Kinetic Studies for the Formation of Glycerol Carbonate from Glycidol and Carbon Dioxide

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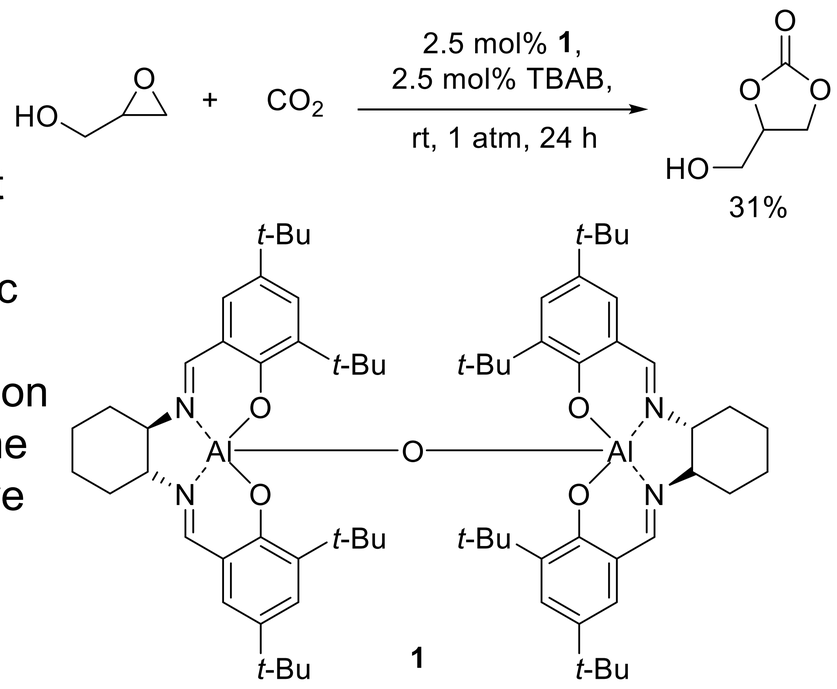
• Introduction

Currently, there is much interest in the utilization of carbon dioxide as a chemical feedstock, both to provide an alternative feedstock to fossil fuels and to help to mitigate global warming. Our group recently developed the synthesis of cyclic carbonates from epoxides and carbon dioxide in the presence of bimetallic aluminium(salen)-based catalyst **1** and tetrabutylammonium bromide (TBAB) at room temperature and atmospheric pressure.[1]

Glycerol carbonate is a target due to both its wide reactivity, numerous synthetic applications and as a means to valorize glycerol, which is becoming widely available as a waste product from bio-diesel production.[2] Under standard reaction conditions, glycerol carbonate is formed from glycidol in only 31% yield (Scheme 1). In order to develop a continuous and efficient process at industrial scales, we have studied the kinetics of the synthesis of glycerol carbonate from glycidol using catalyst **1** under a range of temperatures and pressures. Herein, we present our key results in the field of glycerol carbonate formation from glycidol and CO_2 in the concentration range of catalyst **1** 0.1 mol%-2.5 mol%, temperature range 25-100 °C and CO_2 pressure range 1-100 bar.

