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PAPER

Direct synthesis of cyclic carbonates from olefins and CO_2 catalyzed by a $MoO_2(acac)_2$-quaternary ammonium salt system†

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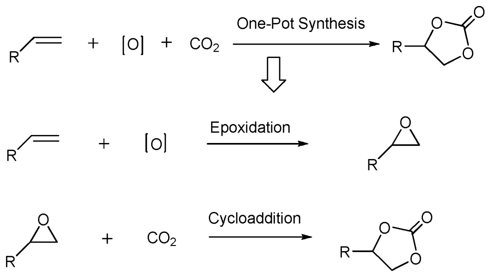
A highly efficient synthesis of cyclic carbonates from olefins and CO_2 has been achieved by the use of a molybdenyl acetylacetonate ($MoO_2(acac)_2$)–quaternary ammonium salt catalytic system with *tert*-butyl hydroperoxide as an oxidant through a one-pot multistep process. This simple and cheap method can be applied to various olefins, such as 1-octene, 1-hexene, allyl chloride, cyclohexene and styrene, affording the highest yields in comparison with the data reported previously except for styrene. A plausible mechanism is proposed based on the results.

Introduction

The chemistry of carbon dioxide (CO_2) has received much attention from both scientific and practical perspectives because CO_2 is not only one of the greenhouse gases but also an inexpensive, nontoxic, nonflammable, naturally abundant and biorenewable C1 resource.[1] The synthesis of cyclic carbonates (CCs), which are excellent aprotic polar solvents, substrates for small molecule synthesis, additives, antifoam agents for antifreeze, and plasticizers, is one of the most promising technologies for chemical fixation and utilization of CO_2.[2] Until now, a number of syntheses of CCs from CO_2 have been described over the last 30 years.[3] Among them, a classical and industrial way is a cycloaddition reaction of CO_2 with epoxide. A remarkable variety of active initiators/catalysts,[3] such as metal and quaternary ammonium salts,[4] phthalocyanine and salen complexes,[5] ionic liquids,[6] metal oxides[7] and immobilized molecular catalysts[8] have been reported for this transformation so far. However, the toxicity and the complicated production process of epoxide, coupled with its high cost, hamper its widespread use as an original material and clearly decrease the number of applications for CC. The search for an environmentally benign and economical process for the synthesis of CCs from CO_2 is therefore of significant importance and interest.

The direct synthesis of CCs from olefins and CO_2, which can be regarded as an oxidative carboxylation process in combination with two sequential reactions of epoxidation of the olefin and the subsequent cycloaddition reaction of CO_2 to the epoxide formed in one pot, is a more economically viable process because of the low-priced and easily available raw material olefins compared with the epoxides and the avoidance of the separation of the epoxide after its synthesis in the first step (Scheme 1). Although the oxidative carboxylation of olefins has been known for a long time, since 1962,[9] however, only a few reports are known thus far about such a useful process in contrast to extensive studies on the cycloaddition reaction of CO_2 and epoxide.[10–19] At first, some known catalysts previously reported for the epoxidation of olefins were tried as active catalysts for the oxidative carboxylation process.[11–12] Subsequently, in view of the remarkable catalytic reactivity of quaternary ammonium salts in the cycloaddition reaction of CO_2 with the epoxide, Arai *et al.* found that quaternary ammonium halides or imidazolium salts were suitable catalysts and/or solvents for the oxidative carboxylation of styrene using *tert*-butyl hydroperoxide (TBHP) as oxidant.[13] Under optimum reaction conditions, tetrabutylammonium bromide (TBAB) was the most effective catalyst and the yield of styrene carbonate (SC) could reach 39%. The yield of SC in this one-pot reaction was significantly increased up to 70% by the TBAB/organic base 1,8-diazabicylco[5.4.0]undec-7-ene (DBU) system using H_2O_2 as an oxidant in water, reported by Li *et al.*[14] In order



Scheme 1 The synthesis of cyclic carbonates *via* the oxidative carboxylation of olefins.

