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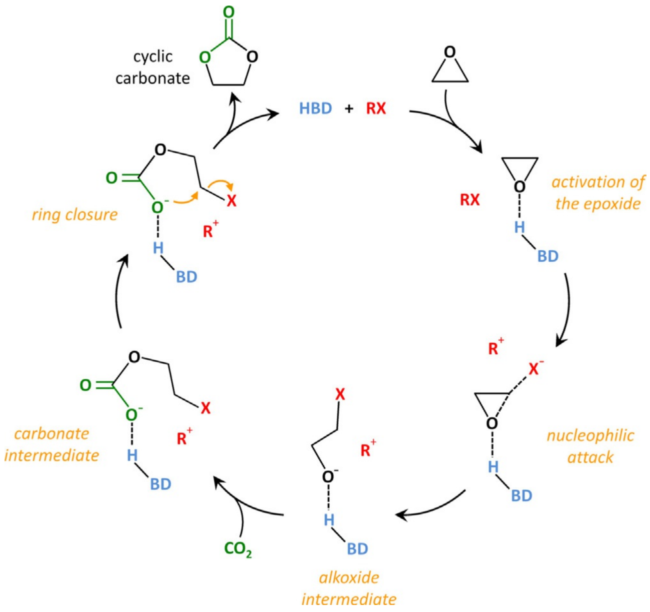
The Role of Water Revisited and Enhanced: A Sustainable Catalytic System for the Conversion of CO_2 into Cyclic Carbonates under Mild Conditions

Yasser A. Alassmy[a, b] and Paolo P. Pescarmona*[a]

The role of water as highly effective hydrogen-bond donor (HBD) for promoting the coupling reaction of CO_2 with a variety of epoxides was demonstrated under very mild conditions (25–60 °C, 2–10 bar CO_2). Water led to a dramatic increase in the cyclic carbonate yield when employed in combination with tetrabutylammonium iodide (Bu_4NI) whereas it had a detrimental effect with the corresponding bromide and chloride salts. The efficiency of water in promoting the activity of the organic halide was compared with three state-of-the-art hydrogen bond donors, that is, phenol, gallic acid and ascorbic acid. Although water required higher molar loadings compared to these organic hydrogen-bond donors to achieve a similar degree of conversion of CO_2 and styrene oxide into the corresponding cyclic carbonate under the same, mild reaction conditions, its environmental friendliness and much lower cost make it a very attractive alternative as hydrogen-bond donor. The effect of different parameters such as the amount of water, CO_2 pressure, reaction temperature, and nature of the organic halide used as catalyst was investigated by using a high-throughput reactor unit. The highest catalytic activity was achieved with either Bu_4NI or bis(triphenylphosphine)iminium iodide (PPNI): with both systems, the cyclic carbonate yield at 45 °C with different epoxide substrates could be increased by a factor of two or more by adding water as a promoter, retaining high selectivity. Water was an effective hydrogen-bond donor even at room temperature, allowing to reach 85 % conversion of propylene oxide with full selectivity towards propylene carbonate in combination with Bu_4NI (3 mol %). For the conversion of epoxides in which PPNI is poorly soluble, the addition of a cyclic carbonate as solvent allowed the formation of a homogeneous solution, leading to enhanced product yield.

Introduction

The use of CO_2 as a feedstock for the synthesis of useful chemical products is receiving growing interest in the context of sustainable chemistry because CO_2 is an inexpensive, widely available, non-toxic, and renewable compound.[1–3] However, the fixation of CO_2 into chemical products is a challenging task owing to its high thermodynamic stability. This issue can be overcome by reacting CO_2 with high-free-energy substrates such as H_2, amines, and epoxides.[1,4] Among these options, the reaction of CO_2 with epoxides to produce cyclic carbonates (Scheme 1) has been widely investigated in recent years.[5] The obtained cyclic carbonates are useful compounds finding relevant applications as intermediates for the preparation of fine chemicals and polymers, as green aprotic polar solvents, and as electrolytes in Li-ion batteries.[5–9] The cycloaddition of CO_2 to epoxides requires a catalyst to proceed at a high rate under mild conditions. The most active catalytic systems for this reaction comprise Lewis acid sites for the activation of the epoxide and Lewis bases acting as nucleophiles for the subsequent



Scheme 1. Proposed mechanism for the cycloaddition reaction of CO_2 to epoxides catalyzed by an organic halide (RX) with the cooperation of an HBD.

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ring-opening of the epoxide.[5] Many highly active and selective metal-based catalysts containing Lewis acid sites have been reported, such as metal complexes[10] and metal–organic frameworks (MOFs).[11] However, metal catalysts tend to display drawbacks such as the generally high cost of their preparation, the toxicity of some metals, and in some complexes and MOFs, low stability against hydrolysis and/or oxidation.[1,12]