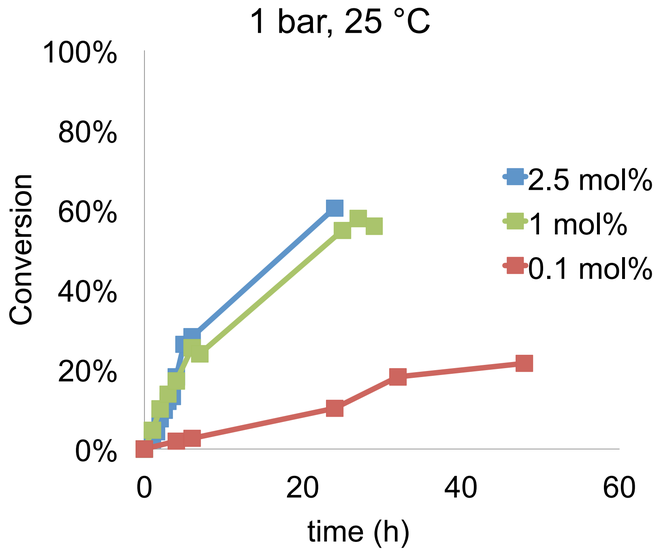


Scheme 1

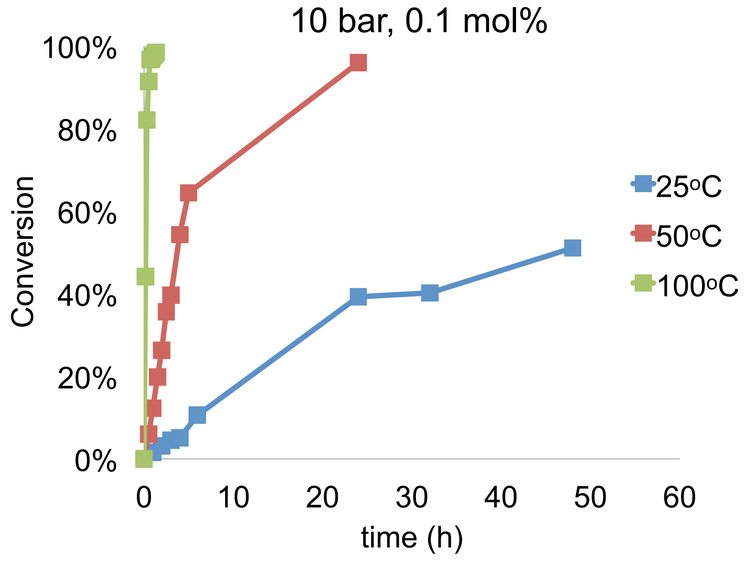
• Results from Kinetic Studies

Representative results from the kinetic study for the formation of glycerol carbonate are shown here.

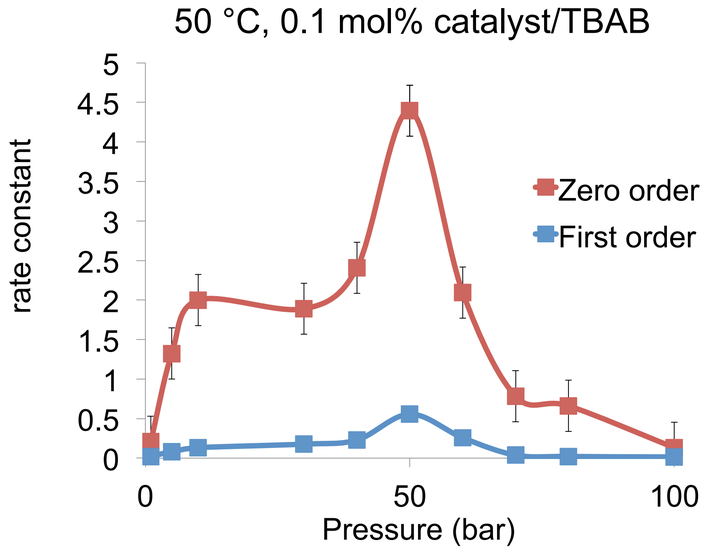
◆ Influence of catalyst concentration



◆ Influence of temperature



◆ Influence of pressure



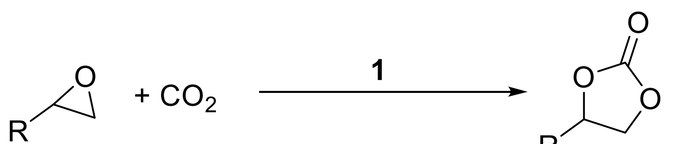
• Synthesis of Cyclic Carbonates using Halide-Free Conditions

The rate law for the formation of glycerol carbonate from glycidol and CO_2 under first order kinetic is determined to be:

Rate = k^1[epoxide][CO_2][Al][TBAB] + k^2[epoxide][CO_2][Al] + k^3[epoxide][CO_2][TBAB]

Rate = k_{obs}[epoxide] k_{obs} = k^1[CO_2][Al][TBAB] + k^2[CO_2][Al]+ k^3[CO_2][TBAB]

The kinetic results suggest that the formation of glycerol carbonate could be achieved without TBAB. Using catalyst **1** alone, various terminal epoxides have been converted to its corresponding cyclic carbonates (Table 1).



a: R=*n*-Bu; b: R=Ph;
c: R=4-ClC_6H_4; d: R=CH_2OH: e: $PhOCH_2$

Table 1

Epoxide	Cat (mol %)	Temp (°C)	Pressure (bar)	Conversion (%)[a]
2a	0.5	50	10	100
2b	0.5	50	50	95
2c	0.5	50	50	96
2d	0.5	50	50	97
2e	2.5	50	10	100

[a]: Reaction was carried out for 24 h. Conversion is determined by GC or ^{1}H NMR spectrum analysis of the crude reaction mixture.

References:

1. Meléndez, J.; North, M.; Pasquale, R. *Eur. J. Inorg. Chem.*, **2007**, 3323. 2. (a) Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.*, **2008**, 1, 13. (b) Sonnati, M. O.; Amigoni, S.; Taffin de Givency, E. P.; Darmanin, T.; Choulet, O.; Guittard, F. *Green Chem.*, **2013**, 15, 283.

Acknowledgements:

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SEVENTH FRAMEWORK PROGRAMME
CyclicCOR Fine chemicals from CO_2