Green Chemistry

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Cite this: *Green Chem.*, 2021, **23**, 592

Highly efficient synthesis of alkylidene cyclic carbonates from low concentration CO_2 using hydroxyl and azolate dual functionalized ionic liquids†

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Received 17th October 2020,
Accepted 8th December 2020

DOI: 10.1039/d0gc03510f

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A highly efficient catalytic system was developed for the reaction between CO_2 and propargylic alcohols for alkylidene cyclic carbonates. Ionic liquids (ILs) with different anions and cations were designed as cocatalysts, in order to find out the effect of the cation and the anion on this reaction. The results indicated that the effect of the cation was significant, especially the hydroxyl group on the cation played an important role due to the presence of a hydrogen bond. It was also found that the basicity of the anion was important for its catalytic activity, where the anion with moderate basicity gave the best activity. Moreover, this hydroxyl and azolate dual functionalized catalytic system showed excellent reusability and generality. It is worth mentioning that at a low concentration of CO_2, this dual functionalized catalytic system showed excellent catalytic activity even in a gram-scale reaction, indicating its potential in carbon capture and utilization processes.

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Introduction

CO_2 capture and utilization (CCU) has evoked great interest in the past few decades because CO_2 can be regarded as an abundant, cheap, and environmentally friendly C1 synthon, which is widely used for the synthesis of many fine chemicals.[1–6] Unfortunately, because of its inherent thermodynamic stability and kinetic inertness, the CCU processes usually require high energy input (including high temperature, high pressure) and the addition of metal catalysts or excessive strong base.[7,8] In addition, compared with other CO_2 sources, fixation of CO_2 from flue gas, one of the major CO_2 sources, is still a major challenge due to its low CO_2 concentration (~10 vol%).[9–11] Thus, effective catalysts are still urgently desired for CO_2 upgradation at low concentration.

Ionic liquids (IL) are promising and eco-friendly candidates as CO_2 absorbents, because of their unique properties, such as high thermal stability, negligible vapor pressure, and tunable structures. By finely tuning IL structures and properties, significant achievements could be made in designing ILs with impressive CO_2 capacity.[12–25] At the same time, thanks to their tunable structures and superior CO_2 absorption ability, ILs can be used to realize CCU processes even under mild conditions.[26–33] There have been many systematical reports focusing on the influence of anions in ILs, where the anion plays key roles in CCU processes as an absorbent and catalyst.[34–38] However, few studies could be realized on the important role of the cation in CCU processes such as the synthesis of alkylidene cyclic carbonates.

Recently, carbonates have drawn much attention because of their potential bioactivities and widespread applications in Li-ion batteries and the pharmaceutical industry.[39,40] Based on the principles of green and sustainable chemistry, the carboxylative cyclization of propargylic alcohols and CO_2 is a promising route to obtain α-alkylidene cyclic carbonates.[41,42] Till now, although numerous heterogeneous catalysts have been reported for this reaction,[43–57] most of them suffered from harsh reaction conditions including high CO_2 pressure, excessive catalyst loading and poor reusability of catalysts, which can be ascribed to the poor activity or low stability of catalysts. How to realise these processes efficiently at a low concentration of CO_2 (such as 10%) is still a puzzle for researchers.

Herein, we developed a highly efficient catalytic system used for the reaction between CO_2 and propargylic alcohols. ILs with different anions and cations were used as cocatalysts (Fig. 1), in order to find out the effect of ILs on this reaction. The results indicated that both the cation and anion played a key role. Therefore, a dual functionalized IL with hydroxyl and azolate groups [Ch][Triz] was designed, which exhibited excellent activity and good reversibility in this reaction. It is worth mentioning that under 10% CO_2, the catalytic system ($AgNO_3$/

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† Electronic supplementary information (ESI) available: NMR, and Tables S1 and S2. See DOI: 10.1039/d0gc03510f

