Cyclic carbonate synthesis from CO₂ and epoxides using zinc(II) complexes of arylhydrazones of β-diketones

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Zinc(II) complexes of arylhydrazones of β-diketones (AHBD) were used for the first time as catalysts combined with tetrabutylammonium bromide (TBABr), in the coupling reaction between CO₂ and epoxides. The influence of pressure and temperature on cyclic carbonate formation was investigated, as well as the catalytic activity towards different substrates (e.g. styrene oxide, propylene oxide and cyclohexene oxide). The molar ratio between metal complex and TBABr was determined for maximum catalytic activity.

1. Introduction

CO₂ utilization as a renewable carbon source in the production of cyclic carbonates is an attractive field of research. Cyclic carbonates are valuable synthetic products, with diverse applications, such as polar aprotic solvents, electrolytes for lithium batteries, fuel additives and intermediates in the manufacture of chemicals and materials [1-4]. The possibility of using CO₂ (a by-product of many industrial processes), as an abundant, non-flammable and non-toxic C₁ building block, is promising towards reducing fossil fuels dependence [5-7]. However, the high CO₂ kinetic and thermodynamic stability, mainly responsible for CO₂ successful utilization as clean solvent, poses a challenging barrier to its chemical conversion [8-12]. In this context, catalysis has a crucial role, which is motivating a lot of research under this topic [13-17].
Direct coupling between CO$_2$ and epoxides stands as one of the most attractive strategies for cyclic carbonate formation, as it has the advantage of being a 100% atom economic transformation.

![Catalyst](image)

**Scheme 1.** Synthesis of cyclic carbonates from CO$_2$ and epoxides

Published works were extensively revised in 2010 by North et al. [2] and in 2015 by Martin et al. [3]. Successful catalytic systems are usually homogeneous Lewis acidic metal-based complexes, combined with a nucleophile, very often tetrabutylammonium bromide (TBABr).

The generally accepted mechanism comprises an interaction between the epoxide and the Lewis acid, through M–O coordination. The epoxy ring is then subject to a nucleophilic attack by the Lewis base, which opens the epoxy ring, forming a metal-alkoxide. Attack of the metal-alkoxide intermediate on the carbon centre of the CO$_2$ molecule, originates a metal coordinated carbonate. Finally, the halide acts as a leaving group, closing the five-membered ring. Although the nucleophile can actually catalyse the reaction alone, the presence of a metal complex makes the ring opening procedure energetically less demanding and subsequent CO$_2$ insertion easier [9]. However, high catalytic activities still involve the use of harsh conditions, particularly temperatures above 373.2 K, which spoils the process overall sustainability [3].

Arylhydrazones of β-diketones (AHBDs) are versatile compounds, which are easy to modify, forming a wide range of coordination compounds [18]. AHBDs can easily be prepared by diazotization with subsequent azo-coupling from cheap starting materials (aromatic amines and β-diketones) [19,21]. AHBD complexes were reported to catalyse several reactions, namely alkane or alcohol oxidation and the nitroaldol reaction [22-25]. An important feature is that they are easy to handle, owing to their air stability and high solubility in polar solvents [22-24]. However, the capability of AHBD complexes to catalyse the CO$_2$ cycloaddition to epoxides has never been explored before. In this work, three different zinc(II) complexes of AHBDs (1, 2 and 3) (Fig. 1) were used for the first time as catalysts, combined with TBABr, in the coupling reaction between CO$_2$ and epoxides.
The influence of pressure and temperature on cyclic carbonate formation was investigated, as well as the catalytic activity towards different substrates (e.g. styrene oxide, propylene oxide and cyclohexene oxide).

