

Zinc(II)-pyridine-2-carboxylate / 1-methyl-imidazole: a binary catalytic system for the synthesis of cyclic carbonates from carbon dioxide and epoxides

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Dedicated to Professor E. Anders on the occasion of his 65th birthday

Abstract

A new “halogen-free” binary catalytic system for the synthesis of cyclic carbonate from epoxides and carbon dioxide is described. The catalysis relies on a synergy between the main catalyst, zinc(II) pyridine-2-carboxylate, and a Lewis base, 1-methyl imidazole. In this preliminary study four epoxides have been tested and the operating capabilities of this system have been evaluated. Using propylene oxide as test substrate and performing the catalysis in a high-pressure NMR tube, allowed us to gather some spectroscopic information on this catalytic system and to propose a reaction mechanism.

Keywords: Epoxides, carbon dioxide, cyclic carbonate, zinc carboxylate, imidazole

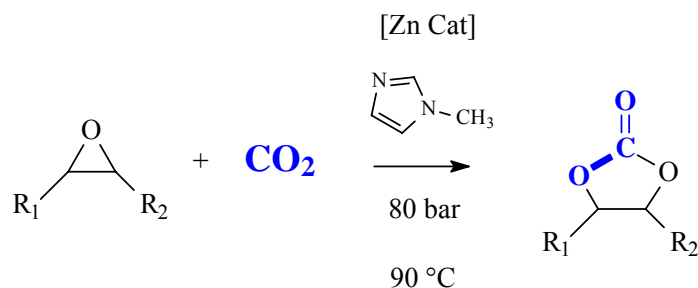
Introduction

The abundance and benignity of carbon dioxide makes it an attractive alternative C₁-synthon for many processes in the synthetic chemistry¹. Moreover the possibility to bind carbon dioxide in useful molecules is one of the tools we definitely have to consider in a global “CO₂-management”. Up to now only four major industrial processes using carbon dioxide as a C₁-building block are known: syntheses of salicylic acid, urea, methanol and cyclic carbonates^{1a}. Other promising synthesis routes have been also documented in the literature but have yet to be up-scaled to reach the volumes found in these four exemplary CO₂-based processes. Typical examples are the synthesis of aliphatic polycarbonates from CO₂ and epoxides² and the synthesis of potential building-blocks for specialty polymers such as, e.g. lactones³, pyrones⁴ or formoxysilane⁵ obtained from butadiene (respectively alkynes or silanes) and CO₂.

Considering the cyclic carbonates, many important technical applications have been reported in the last years. Ethylene- and propylene carbonate owing to their good biodegradability, high boiling points and low toxicities are valuable solvents⁶. These polar molecules find a variety of applications as diluents and components in paint-, coatings and specialty resin formulations⁷ as well as electrolytes (so-called SEI: solid electrolyte interphase) in the production of lithium ion batteries⁸. Cyclic carbonate find also an application in the polymer chemistry: directly via reaction with diols or carboxylic acids to produce polyesters⁹ or indirectly via reaction with ammonia to form more reactive carbamates which eventually lead to polyurethanes¹⁰.

On the whole, the most reported “CO₂-based” synthetic route to cyclic carbonates involves the use of an epoxide as substrate and a halide-containing main catalyst which is used in combination with a co-catalyst, most of the time a halide-containing quaternary onium salt¹¹. Some of the documented systems deal with the use of specifically tailored quaternary onium salt, namely with the use of ionic liquids^{11f-g}, whereas other research group’s focus on the use of transition metal complexes either soluble in the epoxide phase or supported on polymers or silica surface¹². A last way involving basic metal oxides and zeolites has been relatively rarely documented and attracts an ever growing interest¹³.