Several metal-free organic catalysts have also been investigated, such as ammonium halides,[1,13–15] phosphonium halides,[3,16] and imidazolium-based ionic liquids,[17–19] in which the halides are the catalytic species acting as nucleophiles. These systems are less expensive and more readily available than most metal catalysts.[20] However, the lack of metal Lewis acid sites activating the epoxide implies that these metal-free organic catalytic systems often suffer from low activities under mild conditions.[14,21,22] To overcome this issue, hydrogen bond donors (HBDs) such as amino alcohols,[23,24] silane diols,[25] fluorinated alcohols,[26] aromatic compounds with one or multiple hydroxy groups,[14,27–29] and organic acids[30–33] have been recently studied as cocatalysts. In the generally accepted mechanism, these HBDs are able to activate the oxygen atom of the epoxide by hydrogen bonding in a similar way to Lewis acidic metal sites, thus promoting the nucleophilic attack by the halide leading to ring-opening of the epoxide (Scheme 1). Then, the insertion of CO_2 occurs, forming a carbonate intermediate, which undergoes intramolecular ring-closure to generate the cyclic carbonate product (Scheme 1).[20,34] DFT studies indicated that the addition of HBDs leads to lower activation energies to reach the transition states and that more stable intermediates are obtained in the reaction of CO_2 with epoxides.[35,36] Among the several HBD compounds that have been reported for this application,[37–39] one of the most efficient types is represented by aromatic compounds with one or multiple hydroxy groups, such as as phenol, pyrogallol, and gallic acid. Catalytic systems consisting of these HBDs along with tetrabutylammonium iodide (Bu_4NI) were reported to be highly active in the synthesis of cyclic carbonates from CO_2 under mild conditions [25–45 °C, $p(CO_2) = 1–10$ bar].[27,29] Another class of highly efficient HBDs is represented by fluorinated alcohols, which in combination with Bu_4NX ($X = I^-$, Br^-) promoted the reaction of CO_2 with epoxides under mild conditions (60–80 °C, 1–20 bar CO_2) and with complete selectivity towards the cyclic carbonate products. The high activity was attributed to the electron-withdrawing fluorinated groups, which increase the acidity of the alcohol groups and thus the strength of the hydrogen bonding with the oxygen atom of the epoxide.[26,36] Although these HBDs are less costly than most metal-complex catalysts used for this reaction, most of them are still relatively expensive organic molecules and display additional drawbacks such as high toxicity, as in the case of fluorinated alcohols,[26] and/or high boiling points [e.g., 182 °C (phenol); 309 °C (pyrogallol); gallic acid and ascorbic acid tend to decompose around their melting point], which implies the need for energy-demanding vacuum distillation in their separation from the cyclic carbonate products (which also have high boiling points). In this context, the use of a fully environmentally-benign, extremely inexpensive, and relatively low-boiling compound such as water is a potentially attractive alternative. In previous works, water was reported to be beneficial as a cocatalyst at relatively harsh conditions (≥100 °C),[34,35] whereas in other cases it was reported not to help or even be detrimental to the carbonate yield.[40,41] Herein, we demonstrate that using water as HBD in combination with specific organic halides such as Bu_4NI and bis(triphenylphosphine)iminium iodide (PPNI) (Figure 1), and by tuning the reaction conditions carefully, it is possible to match the performance of state-of-the-art HBDs such as phenol,[27] gallic acid,[14] and ascorbic acid[31] and to achieve the selective conversion of CO_2 into several cyclic carbonates under mild conditions (25–60 °C, 2–10 bar CO_2). Additionally, we introduce and evaluate a novel strategy consisting of adding cyclic carbonates to promote the solubilization of PPNI and thus increase its efficiency as a catalyst in the synthesis of cyclic carbonates from CO_2 and epoxides.

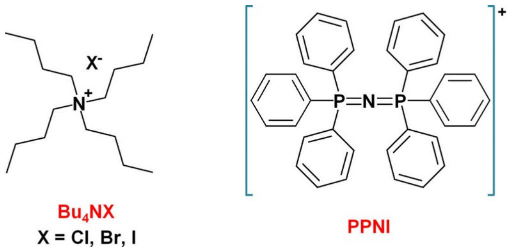

Figure 1. Organic halides used as catalysts in combination with H_2O in this work: tetrabutylammonium halides (Bu_4NX) and bis(triphenylphosphine) iminium iodide (PPNI).

Results and Discussions

The possibility of using water as HBD to promote the reaction of CO_2 with epoxides under mild conditions was investigated as a green and cheap alternative to other HBDs. The first catalytic screenings were performed by using the relatively challenging styrene oxide as a substrate and tetrabutylammonium halides (Bu_4NX, with $X = Cl$, Br, I; 1 mol% relative to the epoxide) as organic catalysts in the presence of water at 45 °C and 10 bar CO_2. The addition of even a small amount of H_2O (0.05 mL) was detrimental for the activity of Bu_4NCl and Bu_4NBr (Table 1, entries 1–4), whereas adding the same amount of water dramatically increased the activity of Bu_4NI, leading to a two-fold higher styrene carbonate yield (Table 1, entries 5 and 7). This trend can be rationalized considering that in a protic medium such as water, the order of nucleophilicity between the halides ($I^- > Br^- > Cl^-$) is the opposite of that in an aprotic solvent. This is related to the shielding effect caused by the protic molecules, which arrange themselves with the partially positively charged hydrogens directed towards the halide ion. These ion–dipole interactions become stronger with increasing strength of the base ($I^- < Br^- < Cl^-$), implying a weaker shielding effect of H_2O for the iodide ion.[42] Our results indicate that for chloride and bromide, the shielding effect of water is more relevant than its role as HBD activating the epoxide, thus leading to an overall decrease in catalytic activity. In contrast,

Table 1. Screening of different organic halide catalysts for the conversion of CO_2 and styrene oxide into styrene carbonate, with or without the addition of an HBD (water, phenol, gallic acid, and ascorbic acid).

