5996 *Macromolecules* **2010**, *43*, 5996–6003
DOI: 10.1021/ma100896x

Macromolecules
ARTICLE

Tuning the Selectivity of the Oxetane and CO_2 Coupling Process Catalyzed by (Salen)CrCl/*n*-Bu_4NX: Cyclic Carbonate Formation vs Aliphatic Polycarbonate Production

Donald J. Darensbourg* and Adriana I. Moncada

Department of Chemistry, Texas A&M University, College Station, Texas 77843

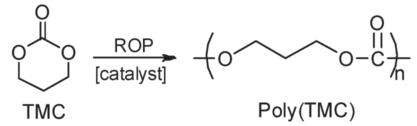
Received April 22, 2010; Revised Manuscript Received June 10, 2010

ABSTRACT: The (salen)$Cr^{III}Cl$ complex **1**, (1,2-cyclohexanediamino-*N,N′*-bis(3,5-ditert-butylsalicylidene)-chromium(III) chloride), in the presence of *n*-Bu_4NX (X = Br, I, Cl, N_3, NCO) as cocatalyst has been shown to be an effective catalytic system for the coupling of oxetane and CO_2 providing the corresponding aliphatic polycarbonate with small quantities of ether linkages at 110 °C. The selectivity of the oxetane and CO_2 coupling process has been effectively tuned for the formation of polycarbonate produced directly from the homopolymerization of preformed trimethylene carbonate (TMC), in the presence of complex **1** along with *n*-Bu_4NBr as cocatalyst, at temperatures lower than 80 °C. Notably, under these conditions the amount of carbonate linkages obtained was remarkably high (> 99%). An investigation of the initial catalytic species involved in the coupling reaction was performed by ESI mass spectral analysis, revealing a Schlenk (ligand redistribution) equilibrium of the three possible anions formed after treatment of the (salen)CrCl with two equivalents of *n*-Bu_4NBr cocatalyst. This catalytic system afforded trimethylene carbonate exclusively from the coupling of oxetane and CO_2 at mild reaction conditions (50 °C and 10 bar of CO_2) via a backbiting process involving mostly a metal−alkoxide intermediate.

Introduction

Biodegradable aliphatic polycarbonates are important components of nontoxic thermoplastic elastomers, which have a variety of medical applications, including sutures, body and dental implants, orthopedic fixation devices, drug delivery systems, and tissue engineering.[1] Therefore, the development of suitable routes for the production of aliphatic polycarbonates has been the subject of multinational research laboratories. One process that has shown significant advances is the alternative copolymerization of CO_2 and aliphatic epoxides such as propylene oxide, in the presence of a metal-based catalyst,[2] a field pioneered by Inoue and co-workers in 1969.[3] This is in part due to the economic and environmental benefits arising from the utilization of biorenewable carbon dioxide for industrial, health, and safety purposes.[4] For example, poly(propylene carbonate) is an industrially relevant polymer because of its biodegradability properties, its sharp decomposition temperature above 200 °C, and its low T_g (~40 °C). However, the production of polycarbonates from propylene oxide has been challenging because of the tendency of aliphatic epoxides to couple with CO_2 to afford the thermodynamically more stable five-membered cyclic carbonate.[5] Nevertheless, recent investigations of cobalt(III) and chromium(III) complexes have demonstrated these derivatives to greatly enhance the catalytic activity and selectivity for copolymer formation from the coupling of propylene oxide and CO_2 under mild reaction conditions.[6]

An alternative methodology for the production of aliphatic polycarbonates involves the ring-opening polymerization (ROP) of six- and seven-membered cyclic carbonates such as trimethylene carbonate (eq 1). The ring-opening polymerization of these cyclic carbonates is thermodynamically favored at all temperatures,[7] and thus it is a suitable route for the production these polymeric materials. Indeed, the production of polycarbonates by this method has been widely investigated by a variety of different mechanisms including cationic,[8] anionic,[9] enzymatic,[10] coordination−insertion,[11] and organocatalytic[12] pathways. It is noteworthy that trimethylene carbonate is readily obtained from 1,3-propanediol, and ethylchloroformate or diethyl carbonate.[9a,13] Consequently, the development of greener routes for the production of this important six-membered cyclic carbonate monomer is of importance. Toward this goal, the coupling of four-membered cyclic ethers such as oxetane and carbon dioxide is an attractive method (eq 2).[14] In this instance the cyclic carbonate product, TMC, is thermodynamically unstable relative to the copolymer, which has limited the employment of this methodology for the exclusive synthesis of trimethylene carbonate. To the best of our knowledge, the only early reports on the ring-expansion of oxetanes with CO_2 to form six-membered cyclic carbonates were published by Baba and co-workers, who employed tetraphenylstibonium iodide or organotin iodide/*n*-Bu_3PO as catalysts.[14c−e]



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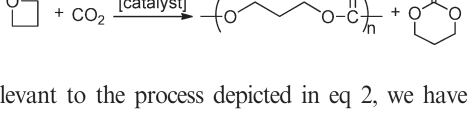

(2)

Relevant to the process depicted in eq 2, we have undertaken detailed mechanistic and kinetic studies on this reaction catalyzed by a (salen)$Cr^{III}Cl$ complex, namely, 1,2-cyclohexanediamino-*N,N′*-*bis*-(3,5-di-*tert*-butylsalicylidene)chromium(III) chloride, (complex **1**),

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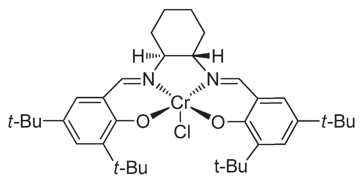
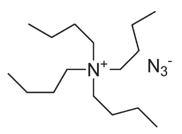
*Corresponding author. E-mail: djdarens@mail.chem.tamu.edu. Fax (979) 845-0158.



