

Catalytic Conversion of Biomass-Derived Carbohydrates into γ -Valerolactone without Using an External H_2 Supply**

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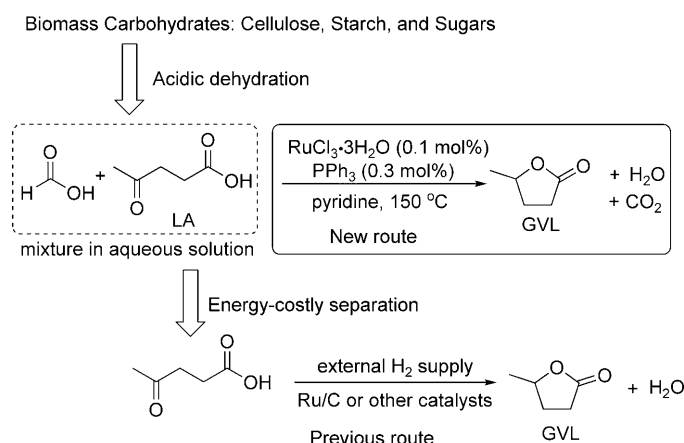
With diminishing fossil fuel reserves, great efforts are now being made worldwide to convert renewable biomass into fuels and value-added chemicals.^[1] The major component of plant biomass, carbohydrates, can be transformed into chemicals including ethanol, *n*-butanol, sorbitol,^[2] hydroxymethylfurfural,^[3] and dimethylfuran.^[4] Recently Horvath et al. demonstrated that the biomass-derived compound γ -valerolactone (GVL)^[5,6] may be used as a liquid fuel, food additive, solvent,^[7] and organic intermediate in the synthesis of fine chemicals.^[8–10]

To produce GVL from biomass, Horvath et al. have developed a pioneering technology^[5] that involves: 1) selective dehydration of carbohydrates to levulinic acid (LA), followed by 2) hydrogenation of LA to give GVL by using an external H_2 supply (1200 psi H_2) (Scheme 1). Transfer hydro-

basic chemical, the invention of novel, more efficient catalytic systems is highly desirable to convert biomass carbohydrates into GVL.

Herein we report a new route to convert various biomass-derived oxygenates (cellulose, starch, and sugars) into GVL without using any external H_2 supply (Scheme 1). We found that LA can be selectively reduced to GVL instead of 1,4-pentanediol by tuning the base and ligand in Ru-based catalytic systems. More importantly, this hydrogenation process can be accomplished only in the presence of the formic acid produced from the original acidic dehydration step. The success of this new route not only improves the atom economy of the process, but also avoids the energy-costly separation of LA from the mixture of LA and formic acid in aqueous solution.

We began our study by examining the product mixture formed by the acidic dehydration of biomass carbohydrates. Under our optimized laboratory-scale conditions, the yields of LA from several types of biomass carbohydrates ranged from 35 to 58 % (Table 1). These values are slightly higher



Scheme 1. Previous and new routes for the production of GVL.

genation of LA with excess $HCOONa$ (37 equiv) catalyzed by $[(\eta^6-C_6Me_6)Ru(bpy)(H_2O)]SO_4$ ($bpy = 2,2'$ -bipyridine) was also examined, but considerable overreduction to 1,4-pentanediol was observed. Thus, for the development of GVL as a

Table 1: Acid-catalyzed transformation of biomass carbohydrates into LA and formic acid at 220 °C.

Entry	Carbohydrate	Yield of LA [mol %]	Yield of formic acid [mol %]
1 ^[a]	microcrystalline cellulose	35.4	45
2 ^[a]	α -cellulose	45.2	49
3 ^[a]	starch	53.7	58
4 ^[b]	glucose	57.7	76

[a] Conditions: 20 g of carbohydrate in 400 mL of aqueous HCl (0.8 M).

[b] Conditions: 15 wt % glucose in 400 mL of aqueous HCl (0.8 M).