Entry	Organic catalyst/HBD	H_2O [mL]	Yield[b] [%]	Selectivity[b] [%]
1	Bu_4NCl/–	0	4	≥99
2	Bu_4NCl/H_2O	0.05	2	85
3	Bu_4NBr/–	0	12	≥99
4	Bu_4NBr/H_2O	0.05	9	87
5	Bu_4NI/–	0	13	≥99
6	Bu_4NI/H_2O	0.025	20	98
7	Bu_4NI/H_2O	0.05	25	95
8	Bu_4NI/H_2O	0.10	29	92
9	Bu_4NI/H_2O	0.20	28	91
10	Bu_4NI/H_2O	0.40	27	90
11	Bu_4NI/H_2O	0.80	22	88
12	Bu_4NI/gallic acid (4:1)[c]	0	26	≥99
13	Bu_4NI/ascorbic acid (4:1)[c]	0	25	≥99
14	Bu_4NI/phenol (4:1)[c]	0	25	≥99
15	Bu_4NI/phenol (2:1)[d]	0	32	≥99
16	Bu_4NI/phenol (1:1)[e]	0	44	≥99

[a] Reaction conditions: styrene oxide (20 mmol), organic catalyst (1 mol% relative to the epoxide), mesitylene (1.5 mmol) as internal standard, 45 °C, 10 bar CO_2,18 h. [b] Yield and selectivity measured by ^1H NMR spectroscopy. [c] 0.25 mol% loading of phenol, gallic acid, or ascorbic acid relative to the epoxide. [d] 0.5 mol% loading of phenol relative to the epoxide. [e] 1 mol% loading of phenol relative to the epoxide.

iodide is less affected by the shielding while H_2O activates the epoxide towards the nucleophilic attack by the halide, resulting in the observed notable increase in catalytic activity. Next, the effect of the amount of water used in combination with the Bu_4NI catalyst was investigated. Water was an effective HBD even upon halving its amount (Table 1, entry 6), although the increase in styrene carbonate yield was less marked than with 0.05 mL H_2O. In contrast, increasing the amount of water used together with the Bu_4NI catalyst to 0.1 mL led to a further increase in the yield of styrene carbonate, reaching 29% (Table 1, entry 8) compared to 13% yield in the absence of water. Further increase in the amount of water did not lead to higher styrene carbonate yield and gradually caused a decrease in the selectivity towards the cyclic carbonate product, owing to the formation of 1-phenyl-1,2-ethanediol (styrene glycol) as a side product (Table 1, entries 9–11). No other side products were observed.

The use of water as HBD was compared to that of state-of-the-art HBDs reported in previous studies such as phenol, gallic acid, and ascorbic acid under the same reaction conditions (Table 1, entries 12–16). Although this comparison demonstrates that water is less effective in promoting the reaction and that a much higher number of moles of water is needed to achieve similar yields to those obtained in the presence of the above-mentioned organic HBDs (2.8 mmol H_2O, i.e., 14 mol% relative to the epoxide, was needed to match the performance of 0.25 mol% of these HBDs), this is counterbalanced by the fact that water is an environmentally friendlier and much less expensive compound. Because the beneficial effect of water as HBD at mild temperature was observed only with Bu_4NI as catalyst, the combination of this halide with H_2O was selected for further investigation and optimization of the catalytic performance.

With the purpose of investigating the effect of the CO_2 pressure on the catalytic performance of the Bu_4NI/H_2O system in the synthesis of styrene carbonate, a set of experiments was performed at 45 °C with the CO_2 pressure ranging from a very low value (2 bar) to above the supercritical point (80 bar). The results demonstrate that using low CO_2 pressure (2–20 bar) results in a higher carbonate yield than that obtained at 80 bar (Figure 2). This means that the access of the CO_2 to the catalytic sites is not a limiting factor for this system and suggests that performing the reaction with CO_2 under supercritical conditions may be detrimental as a consequence of a dilution of the reaction mixture that decreases the contact between the epoxide and the catalyst.[5] These results also allow excluding that the observed increase in activity in the presence of water is caused by the formation of carbonic acid, which in turn could act as HBD. If this were the case, higher CO_2 pressure would have led to higher activity because the concentration of CO_2 dissolved in H_2O is proportional to the partial pressure of CO_2 according to Henry's law. Notably, the selectivity towards the cyclic carbonate obtained in these tests in which a 2 mol% loading of Bu_4NI was used (≥99% for the tests in the 2–20 bar range) is higher than for the tests performed with 1 mol% catalyst loading (see Table 1). This is attributed to the higher catalyst/HBD ratio in the tests performed with higher Bu_4NI loading, which promotes the conversion of styrene oxide to the cyclic carbonate over the competing hydrolysis of the epoxide. Because no significant differences in catalytic activity were observed in the 5–20 bar range (Figure 2), 10 bar CO_2 pressure was chosen for further studies in this work.

