

## Regular Paper

# Kinetic Analysis for the Conversion of Fructose to 5-Hydroxymethylfurfural in 1-Butyl-3-methylimidazolium Chloride with Lower Water Contents

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**Abstract:** Conversion of fructose to 5-hydroxymethylfurfural (HMF) was conducted in an ionic liquid (IL), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), with low-to-middle ( $\leq 0.03$ –10%) water contents at 100°C with *p*-toluenesulfonic acid as a catalyst. When fructose was mixed with [BMIM]Cl to start the reaction, fructose dissolved much faster and more rapidly converted to HMF in [BMIM]Cl with a low water content than it did in that with a middle one, suggesting that the conversion rate greatly depended on the said water content. HMF was stable in pure [BMIM]Cl at 100°C, and there were few possibilities for its rehydration and decomposition to byproducts. Based on these results, we proposed an autocatalytic model of the reaction that considers the effects of water; the formation of HMF was certainly affected by the water produced during the conversion. The kinetic analysis based on this model well expressed the formation of HMF in the IL with a low water content.

**Key words:** fructose, 5-hydroxymethylfurfural, ionic liquid, kinetic analysis, water content

## INTRODUCTION

Given the increasing concern for environmental problems, 5-hydroxymethylfurfural (HMF) has recently garnered attention as a potential substitute for the raw materials of petroleum products. HMF is a decomposition product of saccharides and is a precursor of 2,5-dimethylfuran, 2,5-furandicarboxylic acid, and other platform chemicals,<sup>1</sup> which have been used as new biofuels and raw materials for plastics. Therefore, the production of HMF has been widely investigated for industrial applications.

HMF has been conventionally synthesized in water;<sup>2</sup> mixtures of water and organic solvents;<sup>3–5</sup> and subcritical fluids<sup>6–8</sup> using a catalyst, including inorganic acids,<sup>2,9</sup> organic acids,<sup>9</sup> zeolites,<sup>3</sup> and ion-exchange resins.<sup>4</sup> However, these methods have the disadvantage of a low conversion yield of HMF. Thus, researchers have postulated that HMF could be obtained in higher yields using new reaction media such as ionic liquids (ILs).

ILs are liquid salts at room temperature and primarily consist of anions and organic cations.<sup>10,11</sup> One of the characteristics of ILs is their nonvolatility.<sup>11</sup> Because of this property, ILs can be used repeatedly by extracting products without their release to the environment, and hence, could contribute to a reduction in the use of expensive organic

solvents.<sup>11,12</sup> In addition, ILs are used in many fields of organic synthesis as fine reaction media because many ILs are amphiphilic.<sup>11,13</sup> Given these advantages, the synthesis of HMF in ILs has attracted significant attention. Moreau *et al.* reported that 92% of fructose was converted to HMF at 90°C without any catalyst in 45 min,<sup>14</sup> and Li *et al.* succeeded in achieving a 91% yield of HMF from glucose in 1 min at 100°C with a catalyst.<sup>15</sup> Although many studies have been performed to efficiently synthesize HMF using many kinds of ILs,<sup>15–19</sup> it is insufficient to understand the reaction kinetics of fructose conversion to HMF in ILs. Mechanisms of the HMF formation have not been sufficiently understood and have usually been regarded as a parallel or first-order reaction.<sup>5,19,20</sup> Although a saccharide is initially solvated only with ions, water would eventually affect the reaction behavior, because three water molecules are generated during the conversion of one fructose molecule. However, the effects of these water molecules on the reaction mechanism have not been sufficiently investigated, and there have been some inconsistent results. Li *et al.* reported that water decreased the conversion rate but barely affected the final yield of HMF.<sup>18</sup> On the other hand, Qi *et al.* showed that the water content (below 5%) scarcely affected either the fructose conversion or the HMF yield.<sup>21</sup>

In this study, the conversion of fructose to HMF was conducted in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) with various water contents in order to understand the kinetic effects of water on the reaction behavior.

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Abbreviations: [BMIM]Cl, 1-butyl-3-methylimidazolium chloride; HMF, 5-hydroxymethylfurfural; IL, ionic liquid; TsOH, *p*-toluenesulfonic acid monohydrate; HPLC, high-performance liquid chromatography.

