A facile catalytic synthesis of trimethylene carbonate from trimethylene oxide and carbon dioxide

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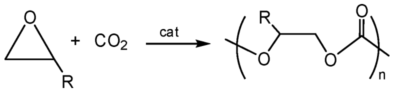
Received 21st May 2010, Accepted 29th June 2010
First published as an Advance Article on the web 19th July 2010
DOI: 10.1039/c0gc00136h

The coupling of oxetane (trimethylene oxide) and carbon dioxide catalyzed by VO(acac)$_2$ in the presence of an onium salt was studied. The process was found to be highly selective and quantitative for the production of the six-membered cyclic carbonate, trimethylene carbonate, under very mild reaction conditions of 60 °C and 1.7 MPa. Other derivatives of trimethylene oxide were shown to similarly selectively afford the corresponding cyclic carbonates upon reaction with CO$_2$.

Carbon dioxide is an abundant, inexpensive, and nontoxic source of chemical carbon. Hence, its utilization as a feedstock for providing value-added products has drawn much attention during the last two decades.[1] Concomitantly, it is a greenhouse gas and a direct effect of its utilization by chemical means plays a role in curtailing CO$_2$ emissions at power-generation plants or industrial processes. Alternatively, an indirect effect would result from waste reduction and the health and safety benefits derived from toxic chemicals substitution. The preparation of aliphatic polycarbonates and/or cyclic carbonates *via* the metal-catalyzed coupling of epoxides with CO$_2$ represents one of the most promising methodologies for achieving these goals (eqn (1) and (2)).[2] Similarly, we have demonstrated that these same catalyst systems, *e.g.*, (salen)CrCl in the presence of onium salts, are capable of affording polycarbonates from oxetane and CO$_2$.[3]



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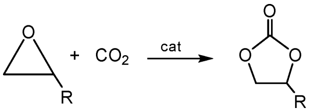
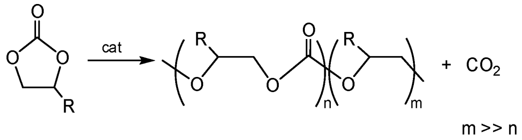


(2)

A major difference between the coupling of CO$_2$ and three- and four-membered cyclic ethers is that the resulting cyclic carbonates have opposite thermal stabilities relative to their respective copolymers.[4] That is, the five-membered cyclic carbonate afforded from epoxides is more stable than its ring-opened polymer, and hence its ring-opening polymerization reaction occurs with significant loss of CO$_2$ (eqn (3)).[5] On the other hand, the six-membered cyclic carbonate is thermodynamically less stable than its polymer, and thus retains CO$_2$ when it undergoes the ring-opening polymerization process (eqn (4)).[6]

The proposed pathway for cyclic carbonate production from cyclic ethers and carbon dioxide involves a backbiting reaction from the initial ring-opening process with subsequent CO$_2$ insertion or later on from the growing polymer chain. This is illustrated below for the coupling of oxetane and CO$_2$ utilizing a metal catalyst and anion initiator (eqn (5)) Although epoxides are easier to ring-open than oxetane because of higher ring-strain, oxetane is a much better ligand for binding to metals. The pK_b of oxetane is 3.13 *vs.* 6.94 for propylene oxide. It should be noted here as well that the process depicted in eqn (5) is enhanced in the initial steps if X is a good leaving group. Recently, we have employed this feature of the reaction mechanism for tuning the reaction pathway for poly(trimethylene carbonate) formation from oxetane and CO$_2$ to proceed *via* preformed trimethylene carbonate by way of ring-opening polymerization.[7] This was accomplished by means of utilizing a less electrophilic cobalt(II) Schiff base complex which prevents polymer chain propagation or using (salen)CrCl in the presence of *n*-Bu$_4$NBr and lowering the reaction temperature where six-membered cyclic carbonate production is enhanced over polymer chain growth. It is worthwhile noting that copolymer formation by way of CO$_2$ and oxetane enchainment generally results in a copolymer with some ether linkages, *i.e.*, not a completely alternating copolymer.



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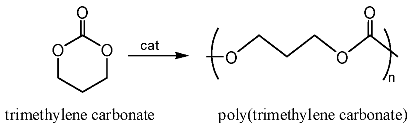

(4)

Trimethylene carbonate is traditionally synthesized from 1,3-propanediol with phosgene or its derivatives (di- and triphosgene) which are highly poisonous gases. Alternatively, it can be produced in a greener more sustainable manner by transesterification of 1,3-propanediol and dialkylcarbonate. This is particularly true since both 1,3-propanediol and dialkylcarbonate are available from renewable resources, namely, glycerol or glucose, and propylene oxide/CO$_2$, respectively.[8] On a related note, numerous reports have demonstrated binary systems composed of a simple metal complex and an onium salt, such as ZnCl$_2$

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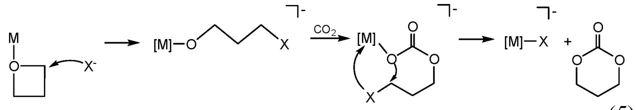
or VCl_3 and n-Bu_4NOAc or n-Bu_4NI to be effective catalysts for the coupling of epoxides and carbon dioxide to provide cyclic carbonates in good yield.[2,9] Trimethylene carbonate has been shown to undergo ring-opening polymerization to yield poly(trimethylene carbonate) with complete retention of its CO_2 content by a variety of benign metal- as well as organo-catalysts.[4,10] This is of importance since these polymers are major components of biomaterials for the preparation of various medical devices.[11]



(5)

