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Biomass

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Highly Selective Decarbonylation of 5-(Hydroxymethyl)furfural in the Presence of Compressed Carbon Dioxide**

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Current plans for the implementation of second-generation biofuels are mainly directed towards the conversion of biomass to synthesis gas and the subsequent formation of synthetic fuels by a Fischer–Tropsch process or the fermentation of cellulose to bioalcohols.[1,2] An alternative pathway to biofuels from carbohydrate feedstock can be envisaged and is based on the effective utilization of the structural input from nature and the development of selective and versatile catalytic defunctionalisation processes.[1,3,4] This strategy also provides access to intermediates and building blocks for chemical products.[1,2] The selective reduction of the oxygen content in the molecular structures is a general theme in these pathways. Currently, this goal is mainly achieved by dehydration and hydrogenation strategies.[3–5] Selective decarbonylation and/or decarboxylation can also be envisaged, but are far less developed at present.

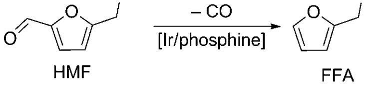
Furan-derived compounds and intermediates are accessible from furfural, an intermediate that is already produced on an industrial scale from pentose sugars.[1,6] In previous years, diverse industrial chemical processes have been established and the products are expected to have significant importance in upcoming biorefinery concepts.[1,6]

Given the more versatile and larger availability of C_6 over C_5 sugars in biomass feedstock, it seems attractive to establish an entry into this product and process network by using 5-(hydroxymethyl)furfural (HMF) as the platform chemical. HMF can be obtained through catalytic processes from hexoses or even cellulose.[7] Recently, a number of examples demonstrated the potential of retaining the furan structure from HMF in the formation of desired biobased target products.[8] Compounds based on the structural motif of furan have also been discussed as potential biofuel candidates.[8] However, processes for the production and further transformation of HMF are often hampered by its low stability under conventional reaction conditions. In particular, the formation of insoluble polymers, so-called humins, is often observed at elevated reaction temperatures.[9] The undesired formation of humins strongly limits the yields of the desired products and lowers the carbon efficiency, thus putting severe constraints on the sustainable utilization of HMF as the platform chemical.

Herein, we demonstrate the possibility to obtain the biogenic C_5 component furfuryl alcohol (FFA) by a highly selective catalytic decarbonylation of HMF. The only previous reports on this approach suffer from low selectivity and/or the need of a stoichiometric amount of an active metal species.[10] The key to the unprecedented high product yields are an integrated development and optimization of catalysts and reaction media that exploit the principles of organometallic chemistry and the properties of compressed carbon dioxide for reactivity control.

The selective decarbonylation of aromatic and aliphatic aldehydes was first demonstrated by Tsuji and Ohno by using stoichiometric amounts of the Wilkinson catalyst ($Rh(PPh_3)_3Cl$).[11] In subsequent years, Doughty and Pignolet further developed the liberation of carbon monoxide (CO) into a catalytic reaction by using bidentate phosphine ligands.[12] Effective catalytic decarbonylation required harsh reaction conditions ($T > 160$ °C) or the addition of stoichiometric amounts of CO scavengers.[13] In 1999, Crabtree and co-workers were able to achieve selective decarbonylation in boiling dioxane with Rh complexes that incorporate tridentate phosphines.[14] Recently, Tsuji and co-workers extended the concept further and showed the beneficial effect of using Ir complexes with monodentate aryl- and alkylphosphines for a selective decarbonylation approach with various aromatic and aliphatic aldehyde substrates.[15] Based on this background, we aimed at an efficient decarbonylation of the temperature-sensitive HMF using Ir catalysts (Scheme 1).

In a first set of experiments, the decarbonylation of HMF was attempted with a catalytic system comprising $[IrCl(cod)]_2$



Scheme 1. Catalytic decarbonylation of HMF.

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Table 1: Catalytic decarbonylation using different phosphine ligands.[a]

Entry	Ligand	Conversion [%]	Selectivity for FFA [%]
1	PPh_3	17	95
2	PCy_3	41	97
3	P*t*Bu_3	25	98
4	P*n*Oct_3	48	98

[a] Conditions: 1 mmol HMF, 25 μmol $[IrCl(cod)]_2$, 100 μmol ligand, 4 mL 1,4-dioxane, 110°C, 48 h.

(cod = 1,5-cyclooctadiene) as the metal precursor in the presence of various monodentate phosphine ligands (Table 1).

