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Note

Solid-state hydrolysis of cellulose and methyl α- and β-D-glucopyranosides in presence of magnesium chloride

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Abstract—Solid-state hydrolysis proceeded with cellulose and methyl α- and β-D-glucopyranosides in the presence of hydrated magnesium chloride. This reaction was effective even at >100 °C since the hydrated water, which is held by $MgCl_2$ up to >200 °C, is utilized as a nucleophile. Excess water made this reaction ineffective due to the competition between water and sugar oxygen atoms in coordinating with Mg^{2+}, a Lewis acid. Consequently, this hydrolysis reaction is characteristic of solid-state reactions.

Keywords: Cellulose; Magnesium chloride; Hydrolysis; Solid-state hydrolysis; Methyl α- and β-D-Glucopyranosides; Lewis acid

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Interactions between carbohydrates and alkaline earth metal halides are important in their thermochemical reactions[1–4] as well as in their biological roles. Many studies relating to the latter topics deal with these interactions in the solid-state[5–9] and in aqueous solution[10–12] in order to understand the biological processes such as calcium storage,[13] calcification,[14] calcium-dependent cell–cell adhesion[15,16] and DNA stabilization.[17] Alkaline earth metal halides also affect carbohydrate pyrolysis.[1–4] Increased yields of char, carbon monoxide, and water and a decreased yield of levoglucosan (1,6-anhydro-β-D-glucopyranoside) have been reported as the major influences of these salts on cellulose pyrolysis.[1–4] Our previous study[4] has shown that alkaline earth metal chlorides ($MgCl_2$ and $CaCl_2$) substantially reduced the pyrolysis temperature of cellulose. This communication deals with the solid-state reaction of cellulose or methyl glucopyranosides in the presence of $MgCl_2$ to identify the activation mechanism of cellulose pyrolysis.

A cellulose sample containing $MgCl_2$ (0.5 mol/mol of the glucose unit of cellulose) was heated in air (1 atm) at 105 °C for 24 h. The resulting cellulose sample is shown in Figure 1 with its X-ray diffraction (XRD) pattern. Although the light-brown color of the sample indicates some reaction occurring during the heat treatment, the XRD pattern shows the native cellulose I-type of crystal structure remained. From the analysis of the methanol extract of the sample, a small amount of 5-hydroxymethyl furfural (5-HMF) was identified.

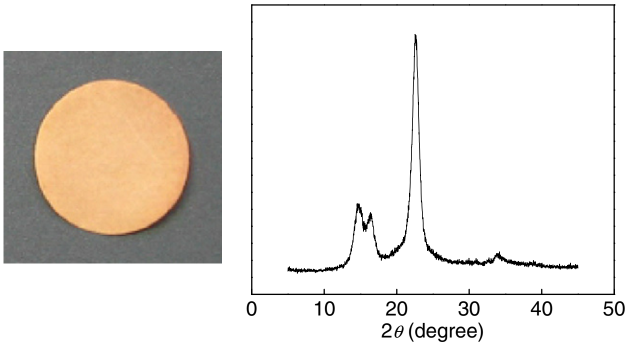

Figure 1. Cellulose sample ($MgCl_2$ content: 0.50 mol/mol of the glucose unit in cellulose) after heat treatment in air (1 atm) at 105 °C for 24 h with the XRD pattern.

Figure 2 summarizes the gel-peameation chromatograms (GPC) obtained for the cellulose samples (in air/105 °C/1–24 h) after conversion into their phenylcarbamate derivatives. The degree of the polymerization (DP) of cellulose decreases from 700 to 400 (polystyrene

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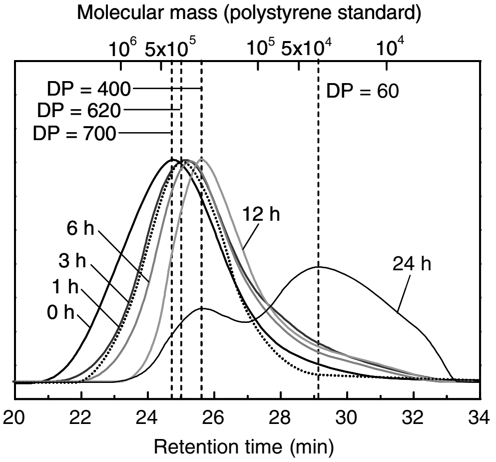


