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Coordination Chemistry Reviews
153 (1996) 155–174

COORDINATION
CHEMISTRY
REVIEWS

Catalysts for the reactions of epoxides and carbon dioxide

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Received 11 August 1995

Contents

Abstract

Oxiranes and carbon dioxide are known to cycloadd and/or copolymerize in the presence of a variety of catalysts. Indeed, cyclic carbonates are prepared on a technical scale by coupling epoxides and carbon dioxide. The fact that cyclic carbonate formation represents one of the

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0010-8545/96/$32.00
SSDI 0010-8545(95)01232-X

few examples of successful carbon dioxide utilization, coupled with the high reactivity of epoxides, has resulted in many papers which reveal a remarkable variety of active catalysts for the CO_2/epoxide coupling processes. Catalysts include simple alkali metal salts, ammonium salts, phosphines, main-group metal complexes, and both non-oxidative and oxidative transition-metal complexes. The purpose of this review is to compile the different catalysts into their general groups of similarity, with the hopes of shedding light on some of the important differences in reaction pathways. There generally appears to be a lack of detailed mechanistic studies; therefore, it is hoped that this review will emphasize where mechanistic clarification is most importantly needed. Furthermore, we anticipate that this review will provide insight into cyclic carbonate vs. polycarbonate production from the CO_2/epoxide coupling process.

Keywords: Carbon dioxide; Catalyst; Epoxide

1. Introduction

The utilization of carbon dioxide as a feedstock for the production of organic products continues to receive scrutiny. Thus far, very few economically feasible processes have been uncovered which utilize carbon dioxide. Walther has recently reviewed carbon dioxide activation in homogeneous-catalytic reactions [1]. As seen from the work described therein, in most cases metal-catalyzed carbon dioxide activation processes remain far inferior to traditional methods of preparation. Metal-catalyzed reactions of carbon dioxide and organic substrates typically result in low conversion numbers and selectivities. However, one of the more successful processes for CO_2 utilization is in polycarbonate and cyclic carbonate synthesis [2]. Indeed, a variety of complexes from simple alkali salts to classical organometallic complexes catalyze the coupling of epoxides and carbon dioxide to form cyclic carbonates and/or polycarbonates.

The search for environmentally beneign processes has been the impetus for much of the research involving epoxide and carbon dioxide coupling. Older conventional methods for cyclic carbonate production involved the use of phosgene, a very toxic chemical. Furthermore, aliphatic polycarbonates and copolymers containing aliphatic carbonate units are being used as biodegradable materials. Cyclic carbonates may be used as aprotic polar solvents and are also monomers for polymer synthesis.

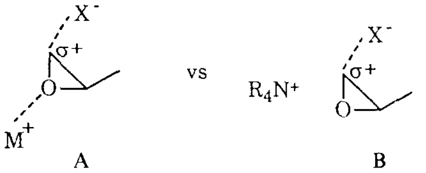
The formation of polycarbonates from oxiranes and CO_2 catalyzed by Et_2Zn/H_2O was first discovered in 1969 by Inoue et al. [3]. This discovery resulted in international efforts in obtaining more efficient catalysts for polycarbonate production. The bulk of this work occured thoughout the 1970s and early 1980s. Many catalysts were found to couple epoxides and carbon dioxide, forming only monomeric species — cyclic carbonates — whereas other catalyts formed both polymers and monomers. Most catalysts which formed polymers also formed cyclic carbonates as contaminants in varying amounts. Kuran and Rokicki reviewed the copolymerization reactions in 1981 [2], and since that time researchers have strived to develop catalytic systems of industrial importance. However, these efforts have been plagued by low reproducibility and the inability to achieve sufficiently high turnovers. A number of detailed mechanistic endeavors have recently been reported in efforts to design more efficient catalysts for both polycarbonate and cyclic carbonate production. However, as will be seen from this review of mechanistic work, these studies are only in their rudimentary stages of development.

The aim of this paper is to present a comprehensive review of the scientific literature which deals with carbon dioxide, epoxides, cyclic carbonates, polycarbonates and poly-alkoxy-carbonates; and the relationship of these species in reaction systems. Earlier work regarding copolymerization catalysts which was reviewed by Kuran and Listos [2] will only be mentioned when relevant to a clearer understanding of the literature described herein. The patents which cover this area will not be included, to avoid the obvious confusions characteristic of the patent literature.

2. Cyclic carbonate and/or polycarbonate synthesis via epoxides and CO_2

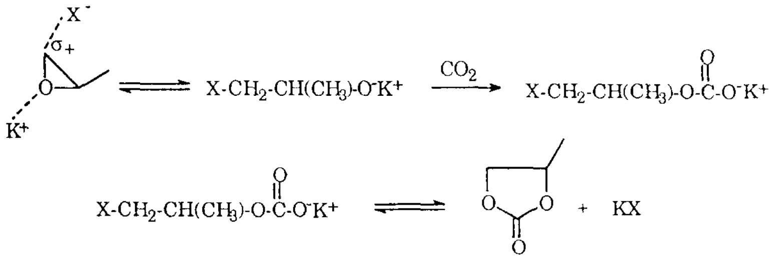
2.1. Cyclic carbonate formation via quaternary ammonium salts, phosphonium salt catalysts and Group 1 metal salts

Simple quaternary salts such as alkyl ammonium or phosphonium halides are extremely effective for high-yield conversions of many epoxides with carbon dioxide to form the corresponding cyclic carbonate [4]. Simple metal salts such as potassium chloride or sodium hydroxide are also effective catalysts. The onium salts having no interaction from the cation are expected to have highly reactive anions capable of nucleophilic attack [**B** in Eq. (1)]. However, the reduced nucleophilicity of the anion in metal salts may be compensated by the electrophilic interaction of the metal ion with an epoxide [**A** in Eq. (1)].



(1)

Though complexes of this type are capable of homopolymerizing epoxides, to date copolymers with CO_2 have not been obtained in these reactions. Until recently most reports have proposed a mechanism similar to Scheme 1, involving nucleophilic



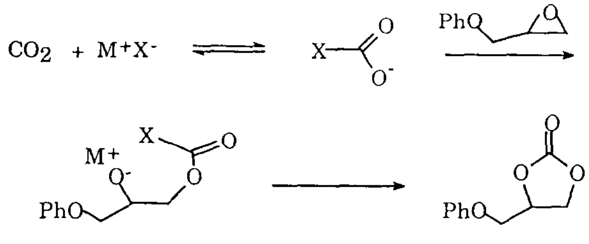
Scheme 1.

attack of the anion at the least-hindered carbon on the epoxide, carbon dioxide addition, intramolecular cyclization, and reformation of the anion. Cyclization has been proposed to be preferred rather than polymer formation, owing to the thermodynamic stability of five-membered cyclic carbonates.