The catalyst formed in situ from triphenylphosphine (PPh_3, 2 equiv) and $[IrCl(cod)]_2$ (1 equiv) gave a low HMF conversion (17%), but a high selectivity (95%) for the desired FFA product (Table 1, entry 1) after 48 h in boiling 1,4-dioxane. Changing the ligand to tricyclohexylphosphine (PCy_3) resulted in 41% conversion while retaining a high selectivity of 97% (Table 1, entry 2). Use of the even more bulky tri-*tert*-butylphosphine (P*t*Bu_3) lead to 25% conversion (Table 1, entry 3). The reaction with the catalyst prepared with tri-*n*-octylphosphine (P*n*Oct_3) resulted in a similarly high conversion as PCy_3 and the almost exclusive formation of FFA (Table 1, entry 4).

Under the relatively mild conditions of this first screening, no formation of humins or other decomposition products of the components was detected, but the formation of FFA did not exceed 50% yield even after 48 h. Increasing the reaction temperature to 220°C and carrying out the reaction with the Ir/PCy_3 catalyst in a closed vessel led to the full conversion of the substrate, but only decomposition products could be isolated from the reaction mixture (Table 2, entry 1; Figure 1). As compressed CO_2 has recently found increasing interest in the conversion of biogenic substrates,[16] and cyclic ethers such as 1,4-dioxane dissolve large amounts of CO_2 to form so-called expanded liquid phases,[17] we investigated whether the undesired intermolecular decomposition pathways could be suppressed in such media.[18] Gratifyingly, the application of pressurized CO_2 (20 bar, 0.5 g) led to a 63% yield of the desired FFA product under otherwise identical conditions (Table 2, entry 2; Figure 1). Increasing the CO_2 pressure to 50 bar (1.1 g) improved the process even further and over 90% yield of FFA was obtained (Table 2, entry 3; Figure 1).

Table 2: Catalytic decarbonylation under different CO_2 pressures.[a]

Entry	*t* [h]	Solvent	*p*(CO_2) [bar]	Conversion [%]	Selectivity for FFA [%]
1	24	dioxane	0	>99	<5
2	24	dioxane	20	>99	63
3	24	dioxane	50	>99	93
4	12	dioxane	50	99	95
5[b]	12	dioxane	50	97	95
6[c]	12	dioxane	50	98	88
7[d]	12	2-MTHF	50	98	96
8[e]	12	THFA	50	95	75[f]
9[g]	12	THFA	50	99	85

[a] 1 mmol HMF, 25 μmol $[IrCl(cod)]_2$, 100 μmol PCy_3 (HMF/Ir = 20:1), 4 mL 1,4-dioxane, 220°C. [b] Recycling experiment. [c] 4 mmol HMF, 50 μmol $[IrCl(cod)]_2$, 200 μmol PCy_3 (HMF/Ir = 40:1), 4 mL 1,4-dioxane, 220°C. [d] 1 mmol HMF, 25 μmol $[IrCl(cod)]_2$, 100 μmol PCy_3 (HMF/Ir = 20:1), 4 mL 2-MTHF, 220°C. [e] 1 mmol HMF, 25 μmol $[IrCl(cod)]_2$, 100 μmol PCy_3 (HMF/Ir = 20:1), 4 mL THFA, 220°C. [f] In situ etherification gave dimeric THFA and FFA ethers as by-products. [g] 2 mmol HMF, 50 μmol $[IrCl(cod)]_2$, 200 μmol PCy_3 (HMF/Ir = 20:1), 4 mL THFA, 220°C.

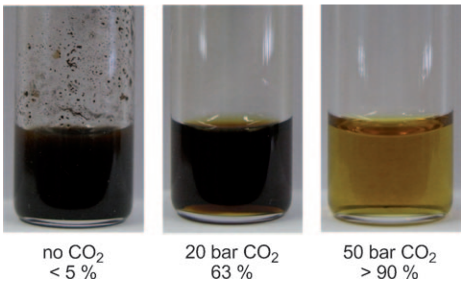


Figure 1. Product mixtures and FFA yields of the decarbonylation reaction under different CO_2 pressures.

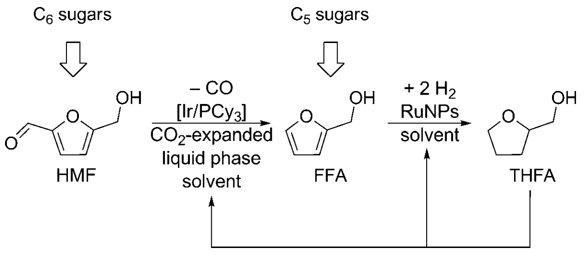
As full conversion was achieved in 24 h, reduction of the reaction time was chosen as the subsequent optimization step. Quantitative conversion and excellent selectivity (Table 2, entry 4) could already be obtained after 12 h, thus emphasizing the beneficial effect of CO_2 on reactivity and selectivity. However, as already observed during the screening experiments, the initial rates and final conversions after 48 h were significantly reduced at lower temperatures (see the Supporting Information).

