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Hydroxy-Functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates

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Hydroxy-functionalized mono- and bisimidazolium bromides were synthesized and applied as catalysts for the cycloaddition of CO₂ and epoxides to cyclic carbonates. A catalyst screening showed the influence of the number of protic hydrogen atoms at the cation for the activation of epoxides. The most active catalyst operates at very mild reaction conditions (70 °C, 0.4 MPa CO₂) and can be easily recycled ten times without loss of activity.

The depletion of fossil carbon sources and the concomitant dependence of the chemical industry on their cracking products are major challenges for the future.^[1] Therefore, the efficient use of renewable carbon resources is of paramount interest in current catalysis research.^[2] For instance, the valorization of CO_2 , as an anthropogenic, nontoxic, and inexpensive C_1 feedstock, is under the spotlight as an abundant renewable carbon source.^[3] The emission of CO₂ from fossil-fuel combustion accounts to more than 30 Gty⁻¹ and it is also available in great quantities as a component in flue gas.^[3c,4] The exceptional stability of CO₂ is, however, a major drawback regarding its economic and biofriendly use as reactant.^[5] Therefore, the use of catalysts for the activation of CO₂ is crucial.^[6] The catalytic cycloaddition of CO₂ with epoxides to form cyclic carbonates, which are used as high-boiling polar solvents and electrolytes in batteries,^[7] is one of the most promising environmentally friendly reactions for the large-scale conversion of CO₂.^[8] Besides homogeneous metal catalysts,^[3c] in the last years, several efficient metal-free tandem catalysts have been developed.^[9] These catalysts consist of an organic compound bearing a hydroxyl group that interacts with an epoxide and thus, polarizes the C-O-ring bond. Additionally, a nucleophile for the epoxide-ring opening is needed, allowing a subsequent reaction with CO₂ to form a cyclic carbonate, as shown by theoretical and experimental studies. Furthermore, several bifunctional

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ionic catalysts are known,^[10] bearing a hydroxyl^[11] or carboxyl^[12] group as an activator for the epoxide, and a halide as nucleophile. In addition, several heterogeneous hydroxyl-functionalized catalysts that use carboxymethyl cellulose,^[13] cellulose,^[14] or chitosan^[15] as supports are known. Nevertheless, these systems often require high temperatures and pressures and have a negative effect on the carbon footprint of the reaction.

Very recently, we reported the influence of cation modifications on the catalytic activity of imidazolium bromides for the cycloaddition of CO_2 and epoxides.^[16] The epoxide is activated by hydrogen bonding of the oxygen atom to the acidic C2 proton of the imidazolium ring, leading to facilitated ring opening by the halide. It was also shown that catalysts with three hydroxyl groups in spatial proximity show superior activity compared with compounds that have one or two adjacent hydrogen-bond donors.^[9c,d] In general, the hydrogen-bond donors are proposed to stabilize intermediates and transition states by inter- and intramolecular hydrogen bonds. This activating effect is also observed in a dual-catalyst system consisting of pentaerythritol and a tetraalkylammonium halide used for the coupling of CO_2 with epoxides.^[9]

In this work, we present single-component catalysts with comparable hydrogen-bond donor capabilities and reactivities. Therefore, we have synthesized OH-functionalized imidazolium bromides and examined their catalytic activity for the cycload-dition of CO_2 and various epoxides. Firstly, a series of imidazolium bromides with three hydrogen-bond donors (1–3, Figure 1) and two hydrogen-bond donors (4–6) were synthesized and characterized by ¹H NMR, ¹³C NMR, IR spectroscopy, and mass spectrometry, as well as by elemental analysis (for further details see the Supporting Information).



Figure 1. Investigated catalysts 1–7 for the synthesis of PC from PO and $\mbox{CO}_{2^{\rm .}}$

details.

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The OH-functionalized ammonium bromide **7** has been investigated previously as a catalyst in batch and continuousflow reactions, reaching turnover frequencies of 3000– 14000 h⁻¹ for the cycloaddition of CO₂ and epoxides.^[11a,17] For this reason, **7** was chosen as a benchmark for the catalysts **1– 6**. Nevertheless, separation of **7** from the product is difficult because of the good solubility of this catalyst in propylene oxide (PO) and propylene carbonate (PC). In addition, the high pressures and temperatures (3.5 MPa CO₂, 180 °C) that are required are highly undesirable from an environmental point of view.