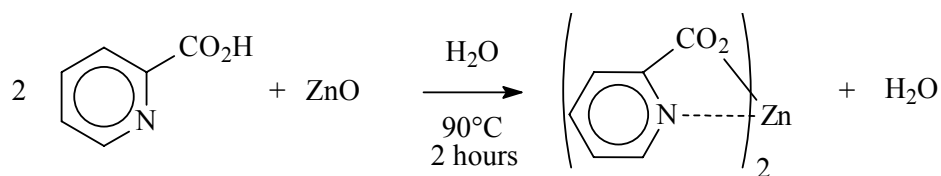
Considering the most reported “metal halide/ quaternary onium salt” way more in detail, it can be noticed that the majority of the systems involves zinc halides (Cl or Br). Since the pioneering work of Kisch and coworkers on catalytic systems involving ZnCl₂ and (n-Bu)₄N^{11a}, many research groups focused on the optimization of this system^{11e-h}. However bearing in mind the general corrosion problems encountered in the industry when using halide-containing catalysts and considering this carbonate chemistry under the aspect of a “Green Chemistry”, it seems advisable to develop catalytic systems involving no halides at all. Several “halogen-free” zinc-based systems were already reported in the activation of CO₂. Zinc(II)-tetraazacycloalkane complexes are well-known to activate and transfer carbon dioxide to acidic substrates to afford for instance alkyl-carbonato derivatives¹⁴. Benzoic acid-based zinc carboxylates are also able to activate CO₂ and catalyze a copolymerization of propylene oxide with CO₂¹⁵. In relation to this, polymeric zinc (II) dicarboxylates like, e.g. zinc glutarate, are effective catalysts for the copolymerization of CO₂ and epoxides¹⁶, although the exact nature of the active site of the catalysis remains speculative. On the search for a new alternative, we decided to focus on binary catalytic systems involving zinc (II) carboxylates with a definite, constrained geometry like 2-pyridine-carboxylic acid (picolinic acid) and a Lewis base as a co-catalyst. The co-catalyst, 1-methyl-imidazole (*N*-methyl imidazole: NMI), is also known to display alone a high reactivity in the curing of epoxy resins¹⁷. 1-methyl imidazole as a co-catalyst should play a dual role in the reaction: by coordinating at the zinc center it should help solubilizing the zinc carboxylate into the epoxide/CO₂ reaction mixture and, on the other hand, it might activate the epoxide due to its high nucleophilicity.



Scheme 1. Zinc picolinate/NMi-catalysed synthesis of cyclic carbonates from epoxides and CO₂.

As a matter of fact, we found that this combination constitutes an effective system for the insertion of CO₂ in terminal epoxides (scheme 1). We report here on the preliminary results of this novel catalytic system.

Results and Discussion



Scheme 2. Synthesis of zinc(II) pyridin-2-carboxylate from zinc oxide and pyridin-2-carboxylic acid.

Zinc 2-pyridine carboxylate was prepared via the “zinc oxide way” according to the literature^{16a} (scheme 2). In a typical reaction zinc pyridine-2-carboxylate is added to the epoxide (20 ml) to form a suspension. Two equivalents of 1-methyl-imidazole are then added to facilitate the solubilisation of the zinc carboxylate, the fastest solubilisation occurring when using styrene oxide as test substrate. The reaction mixture is then put under a CO₂-atmosphere either under 1 bar, carbon dioxide being bubbled into the reaction mixture through a sintered glass or under ca. 60 bar CO₂ in a stainless steel autoclave. The reaction mixture is then heated up to ca. 90°C to allow the reaction to take place. After the reaction time the reaction vessels were cooled down to RT and the carbon dioxide slowly vented, under stirring, in a fume hood. After opening the remaining solution was filtered/separated and analyzed with NMR and IR-FT. In some cases an oily residue could be noticed on the autoclave inner wall. This oil was collected and analyzed via IR- and NMR spectroscopy and revealed to be a mixture containing mainly zinc picolinate, 1-methylimidazole, PO and traces of cyclic carbonate. Comparative tests without catalyst, respectively co-catalyst, were also run in order to evaluate the efficiency of the system. The preliminary results with four epoxides (propylene oxide –PO-, butene oxide -BO-, styrene oxide

–SO- and cyclohexene oxide –CHO-) are summarized in Table I. The zinc-catalyzed conversion to cyclic carbonates was greatly facilitated under CO₂-pressure and delivered, as anticipated, better yields of the carbonate in the presence of the 1-methyl-imidazole co-catalyst (entries 9-12). Performing the tests under 1 bar CO₂ afforded the carbonate only in the case of styrene oxide with low yield (entry 18). The tests ran with 1-methyl-imidazol used alone, as main catalyst, under CO₂-pressure, yielded in the case of styrene oxide significant amounts of the carbonate (entry 5). These results imply a kind of synergy between Lewis acid and Lewis base in the catalysis. In comparison, heating styrene oxide in the presence of 1-methyl-imidazol under argon lead to the expected formation of oligomers, products of the ring opening polymerization of the epoxide. The overall activity of the catalytic system can be ranked as follows: PO > SO > BO >> CHO (entry 9-12). Cyclohexene oxide showed the lowest conversion under the chosen experimental conditions (entries 4, 8, 12, 17).