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to further improve the conversion of olefins to CC, some combined catalytic systems consisting of excellent epoxidation catalysts and quaternary ammonium salts were investigated for this oxidative carboxylation process, using mainly a one-pot single step protocol.[15–18] Arai and Sun demonstrated that supported Au catalysts–zinc bromide/TBAB system or nano-gold catalyst supported R201 resin containing an ammonium salt or amino group could significantly increase the activity using TBHP as an oxidant.[15] For example, a 53% yield of SC was obtained by Au/Fe$(OH)_3$–$ZnBr_2$/TBAB.[15b] He and coworkers reported a sodium phosphotungstate–TBAB catalytic system for the facile synthesis of SC with a 57% yield using H_2O_2 as an oxidant.[16] Liu *et al.* reported a direct synthesis of propylene carbonate with a yield of 48% by a titanosilicate–quaternary ammonium halide system using H_2O_2 as an oxidant.[17] A dioxo(tetraphenylporphyrinato)ruthenium(VI)–quaternary onium salt catalytic system with O_2 as the oxidant was recently developed by Jing as an excellent catalyst for the direct synthesis of CCs at ambient temperature under low pressure, giving a 76% yield for SC.[18] In some cases, however, the poor compatibilities and chemical stabilities between these two kinds of catalysts in one pot cannot be avoided, resulting in undesirable yield or long reaction time. In 2007, Yokoyama *et al.* reported a one-pot synthesis of SC from styrene and CO_2 by the use of methyltrioxorhenium (MTO)–Zn[emim]$_2Br_4$/[bmim]BF_4 (emim = 1-ethyl-3-methylimidazolium, bmim = 1-butyl-3-methylimidazolium) with urea hydrogen peroxide as an oxidant in a multistep protocol, affording SC with an 83% yield.[19] However, the complicated catalyst systems limited their wide uses in industry. Therefore, the search for a simple and highly efficient industrial catalyst for the direct synthesis of CCs from olefins and CO_2 is still of great importance from an industrial point of view.

Selective epoxidation of olefins by alkyl hydroperoxide catalyzed by d^0 transition metal complexes (Mo(VI), V(V), and Ti(IV)) has been known as the most important industrial process for the manufacture of propylene oxide.[20] Although the molybdenum complex is the most active catalyst for the epoxidation reaction using TBHP as the oxidant,[20,21] however, it has never been used as catalyst for the one-pot synthesis of CC from olefins. Herein, we report the direct synthesis of CCs with very high yield from olefins and CO_2, catalyzed by a $MoO_2(acac)_2$–quaternary ammonium salt catalytic system using TBHP as an oxidant through a one-pot multistep process. This simple, cheap, highly-efficient method can be applied to various olefins, such as 1-octene, 1-hexene, allyl chloride, cyclohexene and styrene, affording the highest yields in comparison with the data reported previously except styrene.

Results and discussion

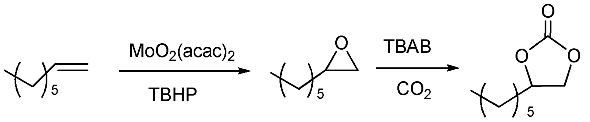
Oxidative carboxylation of 1-octene catalyzed by a $MoO_2(acac)_2$/TBHP–TBAB system

The abilities of molybdenum complexes to catalyze the epoxidation of olefins with organic hydroperoxide as an oxidant were first discovered by Smith in a patent issued in 1956.[21a] Since then, a lot of efforts have been made to develop these efficient catalysts based on the epoxidation mechanism. The results reported by Sheldon and Van Doorn shown that all these molybdenum catalysts gave rise to a common compound, a 1,2-diol complex $MoO_2(OCHRCH_2O)_2$, irrespective of the starting material.[21c] Therefore, our efforts in the end were mainly focused on $MoO_2(acac)_2$, which was easily prepared and commercially available, as a catalyst for the epoxidation of olefins using anhydrous TBHP as an oxidant.[22] TBAB was chosen as an effective cycloaddition catalyst.[3,4b] The simple aliphatic olefin 1-octene was used as a model substrate. Then the one-pot synthesis of 1-octene carbonate from 1-octene and CO_2 by the $MoO_2(acac)_2$–TBAB system was carried out, employing both the single step and multistep protocols, and the representative results were summarized in Table 1.

At first, the epoxidation of 1-octene to 1-octene oxide (OO) and the cycloaddition of CO_2 with OO were separately investigated by $MoO_2(acac)_2$ (**1**) and TBAB in order to know the compatibilities of these catalysts in terms of chemical stabilities in the oxidative carboxylation process in one pot. Consistent with the results reported previously,[21] in the presence of 5.5 mmol of TBHP, 5 mmol of 1-octene was almost completely converted (conversion $>$ 98%) by 0.1 mol% of $MoO_2(acac)_2$ after 1 h at 100 °C without additional solvent, affording an 86% yield of OO (Table 1, Entry 1). In contrast, TBAB was inactive for the epoxidation reaction under the same conditions (Table 1, Entry 2). In addition, adding a catalytic amount of TBAB (5 mol%) to the $MoO_2(acac)_2$/TBHP system markedly prevented the epoxidation reaction proceeding and the expected product 1-octene carbonate was not obtained, suggesting strongly that TBAB had a negative effect on the epoxidation reaction in the $MoO_2(acac)_2$/TBHP system (Table 1, Entry 3).