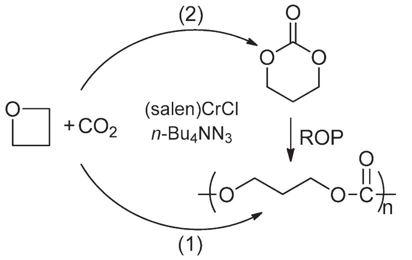
(salen)CrCl Catalyst



Cocatalyst

Figure 1. (salen)CrCl complex **1** and cocatalyst employed in mechanistic and kinetic studies performed on the copolymerization of oxetane and CO_2.[16].

Scheme 1



along with an onium salt, n-Bu_4NN_3, as cocatalyst (Figure 1).[15−17] Our studies have demonstrated that this catalytic system allows for two operative pathways responsible for polycarbonate formation. These are the direct enchainment of oxetane and CO_2 (route 1) and the ring-opening polymerization of preformed trimethylene carbonate (route 2) via a coordination−insertion mechanism (Scheme 1).[16] Complex **1** was employed in this investigation because it was found to be the more active toward copolymer formation among a series of (salen)CrCl catalysts screened for this reaction. As a consequence of our experimental findings with the (salen)CrCl/n-Bu_4NN_3 catalytic system, we first hypothesized that by reducing the electrophilicity of the metal salen complex in conjunction with the appropriate cocatalyst, the selectivity of the oxetane/CO_2 coupling reaction should be modulated. Indeed, we discovered that a (salen)Co^{II} complex in the presence of anions such as bromide that are good leaving groups forms a very active catalyst system for the ring-expansion of oxetane with CO_2 to afford trimethylene carbonate. Subsequently, TMC is polymerized by an anionic ring-opening polymerization mechanism in the presence of bromide ions in the reaction solution.[18]

These results inspired us to further explore the activity and selectivity of the (salen)Cr^{III}Cl catalyst in the presence of anions that are better leaving groups than the azide anion, i.e., bromide and iodide. We surmised that this catalytic system should more effectively tune the selectivity of the oxetane/CO_2 coupling process for cyclic carbonate formation, and/or for polycarbonate produced from the homopolymerization of preformed TMC (Scheme 1, route 2). The isolation of trimethylene carbonate from this process is also of interest because it could be used in melt polymerization processes with other monomers, such as lactides or caprolactones, for the production of important copolymers. In addition, the polycarbonate obtained from ROP of preformed TMC would have no ether linkages, as we have previously demonstrated for the ROP of TMC in the presence of the (salen)CrCl catalyst along with n-Bu_4NN_3 as cocatalyst.[16] This would result in a polymer with better physical properties.

Herein, we wish to report further studies on this transformation as it pertains to the effects of a variety of cocatalysts on the selectivity of the oxetane and CO_2 coupling reaction catalyzed by complex **1**. An investigation of the nature of the catalytic species involved in the reaction will be described. Additionally, the dependence of reaction temperature on the selectivity of the coupling of oxetane and CO_2 as monitored by high-pressure *in situ* IR spectroscopy will be presented. Finally, the effects of temperature and pressure on the selective synthesis of TMC from the coupling of oxetane and CO_2 will be discussed.

Experimental Section

Reagents and Methods. All syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon filled glovebox. Toluene and tetrahydrofuran were freshly distilled from sodium/benzophenone. Ethanol was freshly distilled from Mg/I_2. Diethyl ether, dichloromethane, and hexanes were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. Oxetane (Alfa Aesar) was freshly distilled over CaH_2 and stored in the freezer of the glovebox. Tetra-n-butylammonium bromide (Eastman), tetra-n-butylammonium iodide (Eastman), and tetra-n-butylammonium chloride (TCI) were recrystallized from acetone/diethyl ether before use. Tetra-n-butylammonium azide (TCI), and tetra-n-butylammonium cyanate (Fluka) were stored in the freezer of the glovebox upon arrival. Chromium(II) chloride (Alfa Aesar) and sodium sulfate (EMD) were used as received. Bone-dry carbon dioxide supplied in a high-pressure cylinder and equipped with a liquid dip tube was purchased from Scott Specialty Gases. (PPN)Br ($PPN^+ = (Ph_3P)_2N^+$) was synthesized following the procedure reported in the literature for the synthesis of $(PPN)N_3$.[19] The syntheses of 1,2-cyclohexanediamino-N,N'-*bis*(3,5-di-*tert*-butylsalicylidene), 1,2-phenylenediamino-N,N'-*bis*(3-*tert*-butyl-5-methoxysalicylidene), 1,2-cyclohexanediamino-N,N'-bis(3,5-di-*tert*-butylsalicylidene)chromium(III) chloride (complex **1**), and 1,2-phenylenediamino-N,N'-bis(3-*tert*-butyl-5-methoxysalicylidene)-chromium(III) chloride (complex **2**) were performed as described in the literature.[20] Single crystals of $(salen)Cr(Cl)_x(Br)_y^-PPN^+$ (complex **3**) were obtained by layering hexanes into a saturated dichloromethane solution of the corresponding (salen)CrCl complex (1,2-phenylenediamino-N,N'-bis(3-*tert*-butyl-5-methoxysalicylidene)chromium(III) chloride) containing two equivalents of (PPN)Br. ESI−MS: m/z 608.22 $[(salen)Cr(Cl_2)^-]$, 698.03 $[(salen)Cr(Br_2)^-]$, 654.19 $[(salen)Cr(Cl)(Br)^-]$, 632.20 $[(salen)Cr(Cl)(OAc)^-]$, and 678.15 $[(salen)Cr(Br)(OAc)^-]$.

