Cycloaddition of Epoxide and CO2 to Cyclic Carbonate Catalyzed by VO(IV) Porphyrin

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Cycloaddition of epoxide and CO_2 to cyclic carbonate catalyzed by VO(IV) porphyrin

Dongsheng Bai*, Zhiyong Zhang, Guangjian Wang and Fang Ma

The cycloaddition of epoxide and CO_2 to synthesize cyclic carbonate catalyzed by VO(IV) porphyrin was achieved under 1.4 MPa at 150°C. The effects of reaction temperature, time, CO_2 pressure, co-catalyst and porphyrin framework were investigated. The catalytic results showed that moderate to high yields of cyclic carbonates were obtained under the optimal reaction conditions. Copyright © 2015 John Wiley & Sons, Ltd.

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Introduction

Carbon dioxide (CO_2) chemistry has received much attention in recent decades because CO_2 is the most abundant and inexpensive carbon source and the most significant greenhouse gas.[1–4] Chemical fixation of CO_2 into organic compounds has great significance for the environment and chemistry. One of the most efficient strategies is the cycloaddition of epoxides and CO_2 to synthesize cyclic carbonates (Scheme 1). This is an atomically economic and green reaction. Cyclic carbonates are valuable organic synthetic intermediates, aprotic polar solvents and polymerization reaction monomers.[5–8] Accordingly, various catalytic systems with different yields and turnover frequencies (TOFs) have been developed for the coupling reaction of CO_2 and epoxides, including metal salts,[9–12] metallic complexes,[13–18] ionic liquids,[19–23] metal–organic frameworks,[24–26] organocatalysts[27] and N-heterocyclic carbenes.[28–30]

Porphyrin ligands are widely used due to their planar structure, electron-rich properties and ability to form complexes. Metalloporphyrins such as P-450 are easily synthesized when porphyrin ligands coordinate with metal ions. Therefore, VCl_3 and other Lewis acids have been studied as catalysts for cyclic carbonate synthesis.[31–37] As we know, VO(IV) ions and their corresponding complexes have been studied for their use as catalysts for organic synthesis.[38] For example, Coletti and co-workers reported butylene carbonate synthesis catalyzed by VO(IV) complexes under a CO_2 pressure of 1.0 MPa at 45°C.[39]

Considering the above, in order to expand the types of VO(IV) complexes that can be used as catalysts for cycloaddition of epoxides and CO_2 to synthesize cyclic carbonates, in the work reported herein, several oxygenated vanadium porphyrins (VO(T_RPP); Scheme 2) were synthesized, and their catalytic activities were studied.

Experimental

Materials

Propylene oxide (PO) was distilled from CaH_2. Other epoxides and *N,N*-dimethylaminopyridine (DMAP) were purchased from Alfa Aesar and used directly. *n*-Bu$_4$NF, *n*-Bu$_4$NCl, *n*-Bu$_4$NBr, *n*-Bu$_4$NI and PPh$_3$ were purchased from Sinopharm Chemical Reagent Co. Ltd. Phenyltrimethylammonium tribromide (PTAT) and *n*-Bu$_4$PBr were obtained from Aladdin.

General Procedure of Coupling Reaction of Epoxides and CO_2

All cycloaddition reactions were performed in a 50 ml stainless steel autoclave equipped with a magnetic stir bar. The autoclave reactor was successively charged with VO(T_RPP) (0.05 mmol), co-catalyst (0.1 mmol) and epoxides (100 mmol). The reactor was pressurized with CO_2 to 0.8–1.6 MPa and then heated and stirred at the desired temperature. When the pressure of CO_2 fell to 0.1–0.4 MPa, the reactor was cooled quickly to 0°C in ice water and then slowly vented. The remaining mixture was distilled under reduced pressure or purified using column chromatography to afford cyclic carbonate product.

Preparation of VO(T_RPP) Complexes

VO(T_RPP) were synthesized, purified and characterized using a modified literature procedure.[40] In a typical reaction, freshly distilled *ortho*-substituted benzaldehyde (2.0 ml, 19.6 mmol) was dissolved in 100 ml of argon-purged DMF. Then, concentrated hydrochloric acid (1.0 ml) was added followed by dropwise addition of freshly distilled pyrrole (1.4 ml, 19.6 mmol). The mixture was stirred under argon for 1 h and then 2.5 equiv. of VOSO$_4$ was added. The final reaction mixture was refluxed for 8 h in air. The solvent was removed under reduced pressure and the crude product was washed three times with acidic water and dried. The product was purified using flash chromatography over neutral aluminium oxide using chloroform as eluent.
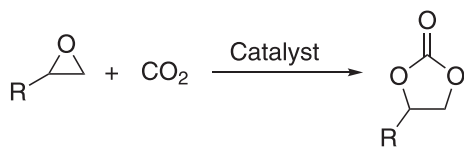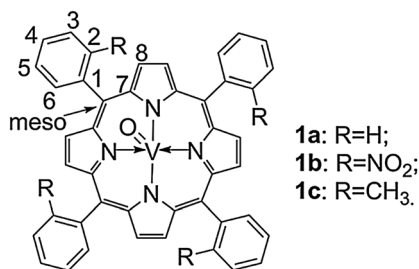
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Scheme 1. Synthesis of cyclic carbonates from CO_2 and epoxides.

