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Phosphonium ionic liquids as catalytic solvents for the bio-based production of alkenes, dienes and acrylic acid

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PURPOSE OF THE ABSTRACT

The global use of fossil feedstocks as the main resource for the production of energy, chemicals and materials results in several issues, most importantly global warming. Consequently, research on alternative resources has become increasingly important in recent years. While for energy needs several possibilities are available, biomass is likely the only realistic option for the sustainable production of chemicals. The components of biomass generally have a high oxygen functionalization degree compared to common industrial chemicals and, as a result, deoxygenation reactions are required. The most common functionality in (hemi)cellulosic compounds is the hydroxy group, hence, this is an ideal target for deoxygenation reactions. In our work, we have focused on dehydroxylation reactions that lead to fully dehydroxylated products with unsaturated carbon-carbon (C=C) bonds, i.e. to alkenes, dienes or unsaturated acids. While producing these unsaturated compounds selectively is more challenging, the presence of the C=C bond(s) in the product is an added value, since it allows for (re)functionalization and/or polymerization reactions. We have discovered that several phosphonium ionic liquids (ILs), most importantly tetrabutylphosphonium bromide (Bu₄PBr), are active catalytic solvents for dehydration reactions in the presence of an acidic co-catalyst.[1] Compared to other ILs, Bu₄PBr results in higher rates, increased stability and an extended substrate scope.[2,3]

First, we have applied this system in the dehydration of several diols, which leads to dienes with decent to excellent selectivity. This is in sharp contrast with purely acid catalyzed dehydrations, which tend to lead to aldehydes, ketones or cyclodehydrated products depending on the substrate.[1] This can be explained by the distinct reaction mechanism, which consists of two steps in both of which the bromide anion of the IL plays a different, important role. The system was optimized for the double dehydration of 1,4-butanediol, which can be produced from biomass by fermentation, to 1,3-butadiene, one of the most important industrial monomers. The typical pitfall in this reaction, i.e. cyclodehydration to tetrahydrofuran, was largely avoided, and butadiene was produced in a 94% yield after 2 hours. Next, we investigated the transformation of lactic acid and lactide, which are available from large scale fermentation processes, to acrylic acid, another important monomer.[4] The carboxylic acid group of lactic acid renders this dehydration more challenging. Not only does it slow down the dehydration; it is also prone to decarboxylation and decarbonylation side reactions to volatile side products. As a result, combined gas and liquid phase analysis was required to complete the mass balance. An optimal yield of 70% acrylic acid could be reached from lactide by minimizing the amount of acid and water in the system. The main advantage of the Bu₄PBr system for the aforementioned reactions is the much lower reaction temperature (200°C) that is applied. For comparison, most reports on the dehydration of 1,4-butanediol or lactic acid involve gas phase reactions of dilute aqueous solutions at 300°C or higher. As a result, these processes are very energy intensive. Furthermore, compared to the gas phase systems, the yields are high for acrylic acid and even the highest reported for butadiene. Finally, we have recently expanded the scope of the system to allow full

deoxygenation of other substrates, such as sugar alcohols, to unsaturated compounds, e.g. olefins.

FIGURES

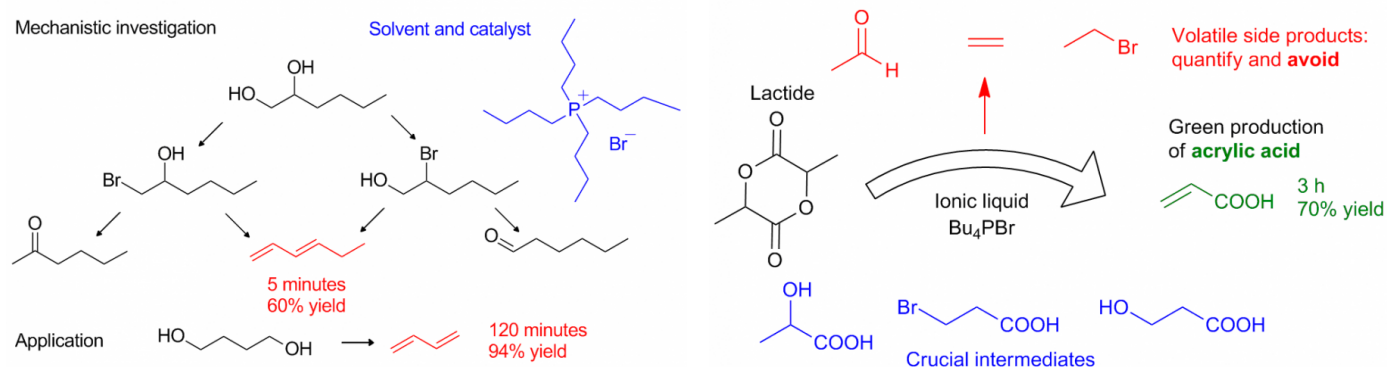


FIGURE 1

Dehydration of diols

Tetrabutylphosphonium bromide catalyzed dehydration of diols: mechanism for 1,2-hexanediol and application in production of butadiene

FIGURE 2

Rearrangement of lactide

Tetrabutylphosphonium bromide catalyzes the rearrangement of lactide in relatively mild conditions

KEYWORDS

ionic liquids | deoxygenation | polyols | lactic acid

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