^1H NMR spectra were acquired on Unity+ 300 MHz and VXR 300 MHz superconducting NMR spectrometers. Molecular weight determinations (M_n and M_w) were carried out with Viscotek Modular GPC apparatus equipped with ViscoGEL^{TM} I-series columns (H + L), and Model 270 dual detector comprised of RI and Light Scattering detectors. High-pressure reactions were performed using an ASI ReactIR 1000 reaction analysis system with stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo).

Copolymerization Reactions Monitored by *in Situ* IR Spectroscopy. In a typical experiment, complex **1** (124.4 mg, 1.96×10^{-4} mol), the appropriate amount of cocatalyst, n-Bu_4NX (X = Br, I, Cl, N_3, NCO), and oxetane (4 g) were dissolved in 10 mL of toluene and delivered via the injection port into a 300 mL stainless steel Parr autoclave reactor that was previously dried in vacuo overnight at 80 °C. The monomer:catalyst:cocatalyst ratio was maintained at 350:1:2. The autoclave is modified with a 30 bounce SiComp window to allow for the use of an ASI ReactIR 1000 system equipped with a MCT detector. In this manner a 128-scan background spectrum was collected

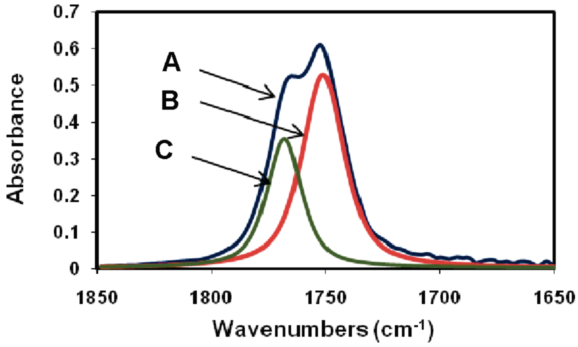


Figure 2. Selected IR spectrum of a reaction solution obtained from the reaction between oxetane and CO_2: (A) undeconvoluted IR spectrum; (B) deconvoluted IR spectrum corresponding to poly(TMC); (C) deconvoluted IR spectrum corresponding to TMC.

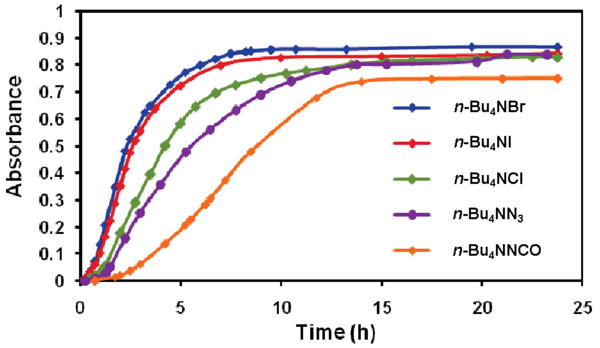


Figure 3. Reaction profiles obtained after deconvolution of selected IR spectra indicating copolymer formation with time for the copolymerization of oxetane and CO_2, in the presence of complex **1** and 35 bar of CO_2 at 110 °C employing various *n*-Bu_4NX salts as cocatalysts.

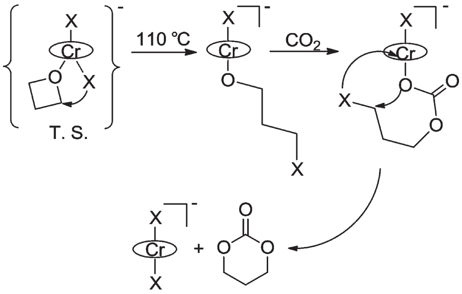
after the reaction mixture was heated to the temperature of the corresponding experiment. The autoclave was pressurized with the appropiate CO_2 pressure, and the infrared spectrometer was set to collect one spectrum every 3 min over a 24 h period. Profiles of the absorbance at 1750 cm^{-1} (polymer) and at 1770 cm^{-1} (TMC) with time were recorded after baseline correction. After the reaction was stopped, the autoclave was cooled down to room temperature, vented in a fume hood, and the reaction solution was extracted with dichloromethane. The percent conversion to products was determined based on the amount of oxetane monomer left in the reaction solution as ascertained by ^{1}H NMR in $CDCl_3$: δ 4.75 (t, 4H, OCH_2) and 2.70 (quint, 2H, CH_2). Furthermore, the quantities of poly(TMC), TMC, and ether linkages in the copolymer were determined by integrating the peak area of the corresponding resonances in $CDCl_3$: poly(TMC), δ 4.23 (t, 4H, OCH_2) and 2.05 (quint, 2H, CH_2); TMC, δ 4.45 (t, 4H, OCH_2) and 2.14 (quint, 2H, CH_2); ether linkages, δ 3.50 (t, 4H, OCH_2) and 1.90 (quint, 2H, CH_2). The reaction solution was dried in vacuo overnight to remove excess dichloromethane and any unreacted oxetane. The polymer residue was purified by precipitation from dichloromethane and 1 M HCl solution in methanol. The supernatant solution containing the catalyst and cyclic carbonate was decanted and the purified polymer was dried in vacuo overnight. (Note: cocatalyst, temperature, and pressure varied within each experiment, and are described in the Results and Discussion section.)

Statistical Deconvolution of FTIR Spectra. When noted FTIR spectra were deconvoluted using Peakfit, version 4.12 (Peakfit for Windows, v. 4.12; SYSTAT Software Inc., San Jose, CA, 2003). Statistical treatment was a residuals method utilizing a combination Gaussian−Lorentzian summation of amplitudes with a linear baseline and Savitsky−Golay smoothing.