A substrate-to-catalyst molar ratio of 1 to 100 and a catalyst-to-cocatalyst molar ratio of 1 to 2 seemed to be an optimal reaction window for this system, a higher dilution (1 / 2 / 1000) of the system afforded only traces of cyclic carbonate (entries 13-17). Interestingly running the test reaction with propylene oxide under high-dilution conditions (1 / 2 / 1000, entry 14) showed no reactivity at all; however performing the same test with bigger amounts of 1-methyl-imidazole (1 / 20 / 1000, entry 15) afforded significant amounts of propylene carbonate with a notably higher carbonate yield than performed in the presence of 1-Me-imidazole alone (- / 1 / 100, entry 6). This again strongly suggests a cooperation between zinc carboxylate and 1-methyl imidazole in the catalysis. We ran a comparative test with a zinc complex containing 1-methyl-imidazole in the coordination sphere, ZnCl₂(NMI)₂. As it might be expected from the literature¹¹ the tests ran with [ZnCl₂(NMI)₂] as catalyst and PO or SO as epoxidic substrates delivered high amounts of the corresponding cyclic carbonates (entries 23-24) clearly showing that the zinc picolinate/NMI system is yet not competitive and needs a tuning of the different reaction parameters.

Table 1. Effects of reaction parameters on the zinc picolinate/NMi₂-catalyzed formation of cyclic carbonate