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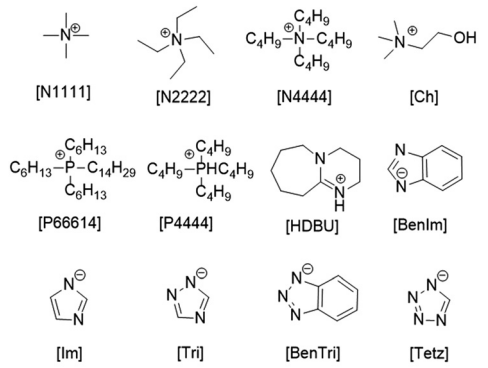


Fig. 1 Structures of the cation and anion of the IL used in this work.

[Ch][Tri]) showed excellent catalytic activity even in a gram-scale reaction.

Experimental

Materials and methods

All chemicals used in this work were commercial available and used without further purification unless otherwise stated. 3-Methyl-1-pentyn-3-ol, 2-phenyl-3-butyn-2-ol and 1-ethynylcyclopentanol were purchased from J&K Scientific Ltd. 2-Methyl-3-butyn-2-ol was purchased from Aladdin Ind. Co., Ltd. 1*H*-Tetrazole (Tetz), 1*H*-benzotriazole (Bentri), 1,2,4-triazole (Triz), benzimidazole (BenIm), tetrabutylammonium hydroxide ($[N_{4444}][OH]$), imidazole (Im), tetraethylammonium hydroxide ($[N_{2222}][OH]$), tetramethylammonium hydroxide ($[N_{1111}][OH]$), choline (Ch) and 1-ethynyl-1-cyclohexanol were purchased from Energy-Chemistry Co., Ltd. CO_2 (99.99%), CO_2 (10%) and N_2 (99.99%) were purchased from Hangzhou Jingong Special Gas Co., Ltd. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz) in DMSO-d_6, which was obtained from Adamas-beta, with DMSO as the standard.

The synthesis of functionalized ILs

These functionalized ILs were easily prepared by the neutralization of superbases or the solution of $[N_{1111}]OH$, $[N_{2222}]OH$, $[N_{4444}]OH$, $[P_{4444}]OH$ or choline with azole compound. In a typical example, the reaction mixture was stirred at 50 °C for 6 h and then the vacuum-rotary evaporation procedure was applied to remove most of the water. After that, ILs were dried under vacuum at 80 °C for more than 24 hours to reduce the possible traces of water. Before use, the water content of ILs was determined by Karl Fisher titration and found to be less than 0.1 wt%.

General procedure for the synthesis of alkylidene carbonates

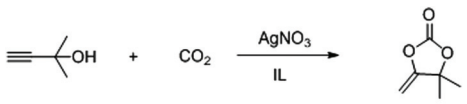
As a typical example, the procedure using 2-methyl-3-butyn-2-ol (**1a**) as a typical substrate is described. $AgNO_3$ (0.066 g, 0.4 mmol), [Ch][Triz] (0.138 g, 0.8 mmol), and **1a** (0.336 g, 8 mmol) were added into a Schlenk flask, connected with a CO_2 balloon filled with CO_2 (99.99%). Then the reaction mixture was stirred at 30 °C for 24 h. The conversion and yield of product **1b** were quantitatively analyzed by gas chromatography (GC) with biphenyl as the internal standard. To investigate the reusability of the catalyst system, the reaction mixture was extracted with *n*-hexane (4 × 15 mL). The upper layer was collected and the solvent was removed to obtain the product, and the lower layer, composed of $AgNO_3$ and [Ch][Triz], was dried in a vacuum at 60 °C for the next cycle.

Results and discussion

At first, various catalysts were applied to the reaction; the results are listed in Table S1.† The effect of different metal catalysts on this reaction was obvious, where $AgNO_3$ and AgOAc catalysts displayed better catalytic reactivity. Considering the basicity of AgOAc that may affect the catalytic reactivity of ILs, we chose $AgNO_3$ for further research.