1a: R=H;
1b: R=NO_2;
1c: R=CH_3.

Scheme 2. Structure of VO(T_RPP).

Complex **1a**. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.83–7.84 (d, 12H, *3, 4*-H of C$_6$H$_5$), 8.13–8.17 (m, 8H, *2*-H of C$_6$H$_5$), 9.13 (s, 8H, *8*-H of pyrrole). ^{13}C NMR (CDCl$_3$, δ, ppm): 121.70 (meso-C), 126.78 (C-*3*), 127.93 (C-*4*), 132.69 (C-*8*), 135.01 (C-*2*), 141.65 (C-*1*), 149.40 (C-*7*). UV–visible (CH$_2$Cl$_2$): λ_{max} = 402, 422, 556, 595 nm. Elemental analysis: calcd for C$_{44}$H$_{28}$N$_4$OV (%): C, 77.76; H, 4.15; N, 8.24. Found (%): C, 77.74; H, 4.19; N, 8.22.

Complex **1b**. H NMR (CDCl$_3$, δ, ppm): 7.85 (s, 8H, *8*-H of pyrrole), 8.17–8.40 (m, 4H, *4, 6*-H of C$_6$H$_5$), 8.63 ppm (s, 8H, *3, 5*-H of C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, δ, ppm): 116.39 (meso-C), 123.71 (C-*8*), 129.04 (C-*3*), 130.13 (C-*4*), 136.97 (C-*5*), 138.10 (C-*1*), 149.24 (C-*6*), 152.50 (C-*7*), 161.31 (C-*2*). Elemental analysis: calcd for C$_{44}$H$_{24}$N$_8$O$_9$V (%): C, 61.48; H, 2.81; N, 13.03. Found (%): C, 61.46; H, 2.85; N, 13.02.

Complex **1c**. ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 3.45 (s, 12H, H–OCH$_3$), 7.31 (s, 8H, *8*-H of pyrrole), 7.74 (s, 4H, *6*-H of C$_6$H$_5$), 8.00 ppm (s, 4H, *4*-H of C$_6$H$_5$), 8.72 ppm (s, 4H, *3, 5*-H of C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, δ, ppm): 53.57 (C–OCH$_3$), 120.89 (C-*3*), 122.28 (meso-C), 126.51 (C-*1*), 131.88 (C-*8*), 134.73 (C-*5*), 135.82 (C-*4*), 136.91 (C-*6*), 143.58 (C-*7*), 150.27 (C-*2*). Elemental analysis: calcd for C$_{48}$H$_{36}$N$_4$O$_5$V (%): C, 72.09; H, 4.54; N, 7.01. Found (%): C, 72.08; H, 4.57; N, 7.00.

Results and Discussion

Effect of Temperature on Propylene Carbonate (PC) Synthesis Catalyzed by 1a

The crucial role played by reaction temperature in PC synthesis from PO and CO_2 was investigated first. As shown in Fig. 1, there is only a 62% yield of PC obtained at 120°C under a CO_2 pressure of 1.4 MPa within 5 h, but the PC yield increases to 99% at 150°C. However, a further increase in the reaction temperature causes a slight decrease of PC yield due to the decomposition of *n*-Bu$_4$NBr (T_i = 114.7°C, T_{Max} = 118.7°C). This hints that 150°C is the optimal temperature for the coupling reaction of PO and CO_2 catalyzed by **1a**/*n*-Bu$_4$NBr.

