cooled and poured into 500 ml. of distilled water. Filtration and repeated triturations with aqueous acetone (1:1) removed all sodium salts from the product, which had swollen but not dissolved during the heating. Failure to dissolve completely did not seem to hinder the iodination, because duplicate preparations gave concordant results.²⁵ Duplicate preparations were also heated at 115° for two hours and at 120° for twelve hours, and the iodine introduced was 5.91 and 5.90%, respectively. The former conditions, used throughout the work, therefore produced maximum iodination.

Iodine estimations (column 7) were made by soaking samples containing 1 to 2 mg. of halogen in 25 ml. of warm ethanol until the material was thoroughly penetrated. Complete dispersion was unnecessary. Potassium hydroxide, 1 g., was added and the mixture boiled under reflux for one hour. After dilution to 100 ml. with water and acidification with dilute sulfuric acid, the estimation was completed by Doering's method²⁶ with the use of 0.01 *N* sodium thiosulfate in the final titration. Iodine contents of 6.54, 6.63, 6.55 and 6.60% were found by the above procedure for an iodo-tosylated cellulose acetate which had 6.53% by the usual Carius method. The latter method was much more tedious and explosions of the sealed Carius tubes, probably owing to the nitration of the samples, used to ruin many estimations.

The calculated sulfur values (Table I, column 9) were based on the iodine content by assuming that the total substitution of the tosylated cellulose ether was not changed by iodination. A satisfactory agreement between the calculated and observed percentages made the existence of any unknown side reaction highly improbable. It was therefore proper to express the moles of tosyl group remaining (column 11) as the difference between the iodine introduced (column 10) and the original tosyl content of each sample (column 6).

Determination of Staudinger Viscosities.—Soluble products, suitable for viscosity determinations, were prepared

(25) *Cf.* Murray and Purves, *THIS JOURNAL*, **62**, 3194 (1940).

(26) Doering, *Ber.*, **70**, 1887 (1937).

TABLE I
 ANALYTICAL DATA OF TOSYLATION AND IODINATION REACTIONS

Sample	Tosylation					After iodination					
	Tosylated hours	Ethoxyl, %	Sulfur, %	Calcd. ^a S, %	Tosyl, moles	Iodine, %	Sulfur, %	Calcd. ^b S, %	Iodine, moles	Tosyl, moles	Calcd. ^c tosyl, moles
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1	1	45.0	1.50	1.42	0.117	5.15	0.28	0.28	0.095	0.022	0.032
2	2	43.6	2.08	2.00	.169	6.00	0.57	.57	.124	.047	.057
3	3	42.6	2.50	2.45	.203	5.75	1.00	.99	.121	.083	.078
4	4	42.2	2.71	2.60	.223	5.82	1.12	1.16	.124	.098	.096
5	5	41.8	2.84	2.84	.237	5.92	1.36	1.33	.126	.109	.110
6	6	41.6	2.90	2.90	.246	5.79	1.39	1.40	.125	.120	.121
7	7	41.5	3.01	2.97	.252	5.77	1.47	1.49	.125	.128	.131
8	8	41.3	3.10	3.03	.260	5.68	1.56	1.58	.123	.137	.136
9	9	41.1	3.21	3.13	.269					.145 ^d	
10	10	41.0	3.25	3.17	.274					.150 ^d	
11	11	40.7	3.25	3.30	.281					.157 ^d	
12	12	40.7	3.30	3.30	.287					.163 ^d	
	Days										
13	1	40.4	3.57	3.42	.312					.188 ^d	.188
14	1.5	39.8	3.70	3.65	.325					.201 ^d	
15	2	39.5	3.74	3.80	.330					.206 ^d	
16	2.5	39.2	3.90	3.92	.346					.222 ^d	.218
17	3	39.2	4.04	3.92	.356					.232 ^d	.245
18	4	38.6	4.25	4.15	.385					.261 ^d	.268
19	7	37.4	4.79	4.65	.450					.326 ^d	.317
20	10	36.2	5.22	5.20	.485					.361 ^d	.347
21	21.3	35.9	5.32	5.30	.510					.386 ^d	
22	147	35.6	5.41	5.40	.517 ^e	4.99	4.12	3.96	.126	.391	

^a Calcd. from ethoxyl substitution of 2.48 throughout. ^b Calcd. from per cent. iodine and ethoxyl substitution of 2.48.