2. Experimental Section

2.1. Materials

All chemicals and solvents were used as received without further purification. Carbon dioxide (99.998 mol % purity) was supplied by Air Liquid. Styrene oxide (97 mol % purity), tetrabutylammonium bromide (TBABr) (≥ 98 % purity), were purchased from Sigma-Aldrich. Complexes 1–3 were synthesized as previously reported [25,26].
2.2. Methods

CO₂ and epoxides coupling reactions were performed in a high-pressure apparatus described in detail elsewhere [17]. Briefly, this apparatus is built around a stainless steel cylindrical cell with two sapphire windows and an internal volume of approximately 4 cm³. The cell was first loaded with styrene oxide (1.75 mmol), metal catalyst, TBABr, and a magnetic stirring bar. The cell was then immersed in a thermostated water bath heated by means of a controller that maintained temperature within ± 0.1 °C. Operating a CO₂-compressor, the desired pressure was brought into the cell. The pressure in the cell was measured with a pressure transducer 204 Setra calibrated between 0 MPa and 34.3 MPa (precision: 0.1 %; accuracy: 0.15 %, at the lowest pressure). After three hours of reaction, the high pressure cell was depressurized to atmospheric pressure into a glass trap immersed in an ice bath. Afterward, the cell was opened and the contents collected using 1 mL of chloroform, to dissolve the reaction mixture. Both contents of the cell and glass trap were mixed and prepared for further analysis as follows. Reaction mixture (0.4 mL) was transferred into a NMR tube, to which 0.1 mL of chloroform-\(d_1\) was added.

\(^1\)H NMR spectra were recorded on Bruker 500 MHz type (400 MHz). Peak frequencies were compared against solvent, chloroform-\(d_1\) at 7.26 ppm. The epoxide conversion and product yield were determined by integrating the relevant peaks in the \(^1\)H NMR spectra: styrene oxide (\(\delta \) = 3.8 ppm) and styrene carbonate (\(\delta \) = 5.6 ppm).

All liquid solutions were prepared gravimetrically using analytical balance (Sartorius model R180D) with the precision of ± 0.0001 g.

3. Results and Discussion

Styrene carbonate synthesis was studied, under solvent free conditions, using complexes 1–3 (Fig. 1) as catalysts. The synthesis and characterization of the three different zinc(II) complexes of AHBDs (1, 2 and 3) were reported earlier by some of us [25,26], and hence will not be discussed herein.

Following our previous study on the use of TBABr as catalyst for the CO₂ cycloaddition to styrene oxide, in this work three different temperatures (313, 333 and 353 K) were investigated at 4 MPa [17]. All reactions were performed for 3 hours, using 3% mol of TBABr and 0.5% mol of zinc complex, in relation to the epoxide. Results obtained are shown in Fig. 2. It is thus clear that complexes 1–3 significantly improved the reaction yield, when compared with the catalytic activity of TBABr.
alone. Among them, complex 1 and 3 presented the highest activities, with the latter showing a slightly greater percentage of carbonate formation.

![Graph showing styrene carbonate formation](image)

**Fig. 2.** Styrene carbonate formation after 3 hours at 4 MPa, using: 3 % mol of TBABr (○); and 3 % mol of TBABr / 0.5 % mol of complex 1 (♦); 3 % mol of TBABr / 0.5 % mol of complex 2 (▲); 3 % mol of TBABr / 0.5 % mol of complex 3 (◇).

Another critical factor was the temperature. For all systems, and as already observed by other authors, cyclic carbonate formation is significantly favoured by the increase of that parameter.

As part of our interest in using CO₂ both as reactant and reaction solvent [17,27,28], this study was extended to the influence of pressure on the catalytic activity of complex 3. Experiments were performed at 353 K for 3 hours, using 3% mol of TBABr and different quantities of zinc complex (0.5% mol and 1% mol), in relation to the epoxide. Results are shown in Fig. 3.

As also noticed in a paper by Taherimehr et al. [29], for epoxides such as styrene oxide that readily dissolves the catalyst, there is no advantage in working under high CO₂ pressure. Actually, experimental results presented in Fig.3 show that carrying on increasing the pressure, had an overall negative effect on styrene carbonate formation. Nevertheless, this influence was not so pronounced when 0.5% mol of the zinc catalyst was used, and was not observed at all for 1% mol of the zinc catalyst. This general pressure negative effect is a result of the reaction mixture separation due to CO₂ addition to the reaction system; as CO₂ pressure increases, the epoxide totally solubilizes into the gas phase, precipitating the catalyst.
Fig. 3. Styrene carbonate formation after 3 hours at 353 K and different pressures, using: 3 % mol of TBABr (○); and 3% mol of TBABr / 0.5 % mol of complex 3 (♦); 3 % mol of TBABr / 1% mol of complex 3 (♦).

