Very Important Paper

Direct Transformation of HMF into 2,5-Diformylfuran and 2,5-Dihydroxymethylfuran without an External Oxidant or Reductant

Gang Li, Zhen Sun, Yueer Yan, Yahong Zhang,* and Yi Tang^[a]

The selective transformation of 5-hydroxymethylfurfural (HMF) to valuable 2,5-diformylfuran (DFF) and 2,5-dihydroxymethylfuran (DHMF) is highly desirable but remains a great challenge owing to its tendency to over-oxidation and over-reduction. In this work, HMF is directly converted into DFF and DHMF without external oxidant or reductant through a Meerwein-Ponndorf-Verley-Oppenauer (MPVO) reaction. In such a MPVO process, HMF is used as both oxidant and reductant and DFF and DHMF are simultaneously produced with a 1:1 molar ratio in the presence of a Lewis acid catalyst. Under high initial HMF concentration, a HMF conversion of up to 44.7% can be reached within 1 h. Moreover, this atom-efficient transformation route for HMF also provides a promising protocol for the crude separation of DHMF products from DFF products, owing to the lower solubility of DHMF compared to DFF in acetonitrile.

5-hydroxymethylfurfural (HMF), the most promising platform molecule linking biomass to chemicals, is readily accessible from biomass-based carbohydrates.^[1] Interestingly, HMF has both hydroxyl and aldehyde groups, which allows it to be converted into various value-added compounds through feasible transformations such as oxidation and reduction (Scheme 1).^[1c] For example, HMF can be gradually oxidized into 2,5-diformylfuran (DFF), 5-fromyl-2-furancarboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA),^[2] but can also be reduced to 2,5-dihydroxymethylfuran (DHMF), 2,5-dihydroxymethyltetrahydrofuran (DHMTHF), and 2,5-dimethyltetrahydrofuran (DMTHF).^[3] Among these compounds, DFF and DHMF are the two vital intermediates and regarded as versatile precursors for the synthesis of functional polymers^[4] and other chemicals/pharmaceuticals.^[5] However, as a result of easy over-oxidation/over-reduction of HMF, the selective conversion of HMF to DFF and DHMF remains a challenging reaction that usually involves many byproducts (Scheme 1 a, b).^[2c,6] Until now, only a few studies concentrated on the selective transformation of HMF

author(s) of this article can be found under http://dx.doi.org/10.1002/ cssc.201601322. to DFF or DHMF with external oxidants (NaOCI and $O_2)$ or reductants (H $_2$ and ethanol), respectively. $^{\rm [2d,7]}$

The Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction offers an effective route for the highly selective reduction of aldehyde groups or the oxidation of hydroxyl groups, which is typically catalyzed by Lewis acid catalysts via a cyclic six-membered transition state.^[8] Coincidently, both hydroxyl and aldehyde groups exist in HMF. Therefore, the intermolecular hydrogen transfer between two HMF molecules may occur through a MPVO reaction (Scheme 2a).^[9] In this case, the transformation of HMF to DFF and DHMF in a single reaction without an external redox reagent can be achieved. However, DFF and DHMF can also convert to HMF through the reverse MPVO reaction (Scheme 2b), indicating that a MPVO redox equilibrium exists between HMF and DFF/DHMF.^[8d, 10]

Inspired by this, we here report the simultaneous synthesis of DFF and DHMF from HMF through a MPVO reaction by using HMF itself as both oxidant and reductant. HMF is very selectively converted into DFF and DHMF with a 1:1 molar ratio by this special form of the MPVO reaction, and a HMF conversion of 44.7% can be achieved under high initial HMF concentration. Moreover, this route also offers a promising protocol for the crude separation of DHMF from DFF as a result of the poor solubility of DHMF in acetonitrile. These results not only demonstrate the feasibility of the MPVO reaction occurring between two HMF molecules, but also provide a promising, highly selective, and atom-efficient route to valuable intermediates from biomass-derived platform chemicals.