^c The sum $Z_a + Z_b$, calcd. from equations (1) and (2) as described in text. ^d Calcd. from column 6 and a constant iodine substitution of 0.124. ^e Complete substitution required tosyl, 0.520 mole.

TABLE II

VISCOSITIES OF ETHYLCELLULOSE AND DERIVATIVES

Sample ^a	Ethoxyl, %	Mol. wt. ^b	η_{sp}/c
Ethylcellulose ^c	48.5	232	26.8
Ethylcellulose	48.5	232	25.5
Tosylated (5)	47.0	239	33.8
Tosylated (8)	43.2	260	31.7
Tosylated (22)	39.3	286	26.5
Iodinated (5)	41.4	272	35.6
Iodinated (8)	47.8	235	31.6
Iodinated (22)	39.5	285	31.4

^a The samples were those with the same number in Table I. ^b Per anhydroglucose unit. ^c Original ethylcellulose. Not treated with the alcoholic alkali.

from the insoluble tosylated and iodo-tosylated ethylcelluloses by hydrolyzing a portion of the ester linkages with alkali. Samples, 0.2 g., readily dissolved when boiled in an atmosphere of nitrogen with 100 ml. of 0.02 *N* potassium hydroxide in methanol. After cooling and neutralizing with acetic acid, the ethylcellulose was precipitated and thoroughly washed in water. Solution in acetone and reprecipitation in water left a pure product in practically quantitative yield. After drying *in vacuo* at 60°, viscosities in glacial acetic acid were determined at 25° as previously described,²⁰ and Staudinger's η_{sp}/c quotient became approximately constant in each case when *c* was 0.01 mole per liter or less. The molecular weights required for the calculation of *c* (Table II) were obtained readily

from the ethoxyl analyses because the latter represented a substitution of 2.48 throughout.

Degradation during alkaline hydrolysis was insignificant (Table II, lines 1 and 2) and the variations in η_{sp}/c from the average value of thirty were not large enough to suggest that tosylation or iodination had caused degradation in a series where the substitution was not constant. If 10^{-3} was accepted as Staudinger's K_m value,¹⁴ all the samples had an average chain length of about one hundred and thirty. The specific viscosities, indeed, were surprisingly constant in view of the fact that the alkaline hydrolysis of the tosyl and iodine substituents doubtless caused Walden inversions and anhydro-ring formation in some of the glucose residues.^{27,28}

Reference to Table I, column 10, shows clearly that the number of tosyl groups replaceable by iodine reached a maximum of 0.124 mole per glucose residue within two hours from the beginning of the esterification. Failure to increase the iodination by more drastic conditions or by using samples tosylated for four months strongly supported the conclusion that the tosylation-iodination method differentiated secondary from primary alcohols sharply and quantitatively.²⁰ Although esterification is a bimolecular process, the

(27) Peat, *Ann. Reports, Chem. Soc.*, 258 (1939).

(28) Isbell, *Ann. Rev. Biochem.*, 9, 65 (1940).

more than twelve-fold excess of acid chloride used in the work made the application of the unimolecular formulas free of serious inaccuracy. On this basis, the rate constant for the tosylation of the primary hydroxyl positions in ethylcellulose was about fifteen (days and decimal logarithms) for the conditions used.