Figure 2. GPC chromatograms of cellulose samples ($MgCl_2$ content: 0.50 mol/mol of the glucose unit in cellulose, phenyl carbamate derivates) after heat treatment in air (1 atm) at 105 °C for 1–24 h: ···: 24 h heating in the presence of water (0.5 mL/30 mg of cellulose) (in a closed ampoule).

standard) up to the 12-h treatment. The peak corresponding to DP 60 is also observed along with the peak (DP 400) for the 24-h treated sample. Thus, the DP of cellulose is reduced stepwise in the presence of $MgCl_2$ from 700 to 400 and then to 60. This DP reduction would relate to the leveling-off of the DP of cellulose. In the heterogeneous (suspension) hydrolysis of native cellulose (cellulose I) with inorganic acids such as sulfuric acid, the DP decreases up to the leveling-off DP of 200–300.[18–21] A similar leveling-off DP has been reported under pyrolysis conditions.[22–24] As for regenerated cellulose (cellulose II) such as viscose rayon, some smaller leveling-off DP values around 30–100 have been reported for acid hydrolysis.[18,19,21] Although the details of the mechanism are not presently known, leveling-off DPs of 400 and 60 are close to those of cellulose I and II, respectively. This reduction in DP was substantially inhibited with an excess of water (Fig. 2).

Reduction of DP and 5-HMF formation indicates that the $MgCl_2$ is acting as a Lewis acid in the transglycosilation and dehydration reactions, respectively. To investigate these reactions further, model experiments with methyl α- and β-D-glucopyranosides were conducted under similar conditions. Figure 3 shows the XRD patterns of the glucoside–$MgCl_2{\cdot}2H_2O$ mixture at various ratios, which were obtained by grinding these two solid substances in a mortar. Relative peak intensities drastically changed with increasing amounts of $MgCl_2{\cdot}2H_2O$. For methyl α-D-glucopyranoside, the intensities of two large peaks at $2\theta = 10^\circ$ and 15° substantially decrease with 0.5 mol equiv of $MgCl_2{\cdot}2H_2O$, and the XRD pattern changes further with increasing the $MgCl_2{\cdot}2H_2O$ levels [main peaks: $2\theta = 27^\circ$ and 41° (1.0 mol equiv), $2\theta = 33^\circ$ (5.0 mol equiv)]. Similarly, a decrease in the small angle ($2\theta = 11^\circ$) peak intensity is

