

Characterization of Water-Soluble Cellulose Derivatives Produced by Alkali Treatment of Ozonized Allylated Celluloses

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Synopsis

Ozonization products of allylated celluloses such as completely allylated methylcellulose and tri-*O*-allylcellulose, which are insoluble in both organic solvents and water, gave water-soluble derivatives by alkaline treatment. Infrared (IR) and ^{13}C -NMR (nuclear magnetic resonance) spectrometries revealed that the products have many carboxyl as well as carbonyl groups. Allyl ethers in allylated celluloses were found to be cleaved by 30–35% during ozonization, whereas alkyl ethers such as methyl and ethyl ethers in cellulose derivatives were completely stable.

INTRODUCTION

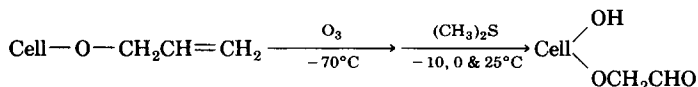
In a previous article,¹ in which aldehydocelluloses were prepared from allylated celluloses (completely allylated methylcellulose, tri-*O*-allylcellulose, and allylated ethylcellulose) by ozonization followed by subsequent dimethylsulfide treatment, a part of allyl groups was found to be removed during ozonization (Scheme 1). The extent of deallylation, however, was not estimated, because the insolubility of aldehydocelluloses in both organic solvents and alkali prevented the determination of hydroxyl groups produced by deallylation. On the other hand, ozonized allylated celluloses were noticed to be alkali soluble and to yield water-soluble products in a weak alkaline solution.

In the present article, ozonized allylated celluloses were subjected to a mild alkaline treatment at pH 10.0 instead of $(\text{CH}_3)_2\text{S}$ treatment, and the products were characterized by various methods. This characterization revealed the formation of aldehyde and carboxyl groups, and gave information on the extent of deallylation.

EXPERIMENTAL

Samples

Cellulose samples were commercially available methylcellulose (DS 1.63, Wako Chemical Ind. Co. Ltd.), cellulose acetate (DS 1.75, 2.24, and 2.39,



Scheme 1. Preparation of aldehydocellulose.

Daicel Chemical Ind. Co. Ltd.), ethylcellulose (DS 1.92, Wako Chemical Ind. Co. Ltd.), and Avicel (cellulose powder, DP 250, Asahikasei Co. Ltd.). These samples were used after being dried at 105°C. Dimethyl sulfoxide (DMSO) and acetone were dehydrated over molecular sieve 3A. Other solvents and reagents of special grade were used without any further purification.

Preparation of Completely Allylated Methylcellulose and Tri-*O*-allylcellulose and Allylated Ethylcellulose

Completely allylated methylcellulose, tri-*O*-allylcellulose, and partly allylated ethylcellulose were prepared according to the procedure in previous reports.^{1,2} The degree of substitution (DS) by allyl groups of completely allylated methylcellulose, tri-*O*-allylcellulose, and allylated ethylcellulose was 1.4, 3, and 0.6, respectively.

Ozonization and Subsequent Alkaline Treatment

Ozonization condition of allylcellulose was the same as that adopted in the previous report.¹ Namely, 1 g of each sample was dissolved in 60 mL of dichloromethane-methanol (5 : 1). Oxygen-containing ozone was bubbled into the solution with a flow rate of 0.5 L/min at -70°C for about 30 min, until the solution turned blue. After ozonization, remaining ozone was purged off from the solution with nitrogen gas, and the solution was evaporated under reduced pressure at 40°C to yield film or filmlike residues. The product was washed thoroughly with water to remove formaldehyde and paraformaldehyde produced by ozonization. The filmlike product was treated at room temperature for 3 days with an alkaline solution, whose pH was kept at 10.0 by the use of a pH stat. The alkaline solution thus produced was dialysed for 3 days and passed through a column of Amberlite IR-120 B (H⁺). Eluates were freeze-dried to yield white cotton-like residues. The residues were characterized by IR and ¹³C-NMR spectrometries.

