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Cycloaddition of Carbon Dioxide and Epoxides using Pentaerythritol and Halides as Dual Catalyst System

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The combination of pentaerythritol with nucleophilic halide salts such as nBu_4NI is used as a dual catalyst system for the cycloaddition of carbon dioxide (CO₂) with a broad range of organic epoxides yielding the respective cyclic carbonates. Due to synergistic effects of the organocatalysts, excellent yields and selectivities could be achieved under mild reaction conditions. Moreover, the nontoxic, cost-efficient, and readily available system is easily recyclable without significant loss of reactivity, representing an exceptional sustainable approach for the fixation of CO₂.

In the last years, catalysis research has increasingly been devoted to finding ways to develop high-performance catalysts for the valorization of renewable carbon sources.^[1] Carbon dioxide is in a special spotlight as a renewable C1 feedstock, because it is ubiquitous and readily available, either from decomposition of organic matter, or artificially by human activities. Of all possible transformations of CO₂ to C1 or higher chemicals with molecular catalysts in solution, one of the most promising reactions in terms of market need, catalyst performance, and reusability is the conversion of CO₂ and epoxides (particularly propylene oxide; PO) to cyclic carbonates (e.g., propylene carbonate; PC) and polycarbonates, respectively.^[2] The synthesis of carbonates and polycarbonates from CO₂ and epoxides is a well-known and established procedure using various highperformance metal catalysts,^[3] with some of them already being applied in industry.^[4] With regards to cheap, sustainable, and green processes, avoiding metal waste by employing (heavy) metal-free catalysts would, however, be much more favorable. In essence, the organocatalysts for the synthesis of cyclic carbonates act as nucleophiles, opening the epoxide ring prior to addition of CO₂ and subsequent cyclization.^[5] Several types of metal-free catalysts have so far been presented, such as halides containing weakly interacting cations (e.g., ammonium, imidazolium),^[6] and nitrogen donor bases.^[7] However, these catalysts require significantly higher temperatures and pressures than metal catalysts. For this reason, more efficient two-component tandem catalyst systems have emerged, con-

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sisting of a hydroxy-containing electrophile (phenols,^[8] glycerol,^[9] chitosan,^[10] lignin,^[11] cellulose^[12]) and a halide. Meanwhile, some of the most active two-component organocatalysts by the teams of Shi,^[13] Kleij,^[8] Han,^[9] and Zhang^[14] exhibit similar activities as metal catalysts under comparable reaction conditions.

Following our previous studies on the cycloaddition of CO_2 and epoxides with halide-based catalysts and electrophilic cocatalysts (NbCl₅,^[15] imidazolium-based ionic liquids^[16]), we focused on investigating the reactivity of pentaerythritol (PETT), which is a cheap and non-toxic compound, as cycloaddition catalyst. The catalytic experiments were performed in a Fisher-Porter bottle charged with equimolar amounts of PETT and halide, flushed with argon, filled with PO, and set under a constant pressure of 4 bar CO_2 for 1 min before the reaction mixture was heated to the desired temperature. The selectivity and yield of PC were determined by gas chromatography. The results are given in Table 1.

The results show that the activity of the binary system originates from a synergistic effect between the catalysts, as no or very little conversion was obtained when using only PETT or nBu_4NI (Table 1, entry 1, 2). Computational studies by Kleij et al.^[8] have shown that the mechanism of the reaction

Table 1. Scro co-catalyst fo	eening of nucleoph or the formation of ————————————————————————————————————	ilic catalysts in combin PC. ^[a] 4 bar CO_2 $70 ^{\circ}\text{C}, 22 \text{ h}$ PETT	nation with PETT as		
Entry	Catalyst [5 mol %]		Yield ^[b] [%]		
1	PETT		0		
2	<i>n</i> Bu₄NI		10		
3	PETT/nBu₄NI		96		
4	PETT/nBu₄NB	r	97		
5	PETT/	_N⊕N ^{-nOc}	79		
6	PETT/	N⊕N- <i>n</i> Oc Br \⊕/	86		
7	PETT/	Br N-nOc	87		
8	PETT/KI		6		
[a] 10.0 mmol PO, 0.5 mmol catalysts, $p(CO_2) = 4$ bar, 70 °C, 22 h. [b] Yields based on GC analysis, selectivity \geq 99% for propylene carbonate.					