The effect of the cation on catalytic activity was investigated, which can be seen in Table 1. At first, the reaction could not take place with no IL as the cocatalyst (entry 1). When a protic IL ([DBU][Tri]) was used as the cocatalyst, the reaction did not occur. It was clear that the type of IL made a big difference. Then, a series of aprotic ILs with different kinds of cations were designed and prepared for the reaction. It was reported that the chain length of the cation affected its catalyst activity significantly. When aprotic ILs, $[N_{1111}][Tri]$, $[N_{2222}][Tri]$ and $[N_{4444}][Tri]$, were used as the cocatalyst, yields of 81%, 69% and 67% were obtained (Table 1, entries 3–5), respectively. In other words, the cation with a shorter chain length gave a higher yield of **2a** in this reaction. We could come to a similar conclusion by comparing entry 5 and entry 6. Besides, $[N_{4444}][Tri]$ and $[P_{4444}][Tri]$ resulted in comparable yields of 67% and 64% (Table 1, entries 4 and 5), which indicated that the impact of the central atom of the cation was weak.

Table 1 The effect of the cation on catalytic activity[a]



1a 2a

Entry	Ionic liquid	Conversion[b] [%]	Yield[b] [%]
1	—	—	<1
2	[DBU][Tri]	4	<1
3	$[N_{1111}][Tri]$	90	81
4	$[N_{2222}][Tri]$	82	69
5	$[N_{4444}][Tri]$	77	67
6	$[P_{4444}]$ [Tri]	75	64
7	$[P_{66614}][Tri]$	70	59
8	$[P_{66614}][Tri]$	70	59
9[c]	[Ch][Tri]	<1	<1

[a] Reaction conditions: **1a** (4 mmol), $AgNO_3$ (0.4 mmol), base (0.8 mmol) and CO_2 (1 bar) for 24 h at 30 °C. [b] Determined by GC using the internal standard method. [c] Without $AgNO_3$.

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Considering that the hydrogen bond played an important role in some CCU processes, a hydroxyl functionalized aprotic IL [Ch][Tri] was designed, prepared, and used in this reaction. The conversion and yield could be improved to 99% and 93% (Table 1, entry 8), respectively. These results indicated that the hydroxyl group of the cation could promote this reaction well. In a control experiment, no reaction proceeded without $AgNO_3$ (Table 1, entry 9). Clearly, both $AgNO_3$ and base (also called a co-catalyst) were indispensable for this reaction.

To investigate the influence of the basicity of the anion, the reaction was carried out using ILs with various basic anions, and the results are listed in Table 2. When [Ch][Cl] was used, only 4% yield of the product was obtained, which implied that the basicity was also significant for this reaction. By tuning the basicity of the anion, it was obvious that this reaction was affected by the strength of the base, where higher conversion was achieved when a stronger basic IL was used. As for the anion with weak basicity, like [Tetz] and [BenTri], the reaction was not complete within 24 hours, implying poor catalytic activity (entries 2 and 3). To our delight, [Tri], whose pK_a was 18.6, could improve the conversion and yield to 99% and 93% (entry 4), respectively. However, strongly basic ILs, [Ch][BenIm] and [Ch][Im], resulted in much lower yields of the product than [Ch][Tri], due to the decreased selectivity (entries 5 and 6). Therefore, a dual functionalized IL with a hydroxyl group and moderate basicity [Ch][Tri] exhibited the best catalytic activity. Besides, compared with other $AgNO_3$-based systems, $AgNO_3$/[Ch][Tri] exhibited excellent performance for CO_2 utilization (Table S4†).

Compared with other CO_2 sources, capturing CO_2 from flue gas is a major challenge due to its low concentration (~10 vol%). Therefore, to further evaluate its practicability, the reaction was also carried out at a low concentration CO_2 of 10%. To our delight, after extending the reaction time to 48 hours, this catalytic system composed of $AgNO_3$ and [Ch][Tri] gave **2a** in a yield of 90% after bubbling CO_2 at 0.1 bar under 30 °C, even at a gram-scale (Fig. 2).

