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Metal Acetylacetonates as Highly Efficient and Cost Effective Catalysts for the Synthesis of Cyclic Carbonates from CO_2 and Epoxides

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Abstract Metal acetylacetonates were found to be efficient and cost effective catalysts for the formation of cyclic carbonates by cycloaddition of carbon dioxide with epoxides, providing high to excellent yields of the corresponding carbonates. Among the various catalysts such as acetylacetonates of Co, Ni, Cu, Zn, Fe, Cr and VO studied, $Ni(acac)_2$ was found to be promising catalyst for this reaction. The present methodology was found to be superior due to the easy accessibility and comparatively inexpensive nature of metal acetylacetonates than salen complexes.

Keywords Carbon dioxide · Epoxide · Cyclic carbonate · Acetylacetonate · Cycloaddition

1 Introduction

Climate change has attained significant prominence in last two decades as atmospheric CO_2 concentrations have indeed increased by almost 100 ppm from pre-industrial level to the present scenario. More than 80 % of our energy comes from the combustion of fossil fuels and it is well-accepted that carbon dioxide is the most prominent anthropogenic greenhouse gas leading to global warming [1, 2]. It is mainly released by burning fossil fuels/biomass as a fuel and by certain industrial and resource extraction processes.

As a solution for this serious problem, the capture of CO_2 and its utilization for the value added chemicals is particularly important rather than just dumping it [3–8]. The coupling of CO_2 with epoxides to form cyclic carbonates is an important reaction as they are valuable compounds that have applications in various fields. Owing to their high solubility, high boiling, low toxicities, and biodegradability, cyclic carbonates are utilized as aprotic polar solvents in degreasing, paint stripping, and cleaning [9, 10]. Methodologies for the formation of cyclic carbonates utilizing CO_2 as a chemical feedstock are well established [11]. Many catalysts such as alkali metal salts [12], metal oxides [13], transition metal complexes [14, 15], ion-exchange resins [16], functional polymers [17], quaternary ammonium and phosphonium salts [17], ionic liquids [18], lanthanide oxychloride [19, 20], cellulose/KI [21] have been developed for the have been developed for the reactions of CO_2 and epoxides to produce cyclic carbonates. Prominent among these, the most successful and popular approach is using metal salens of Al [22, 23], Co [24], Cr [25–27] and other metal derivatives [28, 29]. Nevertheless, concerning an industrial scale synthesis of cyclic carbonates, development of low toxic, cost-effective and high active catalytic system is particularly desired. Metal acetylacetonates, easily accessible and relatively inexpensive as compared to the salen complexes are surprisingly remained unexplored as catalysts for the formation of cyclic carbonates.

In the present paper we describe a systematic study of the catalytic activity of various metal acetylacetonates for the synthesis of cyclic carbonates from the epoxides and carbon dioxide under mild reaction conditions (Scheme 1).

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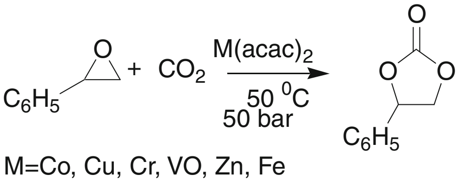
2 Results and Discussion

At first, to evaluate the activity of various metal acetylacetonates such as Co, Ni, Cu, Zn, Cr, VO and Fe, we studied the cycloaddition of CO_2 and styrene epoxide under solvent free conditions. The results of these experiments are presented in Table 1. The catalytic efficiency was found to be mainly depended on the nature of the transition metal and its oxidation state. Among the tested catalysts, $Ni(acac)_2$ was found to be best catalyst in terms of conversion and selectivity of the desired compound. However, $Co(acac)_2$, $Zn(acac)_2$ and $Cr(acac)_2$ were found to be moderate catalysts for this transformation. All the reactions were carried out at in the presence of co-catalyst tetraethylammonium bromide (NEt_4Br) at 50 °C and 50 bar pressure for 4.5 h under solvent less condition in a 100 mL stainless steel high pressure reactor (Fig. 1).

