Tetrabutylphosphonium bromide: a versatile ionic liquid catalyst for the bio-based production of butadiene and acrylic acid

Stalpaert, M.,[a] **Cirujano, F. G.,**[a] **De Vos, D. E.**[a,]*

[a]*Center for Surface Chemistry and Catalysis, KU Leuven, Leuven, 3000, Belgium*
**Corresponding author: dirk.devos@kuleuven.be*

Abstract: The ionic liquid tetrabutylphosphonium bromide, combined with an acid cocatalyst, is an excellent catalyst for dehydration of various substrates. Interestingly, we have discovered that the mechanism is clearly different from purely acid catalyzed dehydration, As a result, increased selectivities to valuable products are obtained. We have focused on two promising reactions for the bio-based production of important monomers, the dehydration of 1,4-butanediol to 1,3-butadiene and the rearrangement of lactide to acrylic acid. Despite working in much milder conditions than for acid catalyzed dehydration, we were able to obtain similar (70% acrylic acid) or greatly increased (94% butadiene) yields.

Keywords: ionic liquid, butadiene, lactic acid.

1. Introduction

Due to the high oxygen functionality of biomass, the valorization of renewable substrates to valuable chemicals requires deoxygenation reactions, such as the dehydration reaction. Recently, different groups have investigated the production of 1,3-butadiene[1] and acrylic acid[2] through dehydration of 1,4-butanediol (BDO) and acrylic acid respectively. Since BDO and acrylic acid can be produced on a large scale through fermentation from bio-based sources, these reactions would allow an attractive, green production of butadiene and acrylic acid, two highly important polymer precursors which are now generally produced from fossil fuels.[1–3] Most research on these dehydration reactions has focused on the use of solid acid catalysts in gas phase reactions. The main disadvantages of these gas phase reactions are high energy consumption, due to high temperatures and diluted aqueous feeds, and low yields, due to acid catalyzed side reactions. Here, we report the use of the ionic liquid tetrabutylphosphonium bromide, together with an acid cocatalyst, as a dehydration catalyst that manages to sidestep this issues because of its distinct reaction mechanism.

2. Experimental

In a typical reaction 0.25 mmol DL-lactide or 0.5 mmol of another substrate was weighed into a glass vial. 1.7 mmol tetrabutylphosphonium bromide (Bu_4PBr), 0.5 mmol of the internal standards hexane and tetradecane and the appropriate amount of other additives was added. The mixture was then heated to 200 °C under a N_2 atmosphere with stirring at 500 rpm. After the reaction, the mixture was cooled on ice and, in the reactions of lactide, a gas phase sample was taken using a syringe. Next, the ionic liquid, was extracted with mesitylene and a sample of the mesitylene layer was taken. After derivatization with BSTFA, another sample of the mesitylene layer was taken. Gas phase samples were analyzed using FTIR spectroscopy, liquid phase samples by gas chromatography coupled with mass spectroscopy.

3. Results and discussion

First, we have shown the activity of Bu_4PBr, combined with an acid cocatalyst, for the dehydration of diols, interestingly leading to selective formation of conjugated dienes.[4] This selectivity is clearly different from purely acid catalyzed dehydrations where typically aldehydes or cyclic ethers are formed depending on the diol, indicating that a different reaction mechanism is at play. We investigated the reaction system and discovered an unusual mechanism consisting of two steps, in both of which the bromide anion plays an important role. The first step is an acid catalyzed bromide substitution, followed by a bromide catalyzed dehydrobromination in the second step (see Figure 1). We have shown that for a broad scope of diols, typical acid catalyzed side products are largely avoided and conjugated dienes are formed in good to excellent yields. We focused on the very promising dehydration of 1,4-butanediol to 1,3-butadiene. Optimizing the conditions for this substrate by increasing the temperature and acid content led to an excellent 94% yield of butadiene at 100% conversion after only 2 hours. The Bu_4PBr system significantly outperforms acid catalyzed gas phase dehydrations, where the cyclodehydration to tetrahydrofuran is problematic.

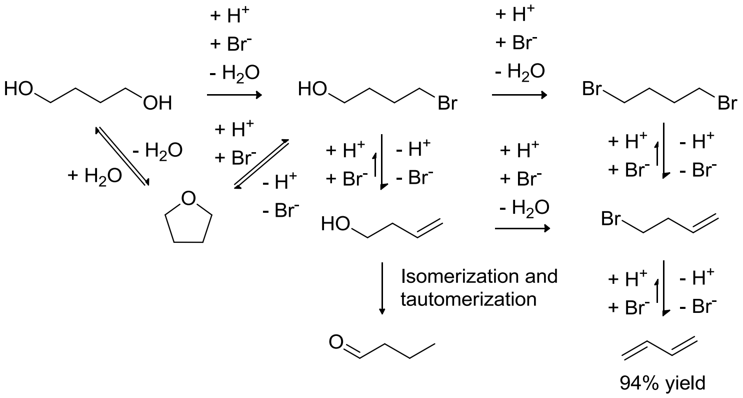

Figure 1 Proposed reaction network for the dehydration of 1,4-butanediol to 1,3-butadiene catalysed by Bu_4PBr and an acid.

Another promising reaction for biomass valorization is the dehydration of lactic acid to acrylic acid. Here again, the Bu_4PBr system proves to be an interesting alternative for gas phase dehydration over solid acid catalysts, where important issues such as high temperatures, dilute lactic acid feeds and mediocre yields (around 60%) persist. By using a combination of gas and liquid phase analysis, we managed to identify and quantify some so far unreported volatile side products. As a result, we could close the mass balance, which up to now was problematic in literature.[5] A reaction network was mapped out, which provided insights in the parameters that control side reactions. Lowering the amount of acid cocatalyst and minimizing the water content in the system, by using lactide as substrate and 98% H_2SO_4 as acid, allowed to increase the acrylic acid yield to 70% at 98% conversion of the cyclic dimer lactide. This result outperforms most gas phase reactions in much milder conditions.

4. Conclusions

In conclusion, the ionic liquid Bu_4PBr is an innovative and highly performant catalyst for the valorization of various renewable substrates, including 1,4-butanediol and lactide. Very good to excellent yields of the important monomers acrylic acid and butadiene can be achieved in mild conditions. This system combines a high solubility for bio-based compounds, excellent stability, high reaction rates, and easy product separation. Furthermore, we are currently working on further extending the substrate scope of the catalytic system by combining it with other catalysts.

References

1. E. V Makshina, M. Dusselier, W. Janssens, J. Degrève, P. A. Jacobs and B. F. Sels, Chem. Soc. Rev. (2014) 43.
2. Y. Fan, C. Zhou and X. Zhu, Catal. Rev. (2009) 51.
3. H. Yim, R. Haselbeck, W. Niu, C. Pujol-Baxley, A. Burgard, J. Boldt, J. Khandurina, J. D. Trawick, R. E. Osterhout, R. Stephen, J. Estadilla, S. Teisan, H. B. Schreyer, S. Andrae, T. H. Yang, S. Y. Lee, M. J. Burk and S. Van Dien, Nat. Chem. Biol. (2011) 7.
4. M. Stalpaert, F. G. Cirujano and D. E. De Vos, ACS Catal. (2017).
5. F. G. Terrade, J. van Krieken, B. J. V. Verkuijl and E. Bouwman, ChemSusChem (2017) 10.