Metal porphyrin/phenyltrimethylammonium tribromide: High efficient catalysts for coupling reaction of CO_2 and epoxides

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Abstract

Novel and high efficient catalysts of metal porphyrin (M(TPP)X, M = Co, Fe, Ru, Mn; X = Cl⁻, Br⁻, OAc⁻, OTs⁻, $Cl_3CCO_2{}^-$)/ phenyltrimethylammonium tribromide (PTAT) were developed to catalyze the coupling reaction of carbon dioxide and epoxides at room temperature.
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1. Introduction

The chemistry of carbon dioxide have recently received much attention from both an economical and an environmental point of view: utilization of the least-expensive carbon source and reduction of global-warming gas [1–6]. The cyclic carbonates are one of products of carbon dioxide fixation and widely used as organic synthetic intermediates, aprotic polar solvents, precursors for biomedical applications, and as raw materials for engineering plastics [7–14]. Various catalysts including alkali metal salts, Lewis acids, transition metal complexes, ionic liquids, and organometallic compounds, have been developed for these coupling reactions of CO_2 with epoxides to yield carbonates [15–23]. While the advances have been significant, most of these catalysts currently suffer from low catalyst reactivity, the need for co-solvent, or the requirement for high pressure and/or high temperature. Very recently, bifunctional catalyst systems of Co(Salen)X/Bu$_4$NY [24–26] were found to be the most efficient catalyst systems for this transformation. But, there are rare reports about the Metal(TPP)X catalyst systems. Kruper and Dellar [27] have reported the synthesis of propylene carbon-

ate from propylene oxide and carbon dioxide using the catalyst system of Cr(TPP)Cl/DMAP operating under 780 psi of CO_2 at 50 °C. Nguyen and co-authors [28] have reported the catalyst system of Co(TPP)X/DMAP. Srinivas and co-authors [29] have reported the catalyst system of Cu(II)porphyrin/DMAP. But the coupling reaction must undergo at 120 °C. Therefore, the exploration of highly efficient catalysts for coupling carbon dioxide with epoxides under low temperature and pressure still remains a challenging.

Herein, we report our excellent results for investigating the catalytic activity of new M(TPP)X/PTAT catalyst systems in the coupling reaction of CO_2 and epoxides.

2. Experimental

2.1. Materials

Propylene oxide was distilled from CaH_2. Other epoxides and PTAT were purchased from Aldrich and used to reaction without further purification.

2.2. Porphyrins

Free-base porphyrins H_2TPP (5,10,15,20-tetraphenyl-porphyrin) [30], H_2TMPP (5,10,15,20-tetra-*o*-methoxyphenyl-

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porphyrin) [31], H$_2$TNPP (5,10,15,20-tetra-*o*-nitrophenylporphyrin), H$_2$TAPP (5,10,15,20-tetra-*o*-aminophenylporphyrin) [32], Fe^{III}(TPP)Cl, Mn^{III}(TPP)Cl [33,34], Ru(TPP)(PPh$_3$)Cl [35–37] were synthesized, purified and characterized following the procedures of literatures described above.

2.3. Cobalt(II) porphyrins

Cobalt(II) porphyrins were obtained by metallation of free base porphyrin with Co(OAc)·2H$_2$O in DMF using the method of literature [33]. The cobalt porphyrins were purified by column chromatography of silica gel, using chloroform as eluent.

2.4. Cobalt(III) porphyrins

To a suspended solution of Co^{II}(TPP) complex (67.1 mg, 0.1 mmol) in 5 ml toluene, glacial acetic acid (0.14 ml, 2 mmol, 20 equiv.) was added. The solution was stirred at room temperature for 4 h. The solvent and unreacted glacial acetic acid were removed under reduced pressure to leave a reddish-brown solid that was used to the oxirane–CO$_2$ reaction as catalyst. Co^{III}(TPP)Cl and Co^{III}(TPP)Br were prepared according to the literature methods [38,39].

