DOI: 10.1002/adsc.200900280

Imidazolium-2-Carboxylate as an Efficient, Expeditious and Eco-Friendly Organocatalyst for Glycerol Carbonate Synthesis

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Received: April 21, 2009; Revised: June 2, 2009; Published online: July 27, 2009

Dedicated to Dr. Danielle Ballivet-Tkatchenko and Dr. Igor Tkatchenko.

Abstract: An improved and greener approach towards the synthesis of glycerol carbonate, *via* transesterification, using 1-*n*-butyl-3-methylimidazolium-2-carboxylate as catalyst is described. The catalyst loading as low as 1% was sufficient to yield quantitative conversions. A plausible mechanism is proposed for the catalytic cycle leading to product formation.

Keywords: dimethyl carbonate; glycerol carbonate; imidazolium-2-carboxylates; organic catalysis; transesterification

The effective utilization of the glycerol that is formed in huge amounts during the production of biodiesel is a key factor to promote biodiesel commercialization and further development. Therefore, using glycerol for the synthesis of value-added chemicals is of great industrial importance. Among these, one of the useful transformations of glycerol is the synthesis of cyclic carbonates *viz.* glycerol carbonate.[1]

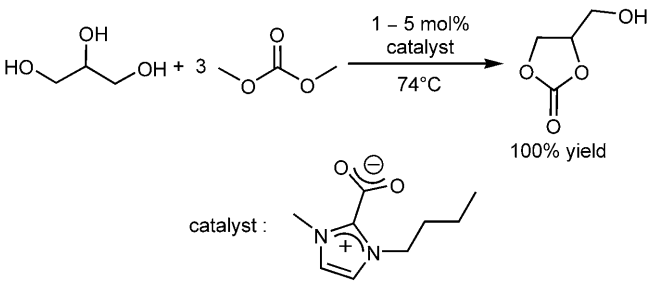
Cyclic carbonates have been widely used as excellent solvents, precursors for polymeric materials, chemical intermediates for pharmaceuticals and many other biomedical applications.[2] They are stable, polar compounds and for this reason they offer useful applications such as components for gas separation membranes or polyurethane foams, a surfactant component, a non-volatile solvent for paint industries, coatings, polycarbonates and additives for detergents.[3] In addition, the multi-electrophilic ability of glycerol carbonate was lucratively utilized for thio-functionalized C-3 synthons.[4]

Several methods have been described for the synthesis of this versatile molecule, including reaction of glycerol with the hazardous phosgene[5] or carbon monoxide and oxygen at a high pressure in the presence of a copper-based catalyst.[6] The carboxylation of glycerol with carbon dioxide by an Sn catalyst, zeolites or ion-exchange resins is also reported.[7] Recently, Kim et al. demonstrated *Candida antarctica* lipase as the first enzymatic example for glycerol carbonate synthesis.[8] Drawbacks pertaining to some of these methods in terms of cost and environmental feasibility is the major issue for the commercialization of glycerol carbonate. Finding a new direct route would be very welcome, as it would avoid multi-step processes reducing energy and waste. In this respect, an interesting method described in the literature is the transesterification from organic carbonates employing homogeneous or heterogeneous catalysts.[9] For example, Rokicki et al. demonstrated the use of the heterogeneous base K_2CO_3 as an efficient catalyst for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate (DMC).[10]

In the search for an alternative homogeneous catalyst for for this transesterification approach, we initiated our investigations using 1-*n*-butyl-3-methylimidazolium-2-carboxylate (BMIM-2-CO_2) as catalyst.

Indeed, imidazolium-2-carboxylates have been extensively studied in our laboratory for their easy synthesis with high yields from the reaction of dimethyl carbonate (DMC) with imidazoles.[11] They are convenient precursors of halide-free ionic liquids[12] or of ligands in organometallic catalysis.[13] Moreover, they can act as organocatalysts in reactions such as oligomerization of isocyanates[14a,b] or as carbon dioxide transfer agents in the formation of ketoacetates,[14c,d] carboxylation of epoxides[14e] or the formation of 5-methylene-1,3-dioxolan-2-ones from propargylic alcohols.[14f] We report here our initial results in the use of such species for the transesterification of glycerol.