This is maybe due to the complete consumption of the $MoO_2(acac)_2$/TBHP system by excess TBAB since the bromide ion can catalyze the unwanted and non-productive decomposition of *tert*-butyl hydroperoxide and $MoO_2(acac)_2$ to generate O_2, *tert*-butyl alcohol, and MoO_2Br_2.[21,23] In the cycloaddition reaction, $MoO_2(acac)_2$ was inactive as a catalyst (Table 1, Entry 4), while TBAB afforded a quantitative yield of CC, almost 99%, in the presence of 1-octene epoxide and CO_2 (Table 1, Entry 5). The presence of the $MoO_2(acac)_2$/TBHP system had a slight influence on the catalytic performance of TBAB in the cycloaddition of CO_2 with 1-octene oxide (Table 1, Entry 6), consistent with the previous result that VO$(acac)_2$ and an onium salt could efficiently catalyze the cycloaddition reaction of trimethylene oxide and CO_2 to produce trimethylene carbonate.[24] As a result, when a one-pot single step synthesis of 1-octene carbonate was carried out under the same reaction conditions in the presence of 3 MPa CO_2 at 100 °C for 2 h, the $MoO_2(acac)_2$/TBHP system showed good conversion of olefin to give high yield of OO, *ca.* 85%, whereas no CC was obtained (Table 1, Entry 7). TBAB alone and the combination of the $MoO_2(acac)_2$/TBHP–TBAB system under the same conditions gave disappointing results by yielding only trace amounts of OO and 1-octene carbonate since the $MoO_2(acac)_2$/TBHP system was used up by the reaction with TBAB in the latter case (Table 1, Entries 8–9). Interestingly, a yield of *ca.* 83% of the desired product CC could be achieved by changing to a multistep protocol in which CO_2 and TBAB were subsequently added into the same reactor after the epoxidation of the olefin catalyzed by the $MoO_2(acac)_2$/TBHP system in 1 h, much higher

Table 1 The oxidative carboxylation of 1-octene catalyzed by the $MoO_2(acac)_2$/TBHP–TBAB system[a]

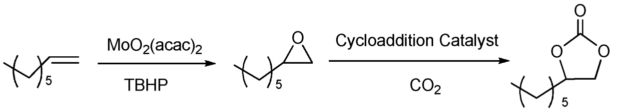


Entry	Catalyst	Temp. (°C)	Time (h)	Yield (%)[b] OO	Yield (%)[b] CC	Type[c]
1[d]	**1**	100	1	86	—	E
2[d]	TBAB	100	1	2	—	E
3[d]	**1**/TBAB	100	1	3	—	E
4[e]	**1**	140	1	—	<1	C
5[e]	TBAB	140	1	< 1	99	C
6[e]	**1**/TBAB	140	1	—	97	C
7	**1**	100	2	85	—	O-S
8	TBAB	100	2	4	2	O-S
9	**1**/TBAB	100	2	5	5	O-S
10	**1**	100/140[f]	1/1[g]	81	—	O-M
11	TBAB	100/140[f]	1/1[g]	< 1	7	O-M
12	**1**/TBAB	100/140[f]	1/1[g]	< 1	83[h]	O-M
13	**1**/TBAB	100/120[f]	1/1[g]	10	74[h]	O-M
14	**1**/TBAB	100/100[f]	1/1[g]	30	55[h]	O-M
15	**1**/TBAB	100/140[f]	2/1[g]	< 1	81[h]	O-M

[a] Conditions: 1-octene 5 mmol, TBHP 5.5 mmol, **1** ($MoO_2(acac)_2$) 0.1 mol%, 5 μmol, TBAB 5 mol%, 0.25 mmol, $P(CO_2)$ 3 MPa, unless otherwise noted. [b] Determined by GC. [c] E, epoxidation reaction; C, CO_2 cycloaddition reaction; O-S, one-pot single step process; O-M, one-pot multistep process. [d] Without CO_2. [e] 1-octene oxide as starting material, 5 mmol. [f] The former is the reaction temperature for epoxidation reaction and the latter is the reaction temperature for cycloaddition reaction. [g] The former is the reaction time for epoxidation reaction and the latter is the reaction time for cycloaddition reaction. [h] Selectivity is close to the yield of cyclic carbonate.