Subtraction of the groups replaced by iodine from the molar amount introduced after t days of tosylation (column 6) left differences, Z_s , which corresponded to the progressive esterification of the 0.396 mole of secondary alcoholic groups in the glucose residues (column 11). Although the tosylation proceeded in a very stiff, highly elastic gel and the general shape of the time plot was consistent with a rapid superficial followed by a slow permutoid reaction,²⁹ this explanation was untenable because the reaction of the primary hydroxyl groups was sharply completed within two hours. When the function $\log 0.396/(0.396 - Z_s)$ was plotted against time, most of the points corresponding to periods of more than one day lay about a straight line (Fig. 1). The shape of the

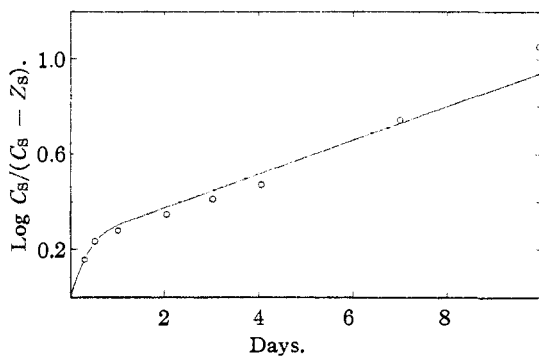


Fig. 1.—The unimolecular tosylation (Z_s) of the hydroxyl groups (originally C_s or 0.396 mole) present in the second and third positions of the ethyl cellulose.

entire curve suggested that the tosylation of the two secondary positions consisted of a slow, first order reaction superimposed on a faster one which was complete in a day. A straight latter portion of the rate curve could then be expressed by the relation

$$\log 0.396/(0.396 - Z_s) = \log 0.396/C_b + K_b t$$

where the subscript b applies to the slower of the two reactions and C_b is the initial molar amount of the corresponding hydroxyl group. By substituting known values for Z_s and t from Table I, C_b and K_b could be determined. As the experimental points were somewhat scattered, C_b and

K_b were also calculated by the method of least squares,³⁰ weighting each point in proportion to its probable experimental accuracy, which naturally decreased toward the end of the tosylation. The error in any value of Z_s was considered to be a function of two errors, those occurring in the analyses of total and of primary substituted tosyl groups. Errors in timing the withdrawal of the samples were neglected because t was relatively large. The average difference between the experimental and calculated values for both primary and total substitution was 1.9% and the combined probable error for any item in column 11, Table I, was accordingly $0.019 [Z_s^2 + (Z_s + 0.124)^2]^{1/2}$. In this manner, C_b was found to be 0.245 mole per glucose unit, and K_b was 0.0700.

The knowledge that the secondary hydroxyl groups that tosylated more slowly did so in accordance with the equation

$$\log 0.245/(0.245 - Z_b) = 0.0700t \quad (1)$$

made it reasonable to assume that a similar equation pertained to the more rapidly reacting positions, denoted by the subscript a. Values of Z_b were calculated from (1) for times between three and eight hours, and the corresponding quantities Z_a found from the relationship $Z_a + Z_b = Z_s$. The initial quantity of "a" hydroxyl group was $0.396 - 0.245$ or 0.151 mole. Substitution in the equation

$$\log 0.151/(0.151 - Z_a) = K_a t \quad (2)$$

gave an average for the rate constant K_a of 2.30 which was also the least square value. The probable errors in the amounts of the more and less rapidly reacting hydroxyl groups (0.151 and 0.245 mole) were found³⁰ to be 5.8 and 3.6%, respectively. Finally, the sums of the quantities Z_a and Z_b at various times were calculated from eq. (1) and eq. (2) and compared with the total amount of tosylation found in the two secondary positions. The satisfactory agreement (Table I, columns 11 and 12) proved the correctness of the assumption that the more rapidly reacting hydroxyl groups also obeyed the unimolecular law.

These rate studies showed that 0.151 mole of hydroxyl group in the second and third position reacted much more rapidly with tosyl chloride than the remaining 0.245 mole. Although it was possible that the faster and slower reactions were characteristic of unsubstituted and half substi-

(30) Chauvenet, "Spherical and Practical Astronomy," Lippincott, Philadelphia, 1888, Vol. II, p. 469, or Whittaker and Robinson, "The Calculus of Observations," London, 1929, p. 209.