Glycerol indeed reacts rapidly with 3.2 equivalents of DMC in the presence of 5 mol% of catalyst, BMIM-2-CO_2, to afford quantitatively glycerol car-



Scheme 1. Synthesis of glycerol carbonate using BMIM-2-CO_2 as catalyst.

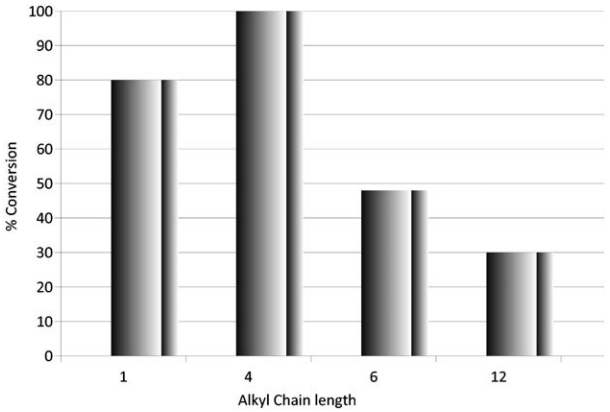


Figure 1. Effect of alkyl chain length on the extent of conversion of glycerol to glycerol carbonate at 74 °C.

bonate within 30 min at 74 °C (Scheme 1). It is noteworthy that this single-pot reaction does not lead to any side products. To the best of our knowledge, this is the first example of an expeditious protocol towards the formation of glycerol carbonate ever reported in the literature. Moreover, with catalyst loading as low as 1 mol%, NMR monitoring of the reaction showed a complete conversion in the product after 80 min. This result outshines the use of K_2CO_3 which requires 3 h heating at the same temperature with a catalyst loading of 3 mol% to reach full conversion.[10]

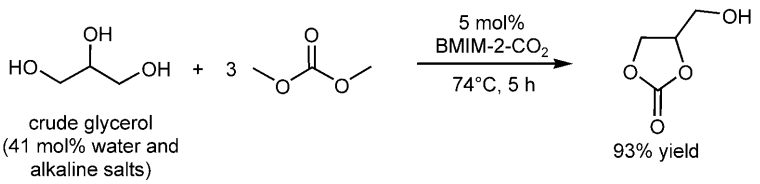
Noting that the reaction conditions used above are very close to those used for the synthesis of 1,3-dialkylimidazolium-2-carboxylates, *viz.* the presence of an excess of DMC in an alcoholic solvent,[11,12d] we anticipated that the formation of the catalyst could be performed *in situ.* Under the same experimental conditions, the reaction was thus executed using 5 mol% of 1-*n*-butylimidazole as catalyst. As compared to 5 mol% of BMIM-2-CO_2 that gave quantitative conversion on NMR within 30 min, no product formation was seen in 30 min. In fact it took a longer time to initiate the process as 55% product formation was seen after 3 h. The observation of an induction period together with an overall less efficient process corelate well with the *in situ* formation of BMIM-2-CO_2 during the course of the reaction. An additional argument to support this hypothesis comes from the systematic study wherein we tried to find the intricacy of the reaction progress. We have indeed studied the effect of the length of the alkyl side chain of the 1-alkylimidazole, by using imidazoles with varying chain lengths, *viz*. methyl, *n*-butyl, *n*-hexyl and *n*-dodecyl under the same conditions. The reaction was performed with 5 mol% of these catalysts for 12 h and the results are summarized in Figure 1. It is noteworthy that increasing the chain length proved detrimental to the extent of conversion as ^{1}H NMR of the crude reaction mixtures revealed the presence of 80, 100, 48 and 30% of glycerol carbonate for 1-methyl-, 1-*n*-butyl-, 1-*n*-hexyl- and 1-*n*-dodecyl-imidazoles, respectively.

