

Cyclic Carbonates from Carbon Dioxide and Alcohols: A Density Functional Theory Study on the Reaction Mechanism.

Willem K. Offermans,^{a} Christoph Gürtler,^a Michael North,^b*

Walter Leitner,^c Thomas E. Müller,^a

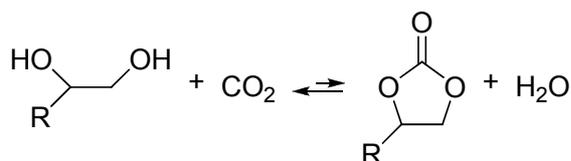
^a *CAT Catalytic Center, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany*

^b *Department of Chemistry, University of York, York, United Kingdom*

^c *Lehrstuhl für Technische Chemie und Petrochemie, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany*

**Willy.Offermans@CatalyticCenter.RWTH-Aachen.de*

Alcohols, such as glycerol or propylene glycol, can react with carbon dioxide to form cyclic carbonates and water (Scheme 1).



Scheme 1: Cyclic carbonates from CO₂ and alcohols

The reaction is equilibrium limited and can be shifted to the right by removing one of the products from the reaction mixture. The use of chemical traps was reported in this context. Acetonitrile, for example, can be hydrolyzed and can consume the water formed as by-product during the reaction.¹ However, the hydrolysis of acetonitrile does not lead to an economically valuable compound and a combination of these two consecutive reactions is not sustainable. It is envisioned that the use of a water permeable membrane will become feasible to overcome this limitation. Membranes are being tested while the search for better catalysts and more sustainable water traps is ongoing.

Several kinds of catalysts, such as CeO₂, MgO, and Sn-compounds were reported to accelerate the reaction of carbon dioxide and alcohols.^{1,2,3} With the focus on more effective and efficient catalysts for the carbonate formation, the presence of several coupled, partially equilibrium-limited reactions might lead to interpretation problems. Any tested catalyst may not only accelerate the formation of carbonates, but also the consecutive reaction of water entrapment.

Thus, we found that zinc-compounds combined with Brønsted acids can catalyze carbonate formation from glycerol and CO₂. It is quite conceivable that this catalytic system can also catalyze the hydrolysis of acetonitrile.

To unravel this ambiguity, we started to model likely reaction mechanisms of the catalyzed reaction of CO₂ and glycerol as well as of the hydrolysis of acetonitrile. Since we suspected that a protic solvent, such as glycerol, will play an important role in elementary steps comprising hydrogen transfer(s), we investigated the hydrolysis in the gas phase and in solution with and without catalyst. The target is to disclose the reaction mechanisms, to calculate the activation barriers for the elementary reaction steps and to calculate free energy changes for all steps. At the end, we intend to link the activity of the investigated catalysts to the actual reaction.

¹ S. Huang, S. Liu, J. Li, N. Zhao, W. Wei, and Y. Sun, *Catalysis Letters* **118**, 290 (2007)

² Y. Du, L.-N. He, and D.-L. Kong, *Cat. Commun.* **9**, 1754 (2008)

³ J. George, Y. Patel, S. M. Pillai, and P. Munshi, *J. Mol. Cat. A: Chem.* **304**, 1 (2009)