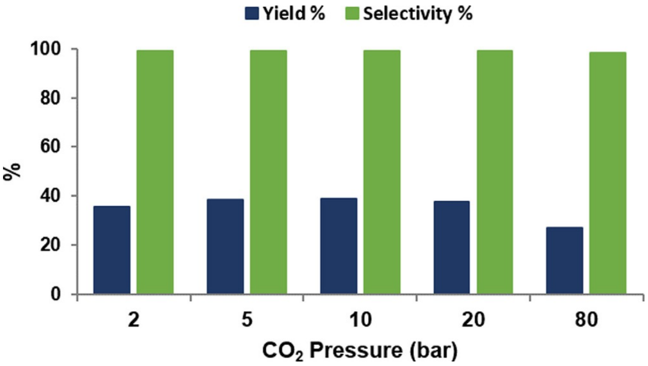

Figure 2. Effect of CO_2 pressure (at the start of the reaction) on the cycloaddition to styrene oxide with a Bu_4NI catalyst in the presence of H_2O as HBD. Reaction conditions: styrene oxide (20 mmol), catalyst (2 mol% loading relative to the epoxide), water (0.05 mL), mesitylene (1.5 mmol) as the internal standard, 45 °C, 18 h. Product yields were determined by ^1H NMR spectroscopy.

After having demonstrated the potential of H_2O as HBD under mild conditions, we further optimized our catalytic system by testing the nature of the cation in the organic halide. For this purpose, PPNI was prepared following a method from the literature,[43] and its catalytic activity was compared to that of Bu_4NI in the presence of water as HBD, under different conditions including reaction at room temperature (Figure 3). PPNI was chosen as a halide salt because the PPN^+ cation is bulkier, and its positive charge is more delocalized compared with Bu_4N^+. As a consequence, the interaction of the PPN^+ cation with the iodide anion is expected to be weaker, thus making the iodide more available for the initial ring-opening of the epoxide.[44,45] Indeed, the PPNI catalyst was consistently more active than Bu_4NI and exhibited high styrene carbonate yields at the three tested reaction temperatures. Remarkably, with longer reaction time, we could successfully react CO_2 with styrene oxide to produce the corresponding cyclic carbonate even at room temperature by using the PPNI/H_2O catalytic system (Figure 3A). The selectivity towards styrene carbonate ranged from 95% for the reaction performed at room temperature to 99% for the reaction performed at 60 °C. To confirm the importance of the presence of water as HBD also with the PPNI catalyst, the reaction at 45 °C was performed without adding water, reaching a much lower carbonate yield (20%) compared with the 38% yield obtained in the presence of water (see Table 2, entries 1 and 2).

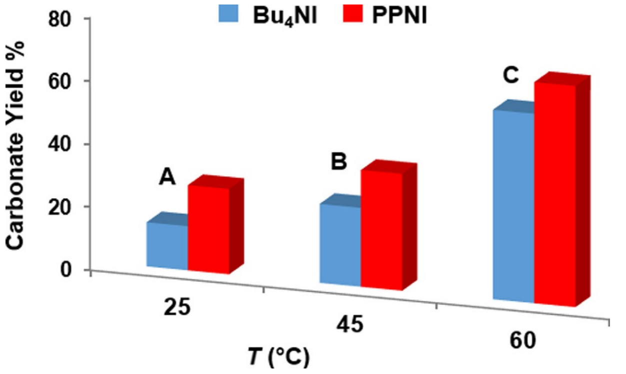

Figure 3. Comparison between Bu_4NI and PPNI as catalysts used in combination with H_2O as HBD, at different reaction temperatures. Reaction conditions: styrene oxide (20 mmol), catalyst (1 mol%), water (0.05 mL), mesitylene (1.5 mmol) as internal standard, 10 bar CO_2; [A] 25 °C, 48 h. [B] 45 °C, 18 h. [C] 60 °C, 18 h.

Table 2. Screening of different epoxides in the reaction with CO_2 to the corresponding cyclic carbonate, with PPNI and Bu_4NI as catalysts, and with or without the addition of water as HBD.

Entry	Substrate	Catalyst/HBD	Yield[b] [%]	Selectivity[b] [%]
1	styrene oxide	PPNI/–	20	≥99
2	styrene oxide	PPNI/H_2O	38	97
3	propylene oxide	Bu_4NI/–	9	≥99
4	propylene oxide	Bu_4NI/H_2O	55	≥99
5	propylene oxide	PPNI/–	1	≥99
6	propylene oxide	PPNI/H_2O	59	≥99
7	1,2-epoxyhexane	Bu_4NI/–	0.2	≥99
8	1,2-epoxyhexane	Bu_4NI/H_2O	23	≥99
9	1,2-epoxyhexane	PPNI/–	0	0
10	1,2-epoxyhexane	PPNI/H_2O	0.7	≥99
11	1,2-epoxyhexane	PPNI/PC[c]	2	≥99
12	1,2-epoxyhexane	PPNI/PC/H_2O[c]	16	≥99
13	cyclohexene oxide	Bu_4NI[d]/–	2	≥99
14	cyclohexene oxide	Bu_4NI[d]/H_2O	9	≥99

[a] Reaction conditions: epoxide (20 mmol), organic halide (1 mol% relative to the epoxide), water (0.05 mL, if added), mesitylene (1.5 mmol) as internal standard, 45 °C, 10 bar CO_2, 18 h. [b] Yield and selectivity measured by ^1H NMR spectroscopy. [c] Propylene carbonate was added as solvent in an amount (1.0 g) that leads to complete dissolution of PPNI in the reaction mixture. [d] 3 mol% Bu_4NI relative to the epoxide.

