

Synthesis of cyclic carbonates from epoxides and CO₂ catalyzed by potassium iodide and amino alcohols



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ABSTRACT

Amino alcohols in combination with potassium iodide represent efficient catalytic systems for the coupling reaction between epoxides and carbon dioxide to give cyclic carbonates. The presence of hydroxyl groups significantly enhances the catalytic activity of the catalyst system. Moreover, polyvalent amino alcohol, triethanolamine was identified as very active catalyst affording the highest yield of cyclic carbonates. We propose that triethanolamine acts as phase transfer catalyst, activates the epoxide via hydrogen bonding and in addition activates CO₂ and hence showing significant synergistic effects. Various non-functionalized and functionalized epoxides were converted into the corresponding cyclic carbonates under mild and solvent free conditions within short reaction time. The catalytic system and reaction conditions represent a readily available and economical alternative for the synthesis of cyclic carbonates.

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Introduction

The global climate change is closely connected to the emission of anthropogenic greenhouse gases. The by far largest part of this emission is accounted to carbon dioxide (CO₂). Besides the reduction of CO₂ output the use of CO₂ as synthetic building block is the central point of the overall CO₂ management strategy [1]. Hence, the utilization of CO₂ as C1-building block in organic synthesis and industrial processes has recently been given great interest and is widely studied in current research [2].

In this context the 100% atom economical reaction between CO₂ and epoxides yielding the corresponding cyclic carbonates is an attractive reaction. Organic carbonates bear some interesting properties including a high boiling point, low toxicity and being odorless. They can be applied as aprotic polar solvents, intermediates for organic and polymeric synthesis as well as electrolytes for lithium ion batteries [3]. The coupling of epoxides with CO₂ is an intensively studied research field. Various homo- and heterogeneous catalysts and catalytic systems for this transformation have been reported [4]. However, many of these catalysts systems suffer from low catalyst stability or reactivity, require co-solvents or -catalysts, or else need harsh reaction conditions. Alkali

metal salts are among the most promising catalysts for this reaction since they are abundant, inexpensive and nontoxic. However, the addition of co-catalyst or solvents is usually necessary to enhance the catalytic efficiency due to the low solubility and activity of these salts itself [5]. Rokicki et al. [6] reported the synthesis of cyclic carbonates from epoxides and CO₂ in the presence of alkali metal salts and crown ethers as phase transfer catalysts. Song et al. [7] described the utilization of potassium iodide in the presence of lecithin. There have been frequently reports on synergistic effect related to the presence of hydrogen bond donors such as alcohols or acids, acting as co-catalysts in the cycloaddition of CO₂ to epoxides. The combination of alkali metal salts and cellulose, β-cyclodextrin, phenol and even water as co-catalysts has been described [8]. Most recently, the combination of these salts with amino acids and amino alcohols as well as formic acid under microwave assistance has been reported [9]. Amino alcohols such as mono- and diethanolamine are known to fix CO₂ and used as absorbents for the chemical absorption of CO₂ [10]. However, so far predominantly drastic reaction temperatures >100 °C and pressures >10 bar are still required. The development of catalyst systems for the cycloaddition of CO₂ with epoxides under solvent free conditions, at temperatures <100 °C, low pressures and short reaction times employing readily available, inexpensive non-toxic reagents is still an attractive topic.

Herein we report the use of simple amines and amino alcohols in combination with alkali metal salts like readily available

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potassium iodide as simple and efficient catalyst system for the synthesis of cyclic carbonates under solvent free and mild conditions. Especially commercially available and inexpensive polyvalent amino alcohols such as diethanolamine and triethanolamine appeared as very reactive phase transfer agents.

Results and discussion

In our initial studies the conversion of 1,2-butylene oxide (**1a**) with CO₂ to 1,2-butylene carbonate (**2a**) served as model reaction for the screening of various additives in combination with potassium iodide (Table 1). The comparatively mild reaction conditions namely a reaction temperature of 90 °C and a CO₂ pressure of 10 bar were chosen in order to identify a novel efficient catalytic system. Amines and amino alcohols were assumed to promote the reaction on the one hand acting as a phase transfer agents and on the other hand activating the substrate and/or CO₂.

