Green Chemistry



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Cite this: *Green Chem.*, 2021, **23**, 3386

CO₂ atmosphere enables efficient catalytic hydration of ethylene oxide by ionic liquids/ organic bases at low water/epoxide ratios†

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The development of an efficient and low-cost strategy for the production of monoethylene glycol (MEG) through hydration of ethylene oxide (EO) at low H₂O/EO molar ratios is an important industrial challenge. We have established that by using CO₂ as the reaction atmosphere, hydration of EO can be achieved at a low H₂O/EO ratio of 1.5 : 1 along with high yields (88–94%) and selectivities (91–97%) of MEG catalyzed by binary catalysts of ionic liquids and organic bases. The results are significantly better than those of experiments conducted under an atmosphere of N₂. Isotope labeling experiments revealed that CO₂ had altered the reaction pathway and participated in the reaction, in which cycloaddition of EO with CO₂ occurred first followed by the hydrolysis of ethylene carbonate (EC) to generate MEG and recover CO₂. The ionic liquids and organic bases synergistically catalyzed the one-pot two-step reaction. DFT calculations confirmed that this route is more kinetically favorable compared to the pathway of direct epoxide hydration.

Received 28th February 2021, Accepted 1st April 2021 DOI: 10.1039/d1gc00758k

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Introduction

Monoethylene glycol (MEG) has many industrial applications, such as for the manufacture of antifreeze and coolants, polyester fibers and resins, desiccants and fuel cells.¹ The global production of MEG was 30.5 million metric tons annually (MMTA) in 2019, which was mainly produced through the industrial process of liquid-phase thermal hydration of ethylene oxide (EO).² However, a high H₂O/EO molar ratio (around 20–25) was required in such a process in order to achieve a high conversion of EO and a high selectivity of MEG. The large excess of water that had been used resulted in additional energy consumption and cost for the distillation of the final MEG product.

A series of catalysts have thus been developed for the hydration of EO^{1*a*} to obtain a high selectivity of MEG, such as sulfuric acid, amines,³ soluble salts,⁴ ion-exchange resins,⁵ acidic poly(ionic liquid)s,⁶ and supported metal oxides.⁷

Catalytic production of MEG under low H_2O/EO ratios has also been achieved in select cases.⁸ Silica-based nanocages encapsulating Co^{III}(salen) or Lewis acids have shown an excellent MEG selectivity with H_2O/EO ratios approaching the stoichiometric value of the reaction.^{8*a,b*} Note that these sophisticated heterogeneous catalysts are complicated to prepare, limiting their practical applications. The development of an effective and simple catalytic strategy for the hydration of EO with low H_2O/EO ratios is still a challenge.

CO₂ utilization through chemical methods has received extensive attention in recent years.9 A number of reports have documented the use of CO₂ as the raw material to produce value-added chemicals, such as carbonates, urea derivatives, carbamates, carboxylic acids, alkanes, and alcohols.¹⁰ Moreover, the use of CO₂ to promote reactions has been reported as well, which provides a novel strategy to efficiently control the reactivity and selectivity of reactions.¹¹ Several studies have focused on CO2-promoted hydration of propargylic alcohols in the presence of metal or ionic liquid catalysts, which involves the generation of α -alkylidene cyclic carbonates by the fixation of CO₂ followed by in situ hydrolysis to produce α -hydroxy ketones and regenerate CO₂.¹² In the whole process, CO₂ was not consumed, but promoted the reaction to generate the product effectively and selectively. The role of CO2 as a promoting reagent (or cocatalyst) to alter reaction pathways inspired us to explore this methodology for the hydration of epoxides.

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 $[\]dagger\, Electronic supplementary information (ESI) available. See DOI: 10.1039/ d1gc00758k$

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Herein, we present the strategy of using CO_2 as the reaction atmosphere to promote the hydration of EO catalyzed by simple catalysts of ionic liquids and organic bases. A high yield and selectivity for MEG were achieved at a H₂O/EO ratio as low as the stoichiometric value of the reaction. CO_2 was found to participate in the reaction through the cycloaddition of EO followed by *in situ* hydrolysis to generate MEG and recover CO_2 , allowing the reaction to occur efficiently at low H₂O/EO ratios.

