THE COUPLING OF EPOXIDES AND CARBON DIOXIDE IN THE PRESENCE OF HOMOGENEOUS TRANSITION-METAL CATALYSTS. PRODUCTION OF POLYCARBONATES *VS* CYCLIC CARBONATES

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Introduction

Over the past decade a variety of efficient homogeneous catalysts or catalyst precursors have been developed to couple the thermodynamically stable carbon dioxide molecule with highly reactive substrates. One of the most promising processes involves the coupling of carbon dioxide and epoxides to afford cyclic carbonates or polycarbonates (eq. 1).[1] The production of polycarbonates from carbon dioxide and epoxides represents an environmentally benign synthetic route to these biodegradable thermoplastics which are mostly prepared by the interfacial polycondensation of diols and phosgene.[2]

Although we and others have made significant advances in the synthesis of these useful thermoplastics from carbon dioxide and epoxides much of the fundamental knowledge concerning the reaction kinetics of these processes is lacking, due in part to the practical challenges associated with sampling and analyzing systems at elevated temperatures and pressures. This information is needed for making this process applicable to the synthesis of a variety of copolymers possessing a range of properties and uses. Here, studies examining in detail the mechanistic aspects of metal catalyzed carbon dioxide/epoxide coupling reactions employing *in situ* infrared spectroscopic methods will be presented.[3] In addition, we have attempted to establish a clear mechanistic view of carbon-oxygen bond forming processes resulting from carbon dioxide insertion into M–O bonds using model organometallic derivatives.[4]

Experimental

Methods and Materials. All syntheses and manipulations were carried out on a double manifold Schlenk vacuum line under an argon atmosphere or in an argon filled glovebox. Glassware was flame dried before use. All solvents were freshly distilled prior to being used. Epoxides were purchased from Lancaster Synthesis and were distilled from calcium hydride. Catalysts were prepared by literature methods. Infrared spectra and kinetic measurements were monitored on ASI's ReactIR 1000 system equipped with a MCT detector and a 30 bounce SiCOMP in situ probe. ^{1}H and ^{13}C NMR spectra were recorded on Unity + 300 MHz or VXR 300 MHz superconducting high resolution spectrometers.

Copolymerization of Cyclohexene Oxide/Propylene Oxide and Carbon Dioxide. A weighed sample of the catalyst complex was dissolved in 20 ml of the appropriate epoxide. The solution was rapidly loaded *via* an injection port into a 300 mL stainless steel Parr autoclave that had been previously dried overnight at 80ºC under vacuum. The reactor was pressurized to 700 psi with CO_2, heated to the desired temperature and stirred for the required time period. After that time, the autoclave was cooled and the CO_2 vented into a fume hood. The reactor was opened and the polymer was isolated from the viscous/solid mixture by dissolution in small amounts of methylene chloride followed by precipitation from methanol.

High Pressure *in situ* Kinetic Measurements. High pressure reaction kinetics were carried out using a stainless steel Parr autoclave modified with a silicon probe to connect to the ASI ReactIR 1000 system (see Figure 1). The formation rates of the polycarbonate and the cyclic carbonate were monitored by following the ν(C=O) of the polycarbonate at ~1750 cm^{-1} and of the cyclic carbonate at ~1825 cm^{-1} (see Figure 2).

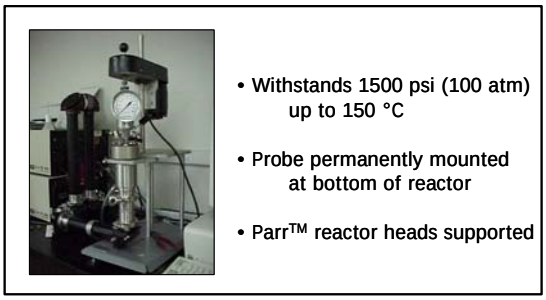


Figure 1. ASI ReactIR™ 1000 with high pressure probe.