than the yields obtained by $MoO_2(acac)_2$ and TBAB alone (Table 1, Entries 10–12). As a result, the one-pot multistep synthetic protocol was viewed as a more attractive and practical route for the oxidative carboxylation of 1-octene and CO_2 catalyzed by the $MoO_2(acac)_2$–TBAB catalytic system. The yield of CC was sensitive to the reaction temperature and time. With the decreasing temperature in the cycloaddition process from 140 to 100 °C, the yield of CC gradually decreased from 83% to 55% (Table 1, Entries 12–14). An extension of the epoxidation reaction time resulted in the decrease of OO yield because of its ring-opening reaction, thus leading to a decreased yield of CC (Table 1, Entry 15).

Table 2 The oxidative carboxylation of 1-octene catalyzed by $MoO_2(acac)_2$/TBHP–various cycloaddition catalysts[a]



Entry	Cycloaddition Catalyst	Yield (%)[b] OO	Yield (%)[b] CC[c]
1	$(n\text{-}C_{16}H_{33})(CH_3)_3NBr$	16	63
2	$(n\text{-}C_2H_5)_4NBr$	12	73
3	$(n\text{-}C_4H_9)_4NBr$	< 1	83
4	$(n\text{-}C_4H_9)_4NCl$	19	64
5	$(n\text{-}C_4H_9)_4NI$	< 1	83
6	$(n\text{-}C_4H_9)_4NHSO_4$	81	3
7	[bmim]Br	2	81
8	[bmim]Cl	45	42
9	$[bmim]BF_4$	84	< 1
10	pyridine	80	4
11	*N*,*N*-dimethylaminopyridine	80	6
12	DBU	86	< 1
13	ethylenediamine	80	3
14	1,2-diaminopropane	82	4
15[d]	$[(n\text{-}C_7H_{15})_4N]_6SiW_{11}CoO_{39}$	80	5
16[d]	$[(n\text{-}C_7H_{15})_4N]_6GeW_{11}MnO_{39}$	79	5

[a] Conditions: 1-octene 5 mmol, TBHP 5.5 mmol, $MoO_2(acac)_2$ 0.1 mol%, 5 μmol, 100 °C, 1 h; cycloaddition-catalyst 5 mol%, 0.25 mmol, 140 °C, $P(CO_2)$ 3 MPa, 1 h, unless otherwise noted. [b] Determined by GC. [c] Selectivity is close to the yield of cyclic carbonate. [d] Cycloaddition-catalyst 0.1 mol%, 5 μmol.

Oxidative carboxylation of 1-octene by $MoO_2(acac)_2$/TBHP-various cycloaddition catalysts through a one-pot multistep process

On the basis of the above results, the $MoO_2(acac)_2$/TBHP–TBAB system showed very good activity and selectivity for the direct synthesis of 1-octene carbonate from 1-octene and CO_2 in a one-pot multistep process. In view of the large-scale application of the $MoO_2(acac)_2$/TBHP system in industry, a lot of highly efficient cycloaddition catalysts, mainly based on quaternary ammonium salts, ionic liquids, organic bases, and transition-metal-substituted Keggin-type polyoxometalates, have been introduced into the $MoO_2(acac)_2$/TBHP system in order to get a novel catalytic system for the one-pot synthesis of CC. The representative results are illustrated in Table 2.