Stability Test of Alkyl Ether Bonds During Ozonization

As commercially available methylcellulose (DS 1.6) was not soluble in dichloromethane-methanol (5 : 1), methylcellulose (DS 2.0) was prepared from Avicel with powdered NaOH and methyl iodide in SO₂-diethylamine-DMSO solutions.^{3,4} This product and commercially available ethylcellulose (DS 1.9) were ozonized under the same conditions as described above, and the elementary compositions of products were compared with those of starting materials.

General Analysis

Infrared spectra were measured by the KBr disk technique and the deposited film technique from chloroform solutions, using Shimadzu IR-435 spectrometer. ¹³C-NMR spectra were measured on JEOL (Japan Electro Optics Laboratory; JEOL) FX-100 type spectrometer and the measuring conditions were as follows: 8000 points, 6000 Hz, pulse delay 0.6 s, and Fydac accumulation method. The contents of aldehyde groups and carbon-carbon double bonds were measured according to the method described previously.^{1,2} The contents of carboxyl groups were determined by the conductometric

titration. The DS by alkyl substituents was calculated based on elementary analyses. The DS by hydroxyl groups was calculated by subtracting DS of the other functional groups from 3.

RESULTS AND DISCUSSION

Alkali Treatment of Ozonized Allylated Celluloses

Ozonized allylated methylcellulose and ozonized tri-*O*-allylcellulose dissolved gradually during the mild alkaline treatment at pH 10.0. The yields of soluble products after alkaline treatment for 3 days were higher than 95 and 70% for ozonized allylated methylcellulose and ozonized tri-*O*-allylcellulose,

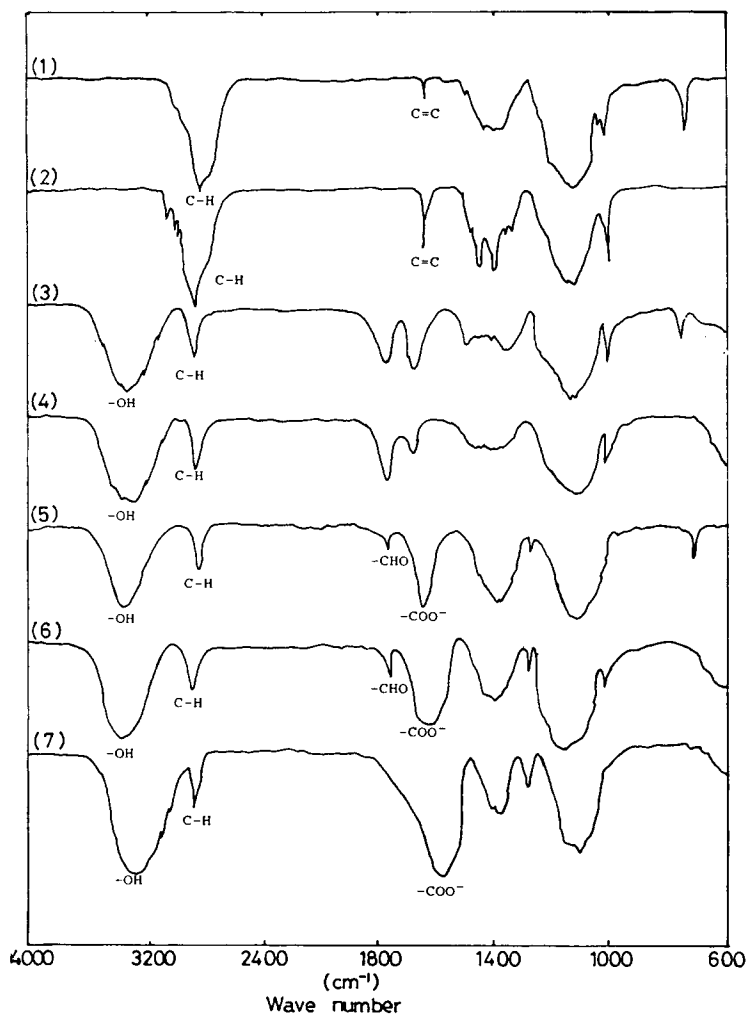


Fig. 1. IR spectra of cellulose derivatives. (1) Completely allylated methylcellulose (DS by allyl: 1.4). (2) Tri-*O*-allylcellulose. (3) Ozonized allylated methylcellulose. (4) Ozonized tri-*O*-allylcellulose. (5) Ozonized allylated methylcellulose after alkaline treatment (pH 10.0). (6) Ozonized tri-*O*-allylcellulose after alkaline treatment (pH 10.0). (7) Carboxymethylcellulose (DS: 0.98).