Results and discussion

CO₂-promoted catalytic hydration of EO with ionic liquids/ organic bases

Hydrations of EO catalyzed by various binary ionic liquid/ organic base catalysts under a CO_2 or N_2 atmosphere were performed (Table 1). Under the CO_2 atmosphere, the hydration of EO catalyzed by VBImBr/VIm (1:1, 2 mol%) gave rise to an excellent yield (89%) and selectivity (97%) of MEG at a molar ratio of H₂O/EO as low as 1.5:1 (entry 1, Table 1). Other reaction conditions such as the amount of catalyst, CO₂ pressure and the H₂O/EO ratio were also tested (Table S1†), while this condition was found to give the best performance in terms of the yield and selectivity of MEG and the amount of water used. In contrast, an atmosphere of N₂ led to a significantly lower yield (21%) and selectivity (32%) for MEG, accompanied by the formation of considerable amounts of by-products such as DEG (12%), TEG (7%) and other polymeric ethylene glycols (entry 2, Table 1).

Various combinations of VBImBr with other common organic bases bearing varying basicities such as DBU, DMAP, DAA, TAA and 4-VP were also tested, and all of them exhibited significantly better catalytic performances under an atmosphere of CO₂ than those under N₂. The reactions under CO₂ generally afforded MEG in yields of 88–91% and selectivities of 94–96%, while only 11–17% in yields and 18–24% in selectivities were obtained under N₂ (entries 3–12, Table 1). Similarly, the combination of the base VIm with other ionic liquids (BMImBr, BnImBr, BdMImBr, and Bu₄NBr) also gave a 4–5

 Table 1
 Hydration of EO under an atmosphere of CO2 or N2 catalyzed by various ionic liquids/organic bases^a

$\frac{A}{CO_2 \text{ or } N_2} + H_2O \xrightarrow{\text{ionic liquid/organic base}} HO \xrightarrow{OH}$											
		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$									
		Organic bases:			N H DAA		N 4-VP				
	Catalysts Yield ^b (%)										
Entry	Ionic liquid	Organic base	Reaction atmosphere	MEG	EC	DEG	TEG	Selectivity of MEG (%)			
1	VBImBr	VIM	CO_2	89	1	1	_	97			
2			N_2	21	—	12	7	32			
3	VBImBr	DBU	CO_2	91	2	1	—	96			
4			N_2	11	_	9	6	18			
5	VBImBr	DMAP	CO_2	90	3	1	—	95			
6			N_2	13	_	9	7	18			
7	VBImBr	DAA	CO_2	91	2	1	—	96			
8			N_2	13	—	10	7	19			
9	VBImBr	TAA	CO_2	90	3	1	—	95			
10			N_2	17	—	11	6	24			
11	VBImBr	4-VP	CO_2	88	3	1	_	94			
12			N_2	13	—	7	6	22			
13	BMImBr	VIm	CO_2	93	2	1	_	96			
14			N_2	13	_	9	6	20			
15	BnBImBr	VIm	CO_2	94	1	1	—	97			
16			N_2	15	_	10	7	19			
17	BdMImBr	VIm	CO_2	93	3	1	_	95			
18			N_2	13	_	10	7	19			
19	Bu ₄ NBr	VIm	CO_2	90	1	4	_	91			
20	-		N ₂	11	_	10	7	16			

^{*a*} Reaction conditions: EO (2.2 g, 50 mmol), H₂O (1.35 g, 75 mmol), and ionic liquid (0.5 mmol, 1 mol%)/organic base (0.5 mmol, 1 mol%), 100 °C, 3 h, 1.5 MPa. ^{*b*} Monoethylene glycol (MEG), ethylene carbonate (EC), diethylene glycol (DEG), and triethylene glycol (TEG).

Note that all the above-mentioned results were obtained at a H₂O/EO ratio of 1.5:1. A yield of 80% and a selectivity of 93% for MEG were also achieved when a stoichiometric H₂O/EO ratio (1:1) was used for the reaction catalyzed by VBImBr/VIm under CO₂ (Table S2†). This performance was even better than the hydration of EO under N₂ at a H₂O/EO ratio of 15/1 in the presence of the same catalysts (Table S2†). The remarkable performance of the current catalytic system is comparable to the pioneering heterogeneous catalysts reported previously,^{8a,b} while the simplicity of the current catalysts and the versatile combination of various ionic liquids and organic bases are noteworthy. Furthermore, the excellent catalytic performance of imidazolium ionic liquids and organic bases with polymerizable vinyl/allyl groups may provide an opportunity to heterogenize the homogeneous catalysts.