Arai and Sun had reported that the catalytic performances of quaternary ammonium salts in the cycloaddition reaction of CO_2 and epoxide were significantly dependent on the nucleophilicities of the anions because their nucleophilic attack to a carbon atom of epoxide can result in ring opening of epoxide to generate a oxygen anion as active species to active CO_2.[13] A quick screening of various quaternary ammonium salts was carried out in the second step of direct synthesis of 1-octene carbonate under 3 MPa CO_2 at 140 °C for 1 h (Table 2, Entries 1–6). The results indicated that the kinds of anions and cations involved in quaternary ammonium salts really did have some effect on the yield of CC. The cation of quaternary ammonium salts played an important role in the second step of one-pot synthesis of CC. The bulkiness of the tetrahedral ammonium ion $[NR_4]^+$ forces the halogen anion away from the cation, thus making the anion more nucleophilic.[4b,13] As a result, the more bulky $[(n\text{-}C_4H_9)_4N]^+$ cation showed higher activity than the less sterically demanding $[(n\text{-}C_{16}H_{33})(CH_3)_3N]^+$ and $[(n\text{-}C_2H_5)_4N]^+$ cations under the same conditions (Table 2, Entries 1–3). Similar to TBAB, quaternary ammonium salts containing strongly nucleophilic halide ions, such as $(n\text{-}C_4H_9)_4NCl$ and $(n\text{-}C_4H_9)_4NI$ also exhibited the same or slightly low activities for the one-pot multistep synthesis of CC from 1-octene under the same conditions (Table 2, Entries 3–5). The decreasing tendency of their activities corresponded with the decreasing nucleophilicity of the halide anion in the order $I^- > Br^- > Cl^-$. Whereas, $(n\text{-}C_4H_9)_4NHSO_4$ with the weakly nucleophilic HSO_4^- anion was almost inactive for the oxidative carboxylation of 1-octene (Table 2, Entry 6).

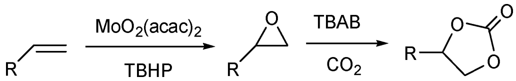
Similarly, ionic liquids with strongly nucleophilic halide ions, such as [bmim]Br and [bmim]Cl were also effective for the direct synthesis of CC from 1-octene, producing CCs with 83% and 42% yields, respectively (Table 2, Entries 7–8). In contrast, $[bmim]BF_4$ could not convert OO to CC under the same conditions (Table 2, Entry 9). Such a result was similar to the MTO–$Zn[emim]_2Br_4/[bmim]BF_4$ catalytic system during one-pot multistep synthetic process,[19] although $[bmim]BF_4$ alone was active for the cycloaddition of CO_2 and epoxide in a long reaction time.[6] A possible reason for the better catalytic performance of quaternary ammonium salts compared with that of the ionic liquids may be ascribed to the different cations in the structure. The planer cation $[bmim]^+$ in the ionic liquid bound the anion more tightly than the $[NBu_4]^+$ (Bu, butyl) cation in the quaternary ammonium salt, which resulted in the relatively low nucleophilicity of the halide anion in the ionic liquid (Table 2, Entries 4 and 8).[4b,13]

Unfortunately, several ammonium bases and transition-metal-substituted polyoxometalates, which were reported as active catalysts for the cycloaddition of CO_2 and epoxides to produce CCs,[3,25] afforded unsatisfactory yields of CCs, maybe due to the absence of the strongly nucleophilic halide ion or coordination with *tert*-butyl alcohol formed in the first step in the one-pot synthesis of CCs (Table 2, Entries 10–16). Thus, quaternary ammonium salts and ionic liquids containing strongly nucleophilic halide anions were found to be effective catalysts in the second step of the one-pot synthesis of CC.

Oxidative carboxylation of various olefins by $MoO_2(acac)_2$/TBHP-TBAB system

To explore the utility of the $MoO_2(acac)_2$/TBHP–TBAB system in a one-pot multistep synthesis of cyclic carbonates, other olefins were then investigated and the results are presented in Table 3. Compared with the previous catalyst systems,[9–19] the $MoO_2(acac)_2$/TBHP–TBAB system demonstrated its superiority in the highly efficient conversion of most olefins to CCs (Table 3, Entries 1–10). Under 3 MPa CO_2, the $MoO_2(acac)_2$/TBHP-TBAB system catalyzed the oxidative carboxylation of 1-hexene, affording 1-hextene carbonate with a moderate yield of *ca.* 49% (Table 3, Entry 2). With further increase of the epoxidation reaction time or the amount of the oxidant TBHP, slightly higher yields of 1-hexene carbonate (*ca.* 56–58%) were obtained (Table 3, Entries 4–5). Allyl chloride carbonate and cyclohexene carbonate were produced in 45% and 33% yields, respectively, under the same conditions; however, with decreasing the epoxidation temperature from 100 °C to 70 °C or with increasing the cycloaddition reaction time from 1 h to 6 h, the yields of allyl chloride carbonate and cyclohexene carbonate were significantly increased up to 80% and 84%, respectively, which are the highest yields reported in the literature (Table 3, Entries 5–8). The only exception was styrene (Table 3, Entries 9–10). Only a 68% yield of styrene carbonate was achieved using this one-pot multistep protocol and the by-product benzaldehyde was simultaneously detected. Although a 68% yield of styrene carbonate was higher than those of most of catalyst systems,[9–17] it was inferior to the