(29) Hess and Trogus, *Z. physik. Chem.*, **B15**, 157 (1931).

tuted glycol units, it was probable that one rate applied to hydroxyl groups in the second, the other to groups in the third, position of the glucose residues. The latter interpretation was conclusively upheld by estimating the completely unsubstituted glycol units in the original ethylcellulose and in the mixtures of ethylated glucoses and ethylglucosides derived from it by degradation.

Oxidation of Ethylated Ethylglucoside Mixture with Periodate.—Ethylcellulose, 2.3 g. or 0.01 mole, was heated with 30 ml. of 1.14% hydrogen chloride in ethanol in a sealed tube for fifty hours at 130°. After isolation,³¹ the very pale brown sirup (2.7 g., theory, 2.77 g.) was dried over calcium chloride *in vacuo* at 60° for sixteen hours to remove traces of ethanol.

Anal. Calcd. for the ethylated mixture derived from the ethylcellulose, C₂H₅O, 56.3. Found: C₂H₅O, 56.5, 56.2. No ethoxyl groups had been removed during the degradation, the conditions of which precluded the formation of furanosides.

The dried sirup, 0.1355 g. or 0.488 millimole as ethylcellulose, was dissolved in 25 ml. of water and oxidized with 50 ml. of an aqueous solution containing 15.4 g. of sodium para-periodate and 22.2 ml. of glacial acetic acid per liter (0.0524 mole of Na₂H₂IO₆). The temperature was kept at 20 ± 0.5°, and the consumption of oxidant was followed by the sodium arsenite method. Samples of 10 ml. were withdrawn at intervals and the alkalinity required in the titration³² was conveniently obtained by adding a slight excess of 10% potassium hydroxide followed by a small piece of solid carbon dioxide. Figure 2, Curve A, shows that 0.26 to 0.29 mole of periodate were used by a mole of the glucoside mixture. A duplicate experiment with an 0.0951-g. sample gave a consumption of 0.25 to 0.29 mole and the average from both runs was 0.27 mole. The latter figure corresponded to the number of glycol groups in the ethylated ethylglucosides. An attempt to check the data by the lead tetraacetate method³³ failed because the initial glycol oxidation could not be clearly separated from the secondary reactions (Fig. 2, curve B).

Oxidation of Ethylcellulose with Lead Tetraacetate.—A solution containing 2.32 g. (0.01 mole) in 75 ml. of glacial acetic acid was mixed with 25 ml. of 0.1 N lead tetraacetate in the same solvent, and the mixture was kept at 25 ± 0.5°. Samples of 10 ml. were pipeted into 25-ml. volumes of chloroform and the excess oxidizing agent was titrated in the usual way.³³ The chloroform prevented the precipitation of ethylcellulose and the consequent difficulty in determining the end-point. Duplicates checked to ±0.1 ml. of 0.01 N sodium thiosulfate or less, and the results are summarized in the first two columns of Table III. A plot of the time *t* against the moles *M* of tetraacetate consumed per glucose unit closely approximated in its later stages the straight line $M = x + yt$. Taking an average value of *y* as 4.9×10^{-5} for the slope of the line (column 4), the inter-

cept *x* was calculated (column 5) for each time. The agreement was satisfactory evidence that the initial rapid reaction corresponded to 9.5 to 10.5×10^{-3} mole of glycol per glucose unit in the ethylcellulose.

TABLE III
OXIDATION OF ETHYLCELLULOSE WITH LEAD TETRA-
ACETATE

Hours, <i>t</i>	0.01 N Thio, ^a ml.	Moles Pb(OAc) ₄ (10 ³ M)	$\Delta M/\Delta T$ (10 ³ γ)	Moles glycol (10 ³ x)
0.1	0	0		
17.5	1.58	0.79		
41.5	2.06	1.03		
65.5	2.52	1.26		
90.0	2.76	1.38	4.9	9.6
116	3.12	1.56	(6.8)	9.7
165	3.58	1.79	4.7	10.2
282	4.64	2.32	4.5	10.3
450	6.08	3.04	4.3	10.2
				9.7

^a Difference from blank of 30.2 ml.

