

# CATALYTIC TRANSFER HYDROGENATION IN $\gamma$ -VALEROLACTONE-BASED IONIC LIQUIDS

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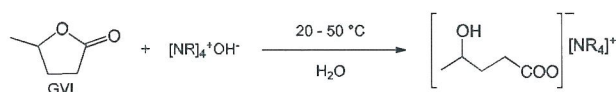
## Introduction

The replacement of conventional organic solvents that usually have high vapour pressure, toxicity, and negative impact on the environment is a crucial part in the development of environmentally benign chemical transformations. Among the proposed „green” reaction media e.g. water, fluorous solvents, supercritical carbon-dioxide etc., the ionic liquids (ILs) have attracted considerable attention as potential alternative solvents due to their attractive properties, such as low vapour pressure, high thermal stability, solvation strength and the quite easily fine-tuned physical properties by proper combination of anion and cation.<sup>1</sup>

The catalytic transfer hydrogenation of organic substrates is a more safe and energy-efficient alternative compared to the high-pressure systems, operating under atmospheric pressure.

The proper combination of transfer hydrogenation with the advantages of ILs could result in an environmentally friendly protocol for the reduction of organic substrates.

We investigated different  $\gamma$ -valerolactone (GVL) based ILs containing 4-hydroxyvalerate anion as reaction media. These solvents can easily be prepared by the combination of GVL (a proposed sustainable liquid)<sup>5</sup> and the aqueous solution of the corresponding tetraalkylammonium hydroxide with excellent yield and high purity (Scheme 1).<sup>3,4</sup>



Scheme 1 Synthesis of 4-hydroxyvalerate based ILs, R: see Table 1

## Results

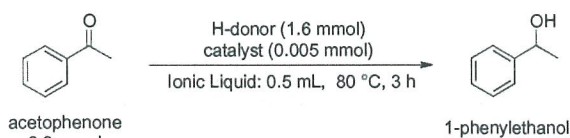
The properties of GVL-based ILs can easily be fine tuned by varying the alkyl chain of the ammonium cation. Accordingly, a series of ILs containing 4-hydroxyvalerate anion were prepared (Table 1).

Table 1 GVL-based ionic liquids with 4-hydroxyvalerate anions

| # | R                               | Ionic liquid                          | Abbreviation        |
|---|---------------------------------|---------------------------------------|---------------------|
| 1 | CH <sub>3</sub>                 | Tetramethylammonium-4-hydroxyvalerate | TMA-HV <sup>4</sup> |
| 2 | C <sub>2</sub> H <sub>5</sub>   | Tetraethylammonium-4-hydroxyvalerate  | TEA-HV              |
| 3 | C <sub>3</sub> H <sub>7</sub>   | Tetrapropylammonium-4-hydroxyvalerate | TPra-HV             |
| 4 | nC <sub>4</sub> H <sub>9</sub>  | Tetrabutylammonium-4-hydroxyvalerate  | TBA-HV <sup>3</sup> |
| 5 | nC <sub>5</sub> H <sub>11</sub> | Tetrapentylammonium-4-hydroxyvalerate | TPeA-HV             |
| 6 | nC <sub>6</sub> H <sub>13</sub> | Tetrahexylammonium-4-hydroxyvalerate  | THA-HV <sup>3</sup> |



The reduction of acetophenone was selected as a model reaction (Scheme 2) to evaluate the solvent effect, type of the H-donor, catalyst precursor, ratio of substrate and H-donor on the efficiency of the transfer hydrogenation.



Scheme 2

Initially common organic solvents (toluene, MeOH, EtOH, PrOH, DMSO) and common ILs ([BMIM][PF<sub>6</sub>], [BMIM][Cl], [BMIM][OH], [BMIM][octyl sulfate], [EMIM][OH]) were tested as reaction media for comparison. It was revealed that only negligible conversion of 1-phenylethanol can be achieved in these solvents. By using GVL-based ILs the reaction rate significantly increased (Table 2), except in case of TMA-HV due to its high melting point (75–85°C). There was > 99 % conversion observed by applying TBA-HV (Table 2, entry 4).

Table 2 Transfer hydrogenation of acetophenone using GVL-based ionic liquids

| Entry | Ionic Liquid        | Conversion (%) |
|-------|---------------------|----------------|
| 1     | TMA-HV <sup>4</sup> | 6              |
| 2     | TEA-HV              | 93             |
| 3     | TPra-HV             | 96             |
| 4     | TBA-HV <sup>3</sup> | >99            |
| 5     | TPeA-HV             | 96             |
| 6     | THA-HV <sup>3</sup> | 94             |

Reaction conditions: 0.005 mmol [Rh(cod)<sub>2</sub>][BF<sub>4</sub>], 0.3 mmol acetophenone, 1.6 mmol HCOOH, 0.5 mL solvent, T = 80 °C, t = 3 h

In order to compare the catalyst systems, several d<sup>8</sup>-metal complexes were tested as catalyst precursor. It was revealed that the highest conversion could be achieved by the use of [Rh(cod)<sub>2</sub>][BF<sub>4</sub>] (Table 3).