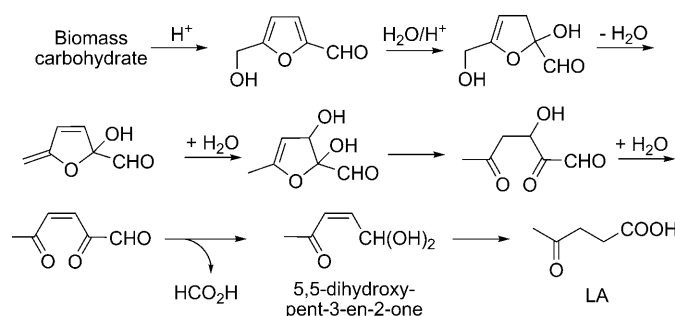
than Horvath's yields (ca. 30–40 %) for the H_2SO_4 -mediated conversion of sucrose into LA.^[5,11] The molar yield of formic acid is found to be always slightly higher than that of LA (Table 1). This observation may be explained by the side reactions of some dehydration intermediates (e.g. 5,5-dihydroxypent-3-en-2-one in Scheme 2).

As the yield of formic acid is higher than that of LA, it should be possible to hydrogenate LA by using the formic acid in the mixture as the sole hydrogen source. However, a previous study showed that transfer hydrogenation of LA with 37 equivalents of $HCOONa$ catalyzed by $[(\eta^6-C_6Me_6)Ru(bpy)(H_2O)]SO_4$ resulted in only 25 % GVL and 25 % 1,4-pentanediol.^[5] We hypothesized that by changing the base and ligand in the catalyst, LA may be reduced selectively to GVL rather than to 1,4-pentanediol. To our delight we

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Scheme 2. Proposed mechanism for the acidic conversion of biomass carbohydrates into LA and formic acid.

found that by using a simple mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.2 mol %) and PPh_3 (0.6 mol %) as the catalyst, the 1:1 neat mixture of LA and formic acid can be selectively transformed into GVL in a closed stainless-steel autoclave without any overreduction (Table 2).

Table 2: Transformation of LA into GVL with 1 equiv of formic acid.

Entry ^[a]	<i>t</i> [h]	<i>T</i> [°C]	Base ^[b]	Yield of GVL [mol %] ^[c]
1	12	100	LiOH	16 ^[d]
2	12	100	NaOH	30 ^[d]
3	12	100	KOH	42 ^[d]
4	12	100	NH_3	16 ^[d]
5	12	100	NEt_3	27 ^[d]
6	12	100	pyridine	20 ^[d]
7	6	150	NaOH	72
8	12	150	NaOH	81
9	6	150	KOH	67
10	12	150	KOH	74
11	6	150	NEt_3	80
12	12	150	NEt_3	94
13	6	150	pyridine	74
14	12	150	pyridine	93
15	3	200	NaOH	78
16	6	200	NaOH	75
17	3	200	KOH	70
18	6	200	KOH	67
19	3	200	NEt_3	89
20	6	200	NEt_3	95
21	3	200	pyridine	82
22	6	200	pyridine	93

[a] Conditions: LA (23.2 g, 200 mmol), formic acid (9.2 g, 200 mmol), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.2 mmol), and PPh_3 (0.6 mmol). [b] 20 mmol base was added. [c] Yield determined by GC-MS. [d] Significant amount of LA was not consumed.

Detailed experiments show that the transformation into GVL is relatively slow at 100 °C (Table 2, entries 1–6). However, by measuring the gas pressure inside the autoclave, we found that the pressure increases rapidly from 0.1 MPa to a maximum value of approximately 8 MPa in about 20 minutes. The rapid increase of the gas pressure can only be explained by the Ru-catalyzed decomposition of formic acid to H_2 and CO_2 , a phenomenon that was exploited recently for developing H_2 -storage systems.^[12] Because this decomposition is found to be very fast, we conclude that the reduction of LA does not proceed through transfer hydro-

genation. Instead, formic acid decomposes to H_2 , which serves in the subsequent hydrogenation of LA to give GVL.