The best catalyst was thus found to be 1-*n*-butylimidazole rather than higher alkyl derivatives. This can be explained as the 2-carboxylate form is less easily obtained by reaction with DMC for increasing chain length and hence is less available for the catalytic reaction.[15] Regarding the lower conversion observed with 1-methylimidazole, we assume that the higher stability of the easily obtained 1,3-dimethylimidazolium-2-carboxylate is detrimental to its reactivity. It should be noted that the reaction was also carried without the catalyst but no product formation was seen on NMR even after 24 h under the reaction conditions.

Hence it is evident that imidazolium-2-carboxylates play an important role to initiate the reaction. Although the exact mechanism of the reaction remains unclear, the formation of the target compound glycerol carbonate can be tentatively rationalized by an *in situ* decarboxylation of imidazolium-2-carboxylates to generate a free N-heterocyclic carbene, the latter being known to promote the transesterification between alcohols and organic esters.[16]

Finally, it is also worthy of mention that our catalyst is efficient on glycerol originating directly from a biodiesel production plant (Scheme 2).[17] Indeed, using 5 mol% BMIM-2-CO_2 allowed us to convert unpurified glycerol into glycerol carbonate with 93% yield after 5 h. This strongly contrasts with the K_2CO_3 system which requires pure glycerol containing less than 2% water.[10]

In summary, we have developed a one-pot, high-yielding synthetic protocol for glycerol carbonate using 1-*n*-butyl-3-methylimidazolium-2-carboxylate as organocatalyst without by-product formation. The most important feature of this methodology can be attributed to the use of catalyst loading as low as 1 mol% for quantitative yields of the product and to the ability of the catalyst to transform raw glycerol. Thus, this simple methodology would be a practical alternative to the existing procedures to cater to the



Scheme 2. Synthesis of glycerol carbonate from crude glycerol coming from a biodiesel production plant.[17]

need of industries. The application of this method in the synthesis of other derivatives of glycerol and higher alcohols is currently underway in our laboratory and will be reported in due course. Further studies regarding the mechanism of the reaction and specially the identification of the reactive intermediates are in progress.

Experimental Section

General Procedure for the Synthesis of Glycerol Carbonate

To a biphasic mixture of glycerol (2.66 g, 28.91 mmol) and DMC (7.84 mL, 93.11 mmol) was added 1-*n*-butyl-3-methylimidazolium-2-carboxylate[12d] (0.053 g, 1 mol%) under an inert atmosphere. The reaction was heated at 74 °C with stirring for 80 min, rapidly becoming homogeneous. The volatile organics were evaporated and dried under vacuum to yield 99% pure product as determined by ^{1}H NMR. ^{1}H NMR (DMSO-d_6, 300 MHz): $\delta = 3.52$ (dd, 1H, $J_1 = 3$ Hz, $J_2 = 12$ Hz, H-2), 3.68 (dd, 1H, $J_1 = 3$ Hz, $J_2 = 12$ Hz, H-2), 4.29 (m, 1H, H-4), 4.49 (t, 1H, $J = 7.5$ Hz, H-4), 4.79 (m, 1H, H-3), 5.29 (bs, 1H, OH); ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): $\delta = 60.5$ (C-2), 65.8 (C-4), 77.0 (C-3), 155.2 (C-1); IR (ATR, neat): $\nu = 3437$, 2932, 1763, 1168 cm^{-1}; IR (NaCl windows, film): $\nu = 3386$, 2931, 1790, 1181 cm^{-1}.

Acknowledgements

The authors thank CNRS, Université de Bourgogne and Region Bourgogne for support and for a postdoctoral fellowship to PN. We also gratefully acknowledge Diester Industrie for generously providing crude glycerol.

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