Results and Discussion

Effects of Various *n*-Bu_4NX Salts as Cocatalysts on the Coupling of Oxetane and CO_2. Our initial efforts were directed at employing complex **1** along with various *n*-Bu_4NX (X = Br, I, Cl, N_3, NCO) salts as cocatalysts to examine the catalytic activity and selectivity for cyclic carbonate vs copolymer formation from the oxetane and CO_2 coupling reaction. The copolymerization reactions were carried out under identical reaction conditions; i.e., 110 °C, 35 bar of CO_2 pressure in toluene solution, and were monitored by *in situ* IR spectroscopy. The growth of the copolymer was monitored by observing its $\nu_{C=O}$ band at 1750 cm^{-1}, and the growth and/or consumption of the cyclic product, TMC, by observing its $\nu_{C=O}$ band at 1770 cm^{-1}. Because of the close proximity of the carbonyl stretching bands of copolymer and cyclic carbonate, it was necessary to deconvolute selected IR spectra employing the band parameters for the pure components in order to get accurate reaction profiles. Figure 2 shows an example of such a deconvoluted spectrum. The reaction profiles for copolymer formation as a function of various *n*-Bu_4NX cocatalysts present in two equivalents relative to complex **1** are shown in Figure 3. It can be readily seen that the rates for copolymer formation differ slightly from each other, and the order of decreasing reaction rate was Br^-, I^- > Cl^-, N_3^- > NCO^-. As we have previously noted, a more remarkable induction period is observed when utilizing the anion NCO^- as cocatalyst.[17] This is consistent with this anion being a stronger field ligand, and thus displacing the chloride from (salen)CrCl more easily, forming the corresponding [*trans*-(salen)CrX_2]-[*n*-Bu_4N^+] (X = NCO) complex. Concomitantly, this ligand is more difficult to be displaced by the oxetane monomer, hence retarding the initial stage of the ring-opening reaction.

Scheme 2



Relative to the initiation step of the copolymerization process, we showed that the ring-opening of oxetane in the presence of (salen)Cr^{III}Cl complexes by *n*-Bu_4NX (X = Cl, N_3) salts is a higher energy process compared to the corresponding reaction involving epoxides.[17] Recently, Jacobsen and co-workers have reported the enantioselective intramolecular openings of oxetanes-containing *O*-centered nucleophiles catalyzed by (salen)Co^{III} complexes, producing good yields of enantioenriched tetrahydrofurans under mild reaction conditions.[21] However, under the catalytic conditions utilized for the copolymerization reaction of oxetane and CO_2, a good nucleophile (X) is required for the ring-opening step (Scheme 2). On the contrary, the formation of trimethylene carbonate which is due to a backbiting process would need a good leaving group (X) (Scheme 2). It should be noted that the transition state in Scheme 2 is currently not well-defined. That is, it involves some level of dissociation of X and binding of oxetane prior to the ring-opening process, similar to an I_a mechanism. Figure 4 illustrates the reaction profiles for the series of reactions performed at 110 °C utilizing complex **1**, in the presence of the various cocatalysts. Among

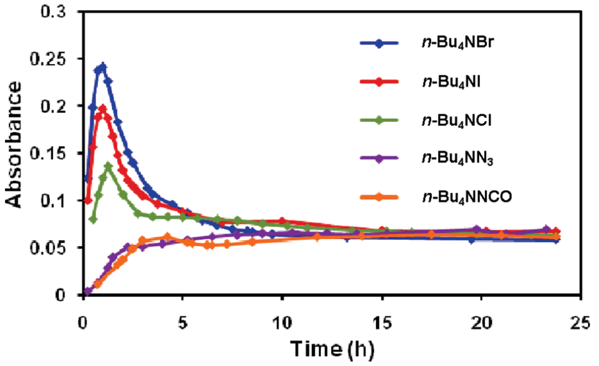


Figure 4. Reaction profiles obtained after deconvolution of selected IR spectra indicating TMC formation with time for the copolymerization of oxetane and CO_2 in the presence of complex **1** and 35 bar of CO_2 at 110 °C employing various *n*-Bu_4NX salts as cocatalysts.

the cocatalysts examined, the bromide anion displayed the highest catalytic activity toward trimethylene carbonate formation at the early stages of the coupling reaction, followed by the iodide, chloride, azide, and cyanate anions. The bromide anion is better at promoting the formation of TMC by a backbiting mechanism under these catalytic conditions. We observed a similar catalytic tendency for the formation of TMC from oxetane and CO_2 utilizing a (salen)Co^{II} complex along with cocatalysts of the type described here, *n*-Bu_4NX ($X = N_3$, Cl, Br, I). Subsequently, TMC polymerizes by an anionic pathway.[18] Others have reported analogous trends for the coupling of CO_2 or CS_2 and aziridines employing alkali metal halides or tetraalkylammonium halides as catalysts.[22] Moreover, Caló reported the formation of five-membered cyclic carbonates from the coupling of oxiranes and CO_2 utilizing molten *n*-Bu_4NBr as catalyst.[23] More recently, North and co-workers reported a detailed mechanistic study on the formation of five-membered cyclic carbonates from the coupling of epoxides and CO_2 catalyzed by a bimetallic aluminum salen complex along with *n*-Bu_4NBr as cocatalyst.[24]

Figure 5 shows the reaction profiles of both copolymer and TMC formation for the copolymerization reaction of oxetane and CO_2 performed using complex **1** in the presence of 2 equiv of *n*-Bu_4NBr as cocatalyst. It is clearly observed that when using this catalytic system and conditions the formation of TMC is enhanced at the early stages of the coupling reaction and its concentration is rapidly decreased over time. On the other hand, the concentration of poly(TMC) is initially inhibited followed by rapidly increasing over the course of the reaction. It is important to recall that a decrease in temperature of ~20 °C is observed following the addition of carbon dioxide to the 110 °C reaction mixture. Thus, the initial inhibition of poly(TMC) formation can be ascribed in small part to a change in selectivity to TMC formation as a consequence of the drop in temperature observed after loading CO_2 into the reaction solution at 110 °C (*vide infra*). In addition, this initial inhibition for poly(TMC) formation can be more remarkable in the presence of anions that are stronger field ligands such as NCO^-, where the initial step of the coupling reaction is retarded. The product distributions for the copolymerization reactions carried out in the presence of complex **1** along with various *n*-Bu_4NX salts as cocatalysts are shown in Table 1, as determined by ^1H NMR spectroscopy. In all the cases good to high activity for copolymer formation was obtained, and the percentages of poly(TMC) were found to be ≥98% with trace quantities of TMC detected after 24 h of reaction. Consistent with the *in situ* IR data, these results strongly suggest that there is an equilibrium process between the cyclic carbonate and the polycarbonate, as the percentage of poly(TMC) did not reach 100% after a 24 h of reaction period. Relevant to this point, anionic equilibrium polymerizations of six-membered cyclic carbonates have been documented in the literature.[9c,25]