Table 3 Transfer hydrogenation of acetophenone in [TBA][HV] using different catalyst precursors

| Entry | Catalyst                                                                   | Conversion (%) | TON |
|-------|----------------------------------------------------------------------------|----------------|-----|
| 1     | CIRh(PPh <sub>3</sub> ) <sub>3</sub>                                       | 92             | 55  |
| 2     | [Rh(cod)Cl] <sub>2</sub>                                                   | 93             | 56  |
| 3     | Pd(OAc) <sub>2</sub>                                                       | 38             | 23  |
| 4     | [Rh(cod) <sub>2</sub> ][BF <sub>4</sub> ]                                  | > 99           | 60  |
| 5     | [Rh(cod) <sub>2</sub> ][SbF <sub>6</sub> ]                                 | 97             | 58  |
| 6     | [Rh(cod) <sub>2</sub> ][Ph(CF <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub> B | 86             | 52  |
| 7     | Shvo-catalyst <sup>6</sup>                                                 | 34             | 21  |

Reaction conditions: 0.005 mmol catalyst, 0.3 mmol acetophenone, 1.6 mmol HCOOH, 0.5 mL ionic liquid, T = 80 °C, t = 3 h;  
<sup>a</sup> ([2,3,4,5-(C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>N<sup>+</sup>-C<sub>6</sub>COO]<sup>-</sup>)(Bu<sub>4</sub>CO)<sub>2</sub>μ-H

Table 4 Transfer hydrogenation of acetophenone using different hydrogen donors

| Entry | Hydrogen donor       | Conversion (%) |
|-------|----------------------|----------------|
| 1     | HCOOH                | >99            |
| 2     | NaHCOO               | >99            |
| 3     | KHCOO                | 89             |
| 4     | NH <sub>4</sub> HCOO | 0              |
| 5     | iPrOH                | 0              |

Reaction conditions: 0.005 mmol [Rh(cod)<sub>2</sub>][BF<sub>4</sub>], 0.3 mmol acetophenone, 1.6 mmol H-donor, 0.5 mL TBA-HV, T = 80 °C, t = 3 h

The investigation of various hydrogen donors showed that the highest conversion could be achieved in the presence of HCOOH and NaHCOO<sup>6</sup>, respectively (Table 4). Since HCOOH is a proposed bio-based H-source<sup>6</sup> it was chosen as H-donor for the further experiments.

The effect of the HCOOH:acetophenone molar ratio on the reaction rate was significant, a conversion plateau was reached when the molar ratio was between 5:1 and 6:1 (Fig. 1). Over 8:1 ratio, the conversion decreased under 20% due to the increased acidity of the system, which results in the loss of activity of the catalyst.<sup>7</sup>

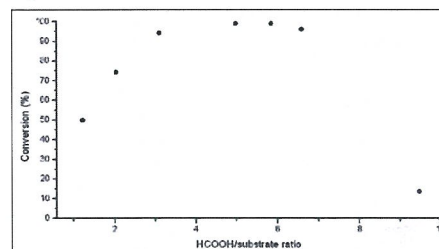
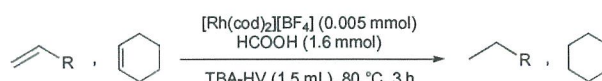


Fig. 1 Effect of H-donor and substrate ratio on the conversion

Contrary to the experiments using GVL-based ILs in high pressure hydrogenation,<sup>4</sup> with phosphine ligand addition the conversion could not be increased. In the presence of 10 eqv. triphenyl phosphine there was 58 % conversion after 3 hours, while with its sulfonated form (TPPTS) only 6 % product was obtained.

Terminal olefins and cyclohexene were also successfully hydrogenated (Scheme 3) in the presence of [Rh(cod)<sub>2</sub>][BF<sub>4</sub>] in TBA-HV.



Scheme 3 Transfer hydrogenation of olefins, R: C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>13</sub>, C<sub>8</sub>H<sub>17</sub>

## Conclusion

$\gamma$ -valerolactone-based ionic liquids were successfully used as reaction media for catalytic transfer hydrogenation of acetophenone, linear and cyclic olefins. It was revealed that the highest conversion can be obtained by the use of [Rh(cod)<sub>2</sub>][BF<sub>4</sub>] precursor in the presence of HCOOH in TBA-HV.

## Acknowledgment

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## References

- Anastas, P.T.; Wasserscheid, P.; Stark, A. Green Solvents, Ionic Liquids, *Handbook of Green Chemistry*, Vol. 6., Wiley-VCH, 2013.
- Baán, Z.; Finta, Z.; Keglevich, G.; Hermecz, I. *Green Chem.* **2009**, *11*, 1937.
- (a) Fegyverneki, D.; Orha, L.; Láng, G.; Horváth, I.T. *Tetrahedron*, **2010**, *66*, 1078.
- Strádí, A.; Molnár, M.; Óvári, M.; Dibó, G.; Richter, F. U.; Mika, L. T. *Green Chem.* **2013**, *15*, 1857.
- Horváth, I. T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L. T. *Green Chem.* **2008**, *10*, 238.
- R. Xing, W. Qi and G. W. Huber, *Energy Environ. Sci.*, **2011**, *4*, 2193–2205
- Joó, F. *Aqueous Organometallic Catalysis*, Kluwer Academic Press, **2001**