The conversion of HMF was performed in a glass reactor under microwave irradiation. AlMe₃, a typical Lewis-acid catalyst, was chosen as catalyst to demonstrate the feasibility of this reaction.^[11] The products obtained under different conditions were analyzed using gas chromatography [GC, Shimadzu GC-2010 plus, equipped with a DM-FFAP capillary column and a flame ionization detector (FID)]. Quantifications of HMF, DFF, and DHMF were obtained from the corresponding response factors and peak areas.^[7c] Initially, different solvents were screened to ascertain the conversion of HMF and the molar ratio of DFF/DHMF because different solvents exhibit different properties (e.g., dielectric constant, acid–base property, and polarity) that could greatly affect the performance of catalysts.^[2a, 12]

As shown in Table 1, the use of dimethyl sulfoxide (DMSO) or *N*,*N*-dimethylformamide (DMF), two common solvents for the dehydration of carbohydrates and HMF oxidation,^[2d,7b] resulted only in low HMF conversion (< 10.0%, Table 1, entries 1 and 2). Moreover, only DFF was detected as a product in the

 [[]a] G. Li, Z. Sun, Y. Yan, Prof. Y. Zhang, Prof. Y. Tang Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, Collaborative Innovation Centre of Chemistry for Energy Materials Fudan University Shanghai 200433 (P.R. China) E-mail: zhangyh@fudan.edu.cn
 Supporting Information and the ORCID identification number(s) for the





Scheme 1. Valuable oxidation and reduction products from HMF: a) over-oxidation, b) over-reduction.



Scheme 2. MPVO reaction of HMF to DFF and DHMF catalyzed by a Lewis acid catalyst: a) disproportionation of HMF, b) reverse MPVO reaction.

Table 1. Results of the MPVO reaction of HMF to DFF and DHMF in various solvents. $^{\rm [a]}$					
Entry	Solvent ^[b]	HMF conversion [%]	DFF/DHMF molar ratio		
1	DMSO	8.3	-		
2	DMF	5.7	-		
3	MIBK	13.4	1.63		
4	dioxane (2.2)	3.9	-		
5	THF (7.4)	9.4	0.71		
6	acetonitrile (37.5)	21.2	1.18		
[a] Reaction conditions: HMF solution of various solvents (0.1 mol L ⁻¹) and AlMe ₃ (AlMe ₃ /HMF molar ratio = 0.10), N ₂ , 80 °C, 10 min, microwave irradiation. [b] The values in parentheses represent the dielectric constants of the solvents.					

two systems (Figure S1 A and B in the Supporting Information), which can be attributed to the presence of an acyl group in both DMSO (S=O) and DMF (CH=O). This acyl group could replace a Lewis-acid site coordinating to one of the HMF molecules necessary to accomplish the MPVO reaction.^[13] Although the HMF conversion was slightly improved to 13.4% in methyl isobutyl ketone (MIBK), the DFF/DHMF molar ratio (1.63) was still much higher than 1.0 (Table 1, entry 3). This high DFF/ DHMF molar ratio indicates that intermolecular hydrogen transfer between the keto group of MIBK and the hydroxyl group of HMF simultaneously occurs in the MIBK system, similar to the case of DMSO and DMF, except for the disproportionation of HMF (Scheme S1).^[14] This intermolecular hydrogen transfer between HMF and MIBK leads to the formation of more DFF than DHMF, which could also be verified by the presence of methyl isobutyl carbinol (MIBC) among the products (Figure S1C). The presence of acyl (DMSO and DMF) and keto groups (MIBK) in the three solvents mentioned above can interfere with the MPVO reaction between HMF molecules and thereby influence the HMF conversion and DFF/DHMF molar ratio.