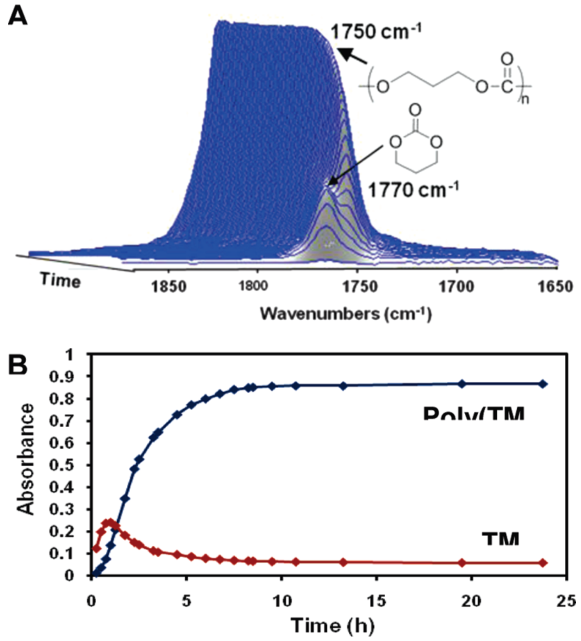


Figure 5. (A) Three-dimensional stack plot of IR spectra collected every 3 min during the copolymerization reaction of oxetane and CO_2. (B) Reaction profiles obtained after deconvolution of selected IR spectra indicating copolymer and TMC formation with time. Reaction carried out at 110 °C in toluene and at 35 bar of CO_2 pressure, in the presence of complex **1** and 2 equiv of *n*-Bu_4NBr.

Table 1. Copolymerization of Oxetane and CO_2 Catalyzed by Complex 1 in the Presence of Various *n*-Bu_4NX salts as Cocatalysts.[a]

cocatalyst	% conversion[b]	% poly-(TMC)[b]	% TMC[b]	% CO_2 content[b]	M_n (GPC)	PDI (GPC)
n-Bu_4NBr	100	98.2	1.8	99	7100	1.42
n-Bu_4NI	100	98.1	1.9	99	7000	1.43
n-Bu_4NCl	75.4	>99	<1.0	97.9	7600	1.20
n-Bu_4NN_3	64.2	>99	<1.0	96.5	5780	1.64
n-Bu_4NNCO	65.6	>99	<1.0	96.9	4700	1.41

[a] Reaction conditions: complex **1** (124.4 mg, 1.96×10^{-4} mol), 2 equiv of cocatalyst, 4 g of oxetane, 10 mL of toluene, M/I = 350, 35 bar of CO_2, 110 °C, and 24 h of reaction time. [b] The % conversion, product distributions, and % of CO_2 content were determined by ^1H NMR spectroscopy.

In this respect, monomers that undergo equilibrium polymerization processes are very useful, because this property of reversibility can be utilized in the recycling of polymeric materials.[26] It should be noted that we have observed more remarkable equilibrium processes between the cyclic carbonate and the corresponding polycarbonate, upon using four-membered cyclic ethers containing two substituents in the 3-position of trimethylene oxide, i.e., 3-methoxy-methyl-3-methyloxetane, and these studies will be reported elsewhere.

Importantly, the highest percentages of CO_2 incorporation were observed for the reactions where *n*-Bu_4NBr, and *n*-Bu_4NI were used as cocatalysts. This result is consistent with the observation that in these reactions there was more TMC formed and thus, more polycarbonate produced by the ring-opening polymerization of preformed trimethylene carbonate via a coordination–insertion pathway. *It should be recalled that we have independently shown that the ROP of*

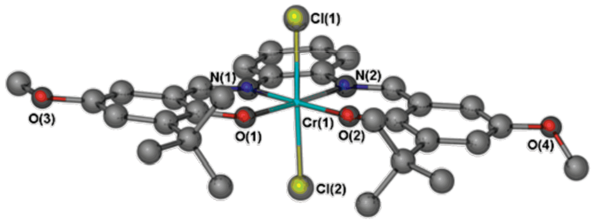
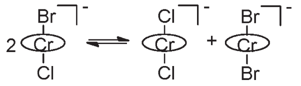


Figure 6. Ball-and-stick representation of the X-ray defined structure of (salen)$CrCl_2^-$ anion, where the salen ligand contains −OMe and −*t*-Bu substituents in the 3,5-positions of the phenolates, respectively, with a phenylene diimine backbone. Tetrabutylammonium cation was omitted for clarity. Data were taken from ref 17.

TMC by these catalytic systems occurs with no CO_2 loss during the copolymerization reaction.[16]

The molecular weight and polydispersities of the copolymers were measured in THF by gel permeation chromatography. Under these reaction conditions the typical M_n value ranged from 4700 to 7100 with PDI of 1.20 to 1.64 (Table 1). A more detailed presentation of M_n as a function of the [monomer]/[initiator] may be found in our earlier report on this catalytic process.[16] At that time it was shown in the absence of toluene under extremely dry conditions the M_n value closely agreed with its theoretical value. A rapid and reversible chain-transfer reaction with water is thought to account for the low values of M_n in Table 1. This is supported by the observation of −OH end groups on the polymer chains.

