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Selectivity of the cyclic carbonate formation by fixation of carbon dioxide into epoxides catalyzed by Lewis bases

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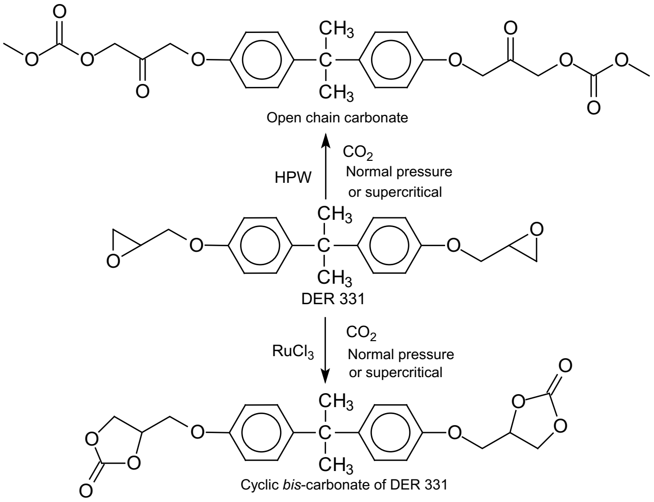
ABSTRACT

Cyclic carbonate and polycarbonate have been selectively obtained with good conversion by coupling carbon dioxide with diglycidylether of bisphenol A. The ruthenium trichloride supported on tetraethylammonium bromide and polyphosphotungstic acid has been found active and selective to produce the corresponding monomeric and polymeric carbonates. These catalysts can be recycled keeping their high product conversion and selectivity. The heteropolyacid itself showed high activity also under supercritical CO_2 conditions to yield polycarbonate.

The formation of cyclic carbonates by cycloaddition of epoxides and carbon dioxide is an industrially interesting route for chemical fixation of CO_2, which has received much attention, since the cyclic carbonates showed interesting applications as polar aprotic solvents, precursors for polycarbonate materials, and intermediates in organic synthesis.[1] Although numerous catalysts have been developed for this transformation,[2] they usually require inert atmosphere, use of co-solvent or co-catalyst, and high pressures and/or high temperatures.

The use of carbon dioxide as starting material is a very promising way to substitute phosgene and related compounds with high toxicity. Hence, the use of carbon dioxide for synthesis can be considered as an interesting alternative for recycling CO_2 and at the same time it constitutes a less pollutant technology with a relative low cost for preparation of several carbonylated compounds. Utilization of CO_2 for synthesis of organic carbonates[3] and carbamates[4,5] has given a great contribution to the environment preservation when compared to other procedures that use phosgene or its derivatives as isocyanate dissolved in benzene[6] or orthochloroformates.[7]

There is one work[8] reporting the utilization of ruthenium chloride ($RuCl_3$) as catalyst for the epoxides ring-opening in the presence of amines to yield the corresponding aminoalcohols. In the present work, we describe the use of $RuCl_3$ supported on tetraethylammonium bromide (TEAB) and polyphosphotungstic acid (HPW) as catalyst for insertion of carbon dioxide into epoxides. These catalysts have shown both good conversion and selectivity. $RuCl_3$ was used without any co-catalyst and also supported on several inorganic solid materials. HPW has shown high activity for copolymerization of CO_2 and DER 331 at both normal and supercritical CO_2 conditions. These catalysts lead the reaction to the selective formation of cyclic carbonate or polycarbonate (Scheme 1).



Scheme 1. Fixation and activation of CO_2 by DER 331 bis-oxirane. Selective catalysis by $RuCl_3$ and HPW.

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Table 1
Results of insertion of CO_2 into DER 331 to selective conversion to cyclic- or polycarbonates.