2.5. General procedure of coupling reaction of CO$_2$ and epoxide

All coupling reactions were performed in a 250 ml stainless steel autoclave equipped with a magnetic stir bar. As a typical procedure, the autoclave reactor was successively charged with Co^{III}(TPP)X (0.1 mmol), PTAT (75.2 mg, 0.2 mmol) and propylene oxide (7 ml, 100 mmol) without additional solvent unless mentioned otherwise. The reactor was pressurized with CO$_2$ to 100 psi, stirred at ambient temperature. After the expiration of the desired time, the reactor was vented. The remained mixture was distilled under reduced pressure or recrystallized with ethanol to obtain the pure cyclic carbonate.
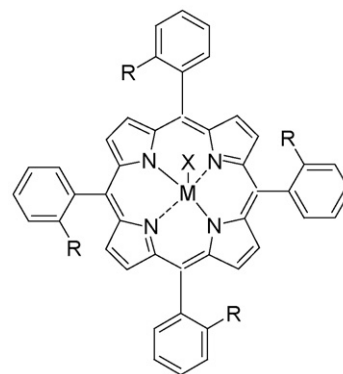
Table 1
Effect of co-catalyst in the coupling reaction of propylene oxide and CO$_2$[a]

Entry	Catalyst	Co-catalyst	Time (h)	Yield (%)	TOF (h^{-1})
1	Co(TPP)Cl	Bu$_4$NBr	4	69.5	174
2[b]	Co(TPP)Cl	DMAP	1	99	248
3	Co(TPP)Cl	PTAT	3	88	293
4	Co(TPP)(OAc)	PTAT	3	90	300
5	Co(TPP)(OAc)	Bu$_4$NBr	5	25.7	51
6[c]	Co(Salen)Cl	Bu$_4$NBr	4	48.2	120
7[c]	Co(Salen)(OAc)	Bu$_4$NBr	2.5	52.4	210

[a] Reaction condition: catalyst (0.1 mmol), co-catalyst (2 equiv.), propylene oxide (100 mmol, 7 ml), CO$_2$ (100 psi), $T = 25$ °C.
[b] Reference [28]: catalyst (0.4% mmol), co-catalyst (2 equiv.), propylene oxide (1 ml), CO$_2$ (100 psi), $T = 120$ °C.
[c] Reference [25]: catalyst (0.5 mmol), co-catalyst (1 equiv.), propylene oxide (500 mmol, 35 ml), $T = 25$ °C.

1a: R=H, X=OAc, M=Co
1b: R=H, X=Br, M=Co
1c: R=H, X=Cl, M=Co
1d: R=H, X=OTs, M=Co
1e: R=H, X=Cl$_3$CCO$_2$, M=Co
1f: R=OMe, X=OAc, M=Co
1g: R=NO$_2$, X=OAc, M=Co
1h: R=NH$_2$, X=OAc, M=Co
1i: R=H, X=Cl, M=Mn
1j: R=H, X=Cl, M=Fe
1k: R=H, X=Cl, M=Ru

Scheme 1.

Table 2
Anion effect of Co(TPP)X on the coupling reaction of propylene oxide and CO$_2$[a]

Entry	Catalyst/co-catalyst	Time (h)	Yield (%)	TON[b]	TOF[c]
1	Co(TPP)(OAc)/PTAT	4.6	93	930	202
2	Co(TPP)Br/PTAT	4	93	930	233
3	Co(TPP)Cl/PTAT	5	93	930	186
4	Co(TPP)OTs/PTAT	7	56	560	80
5	Co(TPP)(O$_2$CCCl$_3$)/PTAT	3	90	900	300
6	Co(TPP)(O$_2$CCCl$_3$)/PTAT	1	66.2	662	662
7	Co(TPP)(OAc)/PTAT	1	62	620	620

[a] Reaction condition: catalyst (0.1 mmol), co-catalyst (2 equiv.), propylene oxide (7 ml, 100 mmol), CO$_2$ (100 psi), $T = 20$ °C.
[b] Moles of propylene carbonate produced per mole of catalyst.
[c] Moles of propylene carbonate produced per mole of catalyst per hour.