Alkali metal salts have been used alone and in conjuction with crown ether or inorganic supports to catalyze the reaction of CO_2 and epoxides to form cyclic carbonates. Rokicki et al. have studied a variety of alkali metal salts in the presence of crown ethers [5]. After 24 h at 120 °C and 40 atm of CO_2, high yields of cyclic carbonates were obtained. Under these conditions the catalytic activity was found to increase with an increase in the anion nucleophilicity and cation diameter. No simple correlation was found between the reactivity of oxiranes and their tendency to form hydrogen bonds. Lack of polycarbonate formation is proposed to be a result of the thermodynamic stability of the five-membered cyclic carbonate. Interestingly, Vogdanis and Heitz have found that ethylene carbonate could be polymerized using a potassium carbonate catalyst under harsher conditions (150 °C) to form copolymer with low CO_2 content (17%) [6]. This investigation will be discussed in greater detail in Section 3.

Though Scheme 1 is the generally proposed mechanism, recent evidence has been presented which suggests alternative pathways for cyclic carbonate formation. A mechanistic study of the reaction of 2,3-epoxypropyl phenyl ether and carbon dioxide under atmospheric pressure has been reported by Kihara et al. [7]. Only halide salts showed a high activity, and their reactivity was as follows: chloride > bromide > iodide ~ fluoride. The lower activity of fluoride anion was attributed to its poor leaving ability. Lithium salts were more active than sodium salts, which in turn were more active than benzyltrimethylammonium salts. This trend correlates with the order of the Lewis acidity of the cation. Recall that under 40 atm of CO_2 pressure Kuran et al. [5] found increased catalytic activity with an increase in cation size; however, Endo et al. [7] have suggested that under high pressures of CO_2 a different mechanism may be at work (Scheme 2). Hence, CO_2 may first be activated by the nucleophile, which in turn interacts with the epoxide. Verification of this alternative mechanism has not yet been established.

Quaternary onium salts on polymer supports were found to be effective cyclic carbonate catalysts at atmospheric pressure of CO_2 [8]. By supporting the onium salts on insoluble polystyrene beads, the catalyst was easily separated by filtration,



Scheme 2.

thereby allowing for recycling of the catalyst. The proposed mechanism is analogous to that in Scheme 1 with the obvious removal of the Lewis-acid interaction of the metal ion. First-order rate constants were obtained and the energy of activation for the reaction of 2-phenoxymethyloxirane with CO_2 was estimated at 70.7 kJ mol^{-1}. The reaction rate was proportional to both catalyst and oxirane concentrations.

2.2. Cyclic carbonate and/or polycarbonate formation via Group 3, 4 and 5 metal complexes

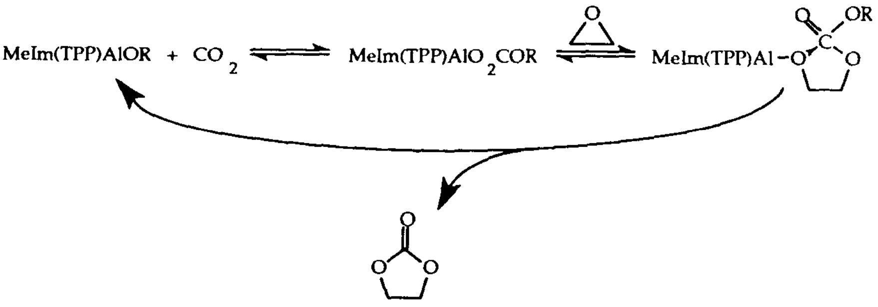
Main-group metal-ion–halide complexes have also been found to catalyze cyclic carbonate formation from carbon dioxide and oxiranes. In this instance the main disadvantage of these catalysts is that the systems require high concentrations of catalyst. In general these processes are run under high pressures of carbon dioxide, 50 kgf cm^{-2}, and temperatures ranging from 100 to 130 °C. However, there are now several reports of main-group metal systems which provide high-yield cyclic carbonate syntheses in atmospheric carbon dioxide.

Most main-group metal complexes which have been studied form only cyclic carbonates. However, Al(III) complexes have been shown in some cases to form polycarbonates. For example, triethylaluminum in the presence of triphenylphosphine has been shown to catalyze the formation of polycarbonates with low carbon dioxide content [9], whereas trichloroaluminum in the presence of triphenylphosphine catalyzes the formation of cyclic carbonates [10]. Al(III) porphyrin complexes have been found to form alternating copolymer with carbon dioxide and propylene oxide [11]. Some success has been observed using this Al(III) porphyrin system to form block copolymers containing polyether and polycarbonate linkages; however, very long reaction times were necessary; 15–40 days at room temperature [12]. The polymers formed were of low molecular weights (1200–9000 $\bar{M}_n$).

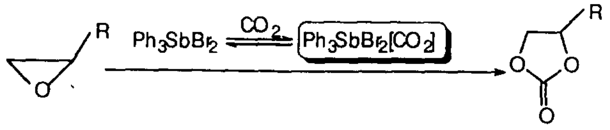
The addition of 1-methylimidazole to this system successfully catalyzes the formation of ethylene carbonate from ethylene oxide and CO_2 under mild conditions [13]. Mechanistic aspects investigated indicate that CO_2 insertion into the Al(III) alkoxide bond is enhanced by the addition of 1-methylimidazole. The addition of ethylene oxide to the CO_2 insertion product resulted in cyclic carbonate formation and reformation of the starting alkoxide. Scheme 3 was proposed based on the above observations.

Matsuda et al. found that triphenylstibonium dibromide and tetraphenylstibonium bromide were very effective catalysts for cyclic carbonate formation [14]. Greater than 90% yields were obtained in 8–16 min at 120 °C under 50 kgf cm^{-2} of CO_2. Relative epoxide reactivity was observed as follows, which is in the same order as the electron-donor ability of the epoxides in hydrogen bonding: propylene oxide > styrene oxide > ethylene oxide > chloromethyl ethylene oxide. It was proposed that CO_2 is activated by the stibonium catalyst, which in turn reacts with the epoxide as shown in Scheme 4 [15]. This mechanism was suggested based upon the observation that the antimony catalysts were more effective than tin catalysts (better Lewis acids).

