



Water as an efficient medium for the synthesis of cyclic carbonate

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ABSTRACT

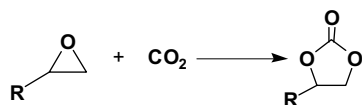
Herein, we report a novel method for the synthesis of cyclic carbonate in water. By tuning the amount of water, cycloaddition of CO₂ to epoxide in aqueous medium leads to cyclic carbonates with moderate to excellent yields and high selectivities. In addition, the presence of water could remarkably improve the activity of ionic liquids by which the turnover frequency of the reaction is about 4–5 times higher in the presence than in the absence of water. The relationship between the higher catalytic reactivity and water was proposed.

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Cyclic carbonates, such as ethylene carbonate and propylene carbonate, are important species in organic chemistry. They have attracted the attention of many chemists, not only because they can serve as excellent aprotic polar solvents and extensively as intermediates in the production of pharmaceuticals and fine chemicals, but also because their current synthesis methods (Scheme 1) are one of the most attractive synthetic protocols utilizing CO₂ as an attractive C1 building block.^{1,2}

Numerous catalysts including ionic liquid (IL) have been developed for this transformation.^{3–23} However, the above catalysts generally suffer from low catalytic activity, water or air sensitivity, and the need for toxic co-solvent. In addition, methods for cyclic carbonate preparation are traditionally in anhydrous systems, which is a critical reaction condition for eliminating unavoidable water in applications.

We recently demonstrated that hydroxyl group when added to traditional ionic liquid catalysts could efficiently catalyze the reaction and yield high cyclic carbonates without Lewis acid.²⁴ Since water is a green, cheap, and hydroxyl group-containing solvent,



Scheme 1. Synthesis of cyclic carbonate from CO₂ and epoxide.

herein, we decided to develop a new method for preparing cyclic carbonate in water.

Using propylene oxide (PO) as a model substrate, the comparison experiments of cycloaddition of CO₂ to PO were carried out under the cases with and without water.²⁵ The results were listed in Table 1. In the presence of water, interestingly, PO conversion and PC yield are considerably increased, and almost all the employed Lewis base catalysts show high activities. When KI and KBr are used, the obtained turnover frequencies (TOFs) are surprisingly about 54 and 236 times higher than those without water, respectively. The activity order of cations is PPh₃Bu⁺ > Bu₄N⁺, [bmim]⁺ > K⁺ > Na⁺ (entries 1, 2, 4, 7, and 12). A longer alkyl chain phosphonium halide, such as butyl-triphenylphosphonium bromide (PPh₃BuBr) or hexyl-triphenylphosphonium bromide (PPh₃HexBr), still exhibits higher activity and selectivity than a shorter chain in the presence of water (Table 1, entries 12, 15, and 16). The activity of anions varies in the order I⁻ > Br⁻ > Cl⁻ > PF₆⁻, BF₄⁻ (entries 7–11), while it is Br⁻ > Cl⁻ > I⁻ > PF₆⁻, BF₄⁻ without water. The results show that the activity of I⁻ is very sensitive to water. Because of the low nucleophilic nature of PF₆⁻ and BF₄⁻ anions,^{9c} low PO conversions and PC selectivities are obtained using 1-butyl-3-methyl-imidazolium-hexafluorophosphate ([bmim]PF₆), and 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim]BF₄) in the presence of water (entries 10 and 11). Due to high water sensitivity of zinc halides, their binary catalytic systems exhibited unsatisfactory results and lost their activities quickly in aqueous reaction system (Table 1, entries 17 and 18). Because of its good performance (entries 14, 19, and 20), PPh₃BuI was chosen for further experiments.

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Table 1
Comparison experiments of cycloaddition of CO₂ to PO under the cases with and without water^a

Entry	Catalyst	With water ^b			Without water ^b		
		X (%)	Y (%)	TOF (h ⁻¹)	X (%)	Y (%)	TOF (h ⁻¹)
1	NaBr	40	30	63	0.8	Trace	1.6
2	KBr	60	52	108	1	Trace	2
3	KI	78	68	142	0.3	Trace	0.6
4	Bu ₄ NBr	95	86	175	56	54	111
5	Bu ₄ NCl	70	46	98	44	42	127
6	Bu ₄ NI	95	88	185	27	26	53
7	[bmim]Br	94	87	180	52	50	104
8	[bmim]Cl	64	42	75	46	44	90
9	[bmim]I	97	90	184	53	51	105
10	[bmim]BF ₄	3.3	Trace	0.7	Trace	—	—
11	[bmim]PF ₆	10	Trace	1.2	2.7	1.7	5.4
12	PPh ₃ BuBr	96	88	177	54	52	108
13	PPh ₃ BuCl	72	51	90	45	44	131
14	PPh ₃ BuI	100	95	194	25	24	49
15	PPh ₃ EtBr	95	85	173	50	49	100
16	PPh ₃ HeBr	97	89	182	61	59	122
17 ^c	ZnBr ₂	1.2	Trace	0.5	3.5	2.7	7
18 ^d	ZnBr ₂ /PPh ₃ HeBr	78	70	142	100	97	199
19 ^e	PPh ₃ BuI	99.6	93	192	24	22	48
20 ^f	PPh ₃ BuI	80	72	150	10	8	16