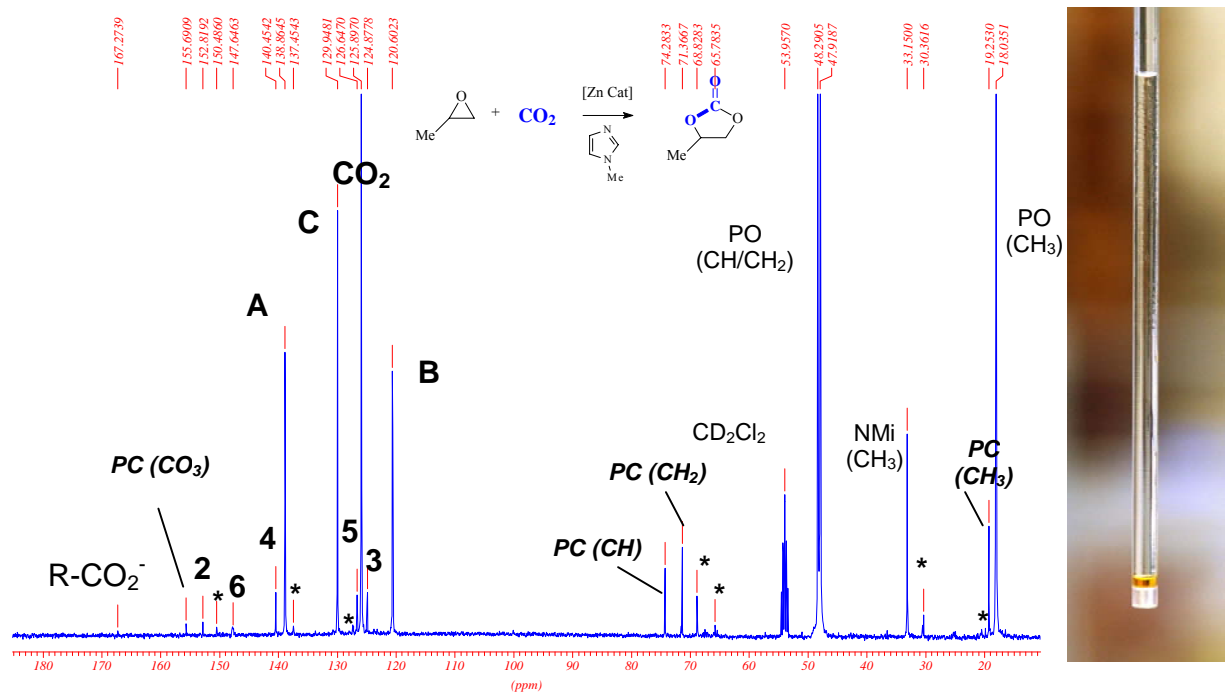
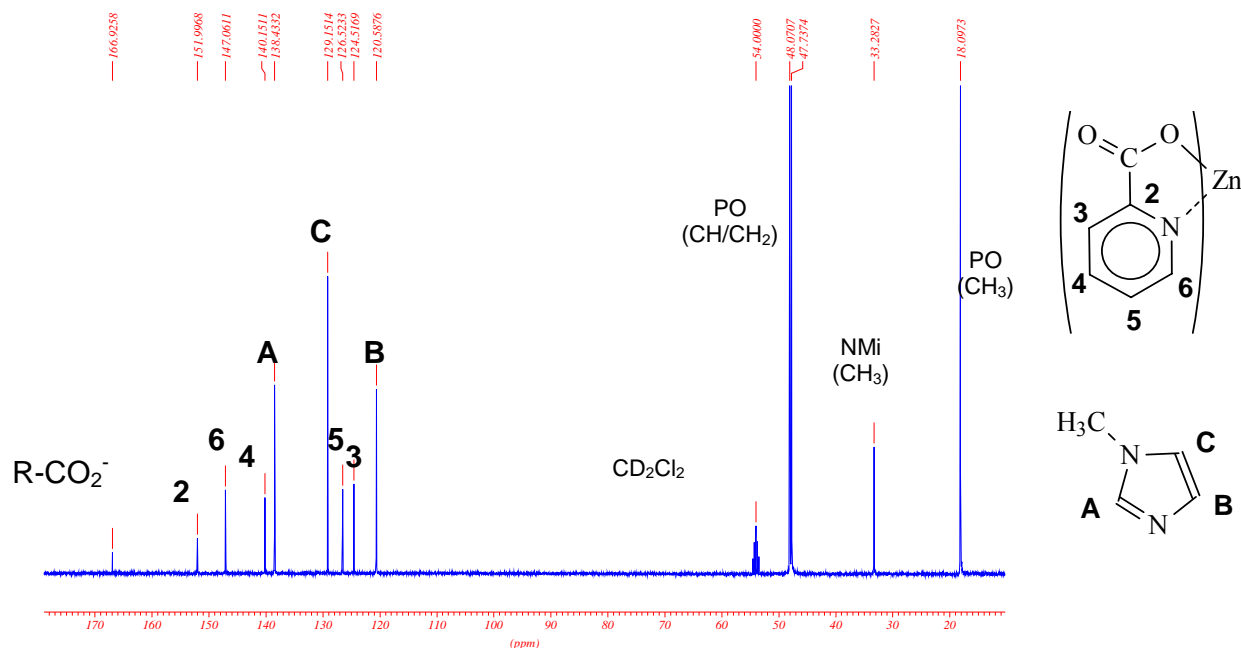
Entry	Temperature Pressure ^a	Substrate	Cat/Co-Cat./ Substrate molar ratio	Products (yields %) ^b
1	90±5°C 60±5 bar	SO (styrene oxide)	1 / - / 100	< 1
2	90±5°C 90±5 bar	PO (propylene oxide)	1 / - / 100	15
3	90±5°C 90±5 bar	BO (butene oxide)	1 / - / 100	< 1
4	90±5°C 80±5 bar	CHO (cyclohexene oxide)	1 / - / 100	-
5	90±5°C 60±5 bar	SO	- / 1 / 100	14
6	90±5°C 90±5 bar	PO	- / 1 / 100	< 1
7	90±5°C 90±5 bar	BO	- / 1 / 100	< 1
8	90±5°C 80±5 bar	CHO	- / 1 / 100	-
9	90±5°C 60±5 bar	SO	1 / 2 / 100	28
10	90±5°C 90±5 bar	PO	1 / 2 / 100	40
11	90±5°C 90±5 bar	BO	1 / 2 / 100	22
12	90±5°C 80±5 bar	CHO	1 / 2 / 100	-
13	90±5°C 60±5 bar	SO	1 / 2 / 1000	< 1
14	90±5°C 90±5 bar	PO	1 / 2 / 1000	< 1
15	90±5°C 90±5 bar	PO	1 / 20 / 1000	26
16	90±5°C 90±5 bar	BO	1 / 2 / 1000	< 1
17	90±5°C 80±5 bar	CHO	1 / 2 / 1000	-
18	90°C 1 bar	SO	1 / 2 / 100	5
19	90°C 1 bar	PO	1 / 2 / 100	< 1
20	90°C 1 bar	BO	1 / 2 / 100	< 1
21	90°C 1 bar	CHO	1 / 2 / 100	-
22	ZnCl ₂ (NMi) ₂ 90±5°C 40±5 bar ^c	PO	1 / 2 / 100	94
23	ZnCl ₂ (NMi) ₂ 90±5°C 20±5 bar ^c	SO	1 / 2 / 100	87