Table 3 The oxidative carboxylation of various olefins by the $MoO_2(acac)_2$/TBHP–TBAB system[a]



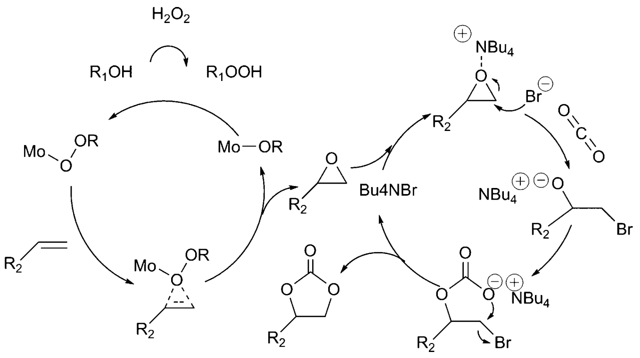
Entry	Olefin	Time (h)	Yield[b] (%)	Yield reported[c] (%)	Ref
1	1-Octene	1/1	83	78	18
2	1-Hexene	1/1	49	47	16
3	1-Hexene	2/1	56	—	—
4	1-Hexene	2/1[d]	59	—	—
5	Allyl chloride	1/1	45	57	18
6	Allyl chloride	1/1[e]	80	—	—
7	Cyclohexene	1/1	33[f]	31	18
8	Cyclohexene	1/6	84	—	—
9	Styrene	1/1	68[g]	83	19
10	Styrene	—	—	76[h]	18

[a] Conditions: olefin 5 mmol, TBHP 5.5 mmol, $MoO_2(acac)_2$ 0.1 mol%, 5 µmol, TBAB 5 mol%, 0.25 mmol, 100 °C for epoxidation reaction and 140 °C for cycloaddition reaction, $P(CO_2)$ 3 MPa, unless otherwise noted. [b] Yield of CC is determined by GC. Selectivity is close to the yield of cyclic carbonate. [c] The highest yield reported previously. [d] TBHP 7 mmol. [e] Reaction temperature for epoxidation reaction is 70 °C. [f] 53% Yield of cyclohexene oxide is detected. [g] 13% Yield of benzaldehyde is detected. [h] Only one example has 100% selectivity for CC.

83% yield offered by MTO–Zn[emim]$_2$Br$_4$/[bmim]BF$_4$ using a multistep protocol and the 100% selectivity obtained by a Ru catalyst,[18,19] maybe due to the attack of TBHP on the epoxide formed and cleavage of the C–C bond in the first step.[20,21] These results strongly indicated that the MoO$_2$(acac)$_2$/TBHP–TBAB system in a one-pot multistep protocol could efficiently promote oxidative carboxylation of various olefins to prepare CCs, which was probably ascribed to avoiding interaction between catalysts themselves and those of the catalyst and intermediate product, resulting from the addition of catalyst at a different stage.

Possible reaction mechanism

Since the one-pot synthesis of cyclic carbonate through a multistep process is viewed as the combination of two separate reactions catalyzed by their respective catalysts, it is apparent that the mechanism of oxidative carboxylation of olefin over catalyst MoO$_2$(acac)$_2$/TBHP-TBAB consists of the mechanism of the epoxidation reaction catalyzed by MoO$_2$(acac)$_2$ and the mechanism of the following cycloaddition reaction catalyzed by TBAB. Due to the industrial importance, the mechanism of the epoxidation reaction catalyzed by MoO$_2$(acac)$_2$ has been studied by several groups. Some represented results have been obtained,[26] for example, the alkylperoxo mechanism proposed by Chong and Sharpless[27] and the metalladioxolane mechanism suggested by Mimoun.[28] Recently, theoretical calculations indicate that the alkylperoxo mechanism in which an oxygen is directly transferred from a hydroperoxide species to olefin is more energetically favorable.[29] Thus, a plausible mechanism is proposed based on these results and presented in Scheme 2.



Scheme 2 The proposed mechanism of the oxidative carboxylation of olefins catalyzed by the MoO$_2$(acac)$_2$/TBHP–TBAB system.