## MATERIALS AND METHODS

**Materials.** Fructose, HMF, *p*-toluenesulfonic acid monohydrate (TsOH), 1-chlorobutane, sodium bicarbonate, formic acid, and levulinic acid (4-oxopentanoic acid) were purchased from Wako Pure Chemical Industries (Osaka, Japan). 1-Methylimidazole was purchased from Sigma-Aldrich Japan K.K. (Tokyo, Japan).

**Preparation of [BMIM]Cl.** [BMIM]Cl was synthesized by refluxing a mixture of 1-methylimidazole (50 g) and 1-chlorobutane (67 g) for 24 h.<sup>22</sup> The reaction mixture was diluted in acetone, and the diluted solution was then transferred to a round-bottom flask. Crude [BMIM]Cl was obtained by removing acetone and unreacted 1-chlorobutane via evaporation. The crude [BMIM]Cl was again dissolved in 80 mL of acetonitrile and kept at room temperature overnight with stirring after gradually adding 50 mL of ethyl acetate. The solution was then settled at 4°C overnight for recrystallization. After removing the solvents via filtration and washing the [BMIM]Cl crystal with cold ethyl acetate, the residual solvent was eliminated under reduced pressure. Recrystallization was repeated at least twice at -10°C, until the supernatant became colorless and transparent to obtain purified [BMIM]Cl. The purified [BMIM]Cl was placed in a round-bottom flask and dried under reduced pressure at 150°C for 2 h.

**Effects of the purification of [BMIM]Cl on the conversion of fructose.** The conversion of fructose to HMF was conducted in both crude and purified [BMIM]Cl without any catalyst. In order to prepare the fructose solution in [BMIM]Cl at a final concentration of 5% (kg/kg [BMIM]Cl), an exactly weighed portion of 60% (kg/kg) fructose aqueous solution (ca. 0.4 g) was added to approximately 5 g of [BMIM]Cl. The mixture was maintained at 50°C with stirring. An aliquot of the reaction mixture was taken at intervals, and concentrations of the remaining fructose and formed HMF were determined via high-performance liquid chromatography (HPLC) after the appropriate dilution of the samples with a saturated aqueous solution of sodium bicarbonate.

Fructose was determined via HPLC with an equipped RID-10A RI detector (Shimadzu Corporation, Kyoto, Japan) and an LC-10AD pump (Shimadzu Corporation) connected to a COSMOSIL Sugar-D packed column (3.0 mm I.D. × 150 mm, Nacal Tesque, Inc., Kyoto, Japan). The eluent was 80% acetonitrile with a flow rate of 0.4 mL/min. HMF was detected by using an SPD-10A UV-Vis detector (Shimadzu Corporation) at 280 nm with the HPLC system, connected to a hydrosphere C18 column (3.0 mm I.D. × 150 mm, YMC Co., Ltd., Kyoto, Japan). The eluent was 5% methanol with a flow rate of 0.4 mL/min.

**Stability of HMF.** The stability of HMF and its potential for rehydration were evaluated in dry [BMIM]Cl and in [BMIM]Cl containing 2% (kg/kg [BMIM]Cl) water for which only purified [BMIM]Cl was used. TsOH (26 mg) was added to 7 g of dry [BMIM]Cl, and the solution was heated to 100°C with stirring. HMF (250 mg), whose amount was equal to 5% (kg/kg [BMIM]Cl) of fructose, was then added to the solution. An aliquot of the reaction mixture was taken at intervals for analysis via HPLC after appropriate dilution. The conditions for the HPLC analysis were the

same as those mentioned above.