General procedure

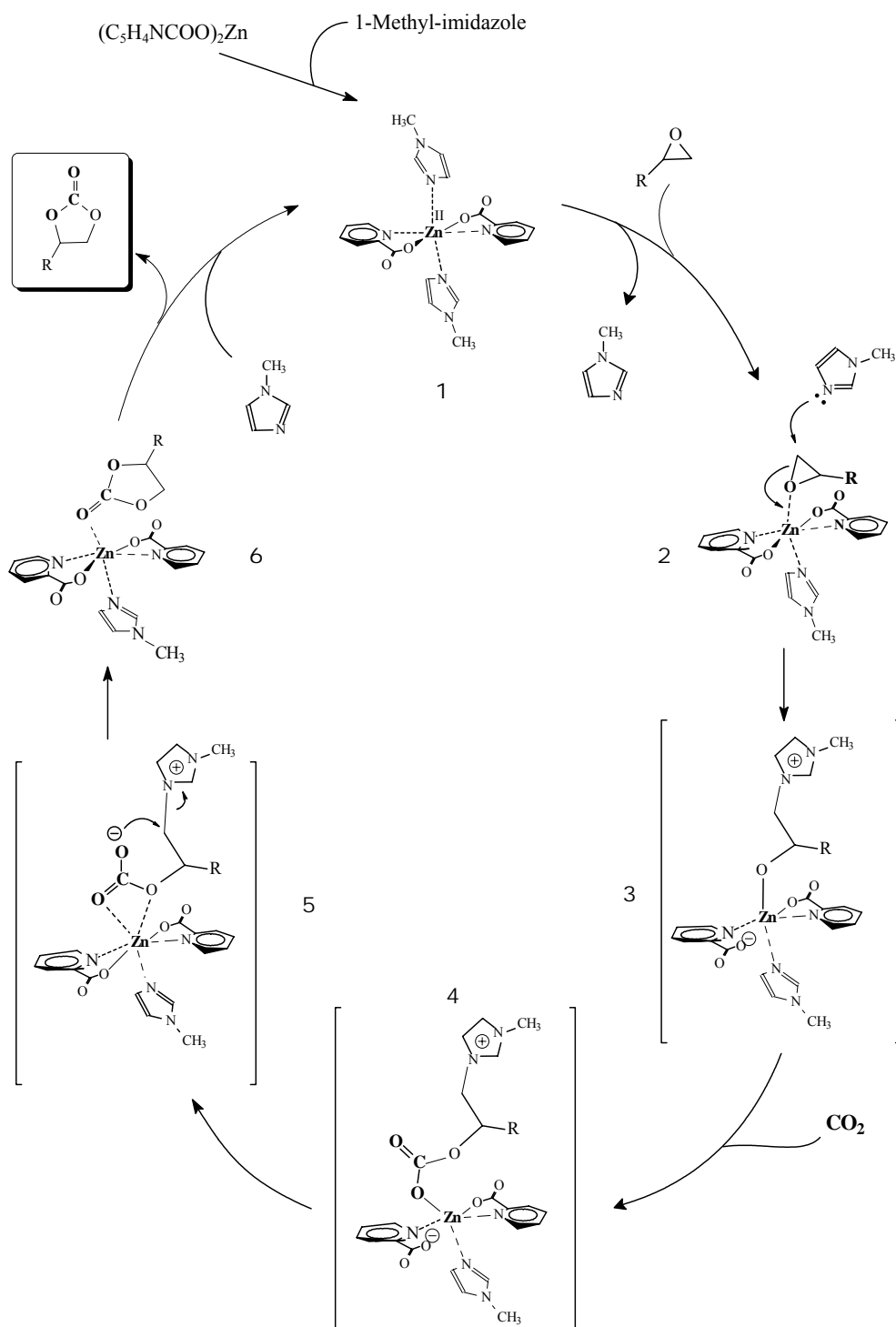
The catalysts were suspended in the epoxide (20ml) in the presence of 1-methyl-imidazole. The reaction mixture was put under a CO₂-atmosphere (ca 25g CO₂) and then heated up to 90°C for ca. 10 hours. a) CO₂ Pressure and temperature read after 4 hours reaction time. b) the cyclic carbonate yield was evaluated with ¹H-NMR: yield % = $\frac{\text{int}(H_{\text{methine carbonate}})}{\text{int}(H_{\text{methine}})}$