In the epoxidation reaction, the hydroperoxide is suggested to coordinate to the metal center through the distal or terminal oxygen, rather than the proximal oxygen, to form the key intermediate alkylperoxo M–OOR. The coordination of the distal oxygen atom is reasonable from steric considerations and the fact that its complexation to the metal center will activate it. Subsequently, the olefin is coordinated with the alkylperoxo M–OOR proceeding with a three-membered transition state, and then the epoxide is produced after complexation and oxygen transfer.[28,30] In the following cycloaddition reaction, the coordination of the [n-Bu$_4$N]$^+$ cation of TBAB with the oxygen atom of the resulting epoxide will promote the nucleophilic attack of the anion Br$^-$ on the less hindered carbon atom of the epoxide, which leads to opening of the epoxide ring and generation of an oxygen anion species. The nucleophilic attack of the newly formed oxygen anion species on the carbon atom of CO$_2$ affords the key intermediate NBu$_4$OCOOCHR$_2$CH$_2$Br. After the intramolecular cycloaddition reaction, the corresponding CC is formed in combination with TBAB being regenerated as the active species in the catalytic cycle.[3,4b]

Remarkably, the MoO$_2$(acac)$_2$–TBAB catalytic system can be recycled by distilling all of the organic solvents, including *tert*-butyl alcohol, toluene, and CC consecutively after the whole reaction, since both of the catalysts are solid and they were left in the bottle. Moreover, their diverse solubilities in ethanol separate them completely. For example, the yield of the first recycle of about 80% was slightly lower than the previous result (83%) using 1-octene as a model olefin. A 78% yield of CC was obtained in the second recycle. Furthermore, the by-product *tert*-butyl alcohol can be converted into TBHP by reacting with H$_2$O$_2$,[30] thus olefins, CO$_2$ and H$_2$O$_2$ were actually consumed during the whole process.

Conclusions

In summary, a simple, cheap, and highly-efficient preparation of cyclic carbonates from olefins and CO$_2$ has been achieved by the MoO$_2$(acac)$_2$/anhydrous TBHP–TBAB system through a one-pot multistep process. Compared with other catalytic systems, the present catalytic system, which is easy to prepare and commercially available, can convert various olefins into the corresponding cyclic carbonates in the highest yields in comparison with the data previously reported, except for styrene. From an economic point of view, the direct synthesis of cyclic carbonates from olefins and CO$_2$ catalyzed by this low-cost and highly-efficient MoO$_2$(acac)$_2$/TBHP–TBAB system employing the multistep protocol would be of great potential in industry for the environmentally benign chemical fixation and utilization of CO$_2$. The investigation of the optimization and application of the MoO$_2$(acac)$_2$/TBHP–TBAB system in industry is under way in our laboratory.

Experimental

Materials and instrumentation

Cyclohexene oxide (98%), 1-octene oxide (97%), styrene oxide (97%) were purchased from Aldrich without further purification. Chloropropylene (98%), 1-hexene oxide (97%), 1-octene (99%), 70% TBHP aqueous solution, and [(n-C$_4$H$_9$)$_4$N]HSO$_4$ (99%) was purchased from J&K Chemical Ltd. Cyclohexene (99%), 1-methylimidazolium (99%) and biphenyl (99%) were purchased from Alfa. Epichlorohydrin, styrene, and other reagents and chemicals with analytical purity were purchased from Sinopharm Chemical Reagent Co., Ltd, P. R. China. CO$_2$ (99.99%) was purchased locally.

Fourier-transform infrared spectra (FT-IR) of the samples were recorded on the Thermal Nicolet 670 FT-IR over the range of 4000–400 cm^{-1} using the KBr pellet technique at room temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz and 100.6 MHz) in CDCl$_3$.

GC analyses were performed on a Kechang GC-9800, equipped with a flame ionization detector (FID) and a SE-30 capillary column using nitrogen as a carrier gas.

Preparations of catalysts and oxidant

$MoO_2(acac)_2$ was synthesized according to the published procedure.[31] $[bmim]BF_4$, [bmim]Br and [bmim]Cl were synthesized according to the literature.[32] Transition-metal-substituted Keggin-type polyoxometalates were synthesized following the published process.[24,33] All these catalysts were determined by IR and were consistent with the literature values.[31–33]

Anhydrous TBHP in toluene was synthesized from refluxing 70% TBHP aqueous solution and toluene following the literature procedure.[22] TBHP concentrations were determined by iodometric titration according to the reference method[21d,22] and was detected to be 3.25 M.