Oxidation of Ethylated Glucose Mixture with Lead Tetraacetate.—An attempt to degrade the ethylcellulose with water saturated with hydrogen chloride at 0°³⁴ eventually left a sirup with 40.8% ethoxyl instead of the calculated 44.9%, and the method of degradation was accordingly discontinued. Degradation of 3.305 g. of ethylcellulose with 16.5 ml. of 72% sulfuric acid was complete in ten days at room temperature³⁵ and a Cajori analysis³⁶ of the aqueous sulfuric acid solution showed the presence of 3.54 g. of aldose where theory was 3.56 g. The methanol solution of the product was centrifuged to remove traces of barium sulfate and after evaporation of the solvent the residual, viscous, colorless sirup crystallized extensively. Drying over calcium chloride *in vacuo* for sixteen hours removed traces of methanol and ethoxyl values of 44.8, 44.6 and 44.9% (calcd., 44.8%) showed that no dealkylation had occurred. Samples of 0.0628 g. and 0.0431 g. in 25 ml. of glacial acetic acid were separately oxidized with 75 ml. of 0.1 N lead tetraacetate in the same solvent.³³ The results

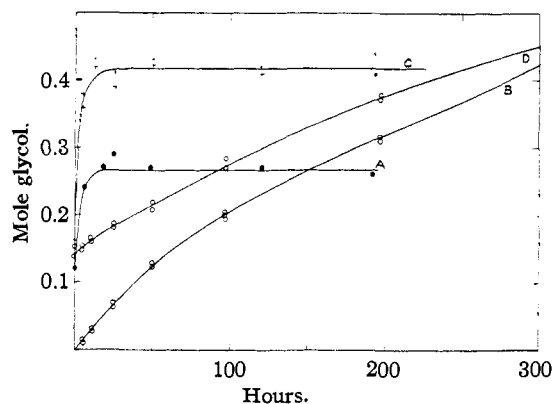


Fig. 2.—Oxidation of ethylated ethylglucoside mixture: Curve A, periodate; Curve B, lead tetraacetate. Oxidation of ethylated glucose mixture: Curve C, periodate; Curve D, lead tetraacetate.

(31) Irvine and Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

(32) Malaprade, *Bull. soc. chim.*, [5] **1**, 843 (1934).

(33) Hockett and McClenahan, *THIS JOURNAL*, **61**, 1667 (1939); see also Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

(34) Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

(35) Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921).

(36) Cajori, *J. Biol. Chem.*, **54**, 617 (1922).

were plotted in Fig. 2, Curve D, whence it appeared that the initial rapid reaction, corresponding to 1:2 glycol units, consumed 0.153 and 0.137 mole of oxidant within fifteen minutes. A parallel experiment with periodate (Fig. 2, Curve C) showed the very rapid consumption of 0.41 to 0.44 mole, corresponding to all glycol groups.

The practically quantitative degradation of the ethylcellulose by acid ethanol left a mixture of ethylglucopyranosides partly ethylated in positions two, three and six to correspond with the original distribution. As positions one and five were protected by glucoside and ring formations, respectively, the 0.25 to 0.29 mole of periodate that the mixture consumed (Fig. 2, Curve A) measured the sum of the 2:3 and 3:4 glycol groups. A lead tetraacetate oxidation of the ethylcellulose determined the number of the former units as 0.01 mole (Table III) and, by difference, 0.24 to 0.28 mole was in the 3,4-position of the glucoside mixture. Because position four had been completely occupied by the glycoside linkages of the ethylcellulose, the fourth hydroxyl group in the corresponding ethylglucosides was completely free. The molar amount of 3,4-glycol therefore gave the number of unsubstituted hydroxyl groups in the third position of the ethylcellulose.