Examination of the Catalytic Species Involved in the Copolymerization Reaction. Subsequent studies were focused on determining the characteristics of the catalytic species formed upon treating a (salen)CrCl with two equivalents of a bromide-based cocatalyst. This catalytic system was demonstrated to have the highest activity toward TMC formation at the initial stages of the coupling reaction at 110 °C. Additionally, the polycarbonate produced displayed a high fixation of carbon dioxide (> 99%). To investigate the nature of this catalytic species a (salen)CrCl, 1,2-phenylenediamino-*N*,*N*′-bis(3-*tert*-butyl-5-methoxysalicylidene)chromium(III) chloride (complex **2**), was treated with two equivalents of (PPN)Br and analyzed by electron-spray ionization mass spectrometry. The parent ions of (salen)$CrCl_2^-$, (salen)-$CrClBr^-$, and (salen)$CrBr_2^-$ were observed in the negative mode of the ESI−MS spectrum at 608.22, 654.19, and 698.03 *m*/*z*, respectively. Moreover, the parent ions of (salen)Cr(Cl)-$(OAc)^-$ and (salen)Cr(Br)$(OAc)^-$ were also detected, which resulted from the reaction of (salen)$CrCl_2^-$ and (salen)$CrBr_2^-$ with acetic acid, which is used during the mass spectral analysis experiment. Because of the presence of excess bromide, the complexes (salen)$CrBr_2^-$ and (salen)$CrClBr^-$ are expected to be the most abundant in solution. These results suggested that when (salen)CrCl is treated with two equivalents of bromide, a Schlenk (ligand redistribution) equilibrium is produced (eq 3.) Pertinent to this point, we have isolated and fully characterized the *n*-Bu_4N^+ salt of the (salen)$CrCl_2^-$ anion by X-ray crystallography (Figure 6).[17]


$$2\,[\mathrm{Br{-}Cr{-}Cl}]^- \rightleftharpoons [\mathrm{Cl{-}Cr{-}Cl}]^- + [\mathrm{Br{-}Cr{-}Br}]^- \qquad (3)$$

Temperature Dependence on the Coupling of Oxetane and CO_2 Catalyzed by (salen)CrCl/*n*-Bu_4NBr. Subsequently, temperature dependence studies were performed in order to examine the selectivity of the oxetane and CO_2 coupling process utilizing the (salen)CrCl/*n*-Bu_4NBr catalytic system.

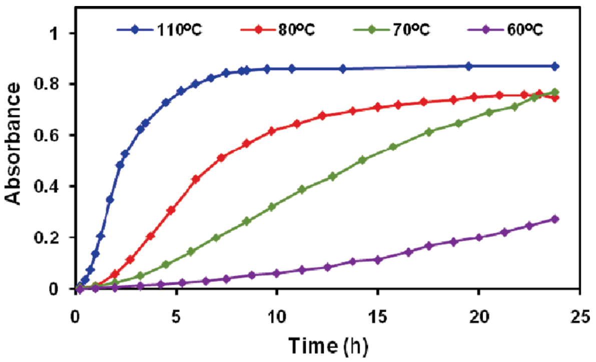


Figure 7. Reaction profiles obtained after deconvolution of selected IR spectra indicating poly(TMC) formation with time for the copolymerization of oxetane and CO_2, in the presence of complex **1**, 2 equiv of *n*-Bu_4NBr, and 35 bar of CO_2 at various reaction temperatures.

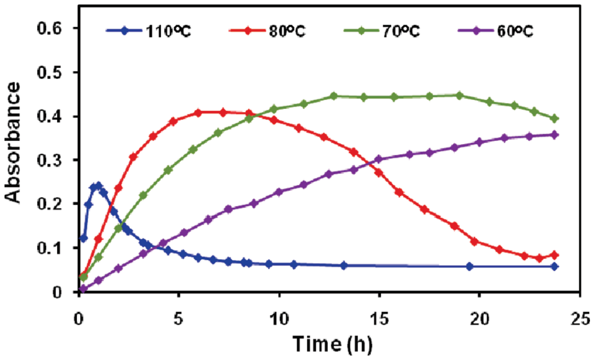


Figure 8. Reaction profiles obtained after deconvolution of selected IR spectra indicating TMC formation with time for the copolymerization of oxetane and CO_2, in the presence of complex **1**, 2 equiv of *n*-Bu_4NBr, and 35 bar of CO_2 at various reaction temperatures.

We previously showed that in the presence of *n*-Bu_4NBr as cocatalyst a higher catalytic activity toward trimethylene carbonate formation is obtained at the early stages of the coupling reaction carried out at 110 °C. It would be anticipated that lowering the reaction temperature would enhance the formation of TMC throughout the course of the reaction. The coupling reactions were carried out under identical reaction conditions, i.e., 35 bar of CO_2 pressure, utilizing complex **1** and 2 equiv of *n*-Bu_4NBr as cocatalyst at various reaction temperatures.

Figure 7 depicts the reaction profiles for copolymer formation with time for a series of reactions performed at various reaction temperatures. As anticipated, the reaction rate for copolymer formation is decreased as the reaction temperature is varied from 110 to 60 °C. Figure 8 illustrates the reaction profiles for trimethylene carbonate formation for the series of reactions carried out at this same temperature range of 110 to 60 °C. It can be clearly observed that upon lowering the temperature from 110 to 60 °C the selectivity for formation of trimethylene carbonate by a backbiting mechanism is enhanced during the course of the coupling reaction. This is the result of the higher temperatures needed to ROP TMC than those required to couple oxetane and CO_2 to form TMC in the presence of bromide ions. The product distributions for the coupling reactions are presented in Table 2, as determined by ^1H NMR spectroscopy.