carbonate) + int(H_{methine} epoxide)] c) Entry 22: 21bar CO_2 at the beginning (11g CO_2); Entry 23: 11 bar at the beginning (6g CO_2).

In order to gather some spectroscopic information on the catalytic system, we ran a couple catalytic tests in high pressure NMR tubes with zinc picolinate, propylene oxide as test substrate and an excess of the co-catalyst to accelerate the solubilisation of the catalyst (molar ratio ca. 1 to 8 instead of 1 to 2). The tests were run in a 5mm sapphire NMR-tube¹⁸ under ca. 50 bar CO_2 , the tube being heated in a silicon-oil bath and regularly shaken. Figure 1 shows the ^1H and ^{13}C spectra of the reaction mixture under argon, prior to the pressurization whereas figure 2 shows the NMR-spectra after 10 hours at 90 °C and ca. 50 bar CO_2 . Interestingly we could notice the formation of small droplets on the inner wall of the tube which lead eventually to the formation of a second phase at the bottom of the NMR-tube (figure 2). Comparing the ^{13}C spectra of the reaction mixture before and after the reaction, it can be seen that, in the upper phase, the concentration of zinc picolinate (signals at 167.0, 152.0, 147.1, 140.1, 138.4, 129.1, 124.5 and 120.6 ppm) decreased whereas the concentration of propylene carbonate increased (155.7, 74.2, 71.4 and 19.2 ppm). In addition, new ^{13}C -signals (68.8, 65.8 and 20.1 ppm) appeared in regions close to the ^{13}C -NMR signals of propylene carbonate as well as in regions close to the signals of 1-methyl-imidazole (150.5, 137.4, 127.1 ppm and 30.4 ppm). These new signals can be tentatively attributed to a stable “alkoxy-imidazolium” specie formed from the reaction of the epoxide with imidazole (*vide infra* for mechanism proposal). After careful depressurisation of the HP NMR-tube, the second phase was investigated with IR and NMR (the isolated oil, hardly soluble in apolar solvents, formed a kind of stable “emulsion” in THF). It can be taken from the first spectroscopic data that the oil displays a composition similar to the upper phase with only traces of propylene carbonate. More work is currently in progress to characterize via the use of 2D-NMR methods (HMQC, HMBC) and ^{13}C -labelled CO_2 the exact nature of the species present in the two phases.



These observations together with the screening tests allow us to propose a tentative mechanism for the catalytic formation of the cyclic carbonate (scheme 3).



Scheme 3. Mechanism proposal for the zinc picolinate/NMi-catalyzed synthesis of cyclic carbonates.

