



## CO<sub>2</sub> cycloaddition to limonene diepoxide: catalysis, kinetics and mass transfer

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### Significance and Relevance

In this work, the reaction kinetics and mechanism of the CO<sub>2</sub> cycloaddition of limonene diepoxide as well as the mass transfer of CO<sub>2</sub> as a function of the conversion, temperature and pressure have been unveiled for the first time. The reaction proceeds via a consecutive mechanism in the presence of homogeneous and grafted catalysts via the formation of a mono-carbonate intermediate. The final product, i.e. limonene dicarbonate can find application as a building block for the synthesis of isocyanate-free polyurethanes.

*Preferred and 2<sup>nd</sup> choice for the topic: CO<sub>2</sub> utilization and recycling, Green chemistry and biomass transformation*

*Preferred presentation: Oral preferred*

### Introduction and Motivations

Limonene is an abundant and cost-effective renewable chemical with a global annual production of approximately 70 kt (2017). Thanks to its very special chemical structure, it can be further functionalized to obtain different monomers for the production of biomaterials<sup>1</sup>. For instance, limonene diepoxide is a promising precursor for the synthesis of non-isocyanate polyurethanes (NIPU). The catalyzed cycloaddition of CO<sub>2</sub> to limonene diepoxide produces a bifunctional five-membered cyclic carbonate i.e., limonene decarbonate (LDC) which is particularly interesting as the precursor of NIPU<sup>2</sup>.

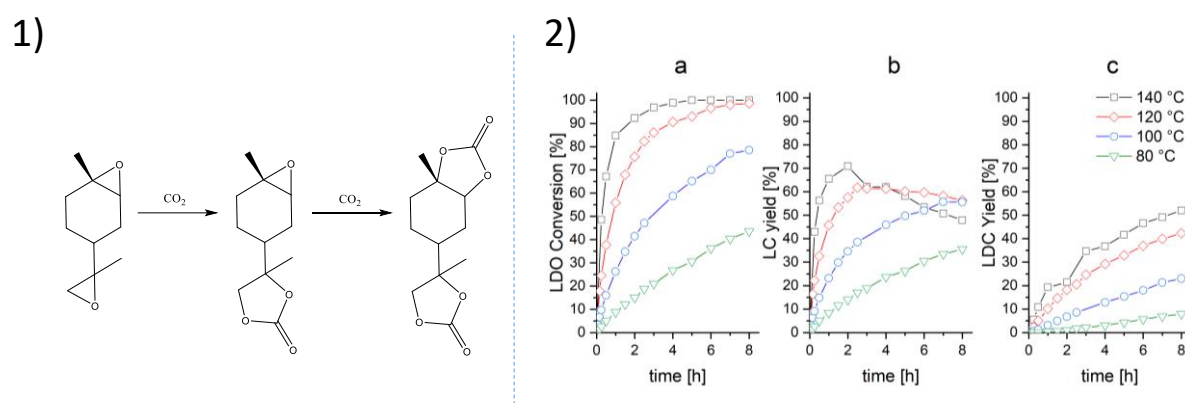
In this work, the carbonation of limonene diepoxide was performed in a stainless-steel reactor autoclave (Parr) under solvent-free conditions, at relatively high temperatures and CO<sub>2</sub> pressures and in the presence of homogeneous and heterogenized catalysts. Different quaternary ammonium salt halides were tested both in the homogeneous phase and grafted on SiO<sub>2</sub>-based supports, and very precise kinetic studies were conducted with the best catalyst by varying the operating parameters. The solubility of CO<sub>2</sub> in the reaction medium was measured at different temperatures and pressures and the gas-liquid mass transfer coefficients were evaluated.

### Materials and Methods

The carbonation of limonene diepoxide (LDO, Nitrochemie), was performed in a stainless-steel reactor autoclave (Parr) in solvent-free mode, at relatively high temperature and pressure of CO<sub>2</sub> and in the presence of homogeneous and heterogenized catalysts. Different homogeneous i.e., quaternary ammonium salt halides and heterogeneous catalysts i.e., SiO<sub>2</sub>-based grafted catalysts were tested. Very precise kinetic studies were conducted with the best catalyst by varying the reaction temperature (80-140 °C), CO<sub>2</sub> pressure (20-50 bar), catalyst loading (1.5-10 wt%) and stirring rate (400-800 rpm). The reaction products were purified with column chromatography and identified by <sup>1</sup>H- and <sup>13</sup>C-NMR as well as by GC-MS. The purified reaction products were utilized as standards for the calibration of the gas chromatographic (GC) method. The limonene diepoxide conversion and the products yields were analyzed with GC (DB-5 60m 0.32 mm column, and flame ionization detector). The solubilities of CO<sub>2</sub> in LDO and LDC were measured at different temperatures and pressures and the gas-liquid mass transfer coefficients were estimated with MATLAB software. Finally, density and viscosity of the reaction mixture were measured as a function of temperature and time of reaction.

## Results and Discussion

The systematic kinetic experiments were conducted with tetrabutylammonium chloride (TBAC) as the catalyst, being the most active among the ones screened. The carbonation of LDO with CO<sub>2</sub> follows a consecutive mechanism through the formation of a monocarbonate intermediate (LC), as displayed in Figure 1.1, being in agreement with the study of Mikšovský et al.<sup>2</sup>. As shown in Figure 1.2, complete conversion of LDO was reached after five hours at the highest reaction temperature and it increases with temperature. The yield of the intermediate LC over time has a maximum while the yield of the dicarbonate product LDC has an inflection point, which are both more pronounced at higher temperatures. As revealed by the kinetic experiments, the reaction temperature and the catalyst amount had a strong influence on both the reactant conversion and the product yields. Varying the CO<sub>2</sub> pressure, it was observed that the two consecutive reactions had a different dependence respect to the CO<sub>2</sub> concentration. Namely, the first reaction showed a zero reaction order with respect to CO<sub>2</sub> while the second one a first reaction order. This behavior can be explained by the variation of the solubility of CO<sub>2</sub> in the reaction media, which is higher at the beginning to then decrease. As a matter of fact, both the pressure and the temperature influenced the absorption of CO<sub>2</sub> in pure LDO and in the reaction mixture at 50% and 100% conversion of LDO. In particular, it decreased by increasing the conversion of LDO and the temperature of the system and increased by increasing the pressure of CO<sub>2</sub>. The limonene dicarbonate was successfully separated from the reaction mixture by crystallization and subsequently fully characterized by NMR, IR and DSC.



**Figure 1.** Reaction scheme of limonene dioxide carbonation (1). Temperature effect on the kinetics of CO<sub>2</sub> cycloaddition of limonene diepoxide (2).

## References

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