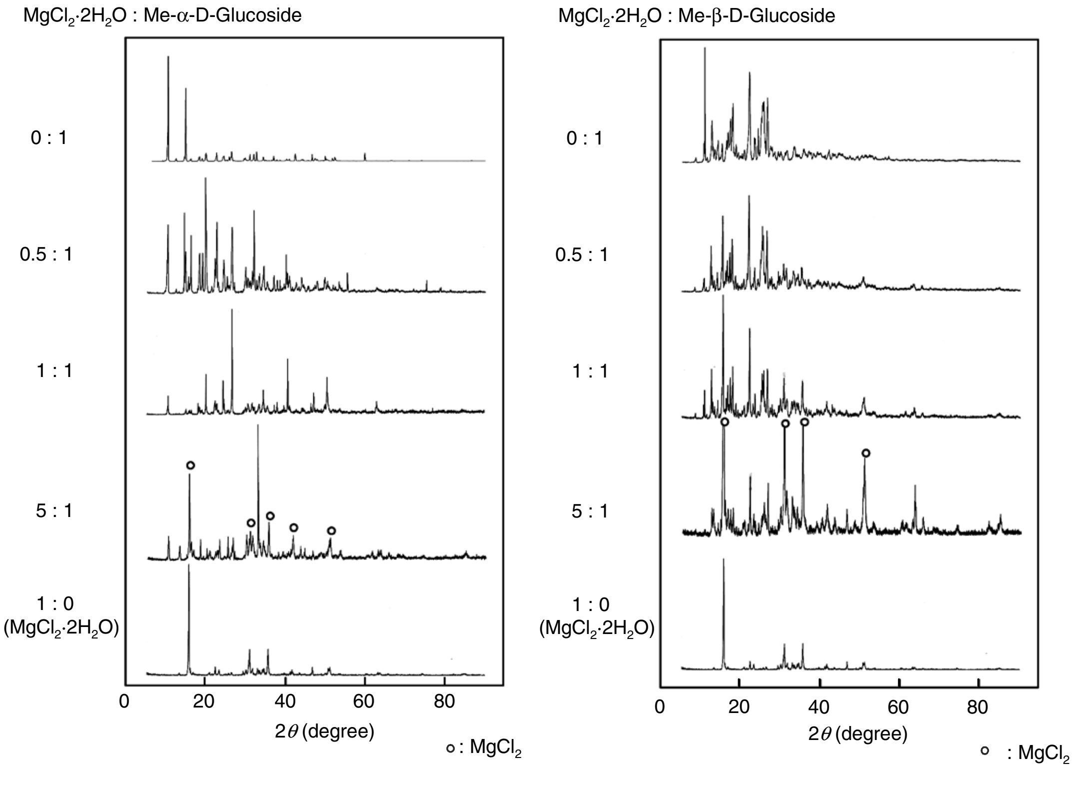


Figure 3. Change in the XRD patterns of methyl α- and β-D-glucopyranosides mixed with increasing amounts of $MgCl_2{\cdot}2H_2O$.

also observed in the methyl β-D-glucopyranoside–$MgCl_2{\cdot}2H_2O$ mixture. Since any transformation of methyl α- and β-D-glucopyranosides was not detected without heat treatment, these changes in the XRD patterns would be derived from glucopyranoside–$MgCl_2$ interactions in the solid state. Changes in the crystal structures of these glucopyranosides were not further studied.

In heating the methyl β-D-glucopyranoside–$MgCl_2{\cdot}2H_2O$ mixture (1:0.5 mol/mol) in air (1 atm) at 105 °C for 4 h, glucose was obtained in a 21.5% yield, which corresponds to about 70% of the reacted glucoside. The influence of water on this solid-state hydrolysis was also studied for both methyl α- and β-D-glucopyranosides. As shown in Figure 4, maximum reactivities were obtained at the water levels (mol/mol of $MgCl_2$) of 6 (β-D-glucopyranoside) and 2 (α-D-glucopyranoside), respectively. Reduced reactivity at higher water levels indicates that this hydrolysis is characteristic of the solid-state and is not effective in water. Competition between water and the glycosidic oxygen in coordinating with Mg^{2+} is considered as a reason for the observed diminished activity in water. Low reactivity at the lower water-level could be explained with the back reaction in transformation into the oxonium ion. Without a nucleophile, the oxonium ion could be converted to the glucoside again by attack of the methoxide anion from the same direction, due to the fact that the other side is blocked in the crystal.