Further experiments showed that the use of tetrahydrofuran (THF) and dioxane as solvents resulted in low HMF conversion (Table 1, entries 4 and 5). However, a relatively high HMF conversion of 21.2% was observed in acetonitrile, which could be caused by its high dielectric constant compared to THF and dioxane (Table 1, entries 4-6).^[15] Moreover, the DFF/DHMF molar ratio in the acetonitrile system was close to 1.0 (Table 1, entry 6), which implies that DFF and DHMF were formed from HMF in almost equal amounts by using acetonitrile as solvent and a Lewis-acid catalyst without external oxidant and reductant (Scheme 2 a).^[9, 16] This could be confirmed further by the GC and GC-MS analysis results of the reaction solution (Figures S2 and S3). Furthermore, no other byproducts could be observed in the acetonitrile system according to the GC analysis results (Figure S3C), indicating its high selectivity. The over-oxidation/reduction of HMF was completely avoided, which can be attributed to the MPVO reaction mechanism.^[8c,d]

Next, the reaction conditions in the acetonitrile system were further optimized in terms of reaction temperature and time. As shown in Figure 1A, the MPVO reaction of HMF to DFF and DHMF is not sensitive to reaction temperature. The HMF conversion slightly increased from 15.9 to 19.1% with the increase of reaction temperature from 60 to 80 °C. Further increase of the reaction temperature caused no further improvement of the HMF conversion at identical reaction times (Figure 1A). This relative independence of temperature for the MPVO reaction of HMF to DFF and DHMF is in accordance with the fact that its enthalpy change (ΔH) is approximately zero ($\Delta H \approx 0$, see the Supporting Information). Moreover, the HMF conversion remained almost constant if the reaction time was increased from 10 to 40 min (Figure 1B).

Table 2 summarizes the influence of the amount of catalyst on the MPVO reaction of HMF to DFF and DHMF. No DFF and



Figure 1. Effect of reaction temperature (a) and time (b) on the MPVO reaction of HMF to DFF and DHMF. Reaction conditions: Acetonitrile solution containing HMF (0.2 mol L⁻¹) and AlMe₃ (AlMe₃/HMF molar ratio = 0.10), N₂, microwave irradiation. a) Reaction time was fixed at 10 min. b) Reaction temperature was fixed at 80 °C.

Table 2. Influence of the catalyst amount on the MPVO reaction of HMF to DFF and DHMF. $^{\rm [a]}$					
Entry	catalyst/HMF molar ratio	HMF conversion [%]	DFF/DHMF molar ratio		
1	0.0	0.0	_		
2	0.04	7.6	1.10		
3	0.1	19.1	1.25		
4	0.2	19.6	1.18		
5	0.4	19.1	0.98		
6 ^[b]	0.4	22.7	1.13		

[a] Reaction conditions: Acetonitrile solution containing HMF (0.2 mol L⁻¹) and AIMe₃ (AIMe₃/HMF molar ratio = 0–0.40), N₂, 80 °C, 10 min, microwave irradiation. [b] All reaction conditions are same as for entry 5, except for the reaction time (1 h).

DHMF were produced in the absence of Lewis-acid catalyst (Table 2, entry 1). With increasing catalyst/HMF molar ratio (0.04–0.10), HMF conversion increased from 7.6 to 19.1% (Table 2, entries 2 and 3). However, a further increase of catalyst amount did not result in further improvement of the HMF conversion (Table 2, entries 3–5). Furthermore, the HMF conversion reached only 22.7% even if the reaction time was increased from 10 min to 1 h with a AIMe₃/HMF molar ratio of 0.40 (Table 2, entries 5 and 6).

These results indicate that the disproportionation of HMF to DFF and DHMF through the MPVO reaction proceeds in the presence of a Lewis-acid catalyst. However, the HMF conversion is still low and exhibits minor changes with variation of the reaction conditions such as reaction time and temperature. This phenomenon can be attributed to the fact that a reversible equilibrium exists between HMF and DFF/DHMF (Scheme 2). $^{\scriptscriptstyle [8d,\,10]}$ This is also in line with the results of the thermodynamic analysis of the MPVO reaction of HMF (see the Supporting Information). The small positive free-energy change ($\Delta G > 0$) in the MPVO reaction of HMF, resulting from its slightly negative entropy change ($\Delta S < 0$) and small enthalpy change ($\Delta H \approx 0$), is not favorable for its conversion to DFF and DHMF (see the Supporting Information). Furthermore, if DFF and DHMF are mixed in the presence of AIMe₃ at 80 °C, they can also transform into HMF through a reverse MPVO process (Scheme 2b), and a 20% conversion of both DFF and DHMF can be achieved. This also implies the existence of a MPVO redox equilibrium between HMF and DFF/DHMF.^[8d, 10b]