The versatility of our optimum catalytic system consisting of PPNI or Bu_4NI and water in the cycloaddition reaction of CO_2 was evaluated by using three additional epoxides (propylene oxide, 1,2-epoxyhexane, and cyclohexene oxide) as substrates at 45 °C and 10 bar CO_2 (Table 2). Under these mild conditions, a very low carbonate yield (1–9%) was found in the absence of water if propylene oxide was used as a substrate with both catalysts (Table 2, entries 3 and 5), whereas the yield was dramatically higher (55–59%) if the reaction was performed in the presence of 0.05 mL H_2O (Table 2, entries 4 and 6), thus confirming the remarkable positive effect of water as HBD in promoting the catalytic activity of the organic iodides. For the tests performed in the presence of water, the higher yield of propylene carbonate compared with that of styrene carbonate under the same conditions (compare entries 6 and 2 in Table 2, or entry 4 in Table 2 and entry 7 in Table 1) follows the expected trend of higher reactivity of propylene oxide in the cycloaddition of CO_2. With this epoxide, the nucleophilic attack occurs mainly at the less hindered carbon atom of the epoxide ring owing to the lower steric hindrance at this position and the electron-donating nature of the methyl group.[5] Conversely, the attack takes place preferentially at the more hindered carbon in styrene oxide owing to the electron-withdrawing nature of the phenyl group, typically resulting in a lower yield of styrene carbonate.[5,46,47] However, such a trend was not followed in the experiments performed with PPNI as catalyst in the absence of water, in which case the yield of propylene carbonate was significantly lower than that of styrene carbonate (compare entries 5 and 1 in Table 2). This shows that the remarkable increase in propylene carbonate yield was not only caused by the role of water as HBD. Indeed, the solubility of the catalyst in the reaction mixture also plays a role in its activity, and the higher solubility of PPNI in styrene oxide compared to that in propylene oxide (Table S1 in the Supporting Information) accounts for the higher carbonate yields obtained with the former epoxide if the reaction was performed without water. However, PPNI is highly soluble in propylene carbonate (Table S2 in the Supporting Information), and if the reaction is performed in the presence of water, the faster formation of the carbonate promotes the dissolution of the organic halide catalyst, which enhances the contact with the unreacted epoxide and thus further increases the activity of the catalyst. This effect is confirmed by the fact that PPNI is fully soluble in the reaction mixture at the end of the catalytic test in the presence of water, whereas it is still largely insoluble if the reaction is performed in the absence of water (Table S1 in the Supporting Information, entries 3 and 4). In the same line of reasoning, the extremely low activity of PPNI in the reaction of 1,2-epoxyhexane with CO_2, both with or without addition of water (Table 2, entries 9 and 10), can be attributed to the negligible solubility of PPNI in this epoxide (Table S1 in the Supporting Information) and to the lower solubility of PPNI in 1,2-hexene carbonate compared with that in propylene carbonate or styrene carbonate (Table S2 in the Supporting Information). As a consequence, the PPNI catalyst was largely insoluble even after the reaction (Table S1 in the Supporting Information, entries 5 and 6). The importance of the solubility of the catalyst in the reaction mixture was confirmed by comparing the activity of Bu_4NI and PPNI as catalysts for the reaction with 1,2-epoxyhexane as substrate. Whereas PPNI is in general a more active catalyst than Bu_4NI (see above), the higher solubility of Bu_4NI in 1,2-hexene carbonate (Table S2 in the Supporting Information) allowed achieving a good yield of this cyclic carbonate (23 %) in the presence of water, whereas only traces of carbonate were observed in the absence of water (Table 2, entries 7 and 8). Accordingly, Bu_4NI was soluble in the reaction mixture at the end of the test in the presence of water (Table S1 in the Supporting Information). It should be noted that the increased solubility of Bu_4NI in the organic phase is caused by the formation of the cyclic carbonate, whereas water does not play a significant role in this as proven by the fact that the reaction mixture consists of an organic phase and a separate aqueous phase (Table S1 in the Supporting Information) and that in the employed ratios water forms a biphasic liquid system with both 1,2-epoxyhexane and 1,2-hexene carbonate (Table S3 in the Supporting Information). An important consequence of the formation of a biphasic liquid system between water and 1,2-hexene carbonate or styrene carbonate in the ratios employed in our tests (Table S3 in the Supporting Information) is that the aqueous phase can be readily separated from the cyclic carbonate product, thus providing a further advantage of our system compared with organic HBDs.