Mechanism investigation through isotope labeling experiments and DFT calculations

The detection of trace amounts of ethylene carbonate (EC) for the reactions under CO₂ implied that CO₂ may have participated in the reaction, affording cycloaddition of EO catalyzed by ionic liquids and organic bases.¹³⁻¹⁶ The presence of this intermediate was further confirmed through monitoring its amounts at different reaction times. As shown in Fig. 1, a considerable amount of EC (19%) was generated at the beginning, while its concentration gradually decreased and almost disappeared after 180 min (1%), accompanied by an increase of the MEG yield. These observations indicate a one-pot two-step procedure for the synthesis of MEG (Fig. 2a). The first step involves cycloaddition of EO with CO2 to form EC, and the second step is the hydrolysis of EC to produce MEG and regenerate CO₂. Apart from the binary ionic liquid/organic base catalysts, CO₂ has not been consumed either, which can be treated as a promoting reagent or a co-catalyst for the hydration of EO.



Fig. 1 Yields of MEG and EC at different reaction times in the hydration of EO. Reaction conditions: EO (2.2 g, 50 mmol), H_2O (1.35 g, 75 mmol), CO_2 (1.5 MPa), VBImBr (0.5 mmol, 1 mol%)/VIm (0.5 mmol, 1 mol%), 100 °C.

(a) Two-step reaction mechanism

$$\overset{O}{\longrightarrow} + \operatorname{CO}_2 \longrightarrow \overset{O}{\longrightarrow} \overset{O}{\longrightarrow} \overset{H_2O}{\longrightarrow} HO \overset{OH}{\longrightarrow} + \operatorname{CO}_2$$

(b) Isotope labeling experiments

$$\stackrel{16}{\longrightarrow} + \stackrel{18}{H^{-0}}_{H} \stackrel{N_{2}}{\longrightarrow} + \stackrel{18}{H^{10}}_{H} \stackrel{N_{2}}{\longrightarrow} + \stackrel{18}{H^{10}}_{H} \stackrel{16}{\longrightarrow} \stackrel{16}{$$

Fig. 2 (a) Proposed two-step reaction mechanism for the hydration of EO under CO₂. (b) Isotope labeling experiments for the investigation of the EO hydration mechanism using isotope-labeled water ($H_2^{18}O$).

To confirm the proposed reaction pathway, three isotope labeling experiments using isotope-labeled water (H2¹⁸O) were conducted and the products were analyzed by GC-MS. The direct hydration of EO with H218O under N2 afforded isotopelabeled MEG (m/z 64) as the main product (eqn (1) in Fig. 2b and Fig. S1[†]), indicating that the ¹⁸O was transferred from H2¹⁸O to MEG. In contrast, the hydration of EO with H2¹⁸O under the CO₂ atmosphere predominantly gave unlabeled MEG (m/z 62), while ¹⁸O was found to be transferred from $H_2^{18}O$ to $C^{18}OO$ (*m*/*z* 46) (eqn (2) in Fig. 2b and Fig. S2[†]). Similarly, the hydrolysis of EC with H218O also produced unlabeled MEG $(m/z \ 62)$ as the main product, while isotopelabeled $C^{18}OO(m/z \ 46)$ was detected (eqn (3) in Fig. 2b and Fig. S3[†]). These results support the proposed two-step mechanism for the catalyzed reaction under CO2, in which the cycloaddition of EO with CO2 occurs first, followed by the hydrolysis of EC with H₂¹⁸O to generate MEG and C¹⁸OO.

The proposed mechanism was further verified by designing cascade reactors. Hydration of EO with $H_2^{18}O$ under a CO_2 atmosphere was designed to occur in the first reactor, and cycloaddition of EO with the released CO_2 vented from the first reactor took place in the second reactor (Fig. S4†). It was found that after completion of the cascade reactions, the isotope ¹⁸O of $H_2^{18}O$ in the first reactor had been transferred to the product in the second reactor, forming ¹⁸O-labeled EC (*m*/*z* 90) (Fig. S5†), through the medium of CO_2 .