Both theoretical analysis (see the Supporting Information) and experimental results (Figure 1 and Table 2, entries 2-6) indicate that the MPVO redox equilibrium between HMF and DFF/DHMF restricts the further conversion of HMF.^[8d, 10] Therefore, effective processes to shift the MPVO redox equilibrium towards DFF and DHMF should be taken into consideration. Fortunately, DHMF shows poor solubility in acetonitrile (Figure S3A and B), and its precipitation from reaction solution can be expected to shift the equilibrium towards the desired products.^[10, 17] As shown in Figure S3 A and B, the relative content of DFF in the supernatant liquid is higher than that of DHMF whereas that of DHMF is higher in the precipitate. Consequently, the more DHMF is removed from the reaction solution the more the equilibrium should shift towards the desired products. Experiments showed that the HMF conversion gradually increased from 19.3 to 26.1% if the initial HMF concentration was simultaneously increased from 0.1 to 1.0 mol L⁻¹ (Table 3, entries 1-4). The higher initial HMF concentration

Table 3. Influence of the initial HMF concentration on the MPVO reaction of HMF to DFF and DHMF. ^[a]							
Entry	C_{HMF} [mol L ⁻¹]	HMF conversion [%]	DFF/DHMF molar ratio				
1	0.1	19.3	1.03				
2	0.2	22.6	1.00				
3	0.5	23.4	1.23				
4	1.0	26.1	0.94				
5	0.2 ^[b]	36.0	0.93				
6	0.6 ^[b]	39.3	1.00				
7	1.0 ^[b]	44.7	1.00				
[a] Reac	tion conditions:	Acetonitrile solution	containing HMF (0.1–				

1.0 mol L⁻¹) and AlMe₃ (AlMe₃/HMF molar ratio = 0.10), N₂, 80 °C, 20 min, microwave irradiation. [b] MPVO-ES process is adopted and the reaction time is 1 h.

causes the formation of more DHMF precipitate, inducing an equilibrium shift of the MPVO reaction of HMF towards DFF and DHMF.^[10a,18] The difference in solubility of DHMF and DFF in acetonitrile not only permits the equilibrium to shift but also provides a promising protocol for the crude separation of DHMF from DFF (Figure S3 A and B).

To further improve the efficiency of this route, various strategies, such as the use of adsorbent or the addition of a cooling step, were utilized to enhance the removal of DHMF. Surprisingly, with the application of these strategies, from now on referred to as MPVO-ES (equilibrium shift) process, the HMF conversion could be increased from 22.7 to 36.0% at 80°C, 1 h reaction time, and an initial HMF concentration of 0.2 mol L⁻¹ (Table 3, entry 5 vs. Table 2, entry 6). In other words, a 59% in-







crease of HMF conversion could be achieved by applying the MPVO-ES process. This clear improvement of HMF conversion suggests that the MPVO-ES process can efficiently promote the precipitation of DHMF and the equilibrium shift of the MPVO reaction towards DFF and DHMF.

Finally, based on the MPVO-ES process, the initial HMF concentration was further increased to improve the efficiency of the catalytic system according to the results of Table 3 (entries 1–4). Indeed, an increase of the HMF conversion from 36.0 to 39.3% was observed if the initial HMF concentration was increased from 0.2 to 0.6 molL⁻¹ (Table 3, entries 5 and 6). Furthermore, the HMF conversion greatly increased to 44.7% if the initial HMF concentration was increased further to 1.0 molL⁻¹ (Table 3, entry 7). As a result, 1.22 mmol of both DFF and DHMF could be obtained within 1 h in acetonitrile (5 mL) (Scheme 3). Moreover, in spite of the high initial HMF concentration, the DFF/DHMF molar ratio remained close to 1.0, demonstrating the high selectivity of the conversion of HMF to DFF and DHMF through the MPVO reaction (Table 3, entry 7).