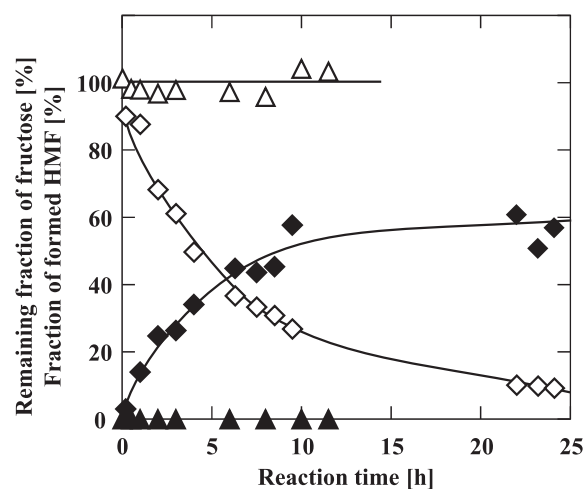
**Measurement of the water content of [BMIM]Cl.** The water content of dry [BMIM]Cl was measured with a Karl Fischer moisture titrator (MKS-510, Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan). The water content of dry [BMIM]Cl was ≤ 0.03%. In order to prepare [BMIM]Cl with water contents of 1, 3, 5, and 10% (kg/kg [BMIM]Cl, d.m.), an appropriate amount of water was added to dry [BMIM]Cl.

**Effects of water on the conversion of fructose.** The conversion of fructose to HMF was conducted in [BMIM]Cl with various water contents [≤ 0.03, 1, 3, 5, and 10% (kg/kg [BMIM]Cl)] and in the presence of 0.35% (kg/kg [BMIM]Cl) TsOH at 100°C. Powdery fructose was directly added to the mixture of [BMIM]Cl and TsOH at a final fructose concentration of 5% (kg/kg [BMIM]Cl) at 100°C with stirring. An aliquot of the reaction mixture was then sampled with time and analyzed via HPLC. Conditions for the HMF analysis were almost the same as those mentioned above, except for the use of a COSMOSIL packed column, HILIC (3.0 mm I.D. × 150 mm, Nacal Tesque). The HPLC analyses of formic acid and levulinic acid were conducted using a UV-Vis detector, SPD-10A (210 nm), connected to a LaChrom C-18-AQ column (4.6 mm I.D. × 250 mm, Hitachi High-Technologies Corporation, Tokyo, Japan). The eluent was 1 mmol/L H<sub>2</sub>SO<sub>4</sub> + 8 mmol/L Na<sub>2</sub>SO<sub>4</sub> (pH 2.8) with a flow rate of 1.0 mL/min.

## RESULTS AND DISCUSSION

### Effects of the purification of [BMIM]Cl on the reaction.

The conversion of fructose was initially conducted in both crude and purified [BMIM]Cl without any catalyst. In crude [BMIM]Cl, fructose decomposed slowly as it was converted to HMF, and only 9% of the fructose remained after 24 h (Fig. 1). On the other hand, neither the decomposition of fructose nor the formation of HMF was observed in purified [BMIM]Cl even after 12 h. Because the crude [BMIM]Cl was dark brown and the purified compound was colorless, the crude compound likely contained many impurities. Some acidic impurities could have played roles as catalysts,



**Fig. 1.** Conversion of fructose (open symbol) to HMF (closed symbol) in crude (diamonds) or purified (triangles) [BMIM]Cl without any catalyst at 50°C.

The solid curves were empirically determined.

although these impurities were not identified. Therefore, [BMIM]Cl itself did not have any catalytic activity for the conversion of fructose. There have been some contradictory reports on the catalytic activity of [BMIM]Cl.<sup>14,16,19</sup> A possible reason for the discrepancy may be the presence of the aforementioned impurities. In order to avoid an inadequate and incomplete kinetic analysis of the conversion of fructose and in order to facilitate reproducibility, only the purified [BMIM]Cl was used in this study.

### Stability of HMF

Researchers have reported that HMF can be rehydrated and decomposed into formic and levulinic acids<sup>19,21,23</sup> during the reaction in other reaction media. In this study, the HMF

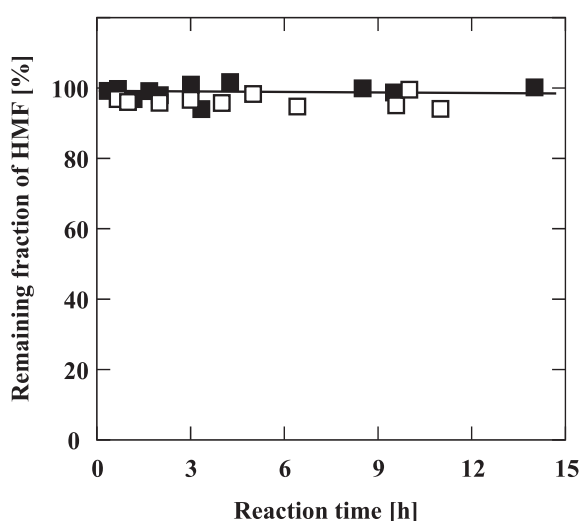


Fig. 2. Stability of HMF in [BMIM]Cl containing 2% (kg/kg [BMIM]Cl) water (□) and dry [BMIM]Cl (■) in the presence of *p*-toluensulfonic acid as a catalyst at 100°C.