Nomura et al. [16] observed that the reactivities of main-group organometallic halides had the following catalytic activity: $Sb > Te > Sn \gg Bi, Ge, Si$. Metal–chlorine bond distances were reported to be in the order $Sb^{V} > Te^{IV} > Sn^{IV}$; therefore, the



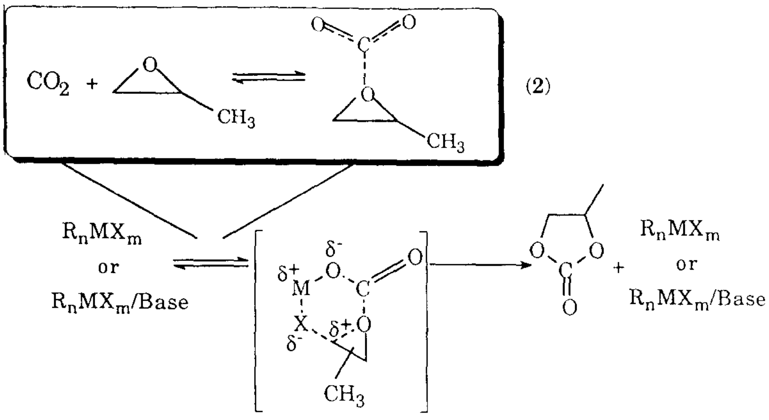
Scheme 3.



Scheme 4.

catalytic activity of the organometallic halides decreases with decrease in the bond length [16]. They further found that the introduction of Lewis bases to the system reversed the order of catalytic activity, Sn > Te > Sb ≫ Bi, Ge, Si. The most active binary systems, Ph_3SnBr-triethylamine and Me_2TeI_2-triphenylphosphine, were more effective than the most effective antimony compound, Ph_4SbBr. The reversed order of reactivities was explained by the following reasoning. The addition of base to a tetravalent organotin halide results in a five-coordinate trigonal bipyramidal complex with increased polarity of the Sn–halogen bonds. Furthermore, there remains an open sixth coordination site. While pentacoordinate organoantimony compounds also react with bases, a six-coordinate complex is formed which may result in a decrease in antimony–halogen bond polarity. These researchers reported a plausible reaction pathway in Scheme 5. Interestingly, they propose an initial CO_2–epoxide [Eq. (2)] interaction based on the appearance of a new absorption band at 260 nm in the UV spectrum upon forming a saturated solution of CO_2 in epoxide.

In contrast to mono- or diorganotin halides, which were found to catalyze the conversion of ethylene oxide and CO_2 to ethylene carbonate at 120 °C and 50 kgf cm^{-2} of CO_2 pressure [17], 1:1 complexes of Bu_3SnI and Bu_4PI are very effective catalysts for epoxide and carbon dioxide coupling [18]. Indeed, a variety of organotin halides exhibited the following reactivity order with 2-ethyloxirane at an atmospheric pressure of CO_2, which is reverse to the order of Lewis acidity: $Bu_3SnI > Me_3SnI > Bu_3SnBr > Ph_3SnI > Bu_3SnCl > Me_2SnI_2$. The addition of a Lewis base such as Et_4NBr was proposed to form a five-coordinate Sn complex with an activated tin–halogen bond. ^{119}Sn NMR was used to confirm formation of five-coordinate complexes. The coupling of typically inactive or acid-sensitive oxiranes with carbon dioxide was also reported using organometallic tin/quaternary onium salt combinations. High-yield conversions to the corresponding carbonates were obtained



Scheme 5.

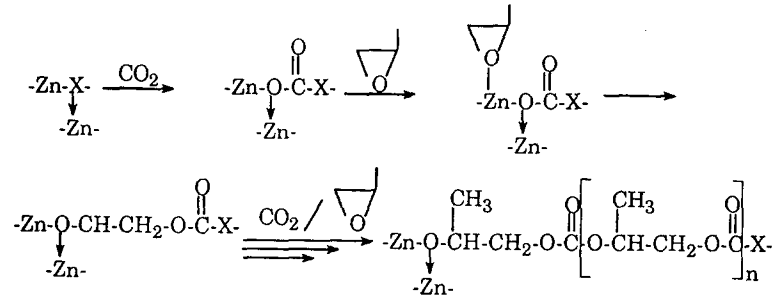
from epoxides such as allyl glycidyl ether and glycidyl methylacrylate at 40 °C and under 50 kgf cm^{-2} of CO_2 pressure. More vigorous conditions, 100 °C, 5 h and 50 kgf cm^{-2} of CO_2, were required for high conversion of 2,2-dimethyloxirane.

2.3. Polycarbonate and/or cyclic carbonate formation via Group 12 metal complexes

2.3.1. M(II) alkoxide and carboxylate catalysts

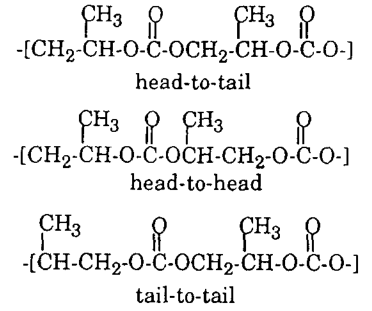
2.3.1.1. General. Of the group 12 metals, Zn(II) complexes have been the most studied, owing to the higher activity in comparison to cadmium catalysts [2]. Indeed, Cd(II) analogs of active Zn(II) copolymerization catalysts are less active. We have recently taken advantage of the relative softness of Cd(II) in comparison with Zn(II) to isolate and structurally characterize some very rare metal epoxide carboxylates [19]. In light of the initial success of a variety Zn(II) species to catalyze the reaction of epoxides and carbon dioxide to form polycarbonates, the bulk of research has focused on Zn(II) chemistry [2]. Some of the initial understandings in these processes were the following. A variety of metal coordination complexes catalyzed polymer synthesis generally at relatively mild temperatures (below 100 °C). In general, Zn(II) carboxylates or alkoxides containing bi- or trifunctional groups such as glutarate or pyrogallol were the most active. Condensed Zn(II) complexes were proposed as necessary for polycarbonate formation owing to an interaction with a neighboring Zn(II) complex as shown in Scheme 6.

Higher temperatures resulted in increased cyclic carbonate yield; therefore, cyclic carbonates are assumed more thermodynamically stable and were not intermediates in polymer formation. Polycarbonate formation was assumed to proceed via an anionic mechanism by the coupling of a carboxylate, alkoxide or carbonate with a epoxide, CO_2 insertion, etc. These mechanistic features have been supported by observing the carboxylate or alkoxide at the end of the polymer chain. Carbon dioxide insertion into metal alkoxide bonds has also been well established.



Scheme 6.