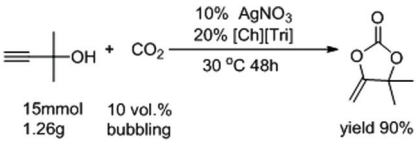


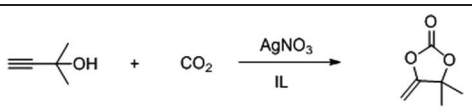
Fig. 2 A gram-scale reaction under low concentration of CO_2 using $AgNO_3$ as the catalyst and [Ch][Triz] as the cocatalyst.

The reusability of the catalytic system is a critical property for CO_2 utilization, which has a direct impact on the cost because it determined the frequency of the replacement of the catalyst. Therefore, we investigated the recycling performance of the $AgNO_3$ and [Ch][Tri] catalytic system under the optimized reaction conditions. The results for 8 cycles are shown in Fig. 3. It was found that good catalytic activity was well-maintained during the 8 cycles.

The substrate scope and generality of this reaction were investigated by using this dual functionalized catalytic system. As illustrated in Table 3, all of these substrates could react with CO_2 under mild conditions, and good to excellent yields were obtained. With an ethyl group, **2b** was given in a yield of 92% (entry 4). By extending the reaction time, a substrate with a large substituent group could also convert totally. The reactivity of phenyl substituted propargylic alcohol was investigated, and a 95% yield of **2c** was obtained (entry 5). In addition, the reaction of **1d** and **1f** was found to occur smoothly with yields of 92% and 89%, respectively, which means that this dual functionalized IL also has a good catalytic activity on propargylic alcohol with a cycloalkane group.

On the basis of the experimental results and previous literature reports, we proposed a plausible mechanism for this reaction (Fig. 4). Firstly, the carbon–carbon triple bond on the substrate **1a** could be activated by silver ions ($AgNO_3$). Meanwhile, [Tri] had a sufficient basicity to extract the proton from the hydroxyl group on **1a** to form intermediate I, and the hydroxyl group on [Ch] could stabilize the intermediate I through inter-

Table 2 The effect of different basic anions on catalytic activity[a]



Entry	Ionic liquid	pK_a of anions[b]	Conversion[c] [%]	Yield[c] [%]
1	[Ch][Cl]	1.8	15	4
2	[Ch][Tetz]	8.2	23	17
3	[Ch][BenTri]	11.9	67	64
4	[Ch][Tri]	13.9	99	93
5	[Ch][BenIm]	18.2	97	67
6	[Ch][Im]	18.9	99	64

[a] Reaction conditions: **1a** (4 mmol), $AgNO_3$ (0.4 mmol), base (0.8 mmol) and CO_2 (1 bar) for 24 h at 30 °C. [b] Values in DMSO. [c] Determined by GC using the internal standard method.

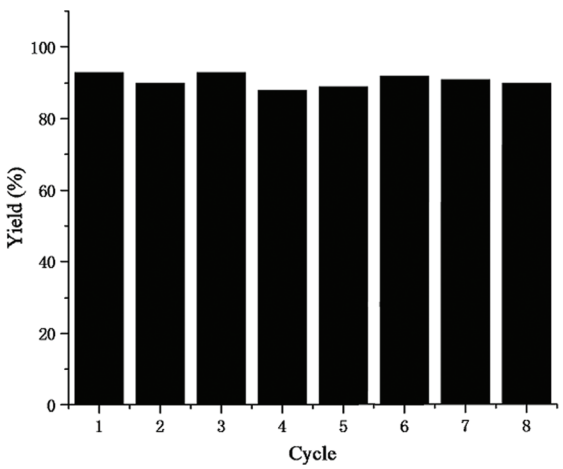


Fig. 3 Recycling experiments using $AgNO_3$ as the catalyst and [Ch][Triz] as the cocatalyst.