changes through the addition of hydrogen-bond donors, when compared to the only use of *n*Bu₄NI. Accordingly, OH-containing electrophiles interact with epoxides via hydrogen bonds, thus polarizing the C–O ring bond and facilitating the nucleophilic attack by the halide and the ring opening, respectively.^[8,17] Further, the intermediates and transition states are stabilized through hydrogen bonds, while the relative energy of the rate-limiting step decreases significantly in comparison to the use of *n*Bu₄NI only.^[8] As a result of this synergistic effect, it is possible to carry out the reaction with our catalytic system based on PETT and nBu₄NI under relatively mild reaction conditions. It is important to note that the catalytic system PETT/KI is active for the cycloaddition of CO₂ and PO, however at significantly higher temperatures and pressures (130 $^\circ\text{C},$ 20 bar CO₂).^[18] Under the reaction conditions applied this mixture leads to only 6% PO conversion (entry 8). This can be attributed to the fact that weaker-interacting cations, that is, the degree of electrostatic interaction between the ions, have a substantial effect on the nucleophilicity of the halide.^[19] That the reactivity of the catalyst system depends on the structure of the cation of the respective nucleophile is further shown by the use of imidazolium-based ionic liquids, which result in lower yields of PC compared to PETT (entries 5-7). This can be explained by the bulkiness of the tetrabutylammonium cation, which weakens the electrostatic interaction between the ions and therefore leads to a higher nucleophilicity of the anion.^[6b] The different reactivity presumably also results from the hydrogen-bonding ability of the imidazolium cation (entry 5), which can interact with the bromide anion^[19] thus competing with the hydrogen bonding of PETT to PO, thereby lowering the product yield. This presumption is further supported by the fact that the C2- and tetramethylated imidazolium-based ionic liquids, which exhibit weaker hydrogen bond donors, give a slightly higher yield (entries 6 and 7). When only imidazolium halides are employed as catalysts, alkylation at the C2-position leads to a decrease of epoxide conversion due to a lack of Hepoxide contacts.[16]

To investigate the influence of the nucleophile on the activity of the dual catalyst PETT/halide, kinetic studies of the catalytic conversion of CO_2 and PO to PC were undertaken using nBu_4NI and nBu_4NBr as co-catalysts. The resulting kinetic curves are shown in Figure 1. Accordingly, under these reaction conditions iodide exhibits a higher catalytic activity since all product yields are higher after the same reaction time than with nBu_4NBr . This behavior is likely caused by the fact that the bromide anion is a stronger hydrogen-bond acceptor than iodide.^[21] Hence, it is stabilized by interaction with PETT, which may also lead to a decrease of the activation of PO through competitive hydrogen bonding. As a result the duration of the reaction can be reduced to 16 h, as compared to 22 h when using nBu_4NI as co-catalyst. For this reason all further investigations were carried out with iodide as nucleophile.

Additionally, the influence of the catalyst loading and the reaction temperature on the PC yield was investigated. A reduction of the temperature from 70 °C to 50 °C results in a strong decreasing yield of PC from 96% to 76%, while the difference in yield at 60 °C is marginal (Figure 2).



Figure 1. Time dependence of the yield of propylene carbonate. Reaction conditions: PO (10.0 mmol), catalysts PETT/*n*Bu₄NX (0.5 mmol), $p(CO_2) = 4$ bar, T = 70 °C.



Figure 2. Effect of the reaction temperature on the yield of PC. Reaction conditions: PO (10.0 mmol), catalysts PETT/*n*Bu₄NI (0.5 mmol), $p(CO_2) = 4$ bar, t = 16 h.

The catalytic activity of the binary system also strongly depends on the concentration of the catalysts. The nearly quantitative conversion of PO with a catalyst loading of 5 mol% (Table 2, entry 5) decreases to 54% yield when the concentration of the catalysts is 1 mol% (Table 2, entry 1).

For a potential application in a green and economic process the recyclability of a catalyst plays an important role. To examine the reusability and the stability of the binary catalytic system PETT/nBu₄NI, the reaction of CO₂ with PO was carried out under the previously described reaction conditions (T= 70 °C, t=16 h, $p(CO_2)$ =4 bar). After the precipitation of the catalysts and extraction of propylene carbonate with diethyl ether, the catalysts were dried in vacuo (see the Experimental Section for details) and used for the next run under the same reaction conditions. The results (Figure 3) show that the activity of the catalytic system remains the same for at least eight catalytic cycles. The slightly irregular yields of PC are within the standard deviation. Notably, leaching effects were not observed. While known catalysts such as pyrogallol^[8] give lower

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Table 2. Influence of catalyst loadings on the formation of propylene carbonate (PC) from PO and $\mathrm{CO}_2^{\mathrm{[a]}}$							
$- \bigvee_{i=1}^{O} \xrightarrow{4 \text{ bar } CO_2}_{i=10} \xrightarrow{O}_{i=10}^{O}$							
Entry	PETT [mol %]	<i>n</i> Bu₄NI [mol%]	Yield ^[b] [%]				
1	1.0	1.0	54				
2	2.0	2.0	67				
3	3.0	3.0	74				
4	4.0	4.0	93				
5	5.0	5.0	96				
[a] 10.0 mmol PO, $p(CO_2) = 4$ bar, $T = 70$ °C, $t = 16$ h. [b] Yields based on							

GC analysis, selectivity \geq 99% for propylene carbonate.