Earlier efforts have reported that the polycarbonates formed from propylene oxide and Zn(II) catalysts was predominantly head-to-tail polycarbonate; however, Lednor and Rol have reported that polycarbonates formed from typical Zn(II) copolymerization catalysts consisted of head-to-tail, head-to-head and tail-to-tail units, with approximately 70% head-to-tail propylene oxide units [20].



$$-[CH_2-\overset{CH_3}{CH}-O-\overset{O}{C}-OCH_2-\overset{CH_3}{CH}-O-\overset{O}{C}-O-]$$

head-to-tail

$$-[CH_2-\overset{CH_3}{CH}-O-\overset{O}{C}-O\overset{CH_3}{CH}-CH_2-O-\overset{O}{C}-O-]$$

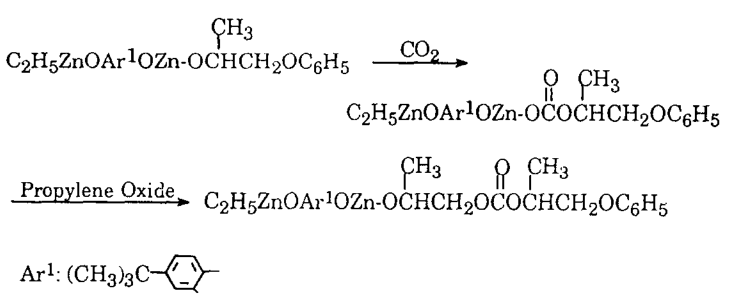
head-to-head

$$-[\overset{CH_3}{CH}-CH_2-O-\overset{O}{C}-OCH_2-\overset{CH_3}{CH}-O-\overset{O}{C}-O-]$$

tail-to-tail

(3)

2.3.1.2. *Mechanistic investigations.* Very recently Kuran and Listos reported mechanistic studies concerning this process using catalysts based on diethylzinc and polyhydric phenols [21]. ^{13}C NMR studies were conducted with a homogeneous $ZnEt_2/Ar^1(OH)_2/PhOPrOH$ (2:1:1) catalyst. Carbon dioxide insertion was observed by NMR. After CO_2 removal, the complex was reacted with propylene oxide at 85 °C for 20 h. Upon work-up the NMR data indicated CO_2 insertion followed by consecutive incorporation of propylene oxide.

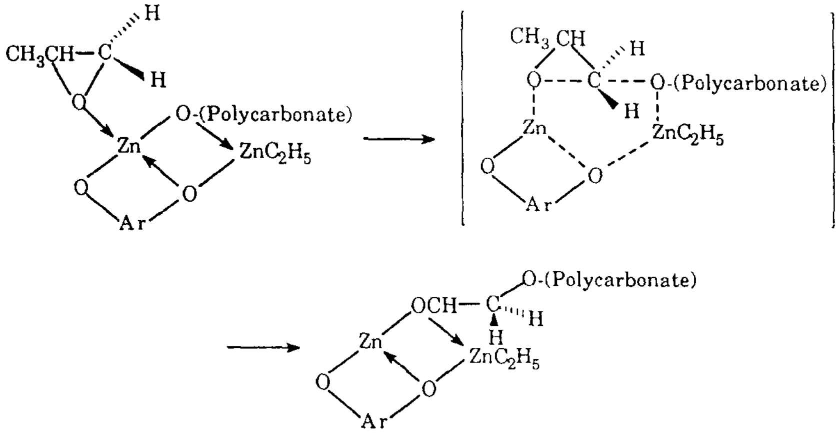


$$C_2H_5ZnOAr^1OZn-O\overset{CH_3}{C}HCH_2OC_6H_5 \xrightarrow{CO_2} C_2H_5ZnOAr^1OZn-O\overset{O}{C}O\overset{CH_3}{C}HCH_2OC_6H_5$$

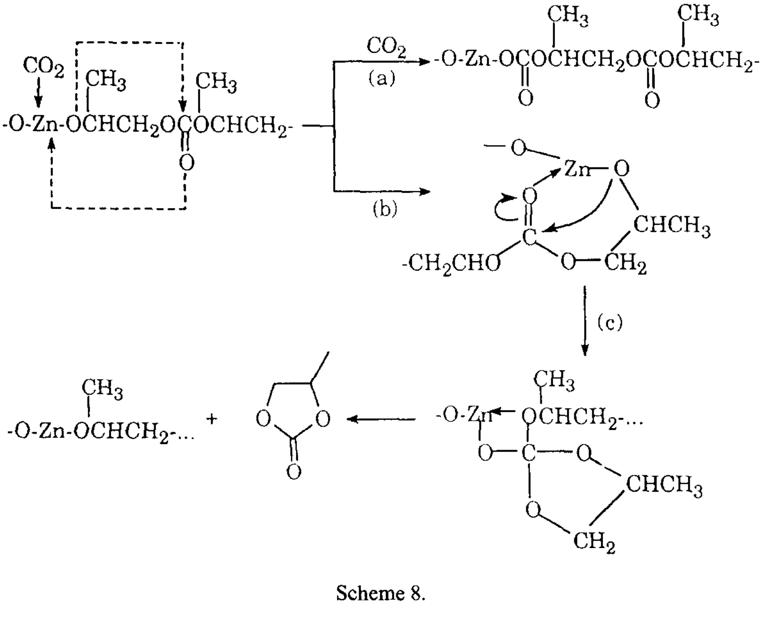
$$\xrightarrow{\text{Propylene Oxide}} C_2H_5ZnOAr^1OZn-O\overset{CH_3}{C}HCH_2O\overset{O}{C}O\overset{CH_3}{C}HCH_2OC_6H_5$$

(4)

Copolymer formation was suggested to proceed via a transition state as described in Scheme 7. Propylene carbonate was proposed to proceed along a reaction pathway illustrated in Scheme 8. The postulated mechanisms rationalize the common observation that Zn(II) complexes containing more than one Zn(II) atom increase the 'probability' that the complex will be catalytically active for copolymer formation. Monoprotic compounds such as ($ZnEt_2$/PhOH (1:2)) appeared to promote the propylene oxide/CO_2 cyclization to propylene carbonate. It was suggested that at least two zinc atoms per complex were necessary in order to promote copolymeriza-



Scheme 7.

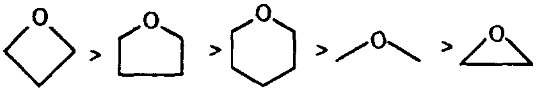


Scheme 8.

tion rather than cyclization. The copolymerization reactions were generally carried out at 35 °C at 60 atm of CO_2. Higher temperatures usually increased the yields of cyclic carbonate, although the yields were generally quite low; 1.5–20.1%.