With the aim of enhancing the solubility of PPNI, 1,2-hexene carbonate was employed as the solvent in the reactions of CO_2 with 1,2-epoxyhexane. Compared with the use of another polar solvent, the choice of 1,2-hexane carbonate is preferable because it does not require any separation at the end of the reaction. Although it can be expected that the addition of 1,2-hexene carbonate (being both solvent and product) could be detrimental for the conversion of the epoxide based on Le Chatelier's principle, we reasoned that the drawbacks could be outweighed by the positive effect on the solubility of PPNI. To test this hypothesis, we compared the effect of using propylene carbonate or 1,2-hexene carbonate as a solvent. For each of them, different amounts were tested whereas the amount of PPNI (0.4 mmol) and water (0.05 mL) was kept constant. Our strategy proved to be successful because the catalytic activity was dramatically enhanced by the addition of either propylene carbonate or 1,2-hexene carbonate (Figure 4). For each solvent, the activity gradually increased upon addition of the cyclic carbonate until a certain quantity, after which the yield of 1,2-hexene carbonate decreased. This drop in activity is most likely caused by a dilution effect, which decreases the probability of an encounter between epoxide and catalyst. The optimum activity as a function of the amount of carbonate used as a solvent was different between propylene carbonate and 1,2-hexene carbonate (Figure 4). This is ascribed to the higher solubility of the PPNI catalyst in the former cyclic carbonate (Table S2 in the Supporting Information). Although the addition of a cyclic carbonate plays a significant role in increasing the solubility of PPNI, this alone is not sufficient to achieve a good 1,2-hexene carbonate yield in the reaction of 1,2-epoxyhexane with CO_2 (Table 2, entry 11), and the presence of water as HBD is crucial for boosting the catalytic activity (Table 2, entry 12).

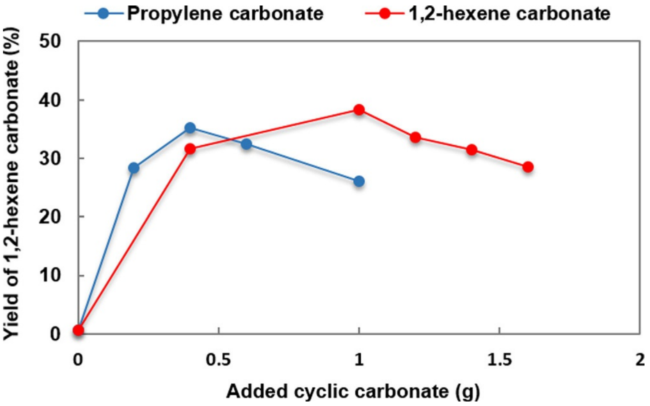

Figure 4. Effect of the use of propylene carbonate and 1,2-hexene carbonate as solvents on the reaction of CO_2 with 1,2-epoxyhexane in the presence of water. Reaction conditions: epoxide (20 mmol), PPNI (2 mol % relative to the epoxide), water (0.05 mL), 45 °C, 10 bar, 18 h. In the case of the use of 1,2-hexene carbonate as a solvent, the yield was calculated by subtracting the amount of 1,2-hexene carbonate added as a solvent from the total amount of carbonate measured at the end of the reaction.

The remarkable enhancement in the catalytic activity by using a cyclic carbonate as a solvent in the synthesis of 1,2-hexene carbonate prompted us to test the same concept in the synthesis of styrene carbonate and propylene carbonate because PPNI was not fully soluble in styrene oxide and propylene oxide before starting the catalytic test (Table S1 in the Supporting Information). However, the results showed that the catalytic activity was not improved, and the cyclic carbonate yield decreased upon adding even small amounts of carbonate (see Figure S5 in the Supporting Information). For these epoxides, the less notable enhancement of the solubility of PPNI is not sufficient to counterbalance the negative effect of adding the cyclic carbonate, and the principle of Le Chatelier and/or a dilution effect become the dominant factor.

The substrate scope of the catalytic system consisting of Bu_4NI and water was extended by investigating the conversion of an internal epoxide, cyclohexene oxide. The steric hindrance around the epoxide group and the geometric strain in the cyclic carbonate caused by the two adjacent rings make the conversion of cyclohexene oxide to cyclohexane carbonate more challenging than that of terminal epoxides.[5,48] Indeed, even upon using a higher catalyst loading (3 mol % Bu_4NI), a very low cyclohexane carbonate yield was obtained in the absence of water (Table 2, entry 13). The addition of water as HBD proved very beneficial in this case as well, leading to a more than four-fold increase in activity, although the achieved cyclic carbonate yield is still moderate under the employed conditions (Table 2, entry 14).