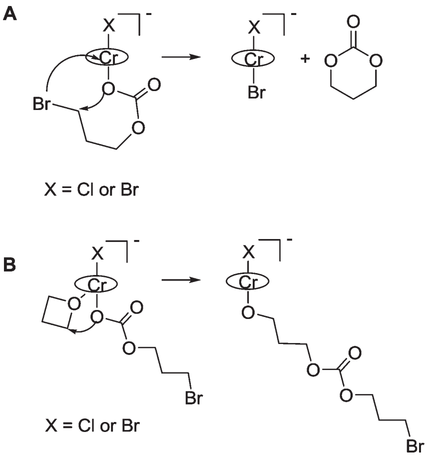
Table 2 clearly illustrates that lowering the reaction temperature from 110 to 60 °C drives the selectivity of the oxetane and CO_2 coupling reaction for TMC production in

Table 2. Coupling of Oxetane and CO_2 Catalyzed by Complex 1/*n*-Bu_4NBr at Various Reaction Temperatures.[a]

temperature (°C)	% conversion[b]	% poly(TMC)[b]	% TMC[b]	% CO_2 content[b]
110	100	98.2	1.8	99
80	100	93.3	6.7	99.3
70	73.7	62.6	37.4	> 99
60	33.9	13.3	86.7	> 99

[a] Reaction conditions: complex **1** (124.4 mg, 1.96×10^{-4} mol), 2 equiv of *n*-Bu_4NBr, 4 g of oxetane, 10 mL of toluene, M/I = 350, 35 bar of CO_2, 110 °C, and 24 h of reaction time. [b] The % conversion, product distributions, and % of CO_2 content were determined by ^1H NMR spectroscopy.

Scheme 3



the presence of complex **1**/*n*-Bu_4NBr. As expected a decrease in catalytic activity is observed as the temperature is decreased, where the ring-opening of oxetane is more difficult. Nevertheless, under these catalytic conditions the formation of TMC and the production of polycarbonate through ROP of preformed TMC via a coordination−insertion mechanism are favored. Concomitantly, the highest percentages of CO_2 fixation are observed in the resulting polycarbonates (Table 2). It is important to note that although ring-opening polymerization of preformed trimethylene carbonate accounts for most of the polycarbonate production at lower reaction temperatures (< 80 °C), we cannot rule out that at least some polycarbonate formation results from the direct enchainment of oxetane and CO_2.

It is evident from our recent experimental results that the formation of trimethylene carbonate is enhanced with the employment of the (salen)CrCl catalyst along with a bromide-based cocatalyst. Additionally, it is suggested that formation of TMC by a backbiting process occurring via a metal−carbonate intermediate is favored at lower reaction temperatures (< 80 °C) (Scheme 3A). By way of contrast, in the chain propagation step the ring-opening of oxetane by a metal−carbonate intermediate is favored at higher reaction temperatures (≥80 °C) (Scheme 3B). As a result, enhancing the process shown in Scheme 3B minimizes the ability of backbiting via a terminal bromide anion (Scheme 3A) forming TMC. Although a dimer of TMC has been observed by us in a related process catalyzed by $(salen)Co^{II}$/*n*-Bu_4NBr, larger carbonate rings have not been observed thus far in the presence of the (salen)CrCl/*n*-Bu_4NBr catalytic system.[18]

It is important to recall that we have performed a cocatalyst concentration dependence study on the coupling reaction using complex **1**/*n*-Bu_4NBr as catalytic system at 110 °C. As expected, the initial formation of TMC increased as the number of equivalents of cocatalyst utilized was increased. This is consistent with the formation of cyclic carbonate by a backbiting mechanism not only aided by the metal catalyst, but also by the free anionic polymer chain. The latter process is thought to have a lower energy barrier and to be assisted in the presence of excess ionic-based cocatalysts which serve to displace the growing polymer chain from the metal catalyst.[27]

Table 3. Coupling of Oxetane and CO_2 to Afford Trimethylene Carbonate.[a]

T (°C)	CO_2 pressure (bar)	% conversion[b]	% poly(TMC)[b]	% TMC[b]
50	35	9.4	0	100
50	10	20.3	0	100
60	35	33.9	13.3	86.7
60	10	46.6	46.5	53.5

[a] Reaction conditions: complex **1** (124.4 mg, 1.96×10^{-4} mol), 2 equiv of *n*-Bu_4NBr, 4 g of oxetane, 10 mL of toluene, M/I = 350, and 24 h of reaction time. [b] The % conversion and product distributions were determined by ^1H NMR spectroscopy.

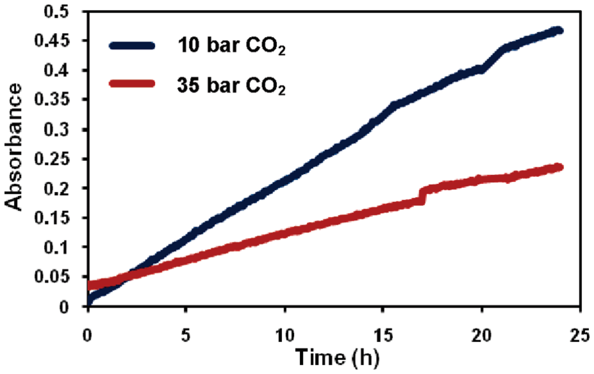


Figure 9. Reaction profiles indicating trimethylene carbonate formation with time for the coupling of oxetane and CO_2. Reactions carried out at 50 °C in toluene in the presence of complex **1** and 2 equiv of *n*-Bu_4NBr at the indicated CO_2 pressures.