^a Reaction conditions: PO (0.2 mol), H₂O (0.067 mol), catalyst (1 mmol), CO₂ pressure (2 MPa), 125 °C, 1 h.

^b X: PO conversion; Y: isolated PC yield; TOF: mole of synthesized PC per mole of catalyst per hour.

^c ZnBr₂ (0.5 mmol).

^d ZnBr₂ (0.165 mmol), PPh₃HeBr (0.67 mmol).

^e After ten times reuse.

^f CO₂ pressure (0.5 MPa).

In order to further investigate the effect of the amount of water in tailoring the synthesis rate of PC, experiments were carried out in which the ratio of H₂O/PO was increased from 0 to 2. As shown in Figure 1, only 26% of PO conversion is observed using PPh₃BuI by itself in the absence of water after 1 h. This might be caused by the difficult ring-opening of epoxide with Lewis base alone,^{5,8,10} while with the presence of water, the activity of PPh₃BuI is sensitively improved. In a low-ratio region (from 0 to 0.33), an increase in ratio could result in remarkable increase in both PC yield and PO conversion. Within this region, PC selectivity keeps above 97%. And the maximal PC yield (97%) obtained at the ratio of 0.33 is about 4 times higher than that without water (25%). While further increasing the amount of water from 0.33 to 2 causes a decrease in the yield and selectivity of PC though PO conversion keeps at 100%. PC selectivity decreases quickly from 97% to 63% correspondingly. It can be explained by the side reaction between water and PO to produce corresponding chemical, 1,3-propylene glycol (PG), which

is another important chemical in organic chemistry. In general, to obtain both high PC yield and high selectivity, the ratio of 0.33 is optimal.

Additional experiments showed that the amount of water could remarkably affect the synthesis rate of cyclic carbonate. For example, the results of PC yield versus reaction time are listed in Figure 2. It can be observed that in the absence of water (A), it takes more than 4.0 h to obtain only 57.0% PC yield with low TOF value (24 h⁻¹). At a low amount of water (B), the synthesis rate of PC is about 2 times faster compared to that without water. The highest synthesis rate obtained in the ratio of 0.33 (E) could be more than 7 times faster than that of curve (A) in 0.5 h. When the ratio is above 1:3, for example, H₂O/PO = 1:1 (F), PC yield is decreased but the PC synthesis rate is still increased. At this amount of water, PC yield could reach its maximal value within 0.5 h. From the above results, water accelerated the cycloaddition reaction of CO₂ to PO, by which the reaction could proceed more smoothly with the pres-

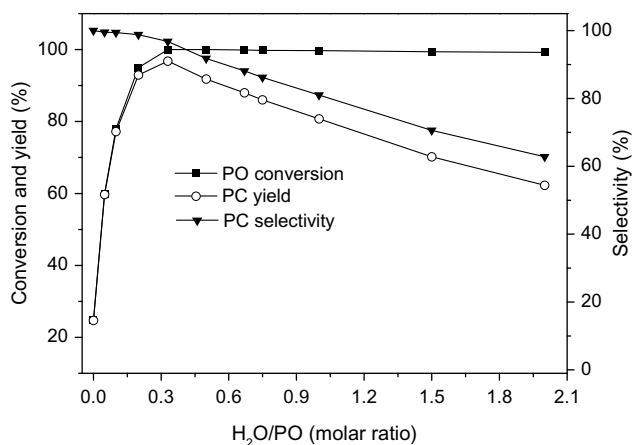


Figure 1. Effect of the amount of water on the synthesis of propylene carbonate. Reaction conditions: PO (0.2 mol), PPh₃BuI (1 mmol), 2 MPa, 125 °C, 1 h.