This one-pot two-step reaction mechanism has been investigated by DFT calculations. As shown in the red pathway in Fig. 3, the ring of EO in the complex **Int-0** (0.0 kcal mol⁻¹) is first activated by VBImBr through the transition state **TS-1** to generate the ring-opening intermediate **Int-2**. Then, CO₂ adds to the hydroxyl oxygen atom of **Int-2** to yield **Int-3**, followed by the formation of the EC ring *via* **TS-4**. The oxygen atom of a H₂O molecule attacks the carbonyl carbon of EC in **Int-5**, while another hydrogen atom of the water is abstracted by VIm. Meanwhile, VBImBr could also stabilize the transition state **TS-6** by forming a H bond with the C–O double bond of EC. The yielded product **Int-7** could complex with another water molecule by forming H bonds in **Int-8**. Through a hexa-ring transition state **TS-9**, the penta-ring is opened to yield **Int-10**,

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which leads to the generation of the product MEG with the release of a $\rm CO_2$ molecule.

Based upon the DFT results, the rate-determining step of the red pathway is the ring-opening step of EO *via* **TS-1**, with an energy barrier of 32.3 kcal mol⁻¹. The barrier is lower than that of direct hydration of EO under N₂ *via* **TS-11** (the pathway in black in Fig. 3) by 6.8 kcal mol⁻¹, which indicates that the CO₂-involved pathway is more kinetically favorable. In particular, this barrier is also 5.7 kcal mol⁻¹ lower than that of the blue condensation pathway of MEG with EO *via* **TS-12**, which leads to the side product DEG. The pathway of hydration of EO involving CO₂ is more favorable than the side reaction of EO with MEG, which highlights the origin of the high selectivity of MEG.

The origin of the MEG selectivity has been further investigated by experiments. Reactions of the product MEG with the starting material EO and the intermediate EC were respectively tested (Fig. 4). It was observed that the reaction of EO with MEG catalyzed by VBImBr/VIm afforded DEG, TEG and other polymeric ethylene glycols with a total yield of 61%. However, no reaction of EC with MEG was observed to occur in the presence of VBImBr/VIm. In fact for the conventional hydration of EO without CO₂, the reactivity of MEG with EO leads to the formation of by-products (DEG and TEG), for which high H₂O/EO ratios are required to prevent the side reactions.^{1,3–7} Note that





Fig. 4 Reactions of the product MEG with EO (a) and EC (b). Reaction conditions: EO (2.2 g, 50 mmol) (a) or EC (4.4 g, 50 mmol) (b), MEG (3.10 g, 50 mmol), and VBImBr (0.5 mmol, 1 mol%)/Vim (0.5 mmol, 1 mol%), 100 $^{\circ}$ C, 3 h, 1.5 MPa.

for our new strategy using CO_2 as the reaction atmosphere, the intermediate EC does not react with MEG, allowing for the high selectivity of MEG at low H_2O /EO ratios.

Synergistic catalysis of ionic liquids and organic bases

Cycloaddition of EO with CO₂ and hydrolysis of EC catalyzed respectively by VBImBr/VIm (1:1), VBImBr or VIm were carried out, in order to investigate the role of each component of the binary catalysts.^{17–20} As shown in Fig. 5a, for the cycloaddition of EO with CO₂, VBImBr and VIm gave EC in the yields of 85% and 22%, respectively, indicating the higher catalytic activity of the ionic liquid than the organic base.¹³ In contrast, for the hydrolysis of EC to MEG, VIm gave a significantly higher yield for MEG (79%) than did VBImBr (6%) (Fig. 5b), implying the higher catalytic activity of the organic base than the ionic liquid in this case. These results were rationalized by DFT calculations (Fig. S7†). The combination of VBImBr and VIm (1:1) afforded excellent performance in both the yields of EC (78%) and MEG (87%) for the two separate reactions.

We have also explored the effect of the molar ratio of the binary catalysts on the hydration of EO under a CO_2 atmosphere. As shown in Table 2, when VIm was used alone (n(VBImBr)/n(VIm) = 0:1), the reaction gave a 10% yield of DEG and a 74% selectivity of MEG. If VBImBr was used alone (n(VBImBr)/n(VIm) = 1:0), the reaction afforded a 28% yield of EC and only a 68% selectivity of MEG (entries 1 and 2, Table 2). These results are consistent with the observations made above that the organic bases or the ionic liquids individually catalyzed a single step of the two-step process efficiently, in which ionic liquids were beneficial for the cycloaddition of CO_2 and organic bases were efficient for the hydrolysis of



Fig. 3 Calculated free energy profiles of reactions under CO_2 or N_2 , in the presence ionic liquid/organic base catalysts. Optimized structures of intermediates and transition states are shown below.