Among the metal derivatives of Co, Cr and Ni, the catalysts having the oxidation state II were found to be more reactive as compared to the catalysts having III oxidation state of the transition metal (Table 1, entry 1–4, 7, 8). This is probably due to the geometrical and structural difference of the +2 and +3 complexes. For example, $Co(acac)_2$ has square planner geometry and therefore its axial positions are free to bind with CO_2 and epoxide in situ during the reaction. In contrast, Co(III) has octahedral geometry in which axial position are occupied and further bonding of substrates to metal will be difficult and may cause steric hindrance as well. Besides these experiments, we also investigated the effect of temperature and pressure on the cycloaddition of styrene oxide and carbon dioxide under otherwise same reaction conditions (Table 1, entry 11–15). It was observed that the temperature and pressure also played an important role on the yield of cyclic carbonate. At ambient temperature (25 °C), the reaction rate was found to be slow and depended on the CO_2 pressure applied. The observed conversion was found to increase as the CO_2 pressure increased. At higher reaction temperatures (60–80 °C), the selectivity of the reaction towards the formation of carbonate was continuously decreased with increasing the CO_2 pressure. This is due to the formation of corresponding polycarbonate by the accelerated polymeri-



Scheme 1 Synthesis of cyclic carbonates

Fig. 1 High pressure autoclave

Table 1 Reaction of styrene oxide with CO_2 using different $M(acac)_2$ catalysts and Et_4NBr at various conditions

Entry	Catalyst	pCO_2/bar	T/°C	Reaction time (h)	Conv. (%)[a]	Yield (%)[b]
1	$Ni(acac)_2$	50	50	4.5	100	97
2	$Ni(acac)_3$	50	50	4.5	22.5	12
3	$Co(acac)_2$	50	50	4.5	70.2	60
4	$Co(acac)_3$	50	50	4.5	Trace	–
5	$Zn(acac)_2$	50	50	4.5	50	37
6	$Fe(acac)_2$	50	50	4.5	Trace	–
7	$VO(acac)_2$	50	50	4.5	Trace	–
8	$Cr(acac)_3$	50	50	4.5	21.7	20
9	$Cr(acac)_2$	50	50	4.5	80	75
10	$Mn(acac)_2$	50	50	4.5	20	–
11	$Ni(acac)_2$	50	25	8.0	50	35
12	$Ni(acac)_2$	10	80	2.0	50	25
13	$Ni(acac)_2$	20	50	4.5	70	60
14	$Ni(acac)_2$	40	50	4.5	85	75

Reaction conditions: styrene oxide (10 mmol), catalyst (1 mol%, 0.1 mmol), n-Et_4NBr (0.1 mmol) without using additional solvent for 4.5 h

[a] Calculated based on the remaining styrene oxide

[b] Isolated yields of the cyclic carbonate

zation between carbonates and CO_2 under high pressure. It was found that efficient and selective conversion into styrene carbonate could be achieved at only 50 °C and 50 bar of CO_2 under otherwise similar reaction conditions. When the reaction of styrene oxide with CO_2 was performed in the presence of tetraethylammonium bromide (NEt_4Br) alone without metal catalyst, the much lower conversions 20.2 % of the styrene carbonate was obtained under similar reaction conditions. This finding established that the metal catalyst is essentially required for the efficient conversion in the present transformation. However, in a blank reaction without tetraethylammonium bromide and metal catalyst, there was no reaction occurred between styrene oxide and CO_2 under similar reaction conditions.

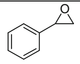
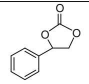
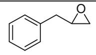
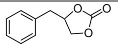
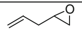
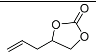
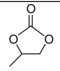
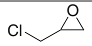
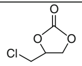
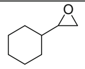
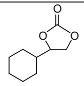
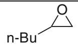
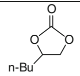
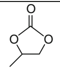
Next, we extended the scope of the reaction with a variety of epoxides, we used Ni(acac)$_2$ as catalyst and studied the cycloaddition in the presence of co-catalyst tetraethylammonium bromide at 50 °C under the 50 bar pressure of CO_2 without using any reducing agent under solvent less conditions (Scheme 2). The results of these experiments are summarized in Table 2. All the epoxides were efficiently and selectively converted to the corresponding carbonates in high to excellent yields.

It is worthy to mention that Ni-based catalytic systems have been less explored for the formation of carbonates by cycloaddition of epoxides and carbon dioxide. In this context, Decortes et al. [30] reported a variety of Ni-based catalytic systems to be effective for the synthesis of cyclic carbonates from epoxides and carbon dioxide. However the need of volatile organic solvents and longer reaction times are the major drawbacks of these methods. Recently, De Pasquale et al. [31] reported an efficient Ni (II) catalyst system for the coupling of carbon dioxide and epoxides under solvent-less conditions. Despite of the inexpensive nature, high stability and higher catalytic reactivity, the need of promoters such as triphenylphosphene and Zn powder as a reducing agent, higher reaction temperature make this method of less applicable. Thus, the method described here is advantageous in many ways over the previous ones like, easy availability and facile synthesis of Ni(acac)$_2$, mild reaction conditions and solvent-less protocol.