Entry	Catalyst	Support	Ee (% E. C)[a]	% Conversion to cyclic carbonate	% Conversion to polycarbonate	IR (cm^{-1})
1	$RuCl_3$	None	376 (42)	50	–	1809
2	$RuCl_3$	SiO_2	700 (25)	73	–	1803
3	**$RuCl_3$**	**TEAB**	**1206 (13)**	**88**	–	**1799**
4	**$RuCl_3$**	**HPW**	**1811 (9)**	–	**89**	**1742**
5	None	HPW	40 (18)	–	78	1749
6	None	TEAB	336 (48)	44	–	1798
7	None	SiO_2	188 (1)	–	–	–

[a] Ee: epoxide equivalent and (% E.C.): percent of epoxide consumed. Epoxide equivalent of DER 331 = 182–192 (100% free epoxide). DER 331 does not show any IR bands in the 1850–1750 cm^{-1} region.

In Table 1 the results of carbon dioxide reaction with DER 331 in the presence of several catalysts are shown.

Characterization of product was performed by solution and solid state NMR and also by FT-IR based on the identification of the bands associated with the carbonyl groups of cyclic carbonates[10] and polycarbonates.[11] For the organic polycarbonates it was observed a band near 1740 cm^{-1}, which corresponds to the asymmetric $\nu(CO_2)$ vibration of the open chain polycarbonate while the $\nu(CO_2)$ vibration of the organic cyclic carbonates has been observed near 1800 cm^{-1}. FT-IR spectra illustrated in Figure 1 (A, B, and C) show a band at ~1800 cm^{-1} associated with the formation of the cyclic carbonate.[9] On the other hand, spectrum displayed in Figure 1D shows a band at ~1750 cm^{-1} associated with the presence of polycarbonate. Results have confirmed the formation of cyclic carbonate from DER 331 and CO_2 under moderated conditions such as normal pressure, minimal solvent amounts, and relatively low temperatures. FTIR analysis has proved the selectivity of the reactions carried out using ruthenium supported on SiO_2 or TEAB, which yielded the cyclic carbonate as the only reaction product.

When $RuCl_3$ itself or supported on both SiO_2 and TEAB was used, a cycloaddition reaction occurred as displayed in Scheme 1. The first stage is the S_N2 ring-opening reaction where presumably the Cl^- ligand (represented for X^- in Scheme 2) could operate as nucleophile, and this is synchronized with the coordination of the oxirane oxygen for a positive the positive $RuCl_2$ molecule (represented for $MX_{n-1}{}^+$ in Scheme 2).

This concerted S_N2 reaction is evidenced by the results shown in entries 1 and 2 in Table 1. Better conversion was observed for the reaction represented by entry 2 in Table 1, which has been achieved by using $RuCl_3{-}SiO_2$ as catalyst. In this case, a possible coordination of ruthenium with the SiO_2 could assist the release of a chloride ligand (presumably by a back-bonding like effect) increasing the concentration of the nucleophilic anion chloride in the reaction media and accelerating the nucleophilic ring-opening reaction.

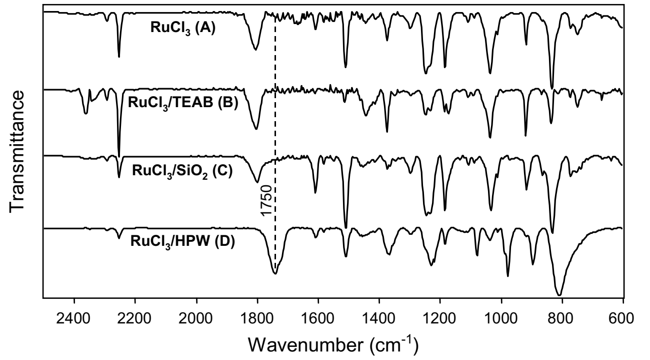
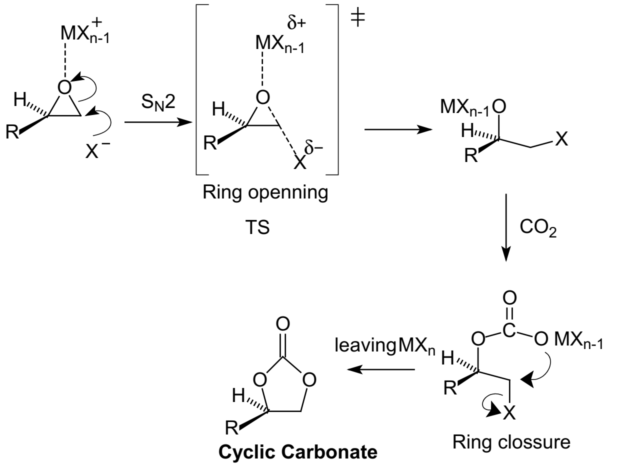


