

Hydroxycarbonylation of olefins and alcohols in ionic liquids

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Transition metal catalysed hydroxycarbonylation of olefins and alcohols is direct one step route for the synthesis of carboxylic acids and esters. However, separation of the product from the catalyst is a serious problem in hydroxycarbonylation as well as in other homogeneous catalytic reactions. A number of ways of overcoming this drawback have been proposed, in particular, immobilising catalyst in water, perfluorated solvents, the use of $scCO_2$. Another promising class of new media are molten salts or ionic liquids. They are good solvents for transition metal complexes and are poorly miscible with non-polar organics such as alkanes and ethers, allowing the formation of two-phase systems.

There have been a few publications on catalytic carbonylation in ionic liquids media and only a little devoted to palladium-catalysed hydroxycarbonylation of olefins and alcohols. We found that olefins and alcohols can be converted into the corresponding acids under CO atmosphere in the presence of palladium catalysts in ionic liquids media. Terminal and internal olefins, cyclohexene, styrene, methanol, ethanol, n-butanol, cyclohexanol, benzyl alcohol and 1-phenylethanol were tested as substrate for carbonylation. A number of molten salts were applied as a reaction medium and tetrabutylammonium bromide (m.p. 103°C) seemed to be the best. Carbon monoxide pressure of 20 atm and reaction temperature of 110°C are suitable conditions to furnish the reaction in 2 hours. The most striking result is high activity of phosphine-free catalyst derived from palladium acetate as a precursor. Moreover, adding phosphine decreased the reaction rate. The critical role of counter anion in molten salt was also recognized. Yield of acids decreased in the order: $Br^- > Cl^- > BF_4^- \approx PF_6^-$. A two-route reaction scheme is proposed to explain the regularities of 1-phenylethanol hydroxycarbonylation. The catalytic system can be used repeatedly by simple extraction of products with diethyl ether. Nine cycles were carried out without loss of activity.