Gorecki and Kuran have also studied the effects of different substituents on the trihydric phenol in the copolymerization of carbon dioxide and propylene oxide using the $ZnEt_2$-trihydric phenol [22]. A variety of different trihydric phenols were used, with polymer yields ranging from 10 to 70% with respect to propylene oxide. Reaction times were either 45 or 90 h at 35 °C. The most active complex was a $ZnEt_2$/4-bromopyrogallol catalyst: however, trends as far as activity vs. the electronic and/or steric properties were not given.

As mentioned earlier, we have used the softer Cd(II) metal ion with tris-3-phenylpyrazolyl hydroborate ligand to isolate and characterize several metal–epoxide carboxylates (Fig. 1), which are proposed as models for the initial step in the Zn(II)-catalyzed copolymerization of epoxides and carbon dioxide [19]. ^{113}Cd NMR was used to observe the epoxide coordination to the metal at low temperatures. As expected, the epoxide coordination is very weak [23]; hence, the coupling of the epoxide to the carboxylate required vigorous conditions.



(5)

2.3.1.3. *Depolymerization and degradation studies.* Besides the back-biting mechanism for cyclic carbonate formation described in Scheme 8, cyclic carbonates were also found to form by the catalytic depolymerization of polycarbonates. In other words, typical catalysts used for copolymerization reactions are also catalysts for

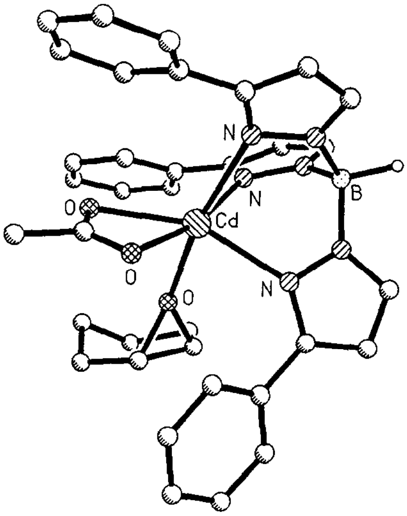
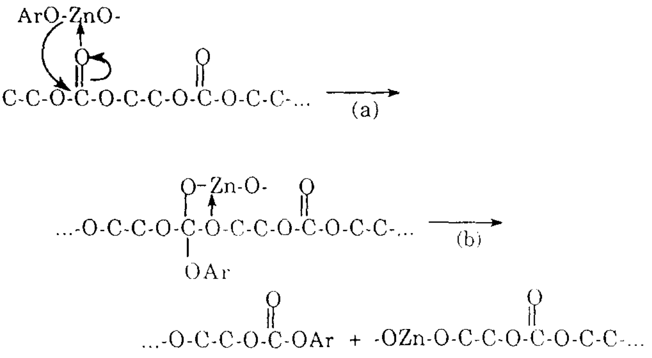


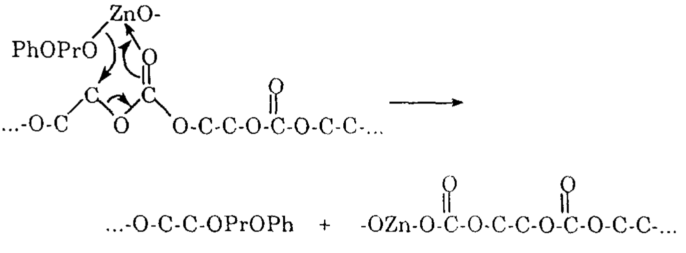
Fig. 1. Ball-and-stick representation of (η^3-HB(3-Phpz)$_3$)Cd(acetate)·cyclohexene oxide.

the degradation and depolymerization of polycarbonate. Yields for cyclic carbonate appear to be similar to the yields of cyclic carbonates formed in actual copolymerization runs. Propylene carbonates are also reported to be formed directly from carbon dioxide and propylene oxide in copolymerization systems. A study of the catalytic depolymerization of polypropylene carbonate was reported by Kuran and Listos [24]. In their study, degradation of the polymer in the presence of high concentrations of catalyst resulted in the incorporation of the catalyst aromatic moiety into the chain as an end group of the polymer. This result was explained by the process in Eq. (6), which results in polymer degradation and a lowering of the polymer intrinsic viscosity.



(6)

Depolymerization was suggested to occur via one of two pathways, which depended on the specific catalyst. For example, propylene carbonate formation was considered to follow a pathway similar to Scheme 8, discussed earlier, using $ZnEt_2/Ar_2(OH)_3$ (2:1) as a depolymerization catalyst, whereas $ZnEt_2$/PhOPrOH (1:2) was inactive in the earlier stages of the reaction for depolymerization reactions. The process depicted in Eq. (7) was suggested as an alternative mechanism for degradation for catalysts in which depolymerization did not also occur.



(7)

2.3.2. Zn(II) halide/quaternary salt catalysts

Kisch et al. have used a variety of zinc halide/onium salt combinations as cyclic-carbonate-producing catalysts [25]. The reactions were carried out at room temperature and under an atmospheric pressure of carbon dioxide. Of the variety of different Zn(II) halide combinations, the highest yields were obtained with a $ZnCl_2/(^nBu)_4NI$ catalyst. A mechanistic study of a variety of catalyst combinations using different halides led the authors to conclude that solvated Zn(II) chloride and trihalogenozincates are the Lewis acids which catalyzed the nucleophilic ring opening of the epoxide by the iodide [26]. The Lewis acid was proposed to stabilize the iodo alcoholate, which in turn reacts with carbon dioxide, forming linear carbonate. Evidence for this Lewis-acid stabilization was shown by the reaction using [2-D]-2-phenyloxirane. The linear carbonate forms cyclic carbonate by intramolecular substitution of iodide. Copolymer was not formed in this system. Electron-releasing groups on the epoxides were found to accelerate the reaction unless the groups were sterically demanding. Activation parameters were estimated at $\Delta H^{\neq} = 71.4 \pm 3.7$ kJ mol^{-1} and $\Delta S^{\neq} = -49.2 \pm 9.3$ J K^{-1} mol^{-1}.