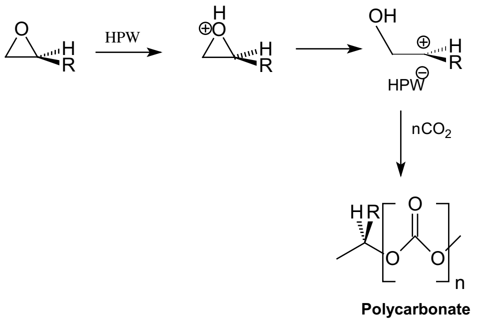
Figure 1. FT-IR spectra of the polycarbonate of DER 331 from reaction catalyzed by $RuCl_3$ (A), $RuCl_3$/TEAB (B), $RuCl_3/SiO_2$ (C) and $RuCl_3$/HPW (D).



Scheme 2. Mechanism proposed for the oxirane ring-opening coupled with CO_2 insertion catalyzed by metal transition halides (e.g., $RuCl_3$ or $RuCl_3{-}SiO_2$).

Otherwise, dispersion of the $RuCl_3$ on the SiO_2 surface can also increase the catalytical activity by increasing the number of the catalytically active surface sites. The high conversion (88%) of the reaction represented by entry 3 in Table 1 can be explained by the participation of support TEAB as co-catalyst where cation TEA^+ also assisted electrophilically the oxirane ring-opening and stabilized the anion intermediaries ($-O^-$ and $-O{-}C(O)O^-$) formed in the reaction sequence, before and after reaction with the CO_2 molecule. However, in agreement with the assumed mechanism the most important role in this case could be attributed to the nucleophilic assistance of the Br, which is at the same time a good leaving group better than the chloride. On the other hand, homogenized mixtures of ruthenium chloride with tetraalkylammonium chloride and bromide salts have showed high efficiency for ruthenium phosphine complexation.[12]

The naked anion nature of the carbonate oxygen coordinated with the TEA^+ and/or $RuCl_2{}^+$ groups together with the good leaving group character of the –Br and –Cl atoms can accelerate the ring-closure step by a S_N2 reaction to complete the cycloaddition and yielding the corresponding cyclic carbonate in a selective way. As it can be observed in Schemes 2 and 3 (below), the results of the reactions catalyzed for unsupported $RuCl_3$ (entry 1 in Table 1) and HPW only, (entry 5 in Table 1) present two significant differences on conversion and selectivity. These differences could be explained considering that the formation of the secondary carbocation intermediate in the Brönsted catalyzed (HPW)



Scheme 3. Mechanism proposed for oxirane ring-opening and formation of open chain carbonates (polycarbonate) catalyzed by HPW.

ring-opening reaction (Scheme 3) could be a less energetic process than the concerted Lewis catalyzed ($RuCl_3$) reaction which needs to achieve an agglomerated transition state. Another important assumption is that for both reactions the rate determining step is justly the oxirane ring-opening.

The selective formation of cyclic carbonate could be also explained by the differences in the relative hardness for the electrophilic sites on the corresponding intermediates. Hardness of the electrophilic centers could also assist the end of the reaction. In fact, relative hardness is linked to the Lewis–Brönsted theory and on the other hand, some calculations will be convenient to explain the observed selectivity using the HSAB theory. Finally, catalysts used for reactions represented by the entries 2–4 in Table 1 were recycled and reutilized with high conversion (73%, 85% and 87%, respectively). This ensured the high reproducibility of the procedure. As conclusion of this work, the selective preparation of the cyclic carbonate from the reaction of an industrial epoxide, DER 331, with carbon dioxide is possible. These reactions have been carried out under normal pressure and using minimal solvent. This result allows proposing the present method as an efficient and eco-friendly protocol for the synthesis of cyclic carbonates in good conversion from CO_2 fixation by epoxide monomer. Original use of ruthenium chloride as catalyst for carbon dioxide captured by epoxides is now claimed. Finally, we have performed the copolymerization of CO_2 with DER 331 under CO_2 supercritical conditions using a Parr Instruments Reactor and a pressurized CO_2/Ar gas mixture. Under these conditions, the conversions of epoxide were similar that under normal pressure (~89%). However, polymerization was more efficient using supercritical CO_2. This was evidenced by formation of a solid film of polycarbonate, which was characterized by SS ^{13}C NMR.[11] A more complete characterization of the polycarbonate was not possible due to the very low solubility of this material.