Therefore, compounds 1–7 were used as catalysts under the previously reported mild reaction conditions (10 mol% catalyst loading, 70 °C, 0.4 MPa CO₂, neat). The cycloaddition reaction was conducted with CO₂ and PO to yield PC.^[16] In a typical experiment, a Fisher–Porter bottle was charged with the catalyst and substrate, pressurized with 0.4 MPa CO₂ for 1 min and heated to the desired temperature for 16 h. The yield and selectivity were determined by using gas chromatography (GC). The results are summarized in Table 1. In all examined cases, the selectivity for PC was higher than 99%. A reaction time of 16 h was needed to reach 95% conversion with catalyst **3** (Figure 2).

Table 1. Synthesis of PC from PO and CO_2 by using catalysts 1–7. ^[a]						
Catalyst	Catalyst amount [mmol]	PO [mmol]	Conversion [%] ^[b]	Selectivity [%] ^[b]		
-	0	10.0	0	-		
1	0.5	10.0	31	\geq 99		
2	0.5	10.0	57	\geq 99		
3	0.5	10.0	95	\geq 99		
4	1.0	10.0	32	\geq 99		
5	1.0	10.0	79	\geq 99		
6	0.5	10.0	58	\geq 99		
7	1.0	10.0	92	\geq 99		
[a] Reaction conditions: 70 $^{\circ}$ C, 0.4 MPa CO ₂ , 16 h. [b] Conversion and selectivity were based on GC analysis.						



Figure 2. Studies of time-dependent conversion of PO; reaction conditions: 10.0 mmol PO, 5 mol% 3, 0.4 MPa CO_{2r} 70 °C; PO conversion based on GC results; Selectivity towards PC \geq 99%.

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In the absence of a catalyst, no conversion of PO occurred under the applied reaction conditions. For a more detailed evaluation of the activity, the molar amount of the bromide anion was constant for all investigated catalysts. Additionally, this allows a direct comparison to previous results.^[16] By varying the substituent of the side chain of the catalyst, the conversion of PO increased in the order methyl < benzyl < *n*-octyl. This trend is mainly attributed to the better solubility of 3 in PO and PC. Catalysts 1 and 2 are insoluble, even in PC, whereas 3 remained in solution during the entire course of the reaction. After 16 h a PO conversion of 95% was achieved. This is the best result for the synthesis of PC under the applied conditions, so far. Compared with our previous results, the reaction time was decreased from 22 h to 16 h.^[16] The high activity of 3 presumably results from three neighboring hydrogen-bond donors (a hydroxyl group and two imidazolium cation units), which activate the epoxide and stabilize the ring-opened intermediate.^[9d] For a better insight into the influence of the OH groups on epoxide activation, imidazolium bromides with only two hydrogen-bond donors were synthesized and applied as catalysts for the cycloaddition of CO₂ and PO. For catalysts 4 and 5, one hydroxyl group and one imidazolium C2 proton can act as hydrogen-bond donors, respectively, and two imidazolium C2 protons for catalyst 6. As mentioned previously for 1-3, the conversion of PO also increases with longer chain length in the order methyl < n-octyl for catalysts **4** and **5**. Nevertheless, using 5 as catalyst resulted in 79% conversion of PO, which is significantly lower than that achieved by using 3 (95%). The solubility of 3 and 5 in PC is comparable; therefore, the observed yields of PC indicate a positive influence of the second imidazolium C2 proton on the catalytic performance. This is in accordance with the results of Kleij and co-workers, who demonstrated that systems containing three hydrogenbond donors exhibit the best catalytic activity.^[9d] For a better understanding of the role of the hydroxyl group of 3, an analogous cation without a hydroxyl group was investigated (compound 6). When using 6 as catalyst, the PO conversion decreased to 58%, hence it can be stated that the hydroxyl group is crucial for an efficient activation of the epoxide. Finally, 3 was compared to 7 to classify the performance of the catalyst. In this regard, compound 3 performed slightly better than compound 7 (95 versus 92% PO conversion). Additionally, PC can be easily separated from 3 with diethyl ether. When using 7 as catalyst, PC can be only separated by distillation, owing to the good solubility of 7 in PC. This is a highly energetic process because of the high boiling point of PC and, therefore, has a negative effect on the carbon footprint of the reaction. Consequently, compound 3 offers the possibility of a sustainable system for the chemical fixation of CO₂. For this reason, further investigations, such as optimization of the reaction parameters, recycling studies, and substrate screening, were performed using 3 as the catalyst.