The first step of the catalysis involves the formation of a soluble octahedrally coordinated specie $[\text{Zn}(\text{pyridine-2-carboxylate})_2(1\text{-methylimidazole})_2]$ (**1**). Related compounds based on 2-quinoline-carboxylic acid have been reported earlier in the literature ¹⁹. The second step is comparable to the mechanism proposed by Kim in the case of the zinc bromide/pyridine-catalysed synthesis of cyclic carbonates ^{11j}, an initial coordination of the epoxide replacing one of the 1-methyl-imidazole being likely to occur first (**2**). The zinc(II) center, as Lewis acid catalyst, should promote the formation of such an intermediate. Some related epoxide-Lewis acid adducts were structurally characterized by Darensbourg *et al.* in the case of cadmium(II) pyrazolylcarboxylato derivatives ²⁰. A nucleophilic attack of the free 1-methyl-imidazole on the less sterically hindered carbon atom of the coordinated epoxide generate a reactive “alkoxy-imidazolium” specie (intermediate **3**). Such intermediates involving epoxide and imidazole were already reported for the imidazole-catalyzed curing of epoxy resins ¹⁷. It is likely that the formation of a second phase observed in some of the test reactions (a.o. in HP-NMR tube with PO) is due to the formation of stable a “alkoxy-imidazolium” zinc carboxylato compound. This zinc-alkoxo specie would react in the third step of the catalytic cycle with carbon dioxide to form, via an insertion into the Zn-O bond, a “carbonato-imidazolium” intermediate (intermediate **4**) ^{11b,11h}. In opposition to the system described by Kim and co-workers ^{11h}, zinc picolinate is not likely to form dinuclear species displaying a bridged “carbonato-imidazolium” which can easily undergo a cyclization to form the cyclic carbonate. In our case, the rearrangement of the “carbonato-imidazolium” intermediate is likely to happen in an intramolecular way (intermediate **5**). However, the possibility that an ancillary zinc picolinate(NMi)₂ monomer might play a role in the cyclization of the “carbonato-imidazolium” specie cannot be completely ruled out. In the last step of the cycle, the Lewis acidity of the zinc carboxylate is not high enough to form a stable zinc picolinate-cyclic carbonate adduct ²¹, the cyclic carbonate is then released and the zinc center is free for a new coordination of the epoxide.

Summary and Conclusions

Despite displaying a lower catalytic activity in the formation of cyclic carbonates than the ZnCl₂-based catalytic systems, this cheap and easy-to-handle zinc carboxylate is a promising starting point for new ways to synthesize cyclic carbonates. More work is currently in progress to optimize this binary system (a.o. broadening the substrate range, tuning the co-catalyst, dealing with the formation of a second phase), to better understand the various reaction steps as well as unequivocally characterize some of the intermediates involved in the catalysis.

Experimental Section

General Procedures. Styrene oxide, butene oxide, propylene oxide and cyclohexene oxide (Aldrich) were distilled under vacuum over CaH_2 . 1-methyl-imidazole (Aldrich, GC grade) was stored immediately after purchase over molecular sieves and used without further purification. Carbon dioxide (Messer Griesheim, purity 99.9990%) was used without further purification. NMR deuteriated solvents (Chemotrade) were degassed, dried over molecular sieves Linde 4 Å and stored under argon. The NMR spectra of reaction mixtures, final products (C_6D_6 or CDCl_3 solutions) and HP-NMR experiments (CD_2Cl_2), were recorded with a Varian Inova 400 spectrometer (^1H 399,81 MHz, ^{13}C : 100.54 MHz). TMS was used as internal standard (^{13}C , ^1H) with different deuteriated solvents. The chemical shifts δ (in ppm) are given relative to the residual signal of the solvent. Infrared spectra (thin films between KBr plates or KBR pellets) were recorded on a BIORAD 175C FT-IR spectrometer in the range of 4000-400 cm^{-1} .

Synthesis of the catalyst

Zinc(II) pyridin-2-carboxylate (zinc picolinate) was prepared according to the “oxide way”^{16a,22}. 0.1 mole of the corresponding acid were dissolved in 50 to 200 ml of deionized water. 0.05 mole of zinc oxide were added to this solution, the suspension was then heated at 90 °C for 2 hours. The resulting solution was filtered and concentrated. Over a period of one day colorless crystals formed (yields ranging from 95% to 98 %). Zinc picolinate was filtered, dried a first time at 120°C, grinded, dried again for 24 hours at 120 °C and eventually stored under argon.