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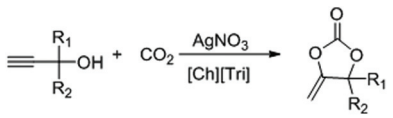
Table 3 The synthesis of alkylidene carbonates from CO_2 using [Ch][Tri][a]



Entry	Substrate	R_1	R_2	T [h]	Yield[b] [%]
1	**1a**	Me	Me	24	93
2	**1a**[c]	Me	Me	48	85
3	**1a**[d]	Me	Me	48	87
4	**1b**	Me	Et	24	92
5	**1c**	Me	Ph	36	95 (87)[e]
6	**1d**	$-(CH_2)_5-$		36	92
7	**1f**	$-(CH_2)_4-$		30	89

[a] Reaction conditions: Substrate (4 mmol), $AgNO_3$ (0.4 mmol), [Ch][Tri] (0.8 mmol) and CO_2 (1 bar) at 30 °C. [b] Determined by NMR using the internal standard method. [c] 10 vol% of CO_2. [d] 15 vol% of CO_2. [e] Isolated yield.

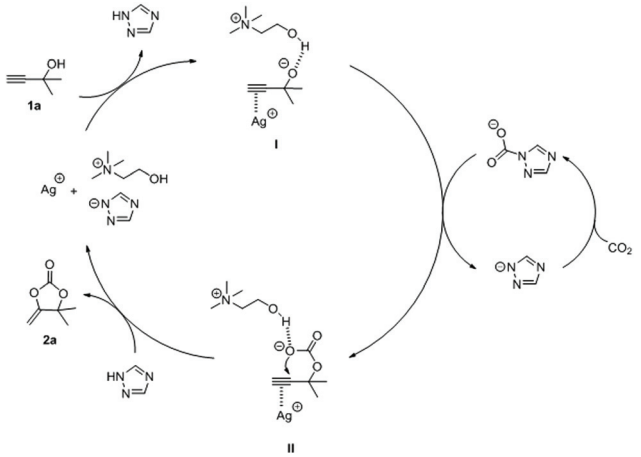


Fig. 4 Possible mechanisms for this reaction.

molecular hydrogen bonding. Subsequently, intermediate II was obtained by intermediate I nucleophilic attacked CO_2, which was captured by [Tri]. Finally, **2a** was generated through an intramolecular ring-closing reaction in II, and silver ions and [Ch][Tri] were regenerated. With this proposed mechanism, ILs acted as a CO_2 absorbent and a base at the same time. As a CO_2 absorbent, it can be seen that ILs with higher basicity could capture more CO_2, while the strong interaction between ILs and CO_2 would impede the reaction of CO_2 and propargylic alcohols. On the other hand, as a base, ILs with weak basicity were hard to initiate the reaction by abstracting hydrogen from propargylic alcohols.

Conclusions

In summary, an efficient catalytic system was developed for the reaction between CO_2 and propargylic alcohols under mild conditions. We found that the effect of the cation on the reaction was significant, where the hydroxyl group on the cation could promote this reaction well. It was also found that the basicity of the anion was important to its activity, where the anion with moderate basicity gave the best activity. Therefore, the catalytic system comprising the dual functionalized IL [Ch][Tri] and $AgNO_3$ exhibited excellent reusability and generality. To be specific, this catalytic system showed excellent performance in a gram-scale reaction even under low concentration of CO_2. We believe that this method developed by us through tuning both the cation and the anion is not only important for CCU processes, but also for gas separation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge the support of the National Natural Science Foundation of China (21776239), the Zhejiang Provincial Natural Science Foundation of China (LZ17B060001), and the State Key Laboratory of Chemical Engineering (No. SKL-ChE-20T05).

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