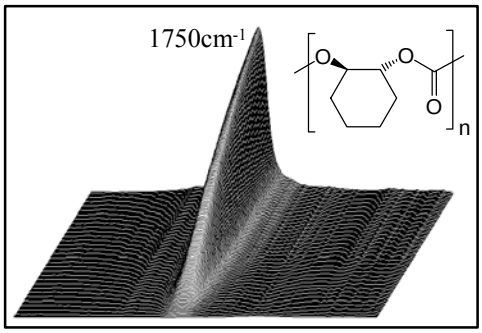


Figure 2. *In situ* infrared monitoring in the ν(CO_2) region for polymer formation from CO_2/cyclohexene oxide.

Polymer Characterization. Polymer samples were first characterized by ^{1}H NMR and IR spectroscopy. The amount of ether linkages were determined *via* ^{1}H NMR by integrating the peaks corresponding to the methine protons of the polyether at ~3.45 ppm and the polycarbonate at ~4.6 ppm. The presence or absence of the corresponding cyclic carbonate was investigated by monitoring the presence or absence of the ν(C=O) of the cyclic carbonate at ~1825cm^{-1}. Finally, M_w and M_n measurements were carried out using GPC.

Results and Discussion

We have examined a wide variety of zinc and chromium based derivatives as catalysts for the coupling of carbon dioxide and propylene oxide or cyclohexene oxide. In these studies, as well as those reported by other researchers, the reaction of carbon dioxide and propylene oxide favors production of cyclic carbonate, whereas, the analogous process involving cyclohexene oxide affords mostly polycarbonates. We have ascribed this difference in product selectivity to the ring strain placed on the five-membered carbonate ring in order to accommodate the conformational requirements of the alicyclic cyclohexyl ring. This is evident from a comparison of the crystal structures of cyclic propylene carbonate and cyclic cyclohexylene carbonate (see Figure 3).[5]

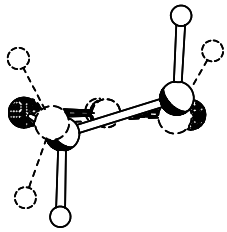


Figure 3. Overlay of the carbonate groups from propylene carbonate (dotted) and cyclohexene carbonate (solid).

Indeed, we have quantified the product selectivity for cyclic carbonate *vs* polycarbonate production in processes catalyzed by (salen)$Cr^{III}Cl$ derivatives. Comparative kinetic measurements were performed as a function of reaction temperature to assess the activation barrier for production of cyclic carbonates and polycarbonates for the two different classes of epoxides, i.e., alicyclic(cyclohexene oxide) and aliphatic(propylene oxide).[6] As anticipated in both instances the unimolecular pathway for cyclic carbonate formation has a larger energy of activation than the bimolecular enchainment pathway. That is, the energies of activation determined for cyclic propylene carbonate and polypropylene carbonate formation were 100.5 kJ-mol^{-1} and 67.6 kJ-mol^{-1} respectively, as compared with the corresponding values for cyclic cyclohexyl carbonate and polycyclohexylene carbonate production of 133 kJ-mol^{-1} and 46.9 kJ-mol^{-1}. The small energy difference in the two concurrent reactions for the propylene oxide/CO_2 process (33 kJ-mol^{-1}) accounts for the large quantity of cyclic carbonate produced at elevated temperatures in this instance.

We have examined a wide variety of (salen)CrNu, where Nu = nucleophile, derivatives as catalysts for the copolymerization of epoxides and carbon dioxide, however at this time we will focus on one of the more active derivatives thus far investigated, complex **1** (see Figure 4). The presence of a cocatalyst which can bind to the axial vacant site at the chromium center has been shown to improve the activity of complex **1** (see Table 1).