stability was evaluated at 100°C in dry [BMIM]Cl and water-containing [BMIM]Cl, and the rehydration behavior of HMF was also investigated. According to the HPLC analysis, no obvious change with time in the HMF concentration occurred during the 14-h storage in either dry [BMIM]Cl or water-containing [BMIM]Cl (Fig. 2), and neither formic nor levulinic acid was detected under these conditions. In addition, Sievers *et al.* reported that HMF itself was stable in [BMIM]Cl with water at 120°C in the presence of sulfuric acid.<sup>24</sup> From these results, HMF is potentially stable, and rehydration did not occur at least in [BMIM]Cl alone at 100°C.

### Effects of the water content on the conversion.

To elucidate the effects of water content on the fructose conversion, we conducted the reaction in [BMIM]Cl with various water contents. As shown in Fig. 3, the reaction behavior obviously depended on the water content. When the water content was low ( $\leq 0.03$  or 1%), fructose rapidly decreased, and the formation of HMF rapidly proceeded. With higher water contents (3–10%), the reaction slowly proceeded, and the HMF yield was low at 75 min. However, no obvious decomposition of HMF and formation of either formic or levulinic acid were observed even at higher water contents.

Moreover, a unique reaction behavior was observed, *i.e.*, fructose rapidly disappeared with the simultaneous formation of HMF in the initial stage. However, the HMF formation slowly continued after the complete disappearance of fructose even though the water content was higher (3–10%). These unique behaviors are discussed below. It was also notable that fructose demonstrated different dissolution behaviors in [BMIM]Cl with various water contents. Fructose instantly dissolved in [BMIM]Cl with  $\leq 0.03\%$  or