Figure 3. Influence of the catalyst recycling on the yield of PC; Conditions: PO (10.0 mmol), catalysts PETT/nBu₄NI (0.5 mmol), $p(CO_2) = 4$ bar, 70 °C, 16 h.

yields in the second catalytic run, PETT is easily recyclable without significant loss of activity. Hence, PETT/*n*Bu₄NI represents a very feasible and reusable catalytic system for the cycloaddition of CO₂ and PO.

The dual catalyst system PETT/nBu₄NI was applied to the cycloaddition of CO₂ with various epoxides (Table 3). The results show that all examined substrates are converted to the corresponding cyclic carbonates with a selectivity of \geq 99%. Because of the electron-withdrawing effect of their substituents, which facilitates nucleophilic attack at the epoxide ring carbon atoms, epichlorohydrin (entry 2) as well as glycidol (entry 3) gave nearly quantitative conversions under the investigated reaction conditions. Also cyclohexene oxide (entry 6), which is known to be a more difficult substrate for the cycloaddition reaction with CO₂, is converted to the corresponding carbonate in 30% yield.

In conclusion, the binary system PETT/nBu₄NI is able to catalyze the formation of cyclic carbonates via cycloaddition of organic epoxides with CO₂. The combination of the cost-efficient, commercially available, and nontoxic components represents one of few metal-free systems that catalyze the conversion of different organic epoxides at rather mild reaction conditions $(T=60-70 \degree C, p(CO_2)=4 \text{ bar}, 4-5 \text{ mol}\%$ catalyst concentration).



16 h. [b] Conversion based on GC analysis, selectivity \geq 99% for propylene carbonate. [c] Conversion determined by integration of the epoxide and cyclic carbonate peaks in the ¹H NMR spectrum.

The dual catalyst system is easily recyclable and can be reused for at least eight times without loss of reactivity. Further, no organic solvents or metals are needed for the cycloaddition reaction, rendering this catalytic system sustainable and economical. Our future research work will focus on the design of tailored hydrogen-bond donor catalysts for the cycloaddition of CO_2 and epoxides without nucleophilic co-catalysts at lower reaction temperatures and pressures in order to improve the sustainability merits of the reaction.

Experimental Section

All organic epoxides and commercially available catalysts were purchased from Sigma Aldrich. Carbon dioxide (99.995%) was obtained from Westfalen AG. All chemicals were used as received without any further purification. The imidazolium-based ionic liquids were synthesized as reported in literature¹⁶ and dried under vacuum for 6 h at 70 °C. The yields of propylene carbonate were analyzed by gas chromatography (GC) on a Hewlett–Packard Instrument HP 5890 Series II with a Hewlett–Packard integration unit 3396 Series II, a FID and a Supelco column Alphadex 120. ¹H NMR spectra were recorded at a 400 MHz Bruker Avance DPX-400 spectrometer in CDCl₃ or [D6] DMSO and referred to the residual signal of the deuterated solvents.

Catalysis experiments: A Fisher-Porter bottle was charged with PETT and nBu_4NI (0.5 mmol each) and a magnetic stirring bar. The epoxide (10.0 mmol) was added under Ar atmosphere and the bottle was pressurized ($p(CO_2) = 4$ bar) for 1 min. The reaction mixture was heated to the desired temperature and stirred for the required time period. After the respective reaction time the bottle was cooled to 0 °C and the excess of CO₂ was vented. The reaction mixture was collected with 5 mL chloroform and a sample for the GC analysis of the yield and selectivity was taken.

Catalyst recycling studies: After the sample for the GC analysis was taken, the solvent and unreacted substrate were removed under

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vacuum and diethyl ether was added. The precipitated catalysts were filtered, washed with diethyl ether, and dried in vacuum for 1 h. The next catalytic cycle was started with the same amount of epoxide (10.0 mmol) as described above.

Determination of the conversion via ¹H NMR: The conversion of all products, except PC, was determined by comparison of the integrals of the OCH protons of the corresponding carbonates and epoxides.

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Doubleteam: The combination of pentaerytrithol with tetrabutylammonium iodide leads to an efficient catalytic system for the cycloaddition of carbon dioxide (CO_2) with various epoxides to cyclic carbonates. The nontoxic, metalfree, and cost-efficient dual catalysts, as well as the easy recyclability result in an exceptional sustainable organocatalytic approach for the fixation of carbon dioxide.



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