Further Optimization of the Oxetane and CO_2 Coupling Process for Trimethylene Carbonate Formation. In an effort to tune the selectivity of the oxetane and CO_2 coupling process exclusively for trimethylene carbonate formation, we have designed a series of experiments where the temperature was kept at 50 or 60 °C, and the CO_2 pressure was varied between 35 and 10 bar as shown in Table 3 and Figures 9 and 10.

The ring-expansion of oxetane with CO_2 catalyzed by complex **1** along with *n*-Bu_4NBr as cocatalyst was found to be most favored at lower reaction temperatures and CO_2 pressures (50 °C, 10 bar of CO_2), even though a low conversion could only be achieved under these reaction conditions (Table 3, Figure 9). This result is consistent with the formation of cyclic carbonate occurring mostly via a metal-alkoxide intermediate (Scheme 4A) rather than by a metal−carbonate intermediate (Scheme 4B). Previously, we have determined an $E^{\ddagger}_{act}$ of 105 kJ/mol for the formation of *trans*-cyclohexylene carbonate in the absence of comonomers from the metal bound polymer chain.[28] On the contrary, the activation barrier for the formation of cyclic carbonate during the copolymerization of cyclohexene oxide and CO_2 at 55 bar was found to be 133 kJ/mol. In this case, cyclic carbonate formation was suggested to occur by way of a metal−carbonate (polymer chain) intermediate.[29] Interestingly, the effect of lowering the reaction pressure from 35 to 10 bar is slightly different when the coupling reaction is performed at 60 °C (Table 3, Figure 10). In this instance, a higher conversion to products was achieved, and the product distribution differed significantly,

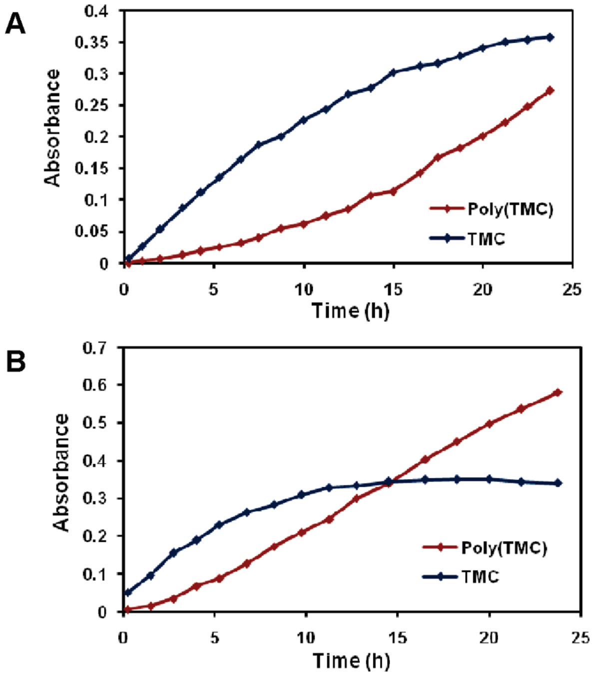
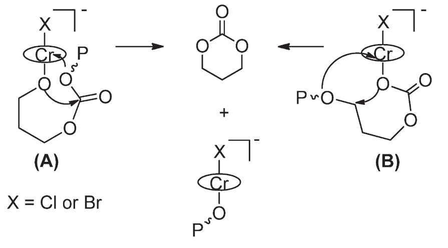


Figure 10. Reaction profiles obtained after deconvolution of selected IR spectra indicating poly(TMC) and TMC formation with time for the copolymerization of oxetane and CO_2. (A) Reaction carried out at 60 °C in toluene and at 35 bar of CO_2 pressure, in the presence of complex **1** and 2 equiv of *n*-Bu_4NBr. (B) Reaction carried out at 60 °C in toluene and at 10 bar of CO_2 pressure, in the presence of complex **1** and 2 equiv of *n*-Bu_4NBr.

Scheme 4



P represents the growing polymer chain

with almost equivalent quantities of poly(TMC) and TMC obtained after 24 h of reaction. This is most likely due to an enhancement of the formation of TMC via a backbiting mechanism through a metal-alkoxide intermediate (Scheme 4A). However, preformed TMC could undergo ring-opening polymerization by a coordination−insertion pathway more readily at 60 °C than at 50 °C.

Concluding Remarks

We have shown that the (salen)CrCl complex along with *n*-Bu_4NX (X = Br, I) is an effective catalyst system for the selective coupling of oxetane and CO_2, providing the corresponding polycarbonate with minimal amounts of ether linkages at 110 °C. The selectivity of the oxetane and CO_2 coupling process can be tuned by altering the nature of the anionic-based cocatalyst. Anions that are good leaving groups such as bromide and iodide, are more effective at yielding trimethylene carbonate by a backbiting process at the early stages of the coupling reaction. Furthermore, at lower reaction temperatures ($T < 80$ °C) the catalyst system (salen)CrCl/*n*-Bu_4NBr is capable of producing polycarbonate directly from the ROP of preformed TMC via a coordination−insertion pathway. Treatment of the (salen)CrCl with two equivalents of a bromide-based cocatalyst forms [*trans*-(salen)$CrClBr^-$] which exits in solution in a Schlenk equilibrium with the corresponding symmetric [*trans*-(salen)CrX_2^-] (X = Cl or Br) complexes as demonstrated by ESI-MS. Additional attempts at tuning the selectivity of the coupling reaction for trimethylene carbonate formation were achieved utilizing the aforementioned catalytic system under lower reaction temperatures and CO_2 pressures, where the formation of TMC by a backbiting mechanism is favored via a metal−alkoxide intermediate. Fundamental studies of the type described in this report should provide us with the knowledge to develop catalyzed methods to synthesize trimethylene carbonate via the ring-expansion of oxetane and carbon dioxide under mild reaction conditions.

Acknowledgment. We gratefully acknowledge the financial support from the National Science Foundation (CHE 05-43133) and the Robert A. Welch Foundation (A-0923).

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