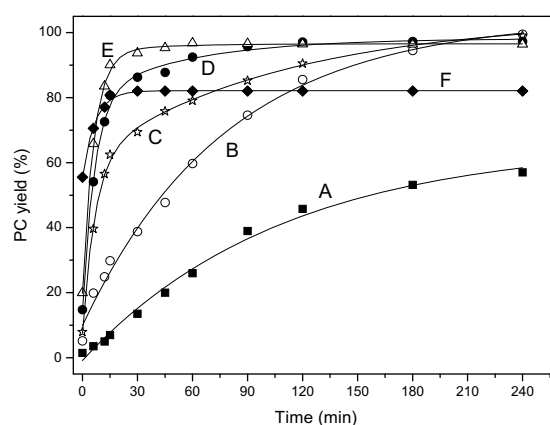



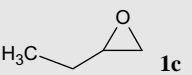
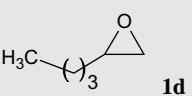
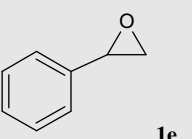
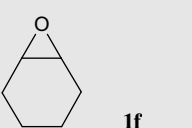
Figure 2. PC yield versus reaction time with different amounts of water. Molar ratio of H₂O/PO: (A) 0, (B) 1:20, (C) 1:10, (D) 1:5, (E) 1:3, (F) 1:1. Reaction conditions: PO (0.2 mol), PPh₃BuI (1 mmol), 2 MPa, 125 °C.

ence of more water content. However, in order to balance both high PC yield and high synthesis rate, 1:3 is the optimal ratio to be considered, which is consistent with the results in Figure 1. It can also be found that at the ratio of 0.33, increasing reaction time beyond 0.5 h up to 4.0 h makes but a slight enhancement in PC yield. In this case, more than 99% PC selectivity and 96% PC yield could be obtained with about 380 h⁻¹ TOF value.

Cycloadditions of CO₂ to other epoxides in water were also examined using PPh₃Bul catalyst at 125 °C and 2 MPa. As shown in Table 2, the reactions proceed smoothly for all the substrates used in the presence of water. High epoxide conversions as well as ≥92% cyclic carbonate selectivities are obtained under the desired reaction conditions (entries 1–5). Aromatic **1e** and aliphatic **1a**, **1c**, and **1d** epoxides are preferred substrates for the reaction. Epoxide **1f** exhibits the lowest activity of the epoxides surveyed as expected from the higher hindrance that originated from the two rings. However, the yields obtained without water are about 3–4 times lower than those in the presence of water. For example, the synthesis of ethylene carbonate (EC) from ethylene oxide (EO) and CO₂ could be completed within 0.5 h at 110 °C with 98% selectivity (Table 2, entry 1) in the presence of water (H₂O/EO = 0.33, molar ratio), while only 30% EO conversion could be obtained under the same reaction conditions without water. If we further increase the molar ratio of H₂O/EO up to 1:1 (entry 1), high EO conversion as well as high EC selectivity could also be achieved. When **1e** is substituted for **1a**, similar tendency could also be observed (entry 4).

To understand the role of the OH group in accelerating the reaction, other solvents with or without OH groups were also tested substituting for water for the synthesis of PC with PPh₃Bul. It can be seen from Table 3 that the activity of PPh₃Bul can also be greatly improved in the presence of OH groups containing chemicals, such as phenol, acetic acid, propylene glycol (PG), ethanol, 2-propanol, and polyethylene glycol (PEG with molecular weight 400). Both high PO conversion and high PC selectivity can be realized under

Table 2
Synthesis of other cyclic carbonates in the presence of water^a

Entry	Epoxide	T/t (°C/h)	Results ^b		
			Y ^c (%)	Y (%)	S (%)
1	 1a	110/0.5	28	95/89 ^d	98/93 ^d
2	 1c	125/1	21	95	97
3	 1d	125/1	20	87	98
4	 1e	125/1	20	83/85 ^d	96/92 ^d
5	 1f	125/2.5	6	47	96

^a Reaction conditions: epoxide (0.2 mol), H₂O (0.067 mol), PPh₃Bul (1 mmol), 2 MPa, 125 °C.

^b X: epoxide conversion; Y: isolated yield; S: selectivity.

^c In the absence of water.

^d H₂O (0.2 mol).

Table 3
Effect of various solvents on the synthesis of PC^a

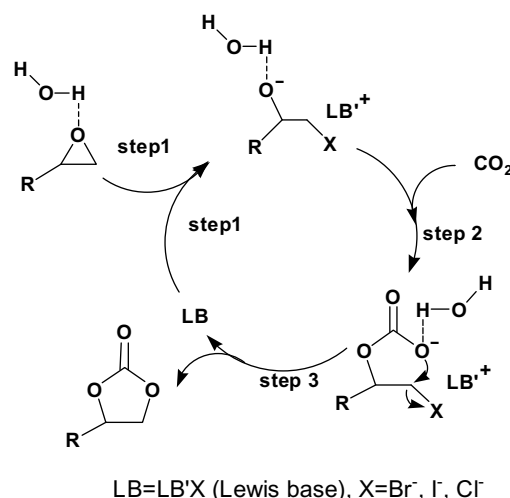
Entry	Solvent	Results ^b		
		X (%)	S (%)	TOF (h ⁻¹)
1	Water	100	97	194
2	Phenol	96	95	185
3	Acetic acid	95	92	174
4	PG	94	97	181
5	Ethanol	81	99	161
6	2-Propanol	79	98	154
7	PEG	75	97	145
8	DMF	36	>99	72
9	PC	35	>99	71
10	Acetone	34	99	68
11	Acetonitrile	31	>99	61
12	Cyclohexane	30	>99	61
13	DMC	18	>99	36
14	Dichloromethane	16	>99	32