In the reactions performed in the presence of water in combination with either Bu_4NI or PPNI, small amounts of diol as side product were typically observed. The amounts were negligible in the synthesis of 1,2-hexene carbonate or cyclohexane carbonate and very small in the synthesis of propylene carbonate (e.g., $\text{yield}_{\text{diol}}=0.26\%$ in entry 4, Table 2), whereas a relatively larger amount of diol was observed in the synthesis of styrene carbonate, particularly in the tests employing a lower catalyst/HBD ratio (e.g., $\text{yield}_{\text{diol}}=0.38\%$ in Figure 2, 10 bar; 1.3% in entry 7, Table 1). Diols can also act as HBDs and thus cooperate with water in promoting the activity of the organic iodide catalysts. To investigate the contribution of diols as HBDs, we performed the reaction of propylene oxide with carbon dioxide by using Bu_4NI as catalyst under our standard conditions, but with the addition of 0.5 mol% propylene glycol and without adding water. The results show that the diol indeed promotes the activity of Bu_4NI (31% cyclic carbonate yield against 9% without any HBD, compare Table S4 in the Supporting Information with entry 3 in Table 2). However, the observed increase in yield is considerably lower than that achieved in the presence of water (55%, see entry 4 in Table 2). This result, in combination with the fact that the diol only forms gradually during the reaction and that the yield of diol in the test with water as HBD reached half of the amount used in this control experiment, indicates that the increased activity in the reaction between propylene oxide and CO_2 (from 9 to 55%) should be ascribed mainly to the role of water as HBD and only to a lesser extent to the formation of the diol. In the reaction between 1,2-epoxyhexane and CO_2 (entry 8, Table 2), no diol was observed, and the increase in activity compared with the reaction without water (entry 7, Table 2) is thus solely ascribed to the role of water as HBD. In contrast, in the reactions between styrene oxide and CO_2 in which a lower catalyst/H_2O ratio was employed (Table 1, entries 7–11), the relatively larger amount of diol formed most likely contributes significantly to the observed increase in activity when water is added to the system.

Finally, we performed catalytic tests with 1,2-epoxyhexane and propylene oxide as substrates and with a higher loading of Bu_4NI (3 mol%) in the presence of water as HBD, with the purpose of achieving high cyclic carbonate yields. The experiment with 1,2-epoxyhexane proved that the use of water as HBD allows reaching virtually full conversion while preserving complete selectivity towards the cyclic carbonate product in the reaction with CO_2 at 60 °C (entry 1, Table 3). The test with propylene oxide demonstrated that in the presence of water as HBD a remarkable 85% conversion with full selectivity towards propylene carbonate was achieved at room temperature, compared with only 17% conversion if the reaction was performed without adding water (compare entries 2 and 3, Table 3). These results are relevant and promising in the perspective of a large-scale exploitation of our catalytic system.

Table 3. Cycloaddition of CO_2 to epoxides with Bu_4NI as catalyst (3 mol%) and water as HBD.[a]

Entry	Substrate	H_2O [mL]	T [°C]	Yield[b] [%]	Selectivity[b] [%]
1	1,2-epoxyhexane	0.05	60	98	≥ 99
2	propylene oxide	–	25	17	≥ 99
3	propylene oxide	0.10	25	85	≥ 99

[a] Reaction conditions: epoxide (20 mmol), Bu_4NI catalyst (3 mol% relative to the epoxide), H_2O as HBD, mesitylene as internal standard (1.5 mmol), 10 bar CO_2, 48 h. [b] Yield and selectivity measured by ^1H NMR spectroscopy.

Conclusions

In this work, we showed that the most sustainable and least expensive hydrogen bond donor (HBD), water, can effectively promote the activity of organic iodide catalysts [i.e., tetrabutylammonium iodide (Bu_4NI) and bis(triphenylphosphine)iminium iodide (PPNI)] in the reaction of CO_2 with a variety of epoxides to produce the corresponding cyclic carbonates with excellent selectivity under very mild conditions (25–45 °C, 10 bar CO_2). To achieve these results, it was crucial to carefully tune the amount of water relative to the epoxide, the nature of the anion and cation constituting the organic halide catalyst, and the remaining reaction conditions. Between the two organic iodide catalysts, Bu_4NI proved to be in general slightly less active than PPNI under the same conditions, but its higher solubility in the reaction mixture, lower cost, and lower toxicity[49] make it a more attractive choice for upscaling.

When the catalytic tests were performed at 45 °C, the addition of water led to an increase of the cyclic carbonate yield by a factor two for styrene oxide as substrate, and to even more notable improvements with other epoxides (propylene oxide, 1,2-epoxyhexane, and cyclohexene oxide). These differences as a function of the epoxide employed as substrate indicate that the behavior of the catalytic system obtained upon addition of water is rather complex. In all cases, the presence of water enhances the catalytic performance mainly by acting as HBD, although with some epoxides (particularly with styrene oxide) it can also promote the formation of small amounts of diol, which in turn acts as an additional HBD. Another important parameter affected by the nature of the epoxide is the solubility of the organic halide catalyst in the reaction mixture. If, as with 1,2-epoxyhexane, the low solubility of PPNI limits the catalytic performance, the addition of a cyclic carbonate as solvent proved to be an efficient strategy to solubilize the organic halide and thus boost the catalytic activity.

Our study showed that for achieving the desired enhancement of the catalytic activity, significantly larger molar loadings of H_2O are needed than those required with the most effective organic HBDs (e.g., phenol, gallic acid, ascorbic acid). However, the lower efficiency of water as HBD is compensated by its assets, which include its environmentally benign nature, very low cost, and easier separation from the cyclic carbonate products, which can be achieved by exploiting either the formation of a biphasic system (in the case of styrene carbonate and 1,2-hexene carbonate) or the relatively low boiling point of water (in the case of propylene carbonate). Additionally, we demonstrated that using water as HBD in combination with Bu_4NI allows reaching very high yields of propylene carbonate at room temperature and to achieve virtually full conversion of 1,2-epoxyhexane with complete selectivity towards the cyclic carbonate (at 60 °C). All these features, in combination with the possibility of upscaling the system, demonstrate that water represents a more sustainable and more economically viable alternative to the use of organic HBDs as promotors for the catalytic fixation of CO_2 into cyclic carbonates under mild conditions.