2.4. *Polycarbonate and/or cyclic carbonate formation via Group 6–11 metal complexes*

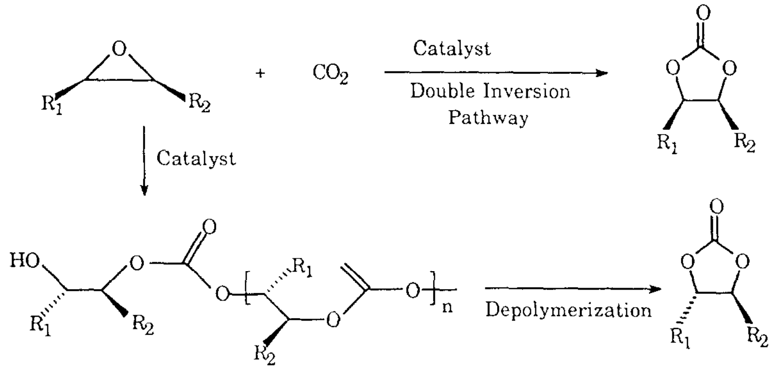
A variety of coordination complexes such as chromium(III) acetate and cobalt(III) acetate have been found to catalyze the copolymerization of carbon dioxide and epoxides [2]. However, these complexes are less effective than Zn(II) complexes and have been studied less. Kisch et al. have observed that $MoCl_5$ and $FeCl_3$ in the presence of phosphine or quaternary salts catalyze the coupling of propylene oxide and carbon dioxide to form propylene carbonate [25]. Similar Zn(II) complexes mentioned earlier are more effective, and therefore more research has been applied in this area.

2.4.1. *Catalysis through non-redox processes*

Chromium(III) tetra-*p*-tolylporphyrinate with amine cocatalysts were reported by Kruper and Dellar to be very efficient catalysts for cyclic carbonate formation via carbon dioxide and epoxide [27]. Various epoxides were investigated, and of these, interestingly, cyclohexene oxide upon reacting with carbon dioxide formed low-molecular-weight polycarbonates. Low-molecular-weight oligomeric carbonates were observed with propylene oxide. In some cases, turnover numbers approached 10000 per metal, and the catalyst was also reported to be recyclable. A temperature range between 60 and 100 °C over a period of 16 to 90 h at 730–780 lbf in^{-2} was observed, depending on the starting material. Two mechanisms were reported for the conversion of starting material to product as depicted in Scheme 9. This mechanistic interpretation was based upon the the stereochemistry of the resulting product. For example, *trans*-polycyclohexane carbonate was obtained from cyclohexene oxide. The reaction of carbon dioxide with cyclopentene oxide resulted in the formation of the *cis*-cyclopentene carbonate which allowed the author to suggest two possible mechanisms. Direct insertion with double inversion with retention of stereochemistry may have occurred, or polymerization/depolymerization with inversion of stereochemistry may be operating, or possibly both mechanisms may be occurring.

2.4.2. *Catalysis through redox processes*

Classical organometallic complexes such as $(Ph_3P)_2Ni$ couple epoxides and carbon dioxide to form cyclic carbonates exclusively [28]. Oxidative addition is proposed to occur, followed by carbon dioxide insertion and subsequent reductive elimination.

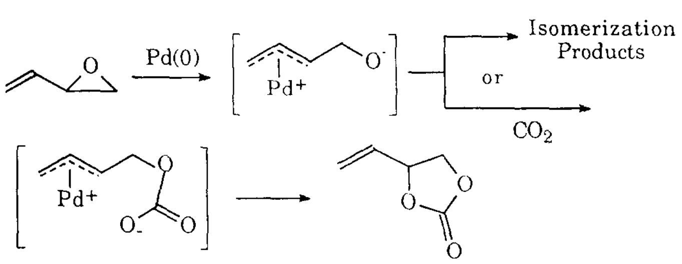


Scheme 9.

Control experiments have revealed that, while phosphines are somewhat active catalysts alone for cyclic carbonate formation, the organometallic complex shows far superior catalytic activity. A microwave study using *trans*-1,2-dideuterioethane as a substrate resulted in the formation of a 1:1 mixture of *cis*- and *trans*-1,2-dideuterioethene carbonate [29]. The loss of stereospecificity is proposed to be the result of a one-electron transfer from nickel(0) to the epoxide. Interestingly, in the same study, the use of a Cu(I) cyanoacetate catalyst which was previously shown to be active towards propylene carbonate production [30] resulted in more than 95% *trans*-1,2-dideuterioethene carbonate.

Organometallic Pd complexes are effective catalysts for carbon dioxide coupling with vinyl epoxides. Fujinami et al. reported 96% yield conversion of 1,3-butadiene monoxide to the corresponding carbonate at 0 °C under a CO_2 atmosphere for 15 min [31]. While there was only limited mechanistic information, Scheme 10 was presented as a possible mechanism in which it is believed that the reaction occurs by oxidative addition of the epoxide to the metal.

Trost and Angle have reacted a variety of vinyl epoxides with carbon dioxide in the presence of a Pd(0) triisopropylphosphite complex catalyst to form high yields of the corresponding cyclic carbonate [32]. By using palladium as a template, the regioselectivty was controlled by converting an intermolecular reaction into a intramolecular reaction with a nucleophile.



Scheme 10.

Aye et al. have reported the use of $PtMe_2$(1,10-phenanthroline), 1, to isolate a complex which results from its reaction with styrene oxide in the presence of carbon dioxide. This complex was suggested to model an intermediate formed in the activation of epoxides/CO_2 by transition-metal complexes which proceed through a redox process. By using (R)-styrene oxide these researchers observed rention of configuration at the chiral carbon center upon oxidative addition [33]. The X-ray crystal stucture of one isomer was determined and is displayed in Fig. 2. An S_N2 mechanism for oxidative addition was shown by following the reaction of 1 with *trans*-CHDCHPhO and carbon dioxide by NMR techniques as seen in Scheme 12.

Recently, Rh(I) has also been found to catalyze the conversion of styrene oxide and CO_2 to form the corresponding cyclic carbonate [34a]. An electrochemical nickel-catalyzed reaction formed cyclic carbonates in good yields from terminal epoxides and carbon dioxide [34b]. Very mild conditions, room temperature and atmospheric pressure, were employed using the catalyst $Ni(cyclam)Br_2$.