The performance of different bases decreases in the order $\text{KOH} > \text{NaOH} > \text{NEt}_3 > \text{pyridine} > \text{NH}_3 > \text{LiOH}$ indicates that a stronger base accelerates the reaction. Increasing the temperature to 150 °C dramatically improves the yield to over 90 %, and NEt_3 and pyridine were found to outperform KOH under these conditions (Table 2, entries 7–14). Increasing the temperature to 200 °C can push the reaction to completion in 6 hours (yield = 95 %) when NEt_3 serves as the base (Table 2, entry 20). KOH gives a lower yield at 6 hours than at 3 hours at 200 °C (Table 2, entries 17 and 18), indicating that the GVL product reacts with the strong base.

These results demonstrate that the product arising from the acidic dehydration of biomass-derived carbohydrates can be converted into GVL without using any external H_2 supply. The next challenge is to make the process practical. Because the acidic dehydration is conducted in water, we sought to accomplish the conversion of LA into GVL in fully aqueous media. To our surprise, the experiments showed that even though PPh_3 is not a water-soluble ligand, the conversion of LA/formic acid (1:1) in 50 wt % aqueous solution can be achieved with a maximum yield of 90 % when NEt_3 is used as the base (Table 3, entry 5). When pyridine is used, the yield is slightly lower (88 %, entry 8).

Strikingly, we found that after the transformation is finished and the resulting solution is condensed (i.e. GVL, water, and other liquids removed through reduced-pressure distillation), the solid residue (presumably containing RuCl_3 and PPh_3) can be reused to convert a mixture of LA and formic acid in approximately a 50 % aqueous solution (Table 3). For the reaction with NEt_3 , the yields in the second and third runs were 78 % and 53 % (Table 3, entries 6 and 7). For pyridine, the yields in the second and third runs

Table 3: Transformation of LA and formic acid into GVL in water and catalyst regeneration at 150 °C.

Entry ^[a]	Ligand	Base ^[b]	Yield of GVL [%] ^[c]
1	PPh_3	LiOH	72
2	PPh_3	NaOH	72
3	PPh_3	KOH	87
4	PPh_3	NH_3	83
5	PPh_3	NEt_3	90
6 ^[d]	PPh_3	NEt_3	78
7 ^[e]	PPh_3	NEt_3	53
8	PPh_3	pyridine	88
9 ^[d]	PPh_3	pyridine	84
10 ^[e]	PPh_3	pyridine	80
11	PCy_3	pyridine	81
12	dppe	pyridine	80
13	tppps	pyridine	54
14	tppts	pyridine	48
15	–	pyridine	21

[a] Conditions for entries 1–10: LA (23.2 g, 200 mmol), formic acid (9.2 g, 200 mmol), H_2O (25 mL), RuCl_3 (0.2 mmol), and ligand (0.6 mmol). [b] 20 mmol base was added; [c] Yield determined by GC-MS. [d] Second run. [e] Third run. dppe = (1,2-bis(diphenylphosphinyl)ethane, tppps = (3-diphenylphosphinyl)benzenesulfonic acid, sodium salt, tppts = 3,3',3''-phosphinetriyltris(benzenesulfonic acid) trisodium salt.

were 84 % and 80 %, respectively (Table 3, entries 9 and 10). The observations indicate that it is possible to recycle the $\text{RuCl}_3/\text{PPh}_3$ catalyst and considerably reduce the cost of the catalytic conversions.

Compared to PPh_3 , other hydrophobic ligands such as PCy_3 and dppe provide slightly lower yields (Table 3, entries 11 and 12). On the other hand, it is surprising to find that water-soluble phosphine ligands including tpms and tppts give significantly lower yields of the products (ca. 50 %; Table 3, entries 13 and 14). Furthermore, in the absence of any phosphine ligand, the yield is even lower (21 %, Table 3, entry 15).

To demonstrate the practical potential of the process, we applied the method to the conversion of glucose into GVL. First, through acidic dehydration (catalyzed by 0.8 M HCl at 220 °C in an autoclave) of glucose (400 mL, 15 wt % aqueous solution), we obtained a mixture of LA and formic acid. After pH neutralization and distillation (to remove some water) to give a total volume of 50 mL, the aqueous mixture contained 42 wt % LA and 17 wt % formic acid. To this mixture we added the $\text{RuCl}_3/\text{PPh}_3$ catalyst (0.1 mol %) and pyridine; catalytic hydrogenation at 150 °C produced GVL in 83 % yield. The overall yield from glucose is 48 %. Thus, we demonstrate that this new technology can be used to convert glucose into GVL with good efficiency.