The time-dependent conversion of PO was investigated by a series of 12 identical experiments. The reactions were stopped after a defined period and samples were taken and analyzed by means of GC. The conversion of PO was plotted versus time (Figure 2), showing that after 16 h almost quantita-

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tive conversion of PO was obtained. A TOF of $14 h^{-1}$ was achieved for catalyst **3**. Additionally, the influence of the temperature on the conversion and selectivity (Figure S1) was investigated. By reducing the temperature from 70 to 50 °C, the conversion of PO decreased from 95 to 73%. This finding could provide an opportunity for further improvement in terms of a sustainable use of CO₂. However, a reduction of the temperature to 25 °C resulted in a low PO conversion of 4%. Thus, a minimum reaction temperature of 50 °C is needed to obtain good PO conversion.

In addition, the influence of the catalyst loading (Figure S2) was investigated. The conversion of PO decreased with reduced amounts of the catalyst. Nevertheless, a PO conversion of 60% was reached with only 1 mol% catalyst loading at 70°C, demonstrating a rather high activity compared with previously reported catalysts.^[16] For this reason, further reactions were carried out at 50°C with 5 mol% catalyst loading and at 70°C with 1 mol% catalyst loading. For both experiments, the reaction time was 24 h to demonstrate the activity and efficiency of the catalytic system under even milder reaction conditions. Under both reaction conditions a small increase, with PO conversions of 78% (50 $^\circ\text{C},$ 5 mol%) and 71% (70 $^\circ\text{C},$ 1 mol%), was detected. Nevertheless, the catalyst was still active and a further increase in reaction time could lead to quantitative conversion of PO. In terms of sustainability, a catalyst loading of 5 mol% is acceptable because of the easy recyclability of 3. Additionally, the amount of catalyst needed for the organocatalytic conversion of epoxides and CO₂ for bifunctional systems spans a wide range.^[10] A favorable scenario requires harsher reaction conditions, but short reaction times, compared with mild reaction conditions and longer reaction times. For this reason, a catalytic run at 140 $^\circ\text{C}$, 1 mol % catalyst loading, 1 MPa CO₂ pressure and 2 h reaction time was performed. Under these reaction conditions the catalyst converts PO to PC in 90% yield, rendering catalyst 3 as active as the state-of-the-art metal-free catalyst [HDBU]Cl (DBU = 1,8-Diazabicycloundec-7-ane).^[18] These results indicate that the limiting parameter is not the catalyst loading, but rather the temperature and the applied CO_2 pressure.

Besides the catalyst activity, the sustainability and recycling potential are also decisive criteria for possible large-scale application. Hence, recyclability studies of **3** were performed to evaluate the sustainability of the system. After each run, **3** could easily be precipitated from the PC solution by the addition of diethyl ether. After filtration, another batch of PO was added and the next catalytic run was started. The conversion of PO remained constant over ten consecutive runs without any loss of activity when using **3** as catalyst (Figure 3).

The differences observed for the conversion of PO are within the standard deviation for GC analysis. Owing to the easy separation of **3** from PC and the slightly higher activity, **3** is a very promising alternative to **7**. Compound **3** can be applied as a catalyst for the cycloaddition of a broad range of different epoxides with CO_2 (Table 2). Electron-withdrawing, electron-donating, and sterically demanding substituents can be converted to the respective carbonates in good to very good yields. In all experiments, the selectivity for the formation of the cyclic



Figure 3. Recycling studies; reaction conditions: 10.0 mmol PO, 5 mol % 3, 0.4 MPa CO_2 , 70 °C, 16 h; PO conversion based on GC results; Selectivity towards PC \geq 99 %.



carbonate was \geq 99%. The very good conversions of epichlorohydrin and glycidol (entries 4 and 5) can be explained by the electron-withdrawing substituents. These substituents result in facilitated nucleophilic attack of the halide during the ring opening of the epoxide. Even cyclohexene oxide, which is known to undergo cycloaddition with CO₂ poorly, is converted to the corresponding cyclic carbonate with a yield of 56% (entry 7).^[10a]

with mesitylene as a standard.