3. Results and discussion

3.1. The effect of co-catalyst for Co(TPP)X on synthesis of propylene carbonate

Taking notice of Lu's results of catalyst system of Co(Salen)X/Bu$_4$NBr, TBAB was firstly chosen as a co-catalyst instead of DMAP in Nguyen's catalyst system Co(TPP)X/DMAP. But the results show that the combination of bifunctional catalyst system is not efficient (Table 1, entries 1 and 5) comparing to the Lu's results (entries 6 and 7). Fortunately, when the phenyltrimethyl ammonium tribromide (PTAT) was used as a co-catalyst, the new bifunctional catalyst system Co(TPP)X/PTAT demonstrated an excellent catalytic ability on

Table 3
Framework effect of porphyrins in the coupling reaction of propylene oxide and CO$_2$[a]

Entry	Catalyst/co-catalyst	Time (h)	Yield (%)	TON	TOF
1	Co(TPP)(OAc)/PTAT	3	90[c]	900	300
2	Co(TMPP)(OAc)/PTAT	3	85[c]	850	283
3	Co(TNPP)(OAc)/PTAT	3	34	340	113
4	Co(TAPP)(OAc)/PTAT	3	31.5	315	105
5	Co(TPP)(OAc)/PTAT	4	20[b]	200	50

[a] Reaction condition: catalyst (0.1 mmol), PTAT (2 equiv.), propylene oxide (100 mmol, 7 ml), CO$_2$ (100 psi), $T = 25$ °C.
[b] Pressure of CO$_2$: 15 psi.

Table 4
Metal effect of catalysts on the coupling reaction of CO_2 and propylene oxide

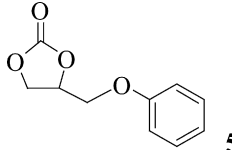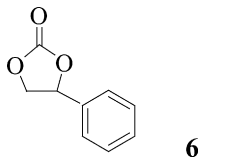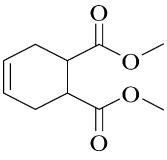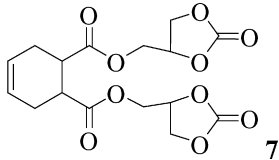| Entry	Catalyst	Time (h)	Yield (%)	TON	TOF
1	Co(TPP)Cl/PTAT	3	88	880	293
2	Mn(TPP)Cl/PTAT	3	27	270	90
3	Fe(TPP)Cl/PTAT	3	10	98	33
4	Ru(TPP)(PPh$_3$)Cl/PTAT	3	14	140	46
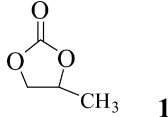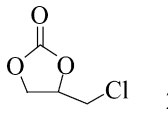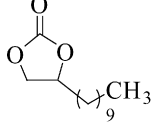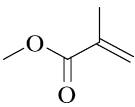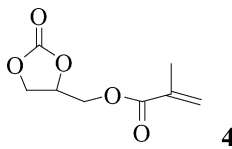
[a] Reaction condition: catalyst (0.1 mmol), PTAT (2 equiv.), propylene oxide (100 mmol, 7 ml), CO_2 (100 psi), $T = 25\,°C$.

synthesis of propylene carbonate at room temperature (entries 3 and 4). These can be explained that the easier leaving group of neucleophile Br_3^- of PTAT has higher activity than that of neucleophile Br^- of TBAB.

3.2. The anion effect of Co(TPP)X on synthesis of propylene carbonate

To select well catalyst system of Co(TPP)X/PTAT, various cobalt(III) porphyrins (Scheme 1) with different counterions were screened for the coupling reaction of CO_2 and propylene oxide (PO). The results are listed in Table 2. It can be seen that all catalyst systems using different anions exhibit high catalytic activity. Among these catalysts, **1e** (Co(TPP)(Cl$_3$CCO$_2$)) exhibits higher catalytic activity than the others used in this study. The activity order is about **1e > 1b > 1a > 1c > 1d**. However, the activity of **1d** (Co(TPP)OTs) is lower due to its bulkiness and high electron-withdrawing ability. The propylene carbonate was obtained with high TOF (entries 6 and 7) and

Table 5
The coupling results of CO_2 and various epoxides catalyzed by Co(TPP)(OAc)/PTAT[a]

