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The CO₂ addition over diols promoted by DBU/alkylating agent dual systems for the synthesis of cyclic and linear carbonates under mild conditions

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PURPOSE OF THE ABSTRACT

The present research aims at investigating in details the reaction between carbon dioxide and a diol to afford cyclic and acyclic carbonates in moderate to good yields. Thanks to its chemical structure, CO₂ has been identified as a promising reagent for the synthesis of organic carbonates as it is non-toxic, cheap and an abundant C1 renewable feedstock [1], and could potentially replace phosgene based carbonates produced industrially. Prior research has been focused on the epoxide/CO₂ coupling to afford cyclic carbonates in good yields [2]. Yet, this coupling suffers from limitations such as restricted substrates and exclusive synthesis of 5 membered cyclic carbonates. In order to extend the products availability through Carbon Dioxide Utilization, more recent research has been carried out with new substrates such as the use of diols [3-5]. Although many different catalysts and reaction routes have already been investigated, efforts are still needed to identify cheaper and more efficient protocols for the selective synthesis of cyclic and acyclic carbonates from the coupling of CO₂ with diols. In this context, the use of organic bases/alkylating agent dual system as promoters and low pressure and temperature conditions (P<1MPa, r.t) seems to be a good alternative to afford organic carbonates.

The present work aims at providing, thanks to an in-situ ATR-IR spectroscopy monitoring, a detailed understanding of the synthesis of propylene carbonate from propylene glycol and CO₂ promoted by DBU and the addition of alkyl halides. This analytical tool enabled to identify several reaction intermediates and to determine how the kinetic profiles, the reaction yields, and the selectivity of the reaction evolves with various parameters (pressure, temperature and nature of the base and alkyl halide). Thus, several experimental conditions have been tested as well as various alkyl halides in order to understand in details the effect on the selectivity and the efficiency of the reaction. Different substrates were also tested such as 1,x diols (2 ? x ? 4) and Isosorbide. The selectivity toward cyclic or biscarbonated compounds is discussed.

Density Functional Theory (DFT) was also performed in this work to understand and validate the reaction pathways proposed via ATR-IR monitoring. Structures of transition states were optimized and comparisons between several reagents and/or paths were calculated, giving capital information about further enhancement of the CO₂-diol conversion into carbonates.

FIGURES

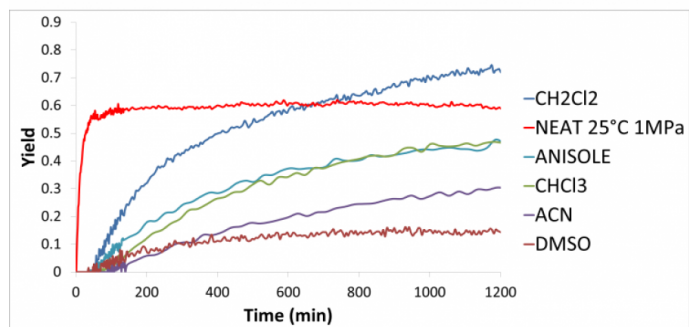


FIGURE 1

In-situ ATR-IR spectroscopy:

Kinetic profiles of the C=O absorption band of propylene carbonate for different solvent conditions

FIGURE 2

KEYWORDS

CO₂ valorisation | Organic carbonates | In situ spectroscopy | DFT calculation

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