^a Reaction conditions: PO (0.2 mol), solvent (1.2 mL, 25 °C), PPh₃Bul (1 mmol), 2 MPa, 125 °C, 1 h.

^b X: PO conversion; S: PC selectivity; TOF: mole of synthesized PC per mole of catalyst per hour.

the same conditions (entries 2–7). But, the results obtained are lower than that in water (entry 1). On the contrary, PO conversions are little improved in the presence of non-OH group containing solvents, such as *N,N*-dimethylformamide (DMF), PC, acetone, acetonitrile, cyclohexane, dimethyl carbonate (DMC), and dichloromethane (CH₂Cl₂) (entries 8–14). Although these polar solvents are commonly used to improve the catalytic activities of catalysts in the previous literatures (e.g., Mg–Al mixed oxides,¹⁵ SmOCl,^{4c} TBD/MCM-41,²² and Cr–salen²³), herein, their functions in accelerating the activity of catalyst are still limited. In addition, some of them are toxic and expensive. From the viewpoint of application and green chemistry, developing cheap, efficient, and safe solvent in catalysis is another requirement aspect. The above results indicate that Brønsted acidic solvents, especially OH group containing solvents, are considerable promoters to improve the activity of the catalyst for the synthesis of PC.

Based on the above results and the previous reports,^{2b,12,24} a mechanism portraying the probable sequence of events is shown in Scheme 2. It was proposed that water (acidic site) and the bromine anion of Lewis base (basic site) coordinately attacked the different parts of epoxide firstly. The coordination of the H atom of water molecule with the O atom of epoxide through a hydrogen



Scheme 2. Proposed mechanism for the reaction in water.

bond resulted in the polarization of C–O bonds, and the halide anion made the nucleophilic attack on the less sterically hindered β -carbon atom of the epoxide at the same time. As a result, the ring of the epoxide was opened easily (step 1). Then, the interaction occurred between the oxygen anion and CO₂, forming an alkylcarbonate anion (step 2) which would be transformed into a cyclic carbonate by the intramolecular substitution of the halide in the next step (step 3). In the reaction, water played a similar function like a Lewis acid on the ring-opening of epoxide, by which the Lewis base could show excellent activity in the absence of Lewis acid. From the above experiments (Table 3, entries 2–7), other solvents containing OH groups might also play the similar role in accelerating the activity of the catalyst.

In conclusion, the synthesis of cyclic carbonates from CO₂ and terminal epoxides in water was reported using a single Lewis base catalyst. The coupling reactions proceeded smoothly with moderate to excellent yields of products. Also water could play a significant role in determining the selectivity in addition to the activity of the catalyst. It was proposed that water and the anion of Lewis base played a synergic epoxy ring-opening effect in accelerating the reactions. Among the catalysts investigated, PPh₃Bul was the best effective Lewis base for the synthesis of cyclic carbonate under the mild conditions (125 °C, 2.0 MPa, and 1.0 h), and showed high stability in activity and selectivity.

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- Cycloaddition procedure for the reaction of propylene oxide (PO) with CO₂*: All the coupling reactions were conducted in a 100 ml stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. A typical reaction was carried out as follows: in the reactor, an appropriate CO₂ (\approx 1.0 MPa) was added to a mixture of PO (14.0 mL, 0.2 mol), H₂O (1.2 mL, 0.067 mol), and catalyst (1 mmol) at room temperature. Then, the temperature was raised to 125 °C with the addition of CO₂ from a reservoir tank to maintain a constant pressure (2.0 MPa). After the reaction had proceeded for a desirable time, the reactor was cooled to 5 °C in an ice-water bath, and the remaining CO₂ was removed slowly. After reaction, the catalyst was separated by distillation under vacuum and reused for further recycling experiment. The crude product mixture was dried over anhydrous sodium sulphate, and then subjected to column chromatography using a 6:1 petroleum ether/EtOAc eluent system on silica gel (200–300 mesh) to give cyclic carbonate as a colorless liquid. The isolated products were analyzed by NMR and Agilent 6890/5973B GC–MS equipped with a MS detector using acetophenone as the internal standard.