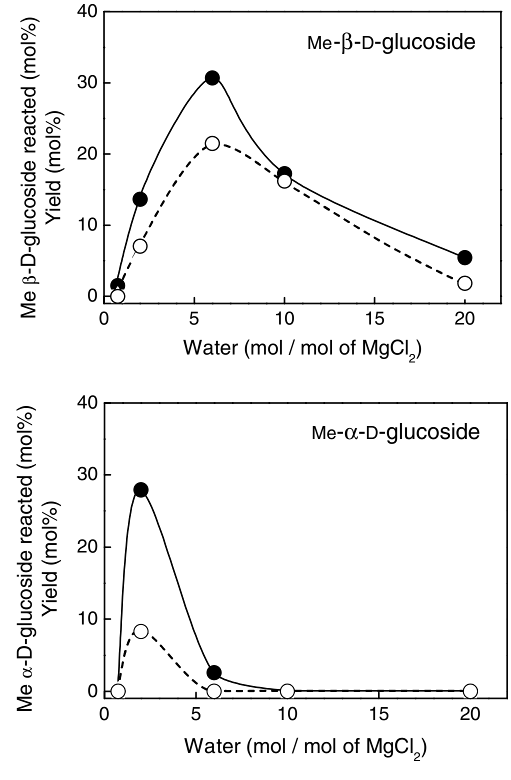
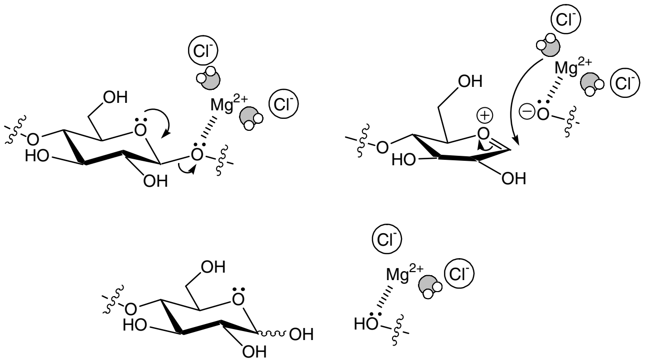


Figure 4. Reactivity and the product yields in heat treatment of methyl α- or β-D-glucopyranoside mixed with $MgCl_2$ (0.50 mol/mol of glucoside) in air (1 atm) at 105 °C for 4 h: (●) glucoside reacted, (○) glucose yield.



Scheme 1. Solid-state hydrolysis mechanism proposed for a mixture of cellulose with hydrated $MgCl_2$.

Based on the present results, a unique solid-state hydrolysis mechanism is proposed by utilizing the hydrated water as a nucleophile (Scheme 1). It is well known that hydrated $MgCl_2$ ($MgCl_2{\cdot}xH_2O$) has the structure of hydrated Mg^{2+} surrounded by the Cl anions.[25,26] The water is also reported to be exchangeable with some electron donors (Lewis bases) such as methanol[27] and ethanol.[28,29] These lines of information indicate that the Mg^{2+} in $MgCl_2{\cdot}xH_2O$ would be able to coordinate with the oxygen atoms, including the glycosidic oxygen, as a Lewis acid, and the latter coordination catalyzes the glycosidic bond cleavage. This is also supported with the strong solid–solid interactions indicated by the change in the XRD patterns (Fig. 3). Coordination of the Mg^{2+} to the oxygen atoms in sucrose in concentrated aqueous solution has also been indicated from both IR and ^{13}C NMR spectra.[12] Although the addition of NaCl or KCl weakened the H-bond network between sucrose and water, the possible interaction between Mg^{2+} and the oxygen atoms of sucrose has been indicated by the addition of $MgCl_2$. With calcium chloride, a similar hydrolysis reaction was also observed. Thus, such reaction should be effective with various alkaline earth metal halides.

A hydrolysis reaction that proceeds in an open reactor even at higher temperatures than the boiling point of water is a characteristic feature of this solid-state hydrolysis. The hydrated water is not easily removed even at such high temperatures as shown in the dehydration properties (Fig. 5) of the hydrated $MgCl_2$ and $CaCl_2$ samples, which were prepared by drying their aqueous solutions (105 °C for 24 h) after evaporation in vacuo.

During the pyrolysis of cellulose impregnated with alkaline earth metal chlorides, such solid-state hydrolysis would proceed to form smaller fragments with reducing end groups, and this would relate to the activation mechanism of cellulose pyrolysis. The present findings also would give useful information for the production

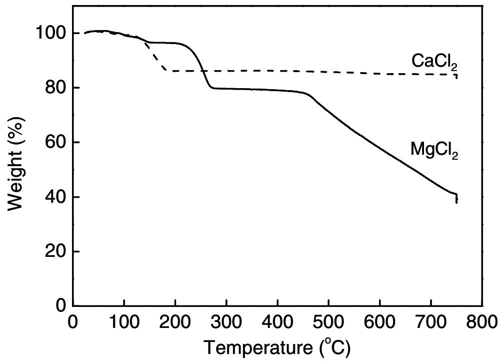


Figure 5. TG curves of the $MgCl_2$ and $CaCl_2$ samples (without any sugar components) obtained by drying their aqueous solutions at 105 °C for 24 h after evaporation in vacuo. TG conditions: room temperature to 750 °C (10 °C min^{-1}) under N_2 flow (50 mL min^{-1}).

of oligosaccharides, the saccharification of cellulose, and polysaccharide stability, among other phenomena.