However, reaction still occurs with relatively good yields, with TBABr/Zinc-complex acting as a heterogeneous (although non-supported) catalyst phase. Experimentally, at 18 MPa it is possible to visualise the catalyst phase through the reactor sapphire window. It consists of a melted TBABr phase in which the zinc-complex is apparently dissolved. At 353 K and 18 MPa, TBABr precipitates as a melted phase due to well-known melting point reduction effect (under high CO₂ pressure) [30].

Fig. 4. Cyclic carbonate formation after 3 hours at 353 K and 4 MPa, using 3 % mol of TBABr / 1 % mol of complex 3. SO: styrene oxide; PO: propylene oxide; CHO: cyclohexene oxide.

These phenomena can be explored for cases in which the catalytic system is not soluble in the substrate, avoiding the use of a harmful organic solvent.

The catalytic activity of complex 3 was further tested for two other epoxides, namely, propylene oxide and cyclohexene oxide (Fig. 4). For propylene oxide (terminal epoxide), the complex presented a
similar catalytic activity when compared with styrene oxide, for the same reaction conditions. The catalytic activity of complex 3 was however less effective for the case of cyclohexene oxide (internal epoxide). This behaviour is explained by the difficulty posed by the restricted geometry of the cyclohexene ring to the formation of the carbonate ring. It should be noted that internal epoxides are considered much more challenging substrates, due to widely natural occurrence. However, these natural epoxides have proven to be mostly unreactive often requiring high pressures [3]. It is known that the outcome of the coupling reactions between CO$_2$ and epoxides, besides being considerably affected by temperature, is also very sensitive to the proportion between the components of the catalytic mixture. In particular, the reaction is affected by the nature of the co-catalyst and its ratio with respect to the metal catalyst. Therefore, a systematic study was performed at 353 K and 4 MPa in order to find out an optimum molar ratio between complex 3 and TBABr for styrene carbonate formation. All reactions were performed for 3 hours.

**Fig. 5.** Optimization of molar ratio between complex 3 and TBABr for styrene carbonate formation. Reactions were performed for 3 hours at 353 K and 4 MPa. Full circles represent styrene carbonate formation (%) and grey bars represent experimental TOFs (h$^{-1}$).
From Fig. 5, it is possible to conclude that, for all molar percentages of TBABr (0.5 %, 1 %, 2 %, 3 %), there was always a specific complex amount yielding the best results. Furthermore, complex 3 / TBABr molar ratios of around 0.17–0.20 were the ones leading to optimal yields. Additionally, the best balance between reaction yield (% mol) and TOF (h⁻¹) was achieved for 1% (mol) of TBABr. In an attempt to further tune this value, similar reactions were performed reducing the catalyst amount, but maintaining the optimal ratio of 0.17 between complex 3 and TBABr.

![Graph showing optimization of reaction yield (black line) and reaction TOF (grey bars).](image)

**Fig. 6.** Optimization of reaction yield (black line) and reaction TOF (grey bars). Reactions were performed for 3 hours at 353 K and 4 MPa, using different quantities of complex 3. Zn complex 3/ TBABr=0.17. TOFs were calculated using the amount of zinc complex used.

As can be seen from the results in Fig. 6, the best compromise between reaction yield and reaction TOF was achieved for TBABr molar percentages of 0.75 % and complex 3 molar percentages of 0.125 %. Under these conditions, the catalyst system is operating at its maximum efficiency, with a reaction yield and reaction TOF of 75 % and 200 h⁻¹, respectively, and presents the highest activity when compared with zinc complexes 1 and 2 (Fig. 7). These results seem to reflect approximately the double number of active metal sites for complex 3, showing that the zinc centers retain the catalytic activity in the tetrametallic structure, however a structure-activity relationship study is needed to establish the influence of ligands electronic and steric properties on the reaction TOF.
**Fig. 7.** Catalytic activities of different zinc complexes at best reaction conditions. Reactions were performed for 3 hours at 353 K and 4 MPa, using 0.75 % of TBABr and 0.125 % of zinc complex (molar percentages in relation to SO).