Finally, intrigued by the surprisingly good performance of the water-insoluble PPh_3 ligand in the Ru-catalyzed hydrogenation in aqueous media, we also examined the $\text{RuCl}_3/\text{PPh}_3$ -catalyzed hydrogenation of LA in 50 wt % aqueous solution with 4 MPa H_2 in the absence of formic acid. Surprisingly the yield of this hydrogenation reaction is actually low (45 %, Figure 1a). In comparing the results from direct hydrogenation and hydrogenation using formic acid as the H_2 source, we suspect that the CO_2 produced in the decomposition of formic acid may be an overlooked factor. Indeed, when we intentionally added CO_2 to the direct-hydrogenation system, a steady increase of yield was observed (Figure 1a). The maximum yield (ca. 100 %) was obtained when the at a CO_2 pressure of 4 MPa (equal to the pressure of H_2).

Additional experiments showed that the concentration of water also has an effect. In neat LA, the yield was 100 % with 4 MPa CO_2 and 78 % without CO_2 . Almost identical yields were obtained with or without CO_2 when 25 wt % water was added. When 50 wt % water was added, the yield was 100 % with CO_2 and 45 % without CO_2 . When 75 % water was added, the positive effect of adding CO_2 vanished. All the above observations indicate that adding CO_2 can greatly improve the Ru-catalyzed hydrogenation. The rationale for of the positive CO_2 effect on hydrogenation remains to be examined future studies. Nonetheless, the positive CO_2 effect explains why simple the $\text{RuCl}_3/\text{PPh}_3$ catalyst can promote the aqueous hydrogenation of LA efficiently.

In summary, we have demonstrated that an inexpensive, recyclable $\text{RuCl}_3/\text{PPh}_3$ /pyridine catalyst system can be used to convert a 1:1 aqueous mixture of levulinic acid and formic acid into γ -valerolactone in high yields. This process may find important applications for the efficient production of GVL from biomass-derived carbohydrates without intermediate

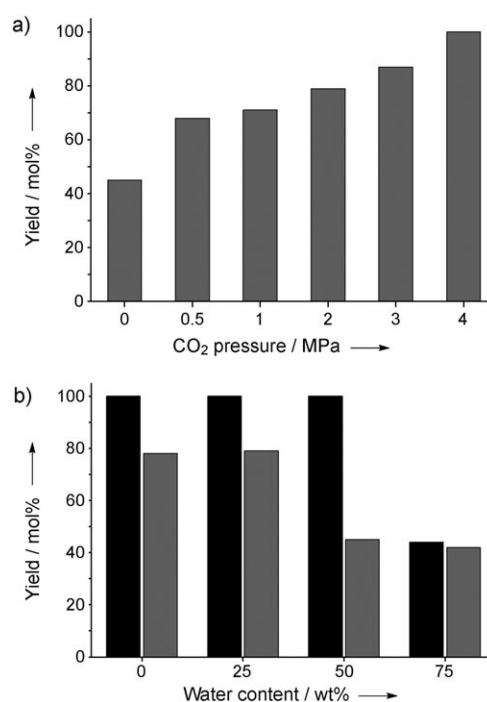


Figure 1. Effect of CO_2 on the hydrogenation of LA. Reaction conditions: 150 °C, 12 h, 200 mmol LA, 20 mmol pyridine, 0.2 mmol RuCl_3 , 0.6 mmol PPh_3 , and 4 MPa H_2 . a) Reaction conducted in 50 wt % water; b) Reaction conducted with 4 MPa CO_2 (black) and without CO_2 (gray).

purification and without using external H_2 supply. A striking positive CO_2 effect on the Ru-catalyzed hydrogenation was observed, which may be used to explain the good results of the aqueous hydrogenation using water-insoluble ligands. In a model experiment with glucose as a biomass-derived carbohydrate GVL was produced in 48 % yield by an operationally simple sequence (i.e. acidic dehydration followed by Ru-catalyzed hydrogenation). Further optimization may eventually make the approach industrially viable for the transformation of non-food biomass into GVL as a valuable chemical.