There are several reports that postulate a mechanism for the cycloaddition of CO_2 and epoxides in the presence of hydrogen-bond donors (e.g. hydroxyl groups).^[10] In combination with the reported results, an analogous mechanism is proposed (Scheme 1). Firstly, the epoxide is activated through hydrogen bonding of the hydroxyl group and C2 protons of the imidazolium moiety. Thus, the C–O bond is weakened and the nucleophilic attack of the bromide is facilitated. The resulting

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Scheme 1. Proposed mechanism for the cycloaddition of CO₂ and PO.

oxyanion species is proposed to be stabilized by the hydrogen-bond donors and reacts with CO_2 to form the cyclic carbonate after intramolecular cyclic elimination ("back-biting"). In comparison with unfunctionalized catalyst **6**, the OH group in the propylene bridge of catalyst **3** enhances the binding strength to the epoxide and thus leads to faster ring opening. To support this hypothesis, DFT calculations were carried out to compare epoxide binding by using the N-dimethylated derivatives of catalysts **1** and **6** for the sake of calculation time.

The calculations show that the first intermediate **B** (binding of the epoxide to H atoms of the cation) is approximately 13 kcal mol⁻¹ lower in energy for the OH-functionalized catalyst (see Scheme 1 and the Supporting Information). Intermediate **C** is also 4 kcal mol⁻¹ lower in energy for the OH-functionalized catalyst. In all steps, besides the imidazolium protons the OH group additionally interacts either with the bromide anion, or with the alcoholate and carboxylate intermediates. These interactions are presumably the reason for the lower energies and relatively higher catalyst activities in comparison with the unfunctionalized catalyst. Notably, in the calculations there are slight deviations in the energy values, which may be caused by using N-methyl groups for the calculations rather than the octyl substituents used for the experiments shown in Tables 1 and 2 (see the difference in the conversion of PO with catalyst 1 versus 3, Table 1). Although for N-methyl substituents, which were used in the DFT calculations, the non-OH-substituted compound has slightly lower energy barriers than the OH-substituted catalyst, this is expected to change with the steric demand of the *n*-octyl groups used in the best catalyst system. It is also worth mentioning that all the barriers in the calculated mechanism are below 30 kcal mol⁻¹, whereas the uncatalyzed reaction of CO_2 and propylene oxide has a barrier (ΔG) of 68.2 kcal mol^{-1} .

The OH-functionalized bisimidazolium bromide **3** is an efficient catalyst for the cycloaddition of various epoxides and CO_2 . Owing to the very mild reaction conditions (70 °C, 0.4 bar CO_2 , 16 h), the easy recyclability, and the absence of any metal

or solvent, this catalyst may be considered as particularly "green". Compound 3 is a rare example of a bifunctional organocatalyst that provides almost quantitative yields of the corresponding cyclic carbonates under such mild reaction conditions. These findings render compound 3 a promising catalyst for efficient CO₂ fixation, minimizing the gap in activity between bifunctional imidazolium halide catalysts and binary phenol-based catalytic systems. Future investigations include a further functionalization of the cation structure for an even more efficient activation of the epoxide. Therefore, the aim is the development of an efficient, bifunctional organocatalyst that allows the conversion of epoxides and CO₂ at low temperature (down to room temperature) and low pressure (down to atmospheric pressure). This development is of interest from an ecological and economical point of view and will help to minimize the carbon footprint of the reaction.

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Keywords: CO_2 fixation \cdot cyclization \cdot hydrogen bonds \cdot organocatalysis \cdot sustainable chemistry

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Hydroxy-Functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates



Just a matter of H bonding: The efficient valorization of carbon dioxide to cyclic carbonates was performed under mild and metal-free conditions by activation of the epoxide through hydrogen bonding of a hydroxyl-functionalized bisimidazolium salt.