1. Experimental

1.1. Materials

Filter paper (Kiriyama No. 704, oven dried at 105 °C for 24 h) was used as the cellulose samples. Aqueous solution (125 μL) of $MgCl_2$ (0.76 mol L^{-1}) was added dropwise to the filter paper (30 mg). This amount of solution was completely absorbed in the filter paper. The resulting paper was dried in an oven (105 °C) for 24 h. The amount of $MgCl_2$ corresponds to 0.5 mol/mol of the glucose unit of cellulose.

Methyl α- and β-D-glucopyranosides (Nacalai Tesque Co.) were used after drying in an oven (105 °C) for 24 h. Hydrated water in methyl β-D-glucopyranoside was completely removed under these conditions. $MgCl_2 \cdot 6H_2O$ was purchased from Sigma–Aldrich Japan K.K. $MgCl_2 \cdot 0.75H_2O$ was obtained from Nacalai Tesque Co. as dehydrated magnesium chloride. Other hydrated magnesium chloride samples ($MgCl_2 \cdot xH_2O$) ($x = 2$, 10, and 20) were prepared from $MgCl_2 \cdot 6H_2O$ as follows. $MgCl_2 \cdot 2H_2O$ was prepared by drying $MgCl_2 \cdot 6H_2O$ in an oven (105 °C) for 24 h. $MgCl_2 \cdot 10H_2O$ and $MgCl_2 \cdot 20H_2O$ were prepared by adding proper amount of water to $MgCl_2 \cdot 6H_2O$. The hydrated water content of these samples was measured by thermogravimetry with a Shimadzu TGA-50 [temperature program: room temperature to 750 °C (10 °C min^{-1}) under N_2-flow (50 mL min^{-1})]. Methyl α- or β-D-glucopyranoside–$MgCl_2 \cdot xH_2O$ mixtures were prepared by grinding the components in a mortar for 20 s under dry nitrogen flow with storage in a sealed vial.

1.2. Reaction and product analysis

A cellulose sample impregnated with $MgCl_2$ or methyl α- or β-D-glucopyranoside (30 mg)–$MgCl_2 \cdot xH_2O$ ($x =$ 0.75, 2 or 6) mixture (1:0.5 mol/mol) was taken in an open vial and heated in an oven (105 °C) for an adequate reaction time. Reaction of the mixture with $MgCl_2 \cdot xH_2O$ ($x = 10$ or 20) was conducted in a closed ampoule to prevent the evaporation of water.

Glucose and unreacted glucoside were quantified via the ^1H NMR spectrum of the reaction mixture extracted with D_2O (1 mL) containing 2-furoic acid as an internal standard. The ^1H NMR spectra were measured with a Bruker AC-400 (400 MHz) spectrometer. XRD patterns of the samples were recorded with a Rigaku RINT 2000V (Cu Kα, $\lambda = 1.542$ Å, 40 kV, 30 mA). The DPs of cellulose samples were evaluated with GPC (polystyrene standard) after conversion into the phenylcarbamate derivative according to the literature procedure.[30] Phenyl isocyanate (0.33 mL) and pyridine (1.0 mL) were added to the cellulose sample, and the mixture was vigorously stirred at 80 °C for 48 h. After the reaction was complete, MeOH (2.0 mL) was added to the mixture to quench the reaction, and then the resulting solution was evaporated in vacuo and dried over P_2O_5 in a vacuum desiccator for 24 h. The mixture thus obtained was redissolved in THF and analyzed by GPC [Shimadzu LC-10A, column: Shodex KF803L + KF806, eluent: THF, flow rate: 0.6 mL min^{-1}, detector: UV 254 nm, column temperature: 40 °C].

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