It should be noted that for all conditions studied reaction selectivity toward cyclic carbonate was always >97%. Furthermore there was no detectable catalytic activity in the absence of TBABr, for conditions explored in this work. The observed results for different Zn complex and TBABr ratios, allow us to propose a similar mechanism of related reported catalytic systems (Fig. 8) [31–33]. The mechanism involves the activation of the epoxide by Zn-AHBD complex (step 1) and subsequent ring-opening with bromide of TBABr (steps 2 and 3). CO₂ could then be inserted into the Zn–O bond with ring-closure giving the cyclic carbonate (steps 4, 5 and 6). Nevertheless, further studies are necessary to corroborate this assumption.

**Fig. 8.** Proposed mechanistic cycle for the coupling reaction of epoxide with CO₂ catalyzed by Zn-AHBD and TBABr.
The interest in exploring AHBD ligands besides their high air stability and synthetic accessibility, arises from their different molecular conformations upon metal complexation and possibility to easy modulate the environment around the metal center. Indeed, from the point of view of large scale manufacturing, the search for a sustainable and versatile catalyst system continues to challenge scientists in the field [34].

A direct comparison between results obtained in this work and other homogeneous Zn(II) complexes reported in literature is not possible, due to differences in experimental conditions. Besides, temperature, pressure, catalyst loading, kind of co-catalyst and time, the mixture composition is also a relevant parameter [17], which further depends on the volume of the reactor used. It is feasible however, to contextualize yield and TOF values obtained for styrene carbonate formation in this work, taking into account experimental differences from those reported in literature. For example, Taherimehr et al. [29] reported the use of zinc complexes of N,N’-phenylene-1,2-bis-salicylidene (salphen ligands) as catalyst and TBAI as co-catalyst for the production of cyclic carbonates. Using a monometallic complex structure, the authors attained a styrene carbonate yield of 86%, at 318K and 4 MPa which corresponds to a TOF of 11.5h\(^{-1}\), as well as, a styrene carbonate yield of 90%, at 318K and 1 MPa which corresponds to a TOF 12h\(^{-1}\). In another work from the same group, Anselmo et al. [35] reported the use of zinc complexes of bis-thiosemicarbazonato (btsc ligands). The authors attained a styrene carbonate conversion of 26% using a monometallic structure and TBAI as co-catalyst, at 318K and 1 MPa which corresponds to a TOF of 1.6h\(^{-1}\). Furthermore, in 2015 Adolph et al. [36] reported the use of zinc complexes based on the N,N-bis-(2-pyridinecarboxamide)-1,2-benzene (bpb ligands) as catalysts for CO\(_2\) cycloaddition to epoxides. The authors attained a styrene carbonate conversion of 27% using monometallic catalyst structure and TBABr as co-catalyst, at 353 K and 5 MPa which corresponds to a TOF of 6.8h\(^{-1}\). In this context, zinc complexes of AHBD ligands used in this work as catalysts in the CO\(_2\) cycloaddition to epoxides (for the first time) showed encouraging activities, although in some of the cited studies, Zn(II)-based catalysts were used at milder conditions.

4. Conclusions

Zinc(II) complexes of arylhydrazones of \(\beta\)-diketones have been used for the first time as catalysts towards the coupling reaction between CO\(_2\) and epoxides. Good catalytic activities and selectivities were achieved at a moderate temperature range of 333-353 K. The reaction requires the use of tetrabutyl-ammonium bromide, but this organic salt can also be used as a liquid heterogeneous support phase for the zinc metal complex (at high pressures). Furthermore, the four potentially zinc active sites
of complex 3 provided almost the double catalytic activity in comparison with the bimetallic complexes 1 and 2. Although it has been proved that the zinc metal sites in tetrametallic structure have maintained it catalytic activity, there was no advantage in using a tetrametallic instead of bimetallic (for the conditions studied in this work). Nevertheless, the high stability and ease of preparation of these kinds of zinc complexes make them good candidates for large scale cyclic carbonate production.

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**References**


