



16th INTERNATIONAL CONFERENCE ON CARBON DIOXIDE UTILIZATION

A detailed investigation of CO₂ addition over diols promoted by organic bases: toward greener cyclic carbonates

A. Brège^{*1,2}, R. Méreau¹, B. Grignard², C. Detrembleur², C. Jérôme², T. Tassaing¹

¹Institut des Sciences Moléculaires, UMR 5255 CNRS Université Bordeaux, F-33405 Talence Cedex, France

²Center for Education and Research on Macromolecules, Université de Liège, 4000 LIEGE, Belgium

*Corresponding author: antoine.brege@u-bordeaux.fr

Keywords: CO₂ utilization, diols, cyclic carbonates, metal-free, ATR-IR, DFT

The present research aims at investigating in details the reaction between carbon dioxide and a diol to afford cyclic carbonates in moderate to good yields. Prior research have been focused on catalytic systems involving metal compounds (e.g CeO₂ ; Cs₂CO₃ ; Bu₂Sn(OMe)₂) in combination with dehydration systems (e.g MeCN ; 2-Cyanopyridine, molecular sieves) giving from poor to good yields in optimized conditions (up to full conversion of alcohol into organic carbonates)^{1,2}.

In addition to the use of carbon dioxide as a non-toxic, cheap and abundant C1 renewable feedstock, more research have been carried out to display greener reagents and milder conditions in order to fulfill the aims of sustainable chemistry. In this context, the use of organic bases as promoters and low pressure and temperature conditions (P<1MPa, r.t) seems to be a good alternative to afford cyclic carbonates^{3,4}. Although many different substrates, 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 carbonates from the coupling of CO₂ with diols.

In this context, 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 organic bases and the addition of alkyl halides. This analytical tool enabled 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 organic bases such as amidines, guanidines and other tertiary amines have been tested as well as various alkyl halides in order to understand in details the effect of the nature of the different promoters

and reactants in the selectivity and the efficiency of the reaction. Different substrates were also tested and the general strategy is presented in Fig. 1.

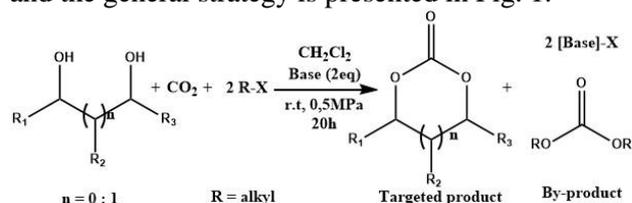


Figure 1 : One-pot/one-step strategy to afford cyclic carbonates

So far, propylene carbonate could be obtained in 70% yield at room temperature, 0.5 MPa, over 20h in a one-pot/one-step reaction. Linear carbonates were also synthesized as by-product of this reaction, leading to more carbon dioxide utilization for organic compounds of great interest.

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

Acknowledgments

We acknowledge the financial support from the “Conseil Régional d’Aquitaine” and the “University of LIEGE” for the PhD fellowship of A. Brege.

References

- [1] Kindermann, N.; Jose, T.; Kleij, A. W., *Top Curr Chem (Cham)* **2017**, *375* (1), 15.
- [2] Honda, M.; Tamura, M.; Nakagawa, Y.; Tomishige, K., *Catal. Sci. Technol.* **2014**, *4* (9), 2830.
- [3] Gregory, G. L.; Ulmann, M.; Buchard, A., *RSC Advances* **2015**, *5* (49), 39404.
- [4] Kitamura, T.; Inoue, Y.; Maeda, T.; Oyamada, J., *Synthetic Communications* **2015**, *46* (1), 39.