In order to further elucidate the origin of the beneficial effect of CO_2, additional experiments were performed. Neither the use of nitrogen gas (50 bar) nor dilution of the reaction mixture with the organic solvent were sufficient to significantly increase the selectivity to comparable values (see the Supporting Information). Additional high-pressure NMR experiments at 80°C did not reveal an interaction between the substrate and CO_2, thus excluding the possibility of an in situ protection of HMF. Visual inspection clearly confirmed the formation of a largely expanded liquid phase, which causes a very significant alteration of the physicochemical properties of the reaction mixture,[17] and thus may at least partly form the basis for the high selectivity in the presence of CO_2.

Although the formation of catalytically active nanoparticles cannot be fully excluded at this stage of our investigation, no indication of particle formation or metal precipitation was observed. Moreover, at the end of the catalytic reaction, the organometallic species $[Ir(CO)(PCy_3)_2Cl]$ could be isolated in high yield (86% after recrystallization). The product was analyzed by using NMR spectroscopy, ESI-MS, and single-crystal X-ray diffraction, and the results are consistent with reported values.[19] The isolated complex could be recycled as a catalyst under identical conditions (Table 2, entry 5). Almost full conversion was achieved with identical selectivity, thus demonstrating the possibility for recycling and repetitive use of the catalyst. An increase in the substrate loading to 12 wt% resulted in 98% conversion with 88% selectivity for FFA, thus further substantiating the preparative potential of this approach (Table 2, entry 6).

In order to replace the petrochemical solvent 1,4-dioxane used in this process, 2-methyltetrahydrofuran (2-MTHF) and tetrahydrofurfuryl alcohol (THFA), which can both be obtained through hydrogenation/dehydration pathways from HMF and FFA, respectively,[1,3] were tested as biomass-based alternative solvents. Excellent conversion and selectivity rates were obtained for the conversion of HMF in 2-MTHF (Table 2, entry 7). The use of THFA as solvent also led to a competitive conversion (95 %), but the detected amount of free FFA dropped to 75 % (Table 2, entry 8). However, the intrinsic selectivity for the decarbonylation remained very high, and ethers of THFA and FFA were formed as the only major by-products (Table 2, entry 9).

Finally, an FFA/THFA mixture obtained from the decarbonylation reaction was subjected to hydrogenation conditions. Ionic liquid (IL) stabilized ruthenium nanoparticles (RuNPs), which were recently described as selective and recyclable systems for the hydrogenation of furan rings, were employed as the catalyst.[20] The IL 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_{12}MIM][BTA]) was used as stabilizer (IL/Ru ≈ 4:1), and Ru nanoparticles with an average size of (3.5 ± 0.6) nm were formed. Without detailed optimization, the FFA in the mixture was hydrogenated with full conversion and 95 % selectivity to THFA under a standard set of reaction conditions (100 bar H_2, 150 °C, 16 h). Additional catalyst optimization for the selective hydrogenolysis of the ether by-products would enable further improvement of the catalytic process. Thus, the decarbonylation of HMF in THFA as solvent and the subsequent hydrogenation of the reaction mixture can be combined to “breed” THFA as the single product; the two catalysts can be recycled via distillation in the individual steps (Scheme 2).



Scheme 2. Integrated synthetic pathways for the C_6 and C_5 platform chemicals HMF, FFA, and THFA using the product as solvent throughout the transformation sequence.

In summary, the highly selective decarbonylation of HMF to FFA using Ir phosphine catalysts has been demonstrated, and yields greater than 90 % could be achieved. If THFA is used as solvent, the primary product FFA can be hydrogenated directly to convert the mixture into a single product stream of THFA at the end of the process. The presence of compressed CO_2 suppresses the formation of humins during the HMF conversion, presumably by forming an expanded liquid phase as the reaction medium. This result suggests that the application of compressed CO_2 could also be envisaged in other HMF-based processes. The results demonstrate that decarbonylation offers a hitherto largely neglected approach for the deoxygenation of biogenic substrates, and the possibility to interconnect the C_5 and C_6 carbohydrate pathways opens new synthetic pathways for biorefinery concepts.

Experimental Section

Reactions and manipulations were performed under argon atmosphere using standard Schlenk techniques. $[IrCl(cod)]_2$ (16.8 mg, 25 μmol) was dissolved in dry and degassed 1,4-dioxane (4.0 mL) in a Schlenk tube. The appropriate phosphine (100 μmol) was added and the mixture was stirred until its color changed from dark-orange to yellow. HMF (126.2 mg, 1 mmol) was added to the stirred solution. After complete dissolution of HMF, the mixture was transferred into a glass-lined stainless steel reactor. Compressed CO_2 (1.1 g) was added to achieve a pressure of 50 bar under the specific reaction conditions, and the pressurised reactor was heated to 220 °C. The reaction was stirred at this temperature for up to 24 h and then quenched by cooling and careful depressurisation. The product solution was analyzed by GC and NMR spectroscopy.

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