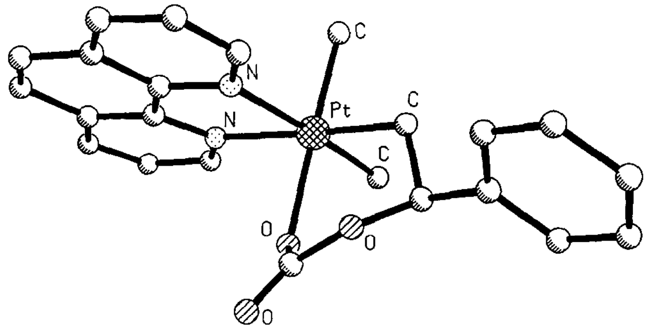
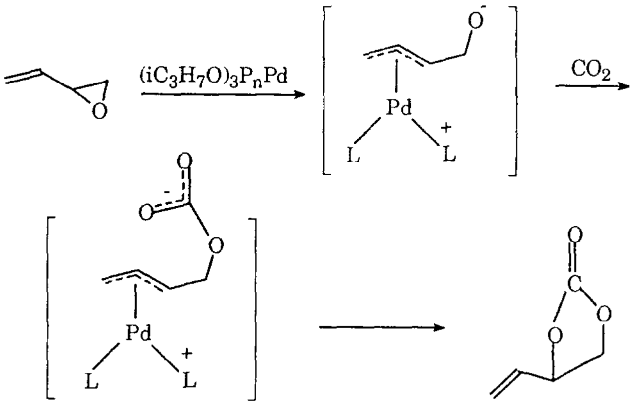
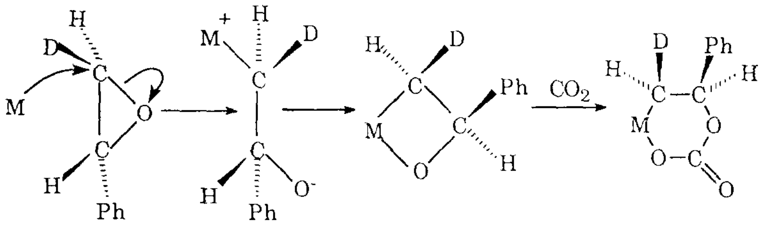


Fig. 2. Ball-and-stick representation of complex resulting from the reaction of $PtMe_2$(1,10-phenanthroline) with styrene oxide and CO_2.



Scheme 11.



Scheme 12.

3. Ring-opening polymerizations of cyclic carbonates

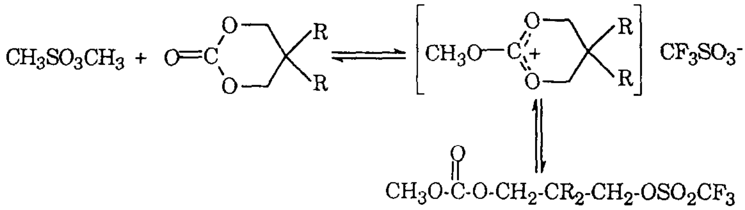
3.1. General

Cyclic carbonates may be polymerized by either anionic or cationic initators. Five-membered ring cyclic carbonates are formed from epoxide and carbon dioxide coupling. Polymerizations of these cyclic carbonates — for example, ethylene carbonate — are known to occur. However, pure poly(ethylene carbonate) is never formed from five-membered cyclic carbonates regardless of the catalyst type or reaction conditions; poly(ether-carbonate) with a maximum of 50% carbonate linkages is formed, in which the polyether formation results from decarboxylation. This carbon dioxide loss has been suggested to help drive the polymerization via the entropy bonus of gas formation [35]. Apparently, the polymerization reaction occurs above the ceiling temperature for polycarbonate formation. In contrast, the polymerization of six-membered cyclic carbonates may result in pure high-molecular-weight polycarbonates.

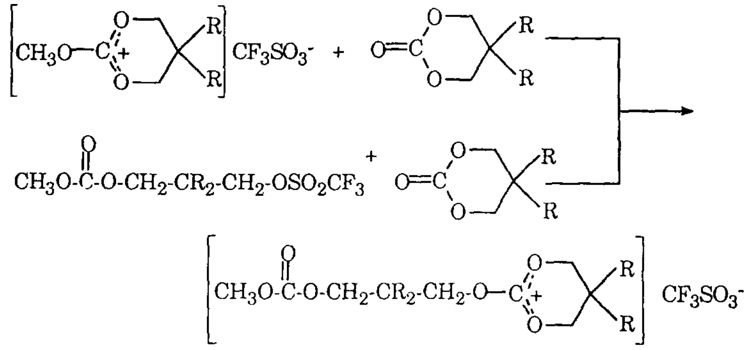
In general the copolymerization of epoxides and carbon dioxide is conducted in the temperature range of 0–100 °C. Ideal temperatures for five-membered cyclic carbonate formation, depending on the nature of the catalyst, ranged from 0 °C to 130 °C. Higher temperatures, 140–180 °C, with a suitable catalyst are required for the polymerization of five-membered cyclic carbonates. Interestingly, six-membered cyclic carbonates are generally polymerized at moderate temperatures (below 100 °C).

3.2. Cationic catalysts

Attempts to polymerize ethylene carbonate by Kricheldorf and co-workers using the cationic initiator methyltriflate resulted in no reaction at 20 or 60 °C, and unidentified decomposition products at 100 °C [36,37]. In contrast, trimethylene carbonate and neopentane-diolcarbonate, six-membered carbonates, were efficiently polymerized to form polycarbonates at 50 or 80 °C with a variety of initiators. Six-membered cyclic carbonates which were polymerized by BF_3, $SnCl_4$ or $SbCl_5$ formed polymer with partial decarboxylation, and are thought to proceed via a cationic mechanism [38]. However, $TiCl_4$ and Bu_3SnOMe were reported to polymerize cyclic carbonates via an insertion reaction without decarboxylation (see below). While high yields of polycarbonates were obtained with trimethylene carbonate, only low-molecular-weight polymer was formed (below 5000) using the initiator methyltriflate. Low molecular weights were due to extensive back-biting degradation reactions that were demonstrated by time/conversion curves. Mechanistic investigations were carried out by monitoring the reactions of 1:1 and 1:2 mixtures of methyltriflate and cyclic carbonate with ^{1}H NMR. The reaction in Eq. (8) was faster than the propagation of the trioxocarbenium ion [Eq. (9)]. The reaction in Eq. (10) was also suggested to occur at higher rates than that of Eq. (9). Ether groups were found in the copolymer, which indicated some decarboxylation had occurred.



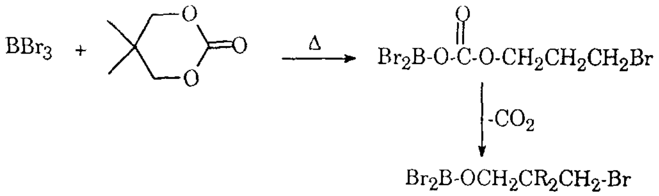
(8)



(9)

(10)

BBr_3, BCl_3, and BF_3OEt_2 were also used as initiators for the polymerization of trimethylene carbonate [39]. BCl_3 was inactive, whereas BBr_3 reacted in the presence of a double molar amount of trimethylene carbonate by a stoichiometric ring-opening with bromine atom transfer [Eq. (11)].