The metal catalyst and co-catalyst tetraethylammonium bromide both are essential for the present reaction. In the presence of organic solvent such as acetonitrile the reaction gave comparable results but solvent-less conditions were found to be best and make this procedure more desirable from environmental viewpoints.

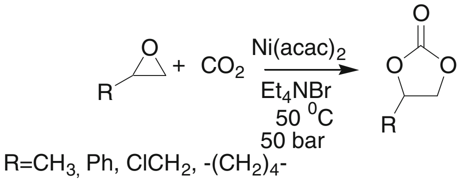
The mechanism of the cycloaddition of epoxides with carbon dioxide in presence of metal catalyst and quaternary salts is well documented in the literature [32]. To understand the mechanistic pathway of the reaction we also performed the experiment by using Zn as reducing agent under described reaction conditions. The reaction remained unaffected and we could obtain the similar conversion and yield of the cyclic carbonate during this course, indicating that the catalytic cycle did not involve the insitu reduction of Ni(II) to Ni (0) as described by De Pasquale et al. [31] Thus, we assume that the reaction probably initiates by the coordinating the metal complex with epoxide followed by the attack of a nucleophilic group (chloride ion from TEAB), leading to epoxide ring-opening and formation of a metal-bound alkoxide [33]. In the subsequent step, insertion of CO_2 in M–O bond to form a metal-bound carboxylate, followed by the production of cyclic carbonate as shown in Scheme 3.

Table 2 Ni(acac)$_2$ catalyzed cycloaddition of various epoxides with CO_2

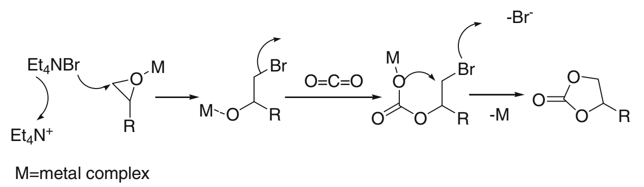
Entry	Epoxide	Product	Reaction Time (h)	Yield (%)^b
1			4.5	97
2			4.0	92
3			3.5	90
4			2.5	98
5			3.0	94
6			6.0	65
7			2.0	98
8			2.0	98

Reaction conditions: substrate (10 mmol), catalyst (1 mol%, 0.1 mmol), n-Et_4NBr (0.1 mmol) at 50 °C under pressure 50 bar without using additional solvent

[a] Isolated yields



Scheme 2 Ni(acac)$_2$-catalyzed synthesis of cyclic carbonates



Scheme 3 Probable mechanistic pathway

3 Conclusion

In summary we have described a highly efficient and cost effective method for the formation of cyclic carbonates from the epoxides and carbon dioxide without any additional solvent and reducing agent. The developed method has many potential advantages (i) metal acetylacetonates are easily accessible and highly stable catalysts; (ii) comparatively inexpensive than salen complexes; (iii) mild and solvent-less condition; (iv) excellent conversions with high selectivity. These remarkable features make the developed protocol attractive and eco-friendly in terms of the industrial applications for the utilization of carbon dioxide by chemical fixation route. Further studies and optimization of the reaction conditions for large scale applications are currently being in progress in our laboratory.

4 Experimental

4.1 Typical Experimental Procedure for the Synthesis of Cyclic Carbonates

All the experiments were performed in a 100 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical reaction, Ni(acac)$_2$ (0.05 g, 0.2 mmol), *n*-Et$_4$NBr (42 mg, 0.2 mmol) and styrene oxide (2.4 g, 20 mmol) were charged into the reactor without using any additional solvent. The pressure of the carbon dioxide was set-up 50 bar and the temperature of the vessel was kept 50 °C during the reaction. After being cooled the reaction mixture at room temperature, the resulting mixture was passed through a short column (SiO$_2$) and washed with dichloromethane. The solvent was evaporated under reduced pressure and crude product was purified by column chromatography, the product styrene carbonate was obtained as a white crystalline solid, mp (52 °C) [34].

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