Degradation of the ethylcellulose by aqueous sulfuric acid gave a practically quantitative yield of the partly alkylated glucoses. Upon treatment with lead tetraacetate, an amount of oxidant equivalent to 0.13 to 0.15 mole of glycol was consumed almost immediately. Further reaction proceeded at a much slower rate and the end of the true glycol oxidation was obscured by oxidation of another nature (Fig. 2, Curve D). It has been shown with various glycols³³ that the oxidation was far more rapid when the configuration was unrestricted than when the grouping was *trans*, as in the 2,3- or 3,4-positions of glucose. Because position one was completely free in the ethylated glucose mixture, the initial, rapid consumption of lead tetraacetate measured the amount of 1,2-glycol present. This amount was obviously equal to that of the free hydroxyl groups in the second position of the ethylcellulose.

A duplicate oxidation with periodate failed because the very rapid nature of this reaction caused the 1,2- (0.13 to 0.15 mole), the 2,3- (0.01 mole) and the 3,4 (0.24 to 0.28 mole) oxidations to overlap and no marked break in the oxidation-time curve occurred until 0.41 to 0.44 mole of periodate had been reduced (Fig. 2, Curve C).

By comparing the data from these oxidation experiments with those from the analysis of the over-all rate at which the secondary hydroxyl groups in ethylcellulose were tosylated, the interpretation of the latter reaction was completely clarified. The 0.151 mole of hydroxyl groups in the second position was esterified fairly rapidly by tosyl chloride while the 0.245 mole in the third position reacted much more slowly. This information will probably make it possible to determine the distribution of substituents in a wide range of cellulose derivatives by the iodination-tosylation technique alone. The method demands a homogeneous system for the rate study and very different reactivities for the second and third positions. The periodate-lead tetraacetate analysis, on the other hand, is possible only when the substituents are not removed during the degradation to partly substituted glucoses.

The authors express their great appreciation of the extensive guidance they received from Dr. G. Scatchard in the mathematical analysis of the tosylation-rate plot.

Summary

1. A technical ethylcellulose, averaging 2.48 ethoxyl and 0.52 hydroxyl groups per glucose residue, was found by oxidation with lead tetraacetate to have 0.01 glycol unit in the second and third positions. The corresponding mixture of partly substituted ethylglucopyranosides was oxidized with periodate and had 0.25 to 0.29 glycol unit distributed between the 2,3 and 3,4 positions. Oxidation of the corresponding mixture of reducing sugars with lead tetraacetate revealed the presence of 0.13 to 0.15 mole of glycol in the 1,2-position. The combined results showed that 0.13 to 0.15 hydroxyl group was unsubstituted in the second position of the ethylcellulose and 0.24 to 0.28 mole in the third.

2. The rate at which the ethylcellulose was esterified in a homogeneous pyridine solution at 20° by a twelve-fold excess of *p*-toluenesulfonyl chloride was followed by sulfur and alkoxyl analyses for four months, or until esterification was practically complete. Samples removed at intervals were converted to the 6-iodo derivatives by heating with sodium iodide in acetylacetone. The analyses showed that 0.124 mole of hydroxyl group was present in the sixth or primary positions of the original ethylcellulose.

3. The data in (2) gave by difference the com-

bined rate at which the two secondary alcohol groups in the ethylcellulose had been esterified. Mathematical analysis of this rate curve showed that the data agreed very closely with a unimolecular, fairly rapid tosylation of 0.151 mole of hydroxyl superimposed on a slow tosylation of 0.245 mole. Comparison with the independent data in (1) made it clear that the ethylcellulose had 0.151 mole of free hydroxyl groups in the

second position and 0.245 mole in the third. These values were probably more accurate than those quoted in (1).

4. The first order rate constants for the tosylation of unsubstituted hydroxyl groups in the ethylcellulose were in the approximate ratio of 2.3 for the second, 0.07 for the third and 15 for the sixth position.