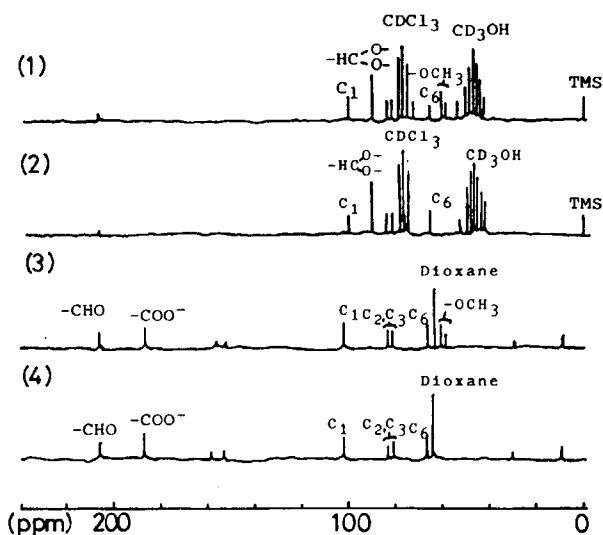


Fig. 2. ^{13}C -NMR spectra of ozonized allylated cellulose and their alkali-treated products. Note: (1) Ozonized allylated methylcellulose in $\text{CD}_3\text{OH}-\text{CDCl}_3$ (1/5). (2) Ozonized tri-*O*-allylcellulose in $\text{CD}_3\text{OH}-\text{CDCl}_3$ (1/5). (3) Alkali-treated product from ozonized allylated methylcellulose in D_2O . (4) Alkali-treated product from ozonized tri-*O*-allylcellulose in D_2O . Internal standards are tetramethylsilane (TMS) for (1), (2), and dioxane for (3), (4).

respectively. Especially for the former, 90% of the ozonized product dissolved after one day's treatment. On the other hand, ozonized allylated ethylcellulose did not dissolve at all even after 7 days treatment.

As shown in spectra (3) and (4) (Fig. 1), the absorption at $1630\text{--}1650\text{ cm}^{-1}$ due to $\text{C}=\text{C}$ stretching vibrations of allyl groups (found for the starting materials) was removed completely by ozonization. Instead, as pointed out in the previous report, the absorption of hydroxyl groups produced by deallylation was detected. Spectra (5) and (6) in Figure 1 showed that the alkaline treatment of ozonized samples caused the formation of carboxyl (around 1600 cm^{-1}) and carbonyl groups ($1710\text{--}1720\text{ cm}^{-1}$). Spectrum (6) is almost the same as that of carboxymethyl cellulose (7) except the presence of the $-\text{CHO}$ absorption band, indicating that alkali solubility of the alkali-treated ozonized products is due to the formation of carboxyl groups.

Structural changes observed by infrared (IR) spectrometry were supported by ^{13}C -NMR spectrometry (Fig. 2). Namely, in the spectra of alkali-treated products [spectra (3) and (4) in Fig. 2], signals due to aldehyde and carboxyl carbons appeared around 200 and 185 ppm, respectively, but no signal around 90 ppm due to ozonides ($-\text{O}-\text{CH}_2-\text{O}-$) was detected. This indicates that alkali decomposed ozonides into aldehyde and carboxyl groups. The mechanism of this decomposition reaction may be formulated as shown in Figure 3.