(11)

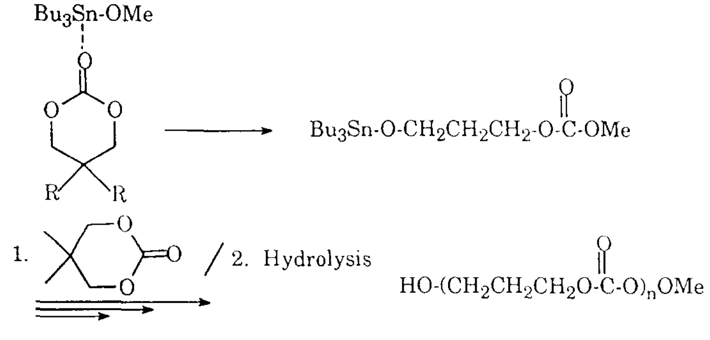
BF_3·trimethylene carbonate was a efficient polymerization catalyst, and molecular weights greater than 100000 were obtained. Ether groups in the polymer suggested some decarboxylation had occurred. $SnCl_4$ and $SnBr_4$, strong Lewis acids, were also good initiators for six-membered cyclic carbonate polymerizations with some carbon dioxide loss. $Bu_3Sn(OMe)_2$ and Bu_3SnOMe, weak Lewis acids, were also good initiators for the polymerization reaction: however, ether linkages were not observed, and therefore Kricheldorf and co-workers propose an insertion mechanism.

3.3. Anionic catalysts

As seen from the work of Kricheldorf and co-workers with the polymerization of six-membered cyclic carbonates, carbon dioxide content is extremely sensitive to the catalyst used [39]. Indeed, by varying the Lewis acidity of the catalyst, the polymerization reaction may vary from a cationic reaction mechanism to an anionic reaction mechanism. Weak Lewis acids such as $Bu_3Sn\text{-}OMe$ are proposed to react with six-membered cyclic carbonates via Scheme 13 to form pure polycarbonates. Complexation of the cyclic carbonate enhances the electrophilicity of the monomer, which is proposed to ring-open via cleavage of the O–acyl bond.

Heitz and co-workers have compared the reactivity of a variety of catalysts in the polymerization of ethylene carbonate, a five-membered ring [6,35]. Transesterification catalysts like dibutyldimethoxytin and zirconium tetrabutalnolate formed polymer containing almost 50% oxycarbonyloxy units. Alkali carbonates were also active catalysts; however, the oxycarbonyloxy content was much lower — 17–22%. The addition of amines to the tin catalysts improved the rate of polymerization but lowered the carbon dioxide content, whereas the addition of phosphines to the tin catalysts increased the copolymerization rate without increasing carbon dioxide loss. In all reports, to date, varying amounts of carbon dioxide are lost throughout the process of polymerizing five-membered cyclic carbonates. Apparently, the polymerization temperature is above the ceiling temperature for the alternating copolymer formation. The entropy bonus of CO_2 loss also helps to drive the polymerization process.

The copolymerization of propylene oxide and ethylene oxide with the five-membered cyclic carbonates, propylene and ethylene carbonates has been reported by Kuran and Listos in which polymer yields were less than 50% after applying a 80 °C temperature for seven days [40]. Systems involving the familiar $diethyl_2Zn$/pyrogallol catalyst contained molecular weights which ranged from 1000 to 2000. Upon using $diethyl_2Zn$/phenol as a catalyst, similar yields were obtained;



Scheme 13.

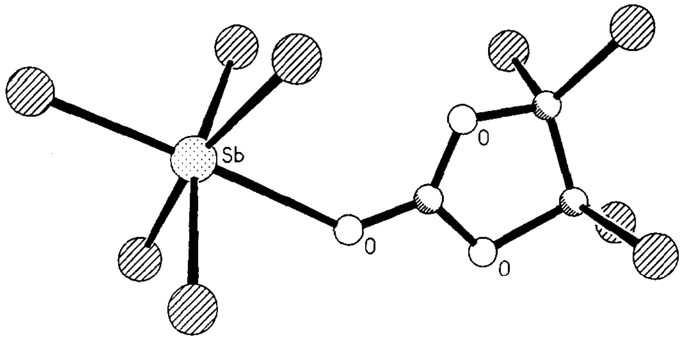


Fig. 3. Ball-and-stick representation of $SbCl_5$(tetrachloroethylene carbonate).

however low molecular weights resulted (135–1500). Polycarbonate content ranged from 5% to 50%. High polycarbonate content (50%) in the polymer was achieved by a high ratio of cyclic carbonate to epoxide.

Ethylene carbonate has also been copolymerized with cyclic amines [41]. The copolymerization of ethylene carbonate with aziridine proceeds spontaneously, and forms oily polymer with low molecular weights (400–2000). These polymers were found to have high polyaziridine content. The addition of base such as triethylphosphine or triethylamine resulted in polymer with alternating copolymers.

3.4. Cyclic carbonate–metal complexes

The formation of cyclic carbonate–metal complexes has also been investigated. Indeed, one might predict metal–cyclic carbonate complexes to be of some importance in the possible reaction schemes for ring-opening and polymer formation, especially in light of the observed sensitivity to the catalyst type. To date there is only one crystal stucture of cyclic carbonate coordination to a metal. This complex, $SbCl_5$(tetrachloroethylene carbonate) [42], shown in Fig. 3, has been described in some detail by Huheey [43]. The bond-length changes of the tetrachloroethylene carbonate upon coordination to the metal were dramatically illustrated by comparing the complexed species with the uncomplexed species. Evidence for metal-catalyzed ring-opening is illustrated by noting that the C–O (ester) bonds are weakened and lengthened upon complexation with the metal halide.

Kricheldorf and Weegen-Schultz have isolated a host of Lewis acid–cyclic carbonate complexes [44]. Examples of these complexes include boron, tin, titanium and antimony halide complexes with coordinated ethylene, trimethylene and 2,2-dimethyltrimethylene carbonates. Evidence for coordination of the carbonate group was obtained by ^{13}C NMR, in which the carbon on the carbonyl moiety shows a larger downfield shift than the other carbons. IR spectra were shown to display a significant bathochromic shift ($100–150\ cm^{-1}$) and a splitting of the carbonyl band.

4. Conclusions

Related areas include the copolymerization and/or cyclic formation of carbon dioxide with oxetanes [45–49], thiiranes [50], and cyclic imines. However, the high reactivity of epoxides coupled with relative cheapness of, for example, propylene oxide has stimulated the majority of research in this area. Future directions are to understand reaction pathways more definitively, and to find more active catalysts for the production of epoxide/CO_2 copolymers.

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