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The Relationship between the Method of Preparation, the Distribution of Substituents and the Solubility in Water or Alkali of Methyl and Ethyl Ethers of Cellulose¹

By JOHN F. MAHONEY² AND CLIFFORD B. PURVES

The ready solubility in organic solvents of the ethylcellulose just studied³ made it possible to follow the rates of tosylation and of oxidation with lead tetraacetate in homogeneous systems. These estimations, together with the selective iodination of the tosylated derivative and the periodate oxidation of the derived ethylated glucose and glucoside mixtures, determined the average distribution of the alkoxy and hydroxyl groups between the second, third and sixth positions of the cellulose structure. It was obvious that the shape of the reaction-rate plot observed for a heterogeneous mixture of pyridine, tosyl chloride and an insoluble less highly alkylated cellulose could not be reliably connected with the different amounts of hydroxyl group in the second and third positions. Although this information could probably be obtained from the corresponding mixture of ethylglucosides, the present work was restricted to adapting the analyses for primary hydroxyl and glycol groups to some water or alkali soluble methyl- and ethyl-celluloses.

Ethers (A), (B) and (C) (Table I) were high grade technical materials prepared in heterogeneous reactions from alkali-cellulose, while (E) and (F) were similar products. Ether (D)⁴ was made

(1) Presented before the Division of Cellulose Chemistry at The Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Abstracted from a thesis submitted by J. F. Mahoney to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941. Present address: Merck and Company, Rahway, New Jersey.

(3) Mahoney and Purves, *THIS JOURNAL*, **64**, 9 (1942). This article contains all data quoted for ether (A).

(4) The authors wish to thank Dr. S. H. Bass, of the Dow Chemical Company, for Methocels (B) and (C). The former had the lot

by ethylating cellulose homogeneously dispersed in aqueous trimethylbenzylammonium hydroxide.⁵

TABLE I
CHARACTERISTICS OF CELLULOSE ETHERS EXAMINED

Ether ^a	Alkoxy ^b	Substitution	Average chain length ^b	Solubility at 0°C.
A	OEt 48.5%	2.48	120	Org. solvents
B	OMe 30.5	1.85	150	Water
C	OMe 10.7	0.588	210	Caustic soda
D	OEt 14.7	0.583	300	Water
E	OEt 27.6	1.20	425	Water ^c
F ^d	OEt 17.5	0.707	...	Caustic soda

^a All data for Ether (A) are quoted from the preceding article.³ ^b By Staudinger's viscosity method (see text). ^c Some granularity. ^d Both (E) and (F) were described as of relatively high viscosity.

The Average Chain Length of Ethers B-E.—Two-gram samples were acetylated for three days at room temperature with a mixture of 60 ml. of pyridine and 20 ml. of acetic anhydride. The products were purified by precipitation from acetone solution into water, and after drying had alkoxy contents of 24.3, 7.62, 13.0 and 20.9%, corresponding to basic molecular weights of 236, 239, 200 and 259, respectively. Viscosities were measured in glacial acetic acid at 25°³ and the Staudinger η_{sp}/c quotients became constant at concentrations of 0.03 to 0.01 mole per liter or less. The η_{sp}/c values were 35.0, 51.9, 60.1 and 110, and the average chain lengths quoted in Table I were derived from them by making the doubtful assumption that Staudinger's K_m constant was 10×10^{-4} in all cases.

number M-453 and a viscosity of 26 centipoises in 2% aqueous solution at 20°. The latter, number MX-267, had a viscosity of 34 centipoises for a 2% solution in 4% caustic soda. We are also indebted to Dr. L. H. Bock, of the Röhm and Haas Company, for ether (D) and to Dr. H. M. Spurlin, of the Hercules Powder Company, for specimens (E) and (F) (Samples X2167-12 and X2167-14). The ash content of the samples was low.

(5) Bock, *Ind. Eng. Chem.*, **29**, 985 (1937). This article reviewed the literature, and discussed the solubility in water of alkylated celluloses in relation to the distribution of the alkyl groups.