Clearly, degradation of cellulose and formation of carboxyl groups make cellulose alkali soluble. It is well known that any oxidized cellulose that contains carbonyl groups at any position of anhydroglucose units is cleaved almost completely by β -alkoxy elimination under very mild alkaline condition to yield degraded cellulose with carboxyl groups at the reducing end. Those

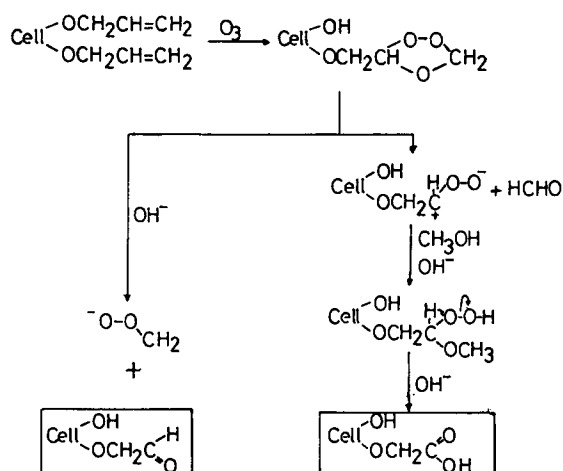


Fig. 3. Reaction mechanism of ozonization and the subsequent alkaline treatment (pH 10.0) of allylated celluloses.

carboxyl groups are of metasaccharinic acid type and are formed by the stopping reaction.⁵ However, ozone has no ability to oxidize hydroxyl groups into carbonyl groups, and thus neither degradation of cellulose nor formation of carboxyl groups based on the above described reactions are expected during alkali treatment of ozonized allylated cellulose.

Interestingly, the extent of dissolution of ozonized products in aqueous alkali decreased with the increase of pH, and as a result, the formation of bead-like residues instead of the dissolution of ozonized allylated celluloses was observed at higher pH than 12.0. This phenomenon was not clarified because of insolubility of the products. Possibly, higher alkalinity accelerates the formation of aldehyde groups which can produce hemiacetal linkages¹ between cellulose chains.

The contents of functional groups in the alkali-treated ozonized celluloses were shown in Table I. Carbon-carbon double bonds in allylated celluloses were removed completely as shown in spectra (5) and (6) in Figure 1. Thus the DS of hydroxyl groups was calculated by subtraction of DS for both aldehyde and carboxymethyl groups from 3. As the hydroxyl group is regenerated by deallylation during ozone treatment (Fig. 3), its content indicated that about 35% of allyl ether bonds were cleaved during ozonization at -70°C . On the

TABLE I
Contents of Functional Groups in Ozonized Allylated Celluloses
After Alkaline Treatment (pH 10.0)

Sample	CHO		COOH		OH
	mEq/g	DS	mEq/g	DS	DS
From AMC	2.0	0.45	1.7	0.38	0.53
From TAC	2.9	0.77	4.6	1.22	1.01

Abbreviations: AMC: Completely allylated methylcellulose (DS by allyl 1.37, by methyl 1.63). TAC: Tri-O-allylcellulose.

TABLE II
Elementary Compositions of Methyl- and Ethylcelluloses
Before and After Ozone Treatment at -70°C

Sample	Elementary composition			DS ^a
	H (%)	C (%)	O (%)	
Methylcellulose				
Before ozonization	6.04	49.62	44.34	2.0
After ozonization	6.64	50.18	43.18	2.0
Ethylcellulose				
Before ozonization	8.60	56.08	35.33	1.9
After ozonization	8.80	57.52	33.68	1.9

^aCalculated on the basis of elementary compositions.

other hand, alkyl substituents in methyl- and ethylcelluloses were completely stable to ozonization as shown in Table II.

CONCLUSION

1. Water-soluble cellulose derivatives containing both aldehyde and carboxymethyl groups were prepared by the mild alkaline treatment (pH 10.0) of ozonized allylated celluloses. The yields were higher than 95 and 70% for ozonized allylated methylcellulose and ozonized tri-*O*-allylcellulose, respectively.

2. The pH value is very important for the formation of water-soluble products. For example, water-insoluble, bead-like products were produced at higher than pH 12.0.

3. About 35% of allyl ether bonds were found to be cleaved during ozonization at -70°C , whereas alkyl substituents in methyl- and ethylcelluloses were completely stable under the same condition.

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