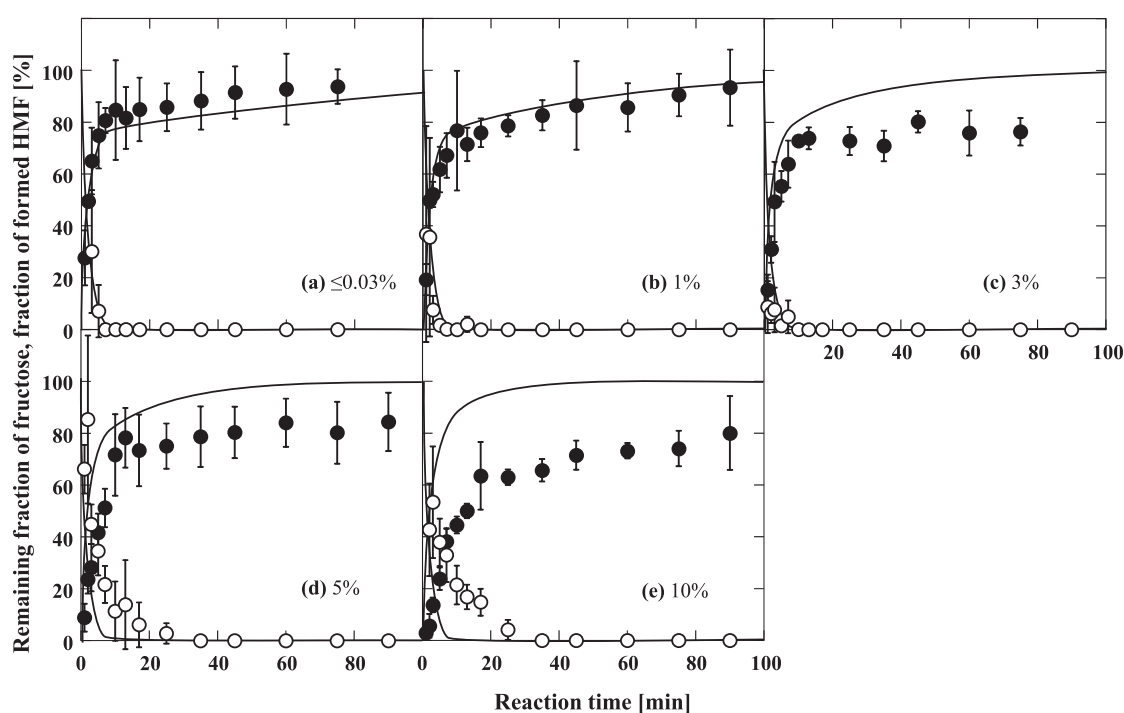


Fig. 3. Conversion of fructose (○) to HMF (●) in [BMIM]Cl with water contents of (a)  $\leq 0.03\%$  (kg/kg [BMIM]Cl), (b) 1%, (c) 3%, (d) 5%, and (e) 10% at 100°C.

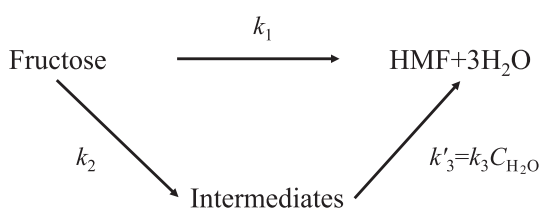
The solid curves are the calculated ones. The symbols represent the (mean  $\pm$  SD) for  $n = 3$ .

1% water; on the other hand, it took approximately 1 min to dissolve fructose in [BMIM]Cl with  $\geq 3\%$  water. These results suggested that the properties of [BMIM]Cl were largely changed by the addition of water.

**Kinetic analysis.** Researchers have suggested that the conversion of fructose to HMF is a consecutive reaction in both super- and subcritical fluids and sometimes in ionic liquids as well. Fructose converts to HMF and other substances, and HMF itself is polymerized or is further rehydrated and decomposed to formic and levulinic acids.<sup>19,21,23</sup> As described above, HMF rapidly formed in the initial stage and continued to form slowly in the latter stage in this study (Fig. 3). These results suggested that there were two pathways to the formation of HMF: a fast one and a slow one. Mechanistically, it has also been reported that there are two major pathways to this formation, a cyclic one and an acyclic one, in which the formation of HMF occurs with and without maintaining the furanose structure of the fructose molecule, respectively.<sup>1,9</sup> The formation through both cyclic and acyclic pathways has also been suggested in the presence of metal catalysts.<sup>15-17</sup> It was proposed that the formation of pyranose-type fructose was involved in the acyclic pathway.<sup>1</sup> Generally, a furanose-pyranose tautomerism occurs when the kind<sup>24</sup> and/or temperature<sup>25</sup> of the solvent change. For the IL, its properties change by the addition of water, which would also change the tautomeric composition. Change in the composition would lead to a change in the reaction pathways, resulting in the decrease of the reaction rate. Therefore, the change of the reaction rate could reflect the tautomeric distribution of fructose.

In addition, neither formic nor levulinic acid was detected in this study. Based on this knowledge, we proposed a simple reaction scheme (Fig. 4) and kinetically analyzed the reaction behavior to evaluate the effects of the water contents on the conversion of fructose to HMF. In our reaction scheme, we made four assumptions: that the conversion was irreversible because the reverse reaction was not generally considered;<sup>1,9,26</sup> that the conversion was an autocatalytic reaction by water formed from fructose; that there were two pathways in the HMF formation; and that the concentration of "reactive fructose," which is one of the structural isomers based on the tautomeric composition and easily converted into HMF, would be changed with increasing water contents as above mentioned, which would affect the kinetics. But the tautomeric composition is presently not known, and its contribution on the kinetic study is not also considered. Based on these assumptions, the reaction rate of each component could be expressed by Eqs. (1)–(4):

$$d(C_F/C_{F0})/dt = -(k_1+k_2)C_F/C_{F0}, \quad (1)$$



**Fig. 4.** Proposed reaction scheme for the conversion of fructose to HMF;  $k_1$ ,  $k_2$ , and  $k_3$  are the rate constants, and  $k'_3$  is the apparent rate constant defined by  $k_3C_{H_2O}$ , where  $C_{H_2O}$  is the molar concentration of water in [BMIM]Cl.