Experimental Section

Materials

Styrene oxide (SO, 97 % purity), propylene oxide (PO, 99.5 % purity), 1,2-epoxyhexane (HO, 97 % purity), propylene carbonate (PC, 99.5 % purity), tetrabutylammonium iodide (Bu_4NI, 99 % purity), tetrabutylammonium bromide (Bu_4NBr, 99 % purity), tetrabutylammonium chloride (Bu_4NCl, 98 % purity), bis(triphenylphosphine)iminium chloride (PPNCl, 98 % purity), potassium iodide ($\geq$ 99 %), mesitylene (98 %), phenol (+99 %), propylene glycol (96 %), ascorbic acid, and deuterated chloroform ($CDCl_3$, $>$99.6 at %, used as solvent for ^{1}H NMR spectroscopy) were purchased from Sigma–Aldrich. Gallic acid (98 %) was purchased from Acros Organics. Diethyl ether and ethyl acetate were purchased from Macron fine chemicals. All chemicals were used without further purification. PPNI was prepared following a previously published procedure (see the Supporting Information for more details).[43] The elemental analysis of the prepared PPNI was performed at Mikroanalytisches Laboratorium KOLBE by using a Metrohm ion chromatograph model IC 883 Plus. Styrene carbonate and 1,2-hexene carbonate were prepared on a large scale by using the Bu_4NI/H_2O catalytic system (see the Supporting Information for experimental details), thus demonstrating the general feasibility of upscaling the use of water as HBD.

Catalytic tests

The catalytic tests were performed by using a high-throughput reactor unit (see Figure S6 in the Supporting Information) manufactured by Integrated Lab Solutions (ILS) and located at the University of Groningen, which allows performing reactions in CO_2 at a temperature between 20 and 200 °C and at a pressure between 1 and 200 bar. The unit consists of two modules: (i) a 10-reactors block that allows performing 10 reactions simultaneously in separate batch reactors (84 mL volume each, 30 mm internal diameter); and (ii) a single batch reactor with the same dimensions and equipped with a borosilicate glass window that allows visualization of the phase behavior within the reactor. Each batch reactor has individual magnetic stirring. In the 10-reactors block, each reactor has an automated closing valve that allows avoiding cross-contamination between reactors. An ISCO pump was used to pressurize the reactors. The temperature of the reactors was controlled by electrical heating cartridges connected to the aluminum blocks hosting the reactors. The risk of overpressure was avoided by automated depressurization protocols and rupture disks.[42] Both the 10-reactors block and the visualization reactor were used in this work. In each experiment, the epoxide (20 mmol), the selected organic catalyst (1–3 mol % loading relative to the epoxide), deionized water (0.025–0.8 mL if added), a cyclic carbonate (0.2–1.6 g if added), and mesitylene (1.5 mmol) as internal standard for NMR spectroscopy were added to a glass vial (46 mL volume, 30 mm external diameter) containing a magnetic stirring bar and closed with a screw cap hosting a silicone/polytetrafluoroethylene (PTFE) septum pierced with two needles allowing the CO_2 gas to enter and exit the vials. Then, the vial was placed into the selected reactor, and the reactor was closed. After this step, a software was used to control all protocols to reach the chosen reaction temperature and pressure. First, the reactor was purged with 5 bar N_2 and then with 10 bar CO_2 to remove air. After this, the reaction block was pressurized with CO_2 (to a lower pressure compared with the target), heated up to the desired reaction temperature, and finally further pressurized with CO_2 (if necessary) to reach the desired pressure. Next, the reactor block was kept under the selected conditions for 18 h with a stirring speed of 900 rpm. After 18 h, the stirring was turned off, and the reactor was cooled to room temperature in 20 min and depressurized to $\leq$1 bar. Finally, the lid of the reactor was opened, the glass vial was removed, and an NMR sample was prepared by adding $CDCl_3$ ($\approx$600 mg) to 50 mg of the reaction mixture. The epoxide conversion, carbonate yield, and selectivity were determined by analyzing the reaction mixture by ^{1}H NMR spectroscopy on a Varian Oxford 300 MHz or a Varian Mercury 400 MHz. The residual solvent resonance was used as a reference for the peak positions in the ^{1}H NMR spectra, which were reported in ppm relative to tetramethylsilane (TMS, 0 ppm). The formation of the diols was confirmed by GC–MS performed on an Agilent Hewlett–Packard-HP 6890 (Rxi-5 Sil MS column, 30 m, 0.25 mm) coupled with an Agilent Hewlett–Packard 5973 MSD MS. Selected catalytic tests were performed in duplicate or triplicate, showing a high degree of reproducibility of the obtained cyclic carbonate yields ($\pm$1 %). In such cases, the average value of the cyclic carbonate yield is reported.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon dioxide · cyclic carbonates · hydrogen bond donor · metal-free catalysts · water

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