Fig. 5 Various catalysts for the cycloaddition of EO with CO₂ (a) and the hydrolysis of EC (b). Reaction conditions: EO (2.2 g, 50 mmol) (a) or EC (4.4 g, 50 mmol) and H₂O (1.35 g, 75 mmol) (b), CO₂ (1.5 MPa), and catalyst (1 mmol, 2 mol%), 100 °C, 3 h.

3 h.

 Table 2
 Effect of the molar ratio of VBImBr and VIm on the hydration of EO^a

		Yield/%			
Entry	n (VBImBr)/n (VIm)	MEG	EC	DEG	Selectivity of MEG/%
1	0:1	61	_	10	74
2	1:0	61	28	1	68
3	1:2	90	1	4	95
4	1:1	89	1	2	97
5	2:1	87	4	1	94
^{<i>a</i>} React CO_2 (1	tion conditions: EO (2 .5 MPa), and catalysts:	2.2 g, 5 : VBImE	0 mn 8r + VI	nol), H ₂ m (1 m	O (1.35 g, 75 mmol), mol. 2 mol%), 100 °C.

EC in the CO_2 -promoted hydration of EO. The combination of VBImBr and VIm in the ratio of 1:2, 1:1 and 2:1 gave rise to both high yields and high selectivities of MEG with trace amounts of DEG and EC being detected (<4%) (entries 3–5, Table 2 and Fig. S6†), demonstrating the synergistic effect of the binary catalysts.

Conclusions

In summary, a new strategy for the selective synthesis of MEG has been established via CO2-promoted hydration of EO catalyzed by ionic liquids and organic bases. The presence of CO_2 significantly improved the catalytic performance for EO hydration, giving excellent yields and selectivities of MEG at a H₂O/EO ratio as low as 1:1. Mechanism investigations indicated a one-pot two-step process including the cycloaddition of EO with CO₂ and the hydrolysis of EC, which was fully demonstrated by isotope labeling experiments and theoretical calculations. During the process, CO₂ played the role of a promoting reagent or a co-catalyst in that it was involved in the reaction but was not consumed. Importantly, the EC formed through the cycloaddition of EO with CO₂ was found to be a crucial intermediate, which accounted for the high yield and selectivity of MEG. Moreover, the simple catalysts consisting of ionic liquids and organic bases exhibited a synergistic catalytic effect for the one-pot two-step mechanism. Considering the availability of CO_2 and the simplicity of the catalysts, we believe that the current work has a great potential for applications in the chemical industries.

Experimental

Chemicals and materials

 N_2 and CO_2 with a purity of >99.9% were supplied by Shanghai Tomoe Gases Co., Ltd. Vinyl imidazole (VIm), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 4-vinylpyridine (4-VP), 4-dimethylaminopyridine (DMAP), diallylamine (DAA), triallylamine (TAA), ethylene carbonate (EC) and $H_2^{-18}O$ were purchased from Macklin. 1-Vinyl-3-butyl-imidazolium bromide (VBImBr), 1-butyl-3-methyl-imidazolium bromide (BMImBr), 1-butyl-2,3dimethyl-imidazolium bromide (BdMImBr) and tetrabutylammonium bromide (Bu_4NBr) were purchased from the Centre for Green Chemistry and Catalysis, LICP, CAS. 1-Benzyl-3-butylimidazolium bromide (BnBImBr) was synthesized according to the literature.¹ Ethylene oxide (EO), monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) were supplied by Sinopharm at CP grade.

Hydration of EO

In a typical experiment, EO (2.20 g, 50 mmol), deionized water (1.35 g, 75 mmol), VBImBr (0.116 g, 0.5 mmol) and VIm (0.047 g, 0.5 mmol) were added into a 30 mL stainless steel Teflon-lined autoclave equipped with a magnetic stirrer and an autoclave with an automatic temperature control system. The autoclave was pressurized with CO₂ or N₂ (1.5 MPa) and heated to 100 °C. After stirring for 3 h, the autoclave was cooled to room temperature in an ice-water bath, followed by slow venting of CO₂ or N₂. The reaction mixtures were analyzed by gas chromatography (GC) (GC-2014, Shimadzu, Japan) with a DM-1701 (30 m × 0.53 mm × 1.0 μ m) capillary column and a flame ionization detector (FID) and biphenyl was used as the internal standard.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2017YFA0403102) and the National Natural Science Foundation of China (21773068, 21811530273).

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