$$\begin{aligned} d(C_{Int}/C_{F0})/dt &= k_2C_F/C_{F0} - k'_3C_{Int}/C_{F0} \\ &= k_2C_F/C_{F0} - k_3C_{Int}C_{H_2O}/C_{F0}, \end{aligned} \quad (2)$$

$$\begin{aligned} d(C_{HMF}/C_{F0})/dt &= k_1C_F/C_{F0} + k'_3C_{Int}/C_{F0} \\ &= k_1C_F/C_{F0} + k_3C_{Int}C_{H_2O}/C_{F0}, \end{aligned} \quad (3)$$

$$\begin{aligned} d(C_{H_2O}/C_{F0})/dt &= 3(k_1C_F/C_{F0} + k'_3C_{Int}/C_{F0}) \\ &= 3(k_1C_F/C_{F0} + k_3C_{Int}C_{H_2O}/C_{F0}), \end{aligned} \quad (4)$$

where  $C_F$ ,  $C_{HMF}$ ,  $C_{Int}$ , and  $C_{H_2O}$  are the molar concentrations of fructose, HMF, the intermediates, and water;  $C_{F0}$  is the initial fructose concentration;  $k_1$ ,  $k_2$ , and  $k_3$  are the rate constants; and  $k'_3$  is the apparent rate constant defined by  $k_3C_{H_2O}$ , respectively.

The kinetic constants were evaluated as follows. The value of  $(k_1 + k_2)$  was tentatively determined from the slope of the semilogarithmic plot of the remaining fructose *versus* time. The tentative value of  $k_1$  was then determined from the slope of the semilogarithmic plot of  $(1 - C_{HMF}/C_{F0})$  *versus* time under the assumption that HMF formed at the initial stage mainly through the fast pathway. From these results, the tentative values of  $k_1$  and  $k_2$  were obtained. The analysis was conducted using the results obtained in [BMIM]Cl with a water content of  $\leq 0.03\%$  and 1% (kg/kg [BMIM]Cl), because fructose dissolved quite rapidly in [BMIM]Cl and the reaction system could be considered to be homogeneous. The kinetic constants were determined using the Solver function in Microsoft Office Excel 2010 (Microsoft Corporation, Redmond, USA) using the above tentatively determined constants as the initial values under the condition  $k_2 < k_1$ . The rate constants  $k_1 = 3.69 \times 10^{-1} \text{ min}^{-1}$ ,  $k_2 = 1.22 \times 10^{-1} \text{ min}^{-1}$ , and  $k_3 = 1.50 \times 10^{-2} \text{ min}^{-1}$  were obtained. The changes in the fructose and HMF concentrations over time, which were calculated using the estimated rate constants, in [BMIM]Cl with water contents of  $\leq 1\%$  fitted the experimental values well (Fig. 3).

On the other hand, when the water content was over 3%, the difference between the calculated and experimental curves became more significant with increasing water content. This result was due to the fact that fructose took much more time to dissolve in [BMIM]Cl with a higher water content, and the properties of [BMIM]Cl as a reaction medium greatly changed with the addition of water. Besides, the reaction mechanism may possibly change, and some other side reactions, such as the conversion of fructose to soluble products,<sup>26</sup> could occur. These results suggested that adding a small amount of water to [BMIM]Cl negatively impacted the production of HMF. Moreover, although Qi et al. reported that much larger water content ( $> 5\%$ ) decreased the reaction rate,<sup>21</sup> this study showed that the addition of water even at 3% greatly and adversely affected the reaction efficiency.

In conclusion, the conversion of fructose to HMF was affected by the water content in [BMIM]Cl. The proposed reaction scheme well expressed the disappearance of fructose and the formation of HMF in [BMIM]Cl with low water content, and the rate constants were evaluated. While the changes in the fructose and HMF concentrations in [BMIM]Cl with high water content were calculated using the rate constants estimated in [BMIM]Cl with low water content, the calculated values did not agree with the experimental ones. The discrepancy between the calculated and experimental values became larger for [BMIM]Cl with higher water content. Therefore, further investigation is

required to fully understand the effects of water on the conversion of fructose to HMF in [BMIM]Cl.

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