General procedure for autoclave experiments and HP-NMR

The catalytic screening tests were performed in a “multi-reactor” system involving 4 high pressure reactors equipped with magnetically coupled stirring systems and electrical heating mantles²³. Temperature and pressure were monitored via a digital multimeter (HP 34970A) connected to a personal computer. The catalytic tests were typically conducted in 70 mL stainless steel (SS316) autoclaves equipped with standard Swagelock fittings. The reactors were heated overnight at 100 °C and purged with argon prior to use. The epoxide (20 ml) were transferred into the autoclave, the catalyst (catalyst/epoxide molar ratio: 1 to 100 or 1 to 1000) and NMI (catalyst/co-catalyst molar ratio: 1 to 2) were added to the epoxide. The reactor was then pressurized with CO_2 (60 bar) for a few minutes under stirring and afterwards weighted, the procedure was repeated until carbon dioxide was clearly in excess (CO_2 / epoxide molar ratio ranging from 1,6 for PO to 3 for CHO, around 25g CO_2). The reactors were heated overnight at 90 °C. After the reaction time the autoclaves were cooled down to RT (water bath) and the carbon dioxide slowly vented, under stirring, in a fume hood. After opening the remaining solution was filtered and analyzed with NMR and IR-FT.

High-pressure NMR experiments were run in a 5 mm HP NMR sapphire tube fitted with titanium-based alloy valves (90% Ti, 6% Al, 4% V)¹⁸. The tube was filled with the different components under argon and then connected to a “pressurizing station” (Vaccum/Argon/ CO_2

lines) via Swagelock fittings. The tube was then sealed and heated in a silicon oil bath for 8 hours at 90°C. During this period of time the tube was occasionally taken from the heating bath, cleaned and shaken on a test tube vortex mixer.

Spectroscopic characterization of the synthesized cyclic carbonates

Propylene carbonate (2-methyl-1,2-ethylene carbonate), C₄H₆O₃, [108-32-7]. IR (nujol, cm⁻³): 2990 (s), 2930 (s), 1793(vs), 1485 (w), 1557 (w), 1388 (m), 1354 (m), 1184 (s), 1120 (m), 1053(s), 777 (m), 712 (m); ¹H NMR (CDCl₃): δ (ppm) = 4.78 (m, R-CH-CH₂), 4.47 (dd, 7.22Hz 8.39Hz R-CH-CHH), 3.92 (dd, 7.71Hz 8.50Hz R-CH-CHH); 1.37 (d, 6.0 Hz, CH₃-CH-CH₂); ¹³C NMR: δ (ppm) = 154.78 (R-CO₃-); 73.01 (R-CH-CH₂), 70.07 (R-CH-CH₂); 18.95 (CH₃-CH-CH₂).

Butene carbonate (1,2-butylene carbonate), C₅H₈O₃, [4437-85-8]. IR (nujol, cm⁻³): 2967 (s), 2936 (s), 2879 (s), 1795 (s), 1457(s), 1062 (s); ¹H NMR (CDCl₃): δ (ppm): 4.57 (m, R-CH-CH₂), 4.42 (dd ~ t, 7.47Hz, R-CH-CHH), 3.97 (dd ~ t, 8.35Hz, R-CH-CHH); 1.64 (m, CH₃-CH₂-CH-CH₂); 0.90 (~t, 6.6 Hz, CH₃-CH₂-CH-CH₂); ¹³C NMR: δ (ppm): 154.88 (R-CO₃-); 77.95 (R-CH-CH₂), 68.99 (R-CH-CH₂); 26.62 (CH₃-CH₂-CH-CH₂); 8.21 (CH₃-CH₂-CH-CH₂).

Styrene carbonate (2-phenyl-1,2-ethylene carbonate), C₉H₈O₃, [4427-92-3]. White crystalline solid (needles, fusion point 52-53°C) isolated via flash chromatography. IR (nujol, cm⁻³): 3067 (m), 2980 (w), 2925 (w), 1778 (vs), 1497(m), 1477(m), 1458(m), 1358, 1392(m), 1328, 1170 (s), 1055 (s), 759 (s), 699 (s); ¹H NMR (CDCl₃): δ (ppm): 5.62 (t, R-CH-CH₂), 4.75 (t, 7.22Hz R-CH-CHH), 4.27 (t, 7.71Hz R-CH-CHH); 7.4-7.3(m, C₆H₅-CH-CH₂); ¹³C NMR: δ (ppm): 154.78 (R-CO₃-); 135.65 (C1), 129.53 (C4), 129.03 (C3,C5), 125.77 (C2,C6), 77.85 (R-CH-CH₂), 71.02 (R-CH-CH₂).

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