Experimental Section

All catalysts and chemicals were obtained commercially and used without further purification. All the catalytic experiments were carried out in a 100 mL autoclave made of zirconium alloy. Before each run the autoclave was purged with N_2 to exclude air. The mixture of substrates and catalyst was heated to the desired temperature in less than half an hour with stirring at 1000 rpm. To recover the catalyst, the reaction mixture was subjected to vacuum distillation to remove water and GVL. The residue was added to the mixture of LA and formic acid for the next run. For direct hydrogenation using H_2 , the autoclave was pressurized with H_2 to 2 MPa at room temperature three times. Then H_2 with or without CO_2 was filled to 8 or 4 MPa. After the reaction, the mixture was analyzed by GC-MS (Thermal Trace GC Ultra with a PolarisQ ion trap mass spectrometer) equipped with a TR-35MS capillary column (30 m \times 0.25 mm \times 0.25 μm).

The carbohydrates were hydrolyzed in 0.8 M HCl at 220 °C in a 500 mL stainless-steel autoclave with vigorous stirring for 1 h. The pH

of the resulting mixture from glucose was adjusted to pH 2 and the mixture was filtered. The filtrate was vacuum-distilled and concentrated. The condensed solution was transferred to a 100 mL autoclave and converted as described above for a typical. The concentrations of LA and formic acid were determined with an HPLC system consisting of a Waters 1525 pump, a Waters 5C₁₈-PAQ column (4.6 × 250 mm), and a Waters 2414 refractive index detector. H₂SO₄ (5 mM) was added to the mobile phase at flow rate of 1 mL min⁻¹ (see the Supporting Information for details).

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- [1] a) G. W. Huber, A. Corma, *Angew. Chem.* **2007**, *119*, 7320; *Angew. Chem. Int. Ed.* **2007**, *46*, 7184; b) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem.* **2007**, *119*, 7298; *Angew. Chem. Int. Ed.* **2007**, *46*, 7164; c) M. Stöcker, *Angew. Chem.* **2008**, *120*, 9340; *Angew. Chem. Int. Ed.* **2008**, *47*, 9200.
- [2] a) G. W. Huber, R. D. Cortright, J. A. Dumesic, *Angew. Chem.* **2004**, *116*, 1575; *Angew. Chem. Int. Ed.* **2004**, *43*, 1549; b) N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. C. Liu, Y. Kou, *J. Am. Chem. Soc.* **2006**, *128*, 8714; c) C. Luo, S. A. Wang, H. C. Liu, *Angew. Chem.* **2007**, *119*, 7780; *Angew. Chem. Int. Ed.* **2007**, *46*, 7636.
- [3] a) G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446; b) H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597; c) J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* **2009**, *131*, 1979.
- [4] Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982.
- [5] H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horvath, *Top. Catal.* **2008**, *48*, 49.
- [6] I. T. Horvath, H. Mehdi, V. Fabos, L. Boda, L. T. Mika, *Green Chem.* **2008**, *10*, 238.
- [7] I. T. Horvath, *Green Chem.* **2008**, *10*, 1024.
- [8] L. E. Manzer, *Appl. Catal. A* **2004**, *272*, 249.
- [9] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.
- [10] D. R. Dodds, R. A. Gross, *Science* **2007**, *318*, 1250.
- [11] The yield of levulinic acid from the acidic dehydration of cellulose can be as high as 70–80% in the industrial-scale processes. See: a) W. F. Stephen, US Patent 5608105, **1997**; b) M. G. Viswas, A. H. Milford, US Patent 5859263, **1999**; c) A. F. William, E. C. John, US Patent 6054611, **2000**.
- [12] a) C. Fellay, P. J. Dyson, G. Laurency, *Angew. Chem.* **2008**, *120*, 4030; *Angew. Chem. Int. Ed.* **2008**, *47*, 3966; b) B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962.
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