Hence, a series of additives in combination with KI as the catalyst were utilized in the coupling reaction of epoxide **1a** and CO₂ to form cyclic carbonate **2a**. Without an additive the formation of **2a** was not observed (Table 1, entry 1). However, in the presence of primary, secondary and tertiary amines the desired product **2a** was formed in up to 73% yield (Table 1, entries 2–4). Interestingly the addition of diamines gave only conver-

sions <5% (Table 1, entry 5). 1,8-diazabicycloundec-7-ene (DBU) and pyridine were also employed as additives and **2a** could be obtained in 73% and 23%, respectively (Table 1, entries 6 and 7). Compared to monofunctional amines we found out that a significant higher yields up to 83% of carbonate **2a** was observed with bifunctional amino alcohol ethanolamine as additive (Table 1, entry 8). In all cases no byproduct was observed and **2a** was formed in selectivities ≥99%. These results clearly showed that in contrast to unsubstituted amines substituted amines with an additional hydroxyl group were more reactive. In this context we studied the performance of different amino alcohols as bifunctional additives (Table 1, entries 8–13).

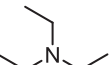



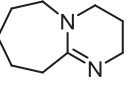





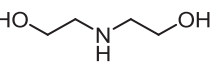
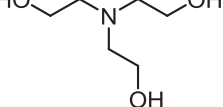
In a first series of experiments we studied the influence of the chain length of simple amino alcohols on the yield of **2a** (Table 1, entries 8–11). However, no considerable influence of the chain length of the amino alcohol was noticed. Furthermore, we employed diethanolamine and triethanolamine and obtained surprisingly remarkable high yields of 93% and 98%, respectively (Table 1, entries 12 and 13). Among the explored amino alcohols, triethanolamine was identified as the most active additive.

It is remarkable that under these mild reactions conditions a quantitative conversion of epoxide **1a** and an excellent yield of 98% of carbonate **2a** are obtained, especially since the reaction is realized under solvent free conditions and the catalytic system is transition metal free, very simple and inexpensive. Usually, reaction temperatures ≥100 °C and longer reactions times are required. Hence, we further explored the influence of the reaction parameters on yield **2a** in our model reaction. In this context we initially studied the effect of the reaction temperature on the yield of carbonate **2a** (Fig. 1). Low conversions are observed at temperatures ≤50 °C. The yield on carbonate **2a** increases considerably up to 82% at 70 °C. Quantitative conversion of epoxide **1a** to carbonate **2a** is obtained at 90 °C within a short reaction time of 3 h.

The dependence of the yield of carbonate **2a** on the reaction time at an initial CO₂ pressure of 10 bar and 90 °C is shown in Fig. 2. The conversion of epoxide **1a** to product **2a** proceeded rapidly within the first 60 min. Notably, after 30 min more than half of the epoxide **1a** was converted to carbonate **2a**. Within 1 h a high yield of 85% is obtained. Subsequently the yield increases up to 98% after 120 min and remains constantly. Consequently further investigations were performed with a reduced reaction time of 2 h.

The effect of the catalyst concentration is shown in Fig. 3. The best result is obtained with equivalent amounts of KI and

Table 1
Screening of different additives in the presence of KI.^a

Entry	Additive	Yield ^b 2a , %	Selectivity ^b 2a , %
1	None	0	≥99
2		25	≥99
3		73	≥99
4		48	≥99
5		2	≥99
6		73	≥99
7		34	≥99
8		83	≥99
9		85	≥99
10		72	≥99
11		88	≥99
12		93	≥99
13		98	≥99

^a Reaction conditions: 25 mmol 1,2-epoxybutane (**1a**), 0.50 mmol KI, 0.50 mmol additive, p(CO₂) = 10 bar, 90 °C, 3 h.

^b Determined by GC with hexadecane as internal standard.

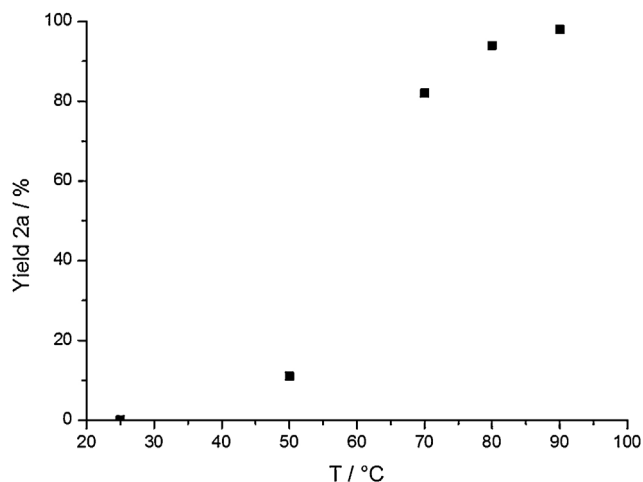


Fig. 1. Effect of the reaction temperature. Reaction conditions: 25 mmol 1,2-epoxybutane (**1a**), 0.50 mmol KI, 0.50 mmol triethanolamine, p(CO₂) = 10 bar, 3 h. Selectivity to cyclic carbonate **2a** ≥99%.

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