Catalytic reactions and analyses

The catalytic reaction was carried out in a 25 mL stainless-steel autoclave equipped with a magnetic bar. In the one-pot single process, the reactor was charged with an appropriate amount of catalysts $MoO_2(acac)_2$ and TBAB, olefin, TBHP at room temperature and CO_2 was pumped in. The reactor was then heated to a desired temperature, and the pressure was adjusted to the desired pressure by a CO_2 boosting pump.

In the one-pot multistep process, the reactor was charged with the appropriate amounts of catalyst $MoO_2(acac)_2$, olefin and TBHP, and then was heated to the desired temperature. After the epoxidation reaction was finished, the autoclave was cooled to room temperature, and was charged with the appropriate amount of catalyst TBAB. CO_2 was then pumped into the reactor and the pressure was adjusted to the desired pressure by a CO_2 boosting pump.

In both processes, the autoclave was cooled to 0 °C in an ice-water bath after the reaction in order to release the remaining CO_2 slowly. The reaction products were determined by gas chromatograph (GC). The mixture was identified by the absolute retention time compared to pure samples, and further purified by column chromatography. The yield and selectivity of products were calculated by peak area using an interstandard technology from ^1H NMR and ^{13}C NMR spectra.

Chloropropylene carbonate. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.73–3.88 (m, 2 H), 4.40–4.43 (dd, J = 6.0, 9.0 Hz, 1 H), 4.60–4.64 (dd, J = 8.0, 9.0 Hz, 1 H), 5.02–5.07 (m, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 44.1, 67.0, 74.5, 154.5.

1-Hexene carbonate. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.87–0.91 (t, 3H, J = 7.0 Hz), 1.30–1.43 (m, 4H), 1.63–1.79 (m, 2H), 4.02–4.06 (dd, 1H, J = 7.2 Hz), 4.49–4.53(t, 1H, J = 8.1 Hz), 4.63–4.71 (1 H, qd, J = 7.5, 5.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 13.8, 22.2, 26.4, 33.5, 69.4, 77.2, 155.2.

Cyclohexene carbonate. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.37–1.62 (m, 4 H), 1.81–1.91 (m, 4 H), 4.65–4.7 (m, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 19.1, 26.7, 75.8, 155.4.

1-Octene carbonate. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.87 (3 H, t, J = 6.9 Hz), 1.38–1.20 (8 H, m), 1.49–1.43 (1 H, m), 1.81–1.63 (2 H, m), 4.06 (1 H, dd, J = 8.3, 7.3 Hz), 4.52 (1 H, t, J = 8.1 Hz), 4.74–4.65 (1 H, m); ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 14.0, 22.4, 24.3, 28.8, 31.5, 33.8, 69.4, 77.1, 155.2.

Styrene carbonate. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.34–4.38 (1 H, m), 4.80–4.84 (1 H, t, J = 8.4 Hz), 5.68–5.72 (1 H, t, J = 8.0 Hz), 7.37–7.48 (5 H, m); ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 71.2, 77.9, 125.9, 129.3, 129.7, 135.9, 154.9.

Recyclability of catalyst and regeneration of TBHP

With respect to recyclability of the present catalyst and regeneration of TBHP, the one-pot multistep reaction was performed on a mole scale. The catalytic reaction was carried out in a 1 L stainless-steel autoclave equipped with a magnetic bar. The reactor was charged with $MoO_2(acac)_2$ (1 mmol, 0.33 g), 1-octene (1 mol, 112 g), anhydrous TBHP in toluene solution (1.1 mol, 340 mL, 3.25 mol L^{-1}), and then the reactor was heated to 100 °C for 1 h. After the epoxidation reaction was finished, the autoclave was cooled to room temperature, and was charged TBAB (0.05 mol, 16.10 g). CO_2 was then pumped into the reactor and the pressure was adjusted to 3 MPa by a CO_2 boosting pump. The autoclave was heated to 140 °C for 1 h. After the reaction, the autoclave was cooled to 0 °C in an ice-water bath in order to release the remaining CO_2 slowly. The mixture was distilled of all of the organic solvent consecutively by vacuum. Then the solid was extracted by a small amount of ethanol. $MoO_2(acac)_2$ was obtained by filtration and TBAB was obtained by recrystallization from ethanol in low temperature after concentration.

The by-product *tert*-butyl alcohol was collected individually and transferred to a 3-necked flask. The same amount of 70% H_2SO_4 was added to the flask and then the flask was placed in an ice-water bath. The same amount of 30% H_2O_2 solution was slowly added. The mixture was stirred overnight. The organic liquid was extracted by toluene and distilled by vacuum to afford anhydrous TBHP in toluene.

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