Entry	Substrate (R=)	Time (h)	Product	Yield[b] (%)
1	CH$_3$	4.6	**1**	93
2	CH$_2$Cl	7.5	**2**	57
3[c]	(CH$_2$)$_9$CH$_3$	7	**3**	68.1
4		3	**4**	34.1
5[d]	CH$_2$OPh	5	**5**	96
6	Ph	10	**6**	20
7[d]		5	**7**	71

[a] Reaction conditions: Co(TPP)(OAc) (0.1 mmol), PTAT (75.2 mg, 0.20 mmol), epoxide (100 mmol), CO_2 (100 psi), $T = 20\,°C$.
[b] Isolated yield.
[c] Ten milliliter DMF as solvent.
[d] Twenty milliliter acetone was used to dilute the substrate.

was obtained with high yield by prolonging the reaction time (entries 1 and 5) using **1a** or **1e** as catalyst.

3.3. The framework effect of Co(TPP)X on synthesis of propylene carbonate

Porphyrins with different framework were investigated on this coupling reaction of PO and CO_2 (Scheme 1). From the results shown in Table 3, we found that substituted groups in the framework of porphyrin influenced the CO_2 insertion reaction. When the catalysts bearing electron-withdrawing groups (**1g**) or electron-donating groups (**1f** and **1h**), they tend to give diminished TOF (Table 3, entries 2–4). This is attributed to the steric effect of substituted groups. We also explored the influence of CO_2 pressure. When the CO_2 pressure was reduced from 100 to 15 psi, propylene carbonate was only obtained with 20% yield (Table 3, entry 5). The concentration of CO_2 in propylene oxide will be reduced when decreased the pressure resulting in low catalytic activity. This is consistent with literature result [28].

3.4. The metal effect of M(TPP)X on synthesis of propylene carbonate

Besides these condition screenings, we also selected different metals as a Lewis acidic center and investigated the catalytic activity of M(TPP)Cl/PTAT in the coupling reaction of CO_2 and propylene oxide (Table 4). It can be seen that the catalytic activity was in the order of Co > Mn > Ru > Fe. From the results mentioned above, we concluded that Co(TPP)(Cl)/PTAT system has higher catalytic activity.

3.5. The cyclic carbonate synthesis from CO_2 with various epoxides catalyzed by Co(TPP)(OAc)/PTAT

Under the optimized reaction condition, we examined the reactions of other terminal epoxides with carbon dioxide. The results are summarized in Table 5. Co(TPP)(OAc)/PTAT was found to be active to other terminal epoxides, producing the responding cyclic carbonates with high yield and TOF. However, styrene oxide seemed to give relatively low activity (entry 6) due to precipitation of solid product. In comparison with that, the phenoxypropylene oxide (entry 5) and the cyclohexenyl-(1,1′-bisglycidyl)-4,5-dicarboxylic ester (entry 7) were took the coupling reaction with some dilute solvent respectively. To a solution of dodecene oxide, some diluter DMF was added for reducing the viscousness and enhancing the yield (entry 3).

4. Conclusions

In summary, we developed a series of novel and high efficient bifunctional catalysts, M(TPP)X/PTAT, in which Co(TPP)(OAc)/PTAT is one of the best catalyst system for the coupling reaction of carbon dioxide and various epoxides yielding relevant cyclic carbonates by which carbon dioxide can be easily introduced into organic molecules at room temperature.