General procedure for synthesis of carbonates from CO_2 and epoxides using ruthenium containing catalysts: Preparation of the catalyst was carried out by adding $RuCl_3$ (1 mmol, 0.5100 g) on the organic or inorganic support (0.5100 g). The catalyst/support mass ratio was previously optimized. The mixture was carefully homogenized using a Teflon mortar and pestle. The amount of the supported catalyst used was equivalent to the oxirane amount, approximately 2.0000 g. The reaction mixture was refluxed with the introduction of CO_2 at normal pressure and a constant flow of ~5 mL/min under magnetic stirring. The reaction temperature was 70–80 °C. Minimal solvent (acetonitrile) was used. Once the reaction was stopped, after around 3 h, the flow of CO_2 was interrupted and the system was stirred until reaching room temperature. Then, the catalyst was recovered by centrifugation. The reactions were monitored by FT-IR measurements and the epoxide equivalent was determined for all the reaction products. Carbonate formation was also confirmed by ^{13}C NMR (C=O) δ = 155.0–154.7 ppm (solution) and ~155 ppm (solid state).

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Supplementary data

NMR conditions. FTIR spectrum of DER 331. Graphics of DSC analysis of cyclic- and polycarbonate. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.101.

References and notes

1. Yoshida, M.; Ihara, M. *Chem. Eur. J.* **2004**, *10*, 2886.
2. Shi, F.; Zhang, Q. H.; Ma, Y. B.; He, Y. D.; Deng, Y. Q. *J. Am. Chem. Soc.* **2005**, *127*, 4182.
3. Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335.
4. Sakakura, T.; Choi, J.; Matsuda, T.; Sako, T.; Oriyama, T. *J. Org. Chem.* **1999**, *64*, 4506.
5. Chu, F. X.; Dueno, E. E.; Jung, K. W. *Tetrahedron Lett.* **1999**, *40*, 1847.
6. Angeles, E.; Santilan, A.; Martinez, I. *Synth. Commun.* **1994**, *24*, 2441.
7. Yadav, J. S.; Reddy, G. S.; Reddy, M. M.; Meshram, H. M. *Tetrahedron Lett.* **1998**, *39*, 3259.
8. Surya, K.; Richard, A. *Synth. Commun.* **2005**, *35*, 2675.
9. Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586.
10. Cyclic carbonate ^{13}C NMR (250 MHz, $CDCl_3$) δ 30.2 (CH_3), 42.4 (Csp^3), 63.3 (CH_2–O), 75.6 (CH–O), 115.2 (HCsp^2), 128.2 (HCsp^2), 145.2 (Csp^2), 154.7 (C=O) and 156.1 (Csp^2); IR ~1800 cm^{-1}.
11. Polycarbonate solid-state ^{13}C NMR δ 31 (CH_3), 41 (Csp^3), 70 (CH_2–O), 78 (CH–OH), 114 (HCsp^2), 127 (HCsp^2), 143 (Csp^2), 155 (C=O), 156 (Csp^2). No signals were observed in the 45–52 ppm region indicating that there are not –CH_2–CH– from oxirane ring. Hence open chain carbonate (polycarbonate) has been obtained as a lineal polymer by polyaddition of two CO_2 molecules by a bis-epoxide molecule; IR ~1745 cm^{-1}.
12. Perez, E. P.; Carvalho, R. M.; Santos, R. H. A.; Gambardella, M. T. P.; Lima-Neto, B. S. *Polyhedron* **2003**, *22*, 3289.