Effect of Reaction Time on PC Synthesis Catalyzed by 1a

The PC yield as a function of reaction time is shown in Fig. 2. The results indicate that this cycloaddition reaction proceeds rapidly within the first 2 h, and there is a yield of 48% within 1 h and 79% within 2 h. For a longer reaction time of 5 h, the yield of PC
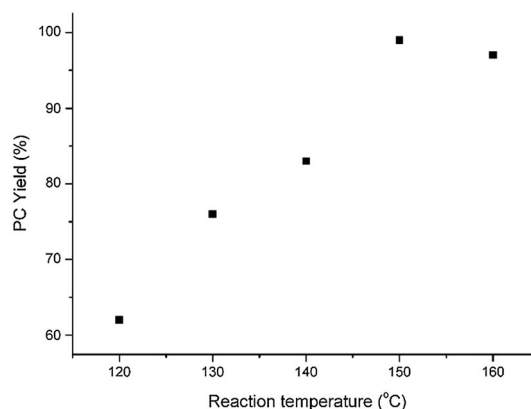
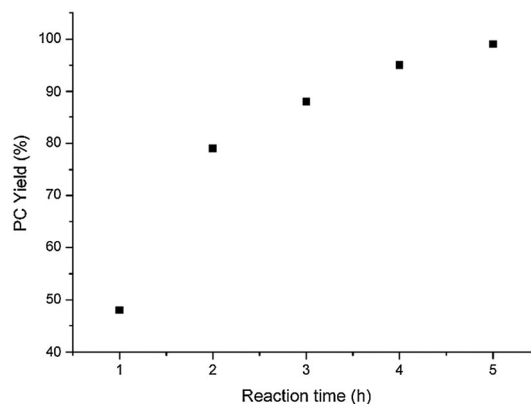**Figure 1.** Effect of temperature on yield of PC.

Figure 2. Effect of reaction time on yield of PC.

exceeds 99%, which suggests the coupling reaction of PO and CO_2 is completed within 5 h.

Effect of Co-catalyst and Porphyrin Framework on Synthesis of PC

Co-catalyst of Lewis base plays an important role in this coupling reaction.[41] The catalytic activity of various co-catalysts was studied. It is evident from Table 1 that *n*-Bu$_4$NBr shows superior activity among the co-catalysts investigated because Br$^-$ is both a better nucleophilic group and leaving group. PC yield increases up to 99% at 150°C under a CO_2 pressure of 1.4 MPa within 5 h catalyzed by **1a**/*n*-Bu$_4$NBr (Table 1, entry 4). Although DMAP and PPh$_3$ as organic bases can catalyze the cycloaddition PO and CO_2, the PC yield is lower than for any quaternary ammonium salt or tetrabutylphosphonium bromide (Table 1, entries 9 and 10 versus 1–8). The yield of PC decreases whether the amount of *n*-Bu$_4$NBr is decreased or increased, and the best **1a**/*n*-Bu$_4$NBr mole ratio is 1:2 for this cycloaddition (Table 1, entries 3–5). The order of catalytic activity of co-catalysts is *n*-Bu$_4$NBr > *n*-Bu$_4$NCl > *n*-Bu$_4$PBr > *n*-Bu$_4$NI > PTAT > *n*-Bu$_4$NF. Oxygenated vanadium porphyrins with various frameworks were also investigated. As evident from Table 1, *ortho*-substituted groups in porphyrin framework strongly influence the coupling reaction (Table 1, entries 4, 11 and 12). When the porphyrin framework bears an electron-withdrawing group (–NO_2) or electron-donating group (–OCH_3) the tendency is to give a decreased yield. This phenomenon can be explained by the steric effect of *ortho*-substituted groups in metalloporphyrins. When **1a** is used without co-catalyst,

Table 1. Influence of co-catalyst and porphyrin framework on PC yield[a]

Entry	Catalyst/co-catalyst (ratio)	Yield (%)[b]	TOF (h^{-1})[c]
1	**1a**/2n-Bu$_4$NF	56	224
2	**1a**/2n-Bu$_4$NCl	95	380
3	**1a**/1n-Bu$_4$NBr	80	320
4	**1a**/2n-Bu$_4$NBr	>99	396
5	**1a**/4n-Bu$_4$NBr	97	388
6	**1a**/2n-Bu$_4$NI	84	336
7	**1a**/2n-Bu$_4$PBr	89	356
8	**1a**/2PTAT	73	292
9	**1a**/2DMAP	17	68
10	**1a**/2PPh$_3$	13	52
11	**1b**/2n-Bu$_4$NBr	49	196
12	**1c**/2n-Bu$_4$NBr	58	232
13	**1a**	—	—
14	n-Bu$_4$NBr	6	12
15[d]	VO(acac)$_2$/1n-Bu$_4$NI	100	14

[a]Reaction conditions: 100 mmol PO, 0.05 mmol VO(T$_R$PP), 0.1 mmol co-catalyst, 1.4 MPa CO$_2$ pressure, 5 h, 150°C.
[b]Isolated yield.
[c]Moles of PC produced per mole of catalyst per hour.
[d]Reported by Coletti *et al.*[39] Reaction conditions: 0.4 M butylene oxide, 0.4 M mesitylene, 0.01 M VO(acac)$_2$, 0.01 M n-Bu$_4$NI, 5 ml solvent (2-butanone), 1.0 MPa, 18 h, 45°C.