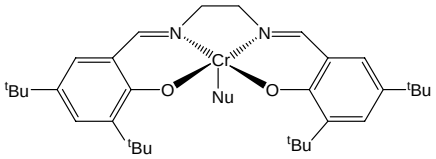


Figure 4. Typical (salen)Cr^{III}Nu (**1**), Nu = Cl(**1a**) , N_3(**1b**), catalyst for the copolymerization of epoxides and carbon dioxide.

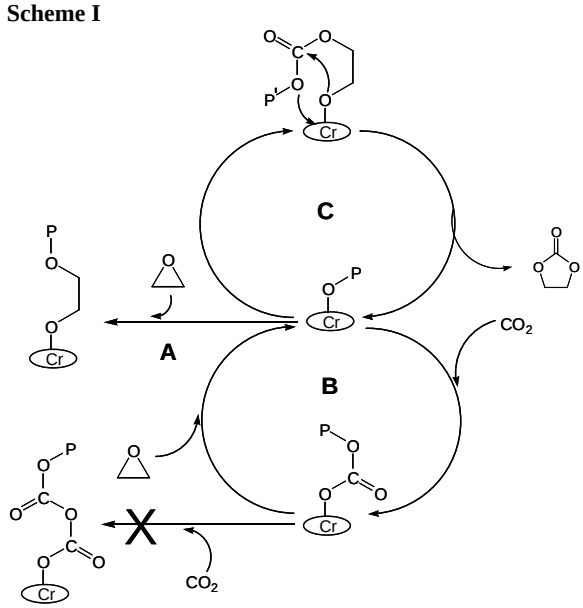
Table 1. Copolymerization Data Using Different Cocatalysts.[a]

Complex	Cocatalyst (eq)	TON[b]	TOF[c]	% carbonate
1a	N-methylimidazole (5)	95	24	69%
	PPh_3 (3)[d]	157	39	96%
	PCy_3 (3)	578	145	99%
	PPNCl (1)[e]	1004	251	>99%
1b	N-methylimidazole (5)	189	47	90%
	PPh_3 (3)	284	71	96%
	PCy_3 (3)[f]	391	98	97%
	PPNCl (1)	1022	255	>99%

[a] 50 mg of catalyst dissolved in 20 mL of cyclohexene oxide and injected into a 300 mL Parr autoclave. The reactor was charged to 55 bar CO_2 pressure and heated to 80ºC for 4 hours. [b] moles of epoxide consumed / mol. of Cr. [c] moles of epoxide consumed / mol. of Cr / hour. [d] For a 24 hr run, M_n = 22,700 and PDI = 1.55. [e] For a 4 hr run, M_n = 5980 and PDI = 2.05, whereas for a 12 hr run, M_n = 16,800 and PDI = 1.92. [f] For a 10 hr run, M_n = 10,800 and PDI = 1.54.

Scheme 1 summarizes the reaction operative during the CO_2/epoxide coupling process. The relative importance of end pathway is closely linked to the nature of the salen ligand, the cocatalyst, and the epoxide. For example, while a more electron donating salen increases the rate of polymerization with cyclohexene oxide, this seems to have the opposite effect for propylene oxide and tends to decrease the rate of conversion for both cyclic and polymer. A similar situation was observed when changing the cocatalyst, where triphenylphosphine has been shown to produce polymer with no cyclic carbonate, while tricyclohexylphosphine produced mostly polyether and a small amount of polymer. This is to be contrasted with the data in Table 1 for cyclohexene oxide and carbon dioxide copolymerization. Furthermore, as previously demonstrated, copolymerization using cyclohexene oxide is further enhanced through the use of anionic cocatalysts. However, when using a PPN^+Cl^- cocatalyst, this was not the case for propylene oxide as cyclic carbonate was the major product.

Scheme I



Finally, the use of other epoxide substrates based on the cyclohexyl backbone in the copolymerization with carbon dioxide, such as [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane, offers the opportunity of affording industrially useful thermoplastics *via* crosslinking of the silane units.[7]

References

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