Chemical Reaction between Cellulose and Formaldehyde

I. Preparation of Methylene Cellulose* and its Methylation[1]

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荒木幹夫**：セルロースとホルムアルデヒドとの反応（第1報）
メチレンセルロースの生成とそのメチル化

Formaldehyde undergoes addition reaction with compounds containing reactive hydrogen atom to form methylol derivatives and particularly under acidic condition the condensation reactions may occur to form methylene derivatives. The probable processes involved in the treatment of cellulose with formaldehyde are similarly considered to be (1) formation of cellulose hydroxymethyl ether (Cel-OCH_2OH), 〔I〕, (2) formation of cellulose polyoxymethylene ethers (Cel-$(OCH_2)_n$-OH), 〔II〕, (3) formation of methylene ether cross-linking (Cel-OCH_2O-Cel), 〔III〕, and (4) formation of polyoxymethylene ether cross-linkings (Cel-$(OCH_2)_nO$-Cel), 〔IV〕, where Cel- shows glucopyranose residue in cellulose molecule.

There have been considerable studies on the chemical reaction between cellulose and formaldehyde. MEUNIER and GYOT[2] postulated the formation of 〔III〕. WOOD[3] discussed their conclusion and asserted that the methylene cross-linkings were formed on two hydroxyl groups of the same glucose residue. SCHENK[4] disputed WOOD's proposed course of reaction and postulated the formation of cross-linking between two hydroxyl groups in adjacent cellulose molecular chain, 〔III〕. Similarly, DILLENIUS[5] supported the formation of 〔III〕 from the effect of this reaction on the products upon the alkali solubility and swelling in water or alkali. GOLDTHWAIT[6] gave the same conclusion from the sharp drop in dye-uptake of the product containing 1.5% combined formaldehyde or less.

From the comparatively earlier papers above mentioned, however, no conclusion as to the actual chemical structure of methylene cellulose has been obtained.

WAGNER and PACSU[7] treated cellulose with paraformaldehyde in a sealed tube in the presence of boric acid as catalyst, and obtained a methylene cellulose containing 5% combined formaldehyde. From the results of methylation with subsequent methanolysis and analysis, they deduced that the product

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* Cellulose treated with formaldehyde.

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obtained was one in which anhydroglucose units of neighboring cellulose chain were cross-linked by methylene dioxy groups preferentially at secondary hydroxyl group. STEELE[8] and LINEKEN[9], from the infrared spectrum of the formaldehyde treated cellulose obtained by the same method as WAGNER and PACSU, observed the reaction proceed mainly to the formation of [IV].

The acids used for the catalyst[10] in these reactions should usually be at least above 10^{-4}, and particularly above 10^{-2}, in dissociation constant. Since boric acid really acts within this range although its dissociation constant is 10^{-10}, it seems to act as a specific catalyst in this reaction. Therefore, the structure of the product obtained by use of this catalyst may differ from that of the products obtained by usual acid catalysts.

The author has been studying the formaldehyde treatments of woods[11] under hydrogen chloride catalyst. And, one part of these experiments, the reaction of pure cellulose with formaldehyde in the presence of hydrogen chloride catalyst in vapor phase was studied, especially as for the structure of the product.

Results and Discussion

Formation of methylene cellulose.—— Hydrogen chloride as a catalyst was absorbed on purified cotton cellulose and the samples treated with hydrogen chloride were reacted with formaldehyde vapor for 7~12 hrs. at 95°C under atmospheric pressure. Sample (No. 4) was obtained by treating with paraformaldehyde in a closed vessel under a pressure of 800 mmHg at 125°C. As shown in Table 1, methylene cellulose containing combined formaldehyde (max. 6.3%) was obtained.

Table 1. Reaction between Cellulose and Formaldehyde in the Presence of Hydrogen Chloride as Catalyst.

Sample No.	Reaction temp., °C	Reaction period, hrs.	Combined HCHO, %
1	95	7	1.28
2	〃	14	3.39
3	〃	21	3.70
4	125	21	6.34

Methylation of methylene cellulose.—— To elucidate the structure of methylene cellulose and to determine the position of hydroxyl groups which have reacted with formaldehyde, complete methylation of methylene cellulose is necessary. As for the methylation of methylene cellulose, WAGNER and PACSU[7] obtained methyl methylene cellulose[+] containing 32% methoxyl group from the methylene cellulose which contains 5.4% bound formaldehyde, where the theoretically obtainable methoxyl content for the methylene cellulose is equal to 37.2%. The results obtained by them seemed to be insufficient for the elucidation of the structure.

Table 2. The Methylation of Methylene Cellulose.