Mass conversion rate (MCR, $gL^{-1}h^{-1}$) of HMF and mass yield rate (MYR, $gL^{-1}h^{-1}$) of DFF/DHMF were also adopted to evaluate the efficiency of this catalytic route because they are often used to assess the practical potential of a catalytic process.^[19] It is clear that if the initial HMF concentration is 1.0 mol L⁻¹, the MCR of HMF can reach 56.4 $gL^{-1}h^{-1}$ and the MYR of DFF and DHMF is 27.7 and 28.7 $gL^{-1}h^{-1}$, respectively (Scheme 3). Clearly, this trend toward high conversion as well as high MCR induced by high substrate concentration is very conducive to an industrial application of this transformation route for HMF.

In conclusion, a transformation route for the simultaneous preparation of 2,5-diformylfuran (DFF) and 2,5-dihydroxymethylfuran (DHMF) from 5-hydroxymethylfurfural (HMF) through a Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction without external oxidant or reductant was successfully developed. Additionally, this catalytic process also provides a promising protocol for the crude separation of DHMF from DFF. Under optimal reaction conditions, a HMF conversion of 44.7% and a MCR of 56.4 g L⁻¹ h⁻¹ can be achieved under high initial HMF concentration through effective precipitation of DHMF from the reaction solution. Owing to its high selectivity and mass conversion rate, this transformation route also shows a promising potential for the conversion of biomass-derived platform chemicals to valuable intermediates. Further work will focus on further improvement of the efficiency of this process.

Experimental Section

Conversion of HMF to DFF and DHMF through the MPVO reaction: All reactions involving an AlMe₃ solution (2м, in toluene) were performed under nitrogen atmosphere using dried solvents, syringe techniques, and oven-dried vials. Typically, HMF (1-5 mmol) was dissolved in dried solvent (5-10 mL, acetonitrile, DMF, DMSO, MIBK, THF, or dioxane (the detailed corresponding information (supplier and purity) of all chemicals is provided in the Supporting Information) in a 30 mL vial. The AIMe₃ solution (AIMe₃/HMF molar ratio = 0-0.40) was then added using syringe techniques, and the vial was sealed under nitrogen atmosphere. The conversion of HMF was performed in the sealed vial under microwave irradiation provided by a single-mode microwave instrument (Nova-2S, Preekem Scientific Instruments Co., Ltd, China). The reaction temperature was held at 60-120°C for 10-60 min. The products were analyzed by GC (Shimadzu GC-2010 plus, equipped with a DM-FFAP capillary column and a FID detector). Quantifications of HMF, DFF, and DHMF were obtained from the corresponding response factors and peak areas. For further details about the product analysis see the Supporting Information.

MPVO-ES process: HMF (1–5 mmol) and Al(OH)₃ (adsorbent, dried at 170 °C overnight, 0.1 g Al(OH)₃ per mmol HMF) were added to acetonitrile (5 mL). The sealed vial was heated at 80 °C for 1 h under microwave irradiation. At 10 min intervals, the sealed vial was cooled with an ice-water bath; AlMe₃ solution was also added to the reaction mixture using syringe techniques to ensure that the AlMe₃/HMF molar ratio remained at 0.40. After a reaction time of 1 h, the products were collected and analyzed by GC. For further details about the product analysis see the Supporting Information.

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COMMUNICATIONS

G. Li, Z. Sun, Y. Yan, Y. Zhang,* Y. Tang

Direct Transformation of HMF into 2,5-Diformylfuran and 2,5-Dihydroxymethylfuran without an External Oxidant or Reductant



Two birds with one stone: A route for simultaneous preparation of 2,5-diformylfuran (DFF) and 2,5-dihydroxymethylfuran (DHMF) from 5-hydroxymethylfurfural (HMF) through a Meerwein-Ponndorf–Verley–Oppenauer reaction is developed. In this Lewis acid-catalyzed reaction, HMF acts as both oxidant and reductant so that no external redox reagent is required. It also provides a promising protocol for the crude separation of DHMF products from DFF products.

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