References

[1] D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps, D.R. Billodeaux, Acc. Chem. Res. 37 (2004) 836.
[2] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.
[3] D.R. Moore, M. Cheng, E.B. Lobkovsky, G.W. Coates, Angew. Chem. Int. Ed. 41 (2002) 2599.
[4] K.C. Nicolaou, Z. Yang, J.J. Liu, H. Ueno, P.G. Nantermet, R.K. Guy, C.F. Claiborne, J. Renaud, E.A. Couladouros, K. Paulvannanand, E.J. Sorensen, Nature 367 (1994) 630.
[5] T. Takata, Y. Furusho, K.-I. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo, M. Sisido, J. Am. Chem. Soc. 120 (1998) 4530.
[6] H.-T. Chang, K.B. Sharpless, Tetrahedron Lett. 37 (1996) 3219.
[7] N. Takeda, S. Inoue, Bull. Chem. Soc. Jpn. 51 (1978) 3564.
[8] N. Takeda, S. Inoue, Macromol. Chem. 179 (1978) 1377.
[9] T. Aida, Macromolecules 15 (1982) 682.
[10] T. Aida, M. Ishikawa, S. Inoue, Macromolecules 19 (1986) 8.
[11] J.H. Jung, M. REE, T. Chang, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 3329.
[12] T. Aida, S. Inoue, J. Am. Chem. Soc. 105 (1983) 1304.
[13] S. Mang, A.I. Cooper, M.E. Colclough, N. Chauhan, A.B. Holmes, Macromolecules 33 (2000) 303.
[14] L.M. Stamp, S.A. Mang, A.B. Holmes, K.A. Kinghts, Y.R. de Miguel, I.F. McConvey, Chem. Commun. (2001) 2502.
[15] A. Baba, T. Nozaka, H. Matsuda, Bull. Chem. Soc. Jpn. 60 (1987) 1552.
[16] F. Li, C. Xia, F. Xu, W. Sun, G. Chen, Chem. Commun. (2003) 2042.
[17] R.L. Paddock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498.
[18] Y. Deng, J. Peng, New J. Chem. 25 (2001) 639.
[19] V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561.
[20] X. Lu, X. Feng, R. He, Appl. Catal. Part A: Gen. 234 (2002) 25.
[21] W.N. Sit, S.M. Ng, K.Y. Kwong, C.P. Lau, J. Org. Chem. 70 (2005) 8583.
[22] J.-L. Jiang, F. Gao, R. Hua, X. Qiu, J. Org. Chem. 70 (2005) 381.
[23] H.B. Xie, S.H. Li, S.B. Zhang, J. Mol. Catal. A: Chem. 250 (2006) 30.
[24] X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo, H. Wang, J. Catal. 227 (2004) 537.
[25] X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang, R. Zhang, J. Am. Chem. Soc. 126 (2004) 3732.
[26] X.-B. Lu, Y.-J. Zhang, B. Liang, X. Li, H. Wang, J. Mol. Catal. A: Chem. 210 (2004) 31.
[27] W.J. Kruper, D.V. Dellar, J. Org. Chem. 60 (1995) 725.
[28] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Tetrahedron Lett. 45 (2004) 2023.
[29] R. Srivastsva, T.H. Bennur, D. Srinivas, J. Mol. Catal. A: Chem. 226 (2005) 199.
[30] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assoup, L. Korsakoff, J. Org. Chem. 32 (1967) 476.
[31] E. Tsuchida, T. Komatsu, E. Hasegawa, H. Nishide, J. Chem. Soc. Dalton Trans. 9 (1990) 2713.
[32] J.P. Collman, J. Am. Chem. Soc. 97 (1975) 1427.
[33] A.D. Alder, F.R. Long, F. Kampas, J. Kim, J. Inorg. Nucl. Chem. 32 (1970) 2443.

[34] R.D. Jones, D.A. Summerville, F. Basolo, J. Am. Chem. Soc. 100 (1978) 4416.

[35] J.P. Collman, C.E. Barnes, P.J. Brothers, T.J. Collins, T. Ozawa, J.C. Gallucci, J.A. Ibers, J. Am. Chem. Soc. 106 (1984) 5151.

[36] S. Apiel, D. Dolphin, G. Domazetis, B.R. James, T.W. Leung, S.J. Rettig, J. Trotter, G.M. Willams, Can. J. Chem. 62 (1984) 755.

[37] B.R. James, D. Dolphin, T.W. Leung, Can. J. Chem. 62 (1984) 1238.

[38] T. Sakurai, K. Yamamoto, H. Naito, N. Nakamoto, Bull. Chem. Soc. Jpn. 49 (1976) 3042.

[39] A.K.-S. Tse, K.W. Mak, K.S. Chan, Organometallics 17 (1998) 2651.