Sample	No. 4		No. 2	
(The methylation with dimethyl sulfate and sodium hydroxide)				
No. of Methylation	%, $-OCH_3$	%, HCHO	%, $-OCH_3$	%, HCHO
0	0	6.34	0	3.39
1	17.9	—	24.5	—
2	25.9	—	25.9	—
3	26.3	—	—	—
4	28.0	—	—	—
5	29.5	—	—	—
6	29.2	4.36(5.02)*	—	—
(The methylation with sodium and methyl iodide in liquid ammonia)				
0	29.2	4.36	25.9	—
1	31.9	—	36.6	—
2	38.6 (39.4)**	3.34(4.20)*	40.5 (41.2)**	2.39(2.92)*

* Calculated from analyzed formaldehyde content of the methylated methylene cellulose by converting to a methoxyl-free basis.

** Theoretically obtainable methoxyl content.

In the present study, the sample of methylene cellulose containing 6.3% combined formaldehyde (Table 1, No. 4) was methylated six times by dimethyl sulfate and sodium hydroxide using the method of STEELE and PACSU[12], and further methylated in liquid ammonia with metallic sodium and methyl iodide by the method of HODGE[13]. The sample containing 3.39% combined formaldehyde (Table 1, No. 2) was methylated two times and further methylated in

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[+] Methylated methylene cellulose.

liquid ammonia. The results were tabulated in Table 2.

As shown in the table, a slight removal of formaldehyde from the products was observed at the methylation, especially in liquid ammonia. It might be caused by the sodium amide formed by liquid ammonia-metallic sodium system[13]. The results of the methylation of two samples of methylene cellulose would lead to the conclusion that the methoxyl contents closely coincide with the theoretical values which were obtained from the calculated number of the free hydroxyl groups remaining after formaldehyde treatment, where the calculation of the free hydroxyl number was based on the assumption that each methylene dioxy group blocks two hydroxyl groups per molecule of formaldehyde. The theoretically obtainable methoxyl contents of formaldehyde-treated cellulose with the same formaldehyde content vary with its structure. In Table 3, the relation between the theoretical methoxyl content and its structure is shown. This fact clearly indicates that the reaction of cellulose with formaldehyde proceeds through the reaction (3) mainly under the condition described.

Table 3. The Relation between the Structure of the Products and Their Theoretically Obtainable Methoxyl Contents.

Products obtained		Theoretically obtainable MeO-%			
Comb. HCHO	MeO-%	for Cel-$(OCH_2)_nO$-Cel			for Cel-$(OCH_2)_n$-OH
%*	obs.	$n=1$	3	5	irrespective of n
4.20	38.6	39.4	42.6	43.3	44.1
2.92	40.5	41.2	43.3	43.8	44.6

* Methoxyl-free basis.

Experimental

Material—— For cellulose sample, absorbent cotton was used, which was prewashed by soap and distilled water, and then made free of water with methanol, which was substituted with ether, and dried under a reduced pressure. The water content of the samples before the reaction was about 3.2%. Formaldehyde was obtained by the thermal decomposition of dried paraformaldehyde.

Reaction with formaldehyde—— Ten grams of the sample was placed in a fully dried desiccator (2L) fitted with a gas inlet tube and then it was evacuated to 20 mmHg. From the gas inlet tube, dry hydrogen chloride was introduce into it to make the concentration of hydrogen chloride about 0.25 g/l and then through calcium chloride tube dry air passed into the vessel gradually to make the pressure in the vessel up to atmospheric pressure. After one hour, the cellulose sample treated with hydrogen chloride was reacted with formaldehyde for 3~17 hrs. at 95°C by the same method as described in the previous reports[11]. The sample 4 (Table 1) was obtained by the reaction of formaldehyde under a pressure of 800 mmHg at 125°C for 21 hrs.

Determination of combined formaldehyde of methylene cellulose and methyl methylene cellulose—— For the methylene cellulose, the sample was refluxed with 28% ammonium hydroxide for one hour and washed with hot distilled water repeatedly to remove absorbed formaldehyde and its polymers. In the case of methylated samples, the treatment of ammonium hydroxide was omitted. Before analysis, the samples were dried over phosphorus pentoxide at a reduced pressure. The analysis was carried out by WOOD's[3] method ; 0.1~0.2 g of the sample was distilled with 1 N- sulfuric acid containing sodium sulfate until 250 ml. distillate was collected. The distillate was made up exactly to 500 ml. From that solution one ml. was pipetted out and the free formaldehyde contained in it was analyzed by BRICKER's[14] method.

Methylation of methylene cellulose——

(A) By dimethyl sulfate and sodium hydroxide: The sample containing 6.3% bound formaldehyde was methylated by the method of STELLE and PACSU[12]. After six times treatments, no further increase of methoxyl content was observed. Another sample containing 3.39% bound formaldehyde was methylated two times by the same method.

(B) By methyl iodide and sodium in liquid ammonia : Commercial anhydrous liquid ammonia, sodium (C. P. grade) and methyl iodide were used. The reaction vessel was a 500 ml., rubber-stoppered, three necked unsilvered DEWAR's flask, fitted with a stirrer and a sodium hydroxide tube for preventing moisture. The method of HODGE, KARRJALA and HILBERT was used. Ten grams of the dried, partially methylated methylene cellulose obtained by the treatment (A) was stirred with 300 ml. of anhydrous liquid ammonia.