there is no PC obtained (Table 1, entry 13). However, there is a 6% yield of PC when only n-Bu$_4$NBr is used as catalyst (Table 1, entry 14). Although there was a 100% yield of butylene carbonate when catalyzed by VO(acac)$_2$/n-Bu$_4$NBr reported by Coletti *et al.*, the TOF value was very low (Table 1, entry 15).[39]

Effect of CO$_2$ Pressure on PC Synthesis Catalyzed by 1a

The effect of CO$_2$ pressure on PC yield was studied under the optimized reaction conditions mentioned above. It can be seen from Fig. 3 that the yield of PC greatly depends on CO$_2$ pressure. The PC yield increases as pressure increases from 0.8 to 1.4 MPa and reaches a maximum (99%) at 1.4 MPa. However, a further increase in CO$_2$ pressure causes a slight decrease of PC yield because the concentration of PO decreases along with an increased amount of dissolved CO$_2$ at higher pressure. This indicates that 1.4 MPa is the optimal CO$_2$ pressure for the coupling reaction of PO and CO$_2$ to form PC catalyzed by **1a**/n-Bu$_4$NBr.
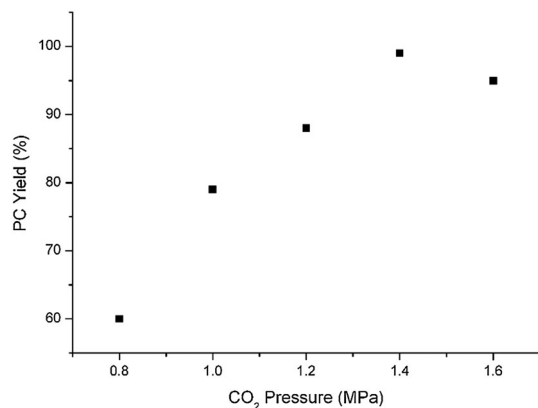

Figure 3. Effect of CO$_2$ pressure on yield of PC.

Table 2. Cycloaddition of CO$_2$ to various epoxides catalyzed by **1a**/n-Bu$_4$NBr[a]

Entry	R	Time (h)	Yield (%)[b]
1	CH$_3$	5	99
2	CH$_3$CH$_2$	8	76
3	ClCH$_2$	4	96
4[c]	Ph	12	71
5[c]	PhOCH$_2$	4.5	93
6	CH$_3$(CH$_2$)$_9$	12	22

[a]Reaction conditions: 100 mmol epoxide, 0.05 mmol **1a**, 0.1 mmol n-Bu$_4$NBr, 1.4 MPa CO$_2$ pressure, 150°C.
[b]Isolated yield.
[c]CH$_2$Cl$_2$ (3 ml) was used as diluent.

Cycloaddition Reaction of Various Epoxides and CO$_2$ Catalyzed by 1a/n-Bu$_4$NBr

Under the optimal reaction conditions, various terminal-substituted epoxides were used and reacted with CO$_2$ to synthesize cyclic carbonates in order to extend the scope of reactants. It is evident from Table 2 that the yields of propylene carbonate (Table 2, entry 1), chloropropene carbonate (Table 2, entry 3) and phenoxylpropylene carbonate (Table 2, entry 5) exceed 93% within 5 h. Epichlorohydrin with a chlorine functional group having larger steric hindrance than PO with a methyl group is also a highly active epoxide due to the good electron-withdrawing capability of chlorine (Table 2, entry 1 versus entry 3). The good conversions of epichlorohydrin and phenylglycidyl ether can also be explained by their good electron-withdrawing capability, allowing for an easier nucleophilic attack of the epoxide ring carbon atoms (Table 2, entries 3 and 5).[42] However, when butene oxide and dodecylene oxide are used as substrate, yields of only 76% of butene carbonate and 22% of dodecylene carbonate are obtained in longer reaction time due to the low reactivity of electron-rich substrate (Table 2, entries 2 and 6). The yield of styrene carbonate is only 71% due to the steric hindrance effect of the phenyl group (Table 2, entry 4).

Conclusions

In summary, we expanded and developed several high-valent vanadium porphyrins as catalysts for the synthesis of cyclic carbonates from epoxides and CO$_2$ with high TOF. The yields of cyclic carbonates were moderate to excellent under a CO$_2$ pressure of 1.4 MPa at 150°C catalyzed by VO(TPP)/n-Bu$_4$NBr.

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