In methylation steps, the sodium was added in small pieces at a rate controlled so that the amount of free sodium present in the reaction mixture did not exceed the amount that would react within the next 15 min. After one hour, methyl iodide was added dropwise to the reaction mixture. The temperature of which was 35°C below zero. The total amount of sodium added in the first three methylation steps was (1) 1.4, (2) 1.0 and (3) 0.8 atom per C_6-unit. Then, after decantation and washing with liquid ammonia, further two times methylation was carried out. The total amounts of sodium in these two steps was (4) 1.0 and (5) 0.8 atom per C_6-unit. The molar ratio of methyl iodide to sodium in each methylation step was 1, excluding the last step (5), where the ratio was 1.5. After five times methylation, the partially methylated methylene cellulose was separated by decantation and washing with liquid ammonia and was re-methylated by the treatments (2), (3), (4) and (5) as described above. No further increase of methoxyl content was observed in the treatments (4), (5). The methylated methylene cellulose was washed with liquid ammonia and then with hot distilled water. The washed sample was dried over phosphorus pentoxide under a reduced pressure.

Determination of methoxyl content—— The methoxyl content of methylated methylene cellulose was determined by the method of Vieböck and Schwappach modified by Hoffman and Wolform[15]. The results were shown in Table 2.

Summary

The methylene cellulose obtained by the reaction of formaldehyde in the presence of hydrogen chloride as a catalyst was fully methylated by methyl iodide and sodim in liquid ammonia after the treatment with dimethyl sulfate and sodium hydroxide. The methoxyl content of the fully methylated methylene cellulose was closely in accord with the theoretical methoxyl content calculated on the assumption that each methylene bridge brocks two hydroxyl groups per molecule of formaldehyde. This fact shows that the reaction of cellulose with formaldehyde proceeds through reaction (3) under the condition used.

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摘要

塩化水素の存在下でセルロースとホルムアルデヒドとを反応させて，最高6.3%の結合ホルムアルデヒドを含有するメチレンセルロースをえた。その結果は表1で示した。

えられたホルムアルデヒド含有量のことなるメチレンセルロースを，それぞれ，ジメチル硫酸と水酸化ナトリウムとでトルエン中で6回前メチル化を行ない，さらに液体アンモニア中でヨウ化メチルと金属ナトリウムとでメチル化して，それぞれのほぼ完全メチル化メチレンセルロースと考えられるものをうることができた。その結果は表2で示した。

それらの最高メトオキシル基含有量は，いずれもホルムアルデヒド1分子がセルロース鎖中の2つの水酸基と反応して，メチレンジオキシ架橋結合を生成するとして計算した理論メトオキシル基含有量に近い値を示す（表3参照）。

このことから，この反応ではホルムアルデヒドはセルロースと反応してセルロース鎖間にメチレンジオキシ架橋結合を主として生成する方向に進行することが明らかになつた。

Literature Cited

1) Presented in part at the Meeting of the Chemical Society of Japan, Tokushima City, Tokushima Pref., September (1962).
2) MEUNIER, L. and R. GYOT : Compt. rend., **188** : 506 (1929).
3) WOOD, F. C. : J. Soc. Chem. Ind. (London), **50** : 4111 (1931).
4) SCHENK, M. : Helv. Chim. Acta, **14** : 520 (1936), *ibid.*, **15** : 1008 (1932).
5) DILLENIUS, H. : Jentgen's Kunstseide u. Zellwolle, **24** : 520 (1942).
6) GOLDTHWAIT, C. F. : Textile Research J., **21** : 55 (1951).
7) WAGNER, R. E. and E. PACSU : Textile Research J., **22** : 12 (1952).
8) STEELE, R. : Textile Research J., **25** : 545 (1955).
9) LINEKEN, E. E., S. M. DAVIS and C. M. JORGENSEN: Textile Research J., **26**: 940 (1956).
10) ROFF, W. J. : J. Textile Institute (Transaction), **11** : T646 (1958).
11) ARAKI, M., T. GOTŌ, R. GOTŌ and S. KADITA : "Wood Research" Bull. of the Wood Research Inst. Kyoto Univ., No. 20: 1, 16, 22 (1958), *ibid.*, No. 21: 51 (1957), *ibid.*, No. 22: 24 (1960).
12) STEELE, R. and E. PACSU : Textile Research J., **19** : 771 (1949).
13) HODGE, J. E., S. A. KARRJALA, and G. E. HILBERT: J. Am. Chem. Soc., **73**: 3312 (1951).
14) BRICKER, C. E., and H. R. JOHNSON : Ind. Eng. Chem., Anal. ed., **17** : 400 (1954).
15) HOFFMAN, D. O., and M. L. WOLFROM : Anal. Chem., **19** : 225 (1947).