Herein, we describe a catalytic system for the efficient synthesis of trimethylene carbonate (TMC) from oxetane and CO_2 involving a readily available complex derived from a biocompatible metal, $VO(acac)_2$ (acac = acetylacetonato or 2,4-pentadiono) which serves as a Lewis acid for the activation of oxetane, and n-Bu_4NBr which provides the nucleophile for ring-opening oxetane. In a typical experiment a green solution of $VO(acac)_2$ (2.5–5.0 mol%) in oxetane (4.0 g or 0.069 mol) containing one equivalent of n-Bu_4NBr, and in some instances with added toluene (10 mL), was introduced into a previously dried at 100 °C under vacuum stainless steel Parr autoclave.[12] The reactor was pressurized with carbon dioxide and heated to 60 °C for the described time. Upon cooling the autoclave in an ice bath and venting the excess CO_2 in a fume hood, the contents of the reactor were extracted with dichloromethane and the conversion to cyclic carbonate was measured by ^{1}H NMR spectroscopy. The product was isolated as a green-brown solid (6.56 g) which contained the $VO(acac)_2/n$-Bu_4NBr catalyst and trimethylene carbonate. The cyclic carbonate product was purified by elution from a silica-gel column by diethyl ether, gradually increasing the solvent's polarity to 10% dichloromethane to provide a white solid in a 60% yield. The melting point, determined by DSC, was found to be 47.1 °C (literature value 45–47 °C).[13] Anal. Calcd. for $C_4H_6O_3$: C, 47.06; H, 5.92; Found: C, 47.22; H, 6.10. ^{1}H NMR in $CDCl_3$ δ (ppm): 4.45(t, 4H, J = 6 Hz, CH_2O), 2.14 (quintet, 2H, J = 6 Hz, CH_2). ^{13}C NMR in $CDCl_3$ δ (ppm): 148.4 ($C{=}O$), 67.8 (CH_2O), 21.5 (CH_2). IR in CH_2Cl_2 (cm^{-1}): 675(s), 756(vs), 779(m), 1064(m), 1110(vs), 1140(s), 1186(vs), 1249(s), 1417(s), 1463(m), 1726(s), 1744(m), 2914(vw), 2927(vw), 2960(vw), 2983(vw) and 3018(vw).

Early reports on the formation of trimethylene carbonate from oxetane and CO_2 have utilized tetraphenylstibonium iodide or organotin iodide/n-Bu_3PO catalysts which operate under harsher reaction conditions.[14,15] Furthermore, these processes were not well-developed as synthetic methodologies for the preparation of TMC. So far there have been no communications for catalyzing the selective coupling of oxetane and CO_2 to provide TMC utilizing transition metal coordination complexes, especially those derived from biocompatible metals such as vanadium. The process described here is much greener, *i.e.*, produces less waste and utilizes less energy, than the synthesis of TMC from 1,3-propanediol and diethylcarbonate.[8b]

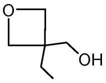
In order to find the best yield and selectivity for TMC formation *vs.* poly(TMC) we have evaluated variation of the reaction conditions of temperature, catalyst loading, CO_2 pressure, as well as the presence of an added solvent. Previous studies involving a closely related process have shown that n-Bu_4NBr is the best cocatalyst for this reaction.[7] Table 1 lists reaction conditions, along with the corresponding product yields and selectivities. As readily seen in Table 1 all reactions are highly selective for cyclic carbonate (TMC) formation.

Table 1 Results of coupling reaction of oxetane and CO_2.[a]

Entry	Reaction time (h)[b]	Pressure (MPa)	Conversion (%)[f]	Selectivity (%)[f]	
				TMC	Poly(TMC)
1[c]	2(4)	3.5	46 (57)	97.8 (98.2)	2.2 (1.8)
2	2	3.5	56	96.4	3.6
3	4	3.5	76	94.7	5.3
4	4	1.7	80	91.3	8.7
5	4	0.6	34	82.4	17.6
6[d]	4	3.5	56	100.0	—
7[e]	2	3.5	59	100.0	—
8[e]	4	3.5	84	100.0	—
9[e]	8	3.5	95	100.0	—

[a] All reactions were carried out with 5.0 mol% $VO(acac)_2/n$-Bu_4NBr loading at 60 °C, except where noted. [b] Values in parenthesis represent 4 h runs. [c] Catalyst loading 2.5 mol%. [d] 50 °C. [e] With added 10 mL of toluene. [f] Determined by ^{1}H NMR spectroscopy.

As noted in entry 1 for 2 and 4 h runs at 60 °C and 3.5 MPa with a catalyst loading of 2.5 mol% the conversion of oxetane to products was 46 and 57%, respectively, with a selectivity for TMC of 98%. Alternatively, an increase in catalyst loading to 5.0 mol% for a 2 h run (entry 2) also provided a 56% conversion with similar selectivity of cyclic carbonate formation. Entries 3, 4, and 5 demonstrate the effect of varying the CO_2 pressure, with runs at 3.5 and 1.7 MPa yielding similar reactivity. However, upon decreasing the CO_2 pressure to 0.6 MPa (entry 5) there was a significant drop in both reactivity and selectivity. The effect of lowering the reaction temperature from 60 °C to 50 °C while keeping the other reaction parameters constant is best seen in comparing entries 3 and 6 where the % conversion decreased from 76 to 56% concomitantly with a slight increase in selectivity from 95 to 100%. Increasing the reaction temperature to 70 °C and higher greatly decreases the selectivity for TMC formation. That is, subsequent ring-opening polymerization of preformed TMC leads to poly(TMC) formation. For the purposes of preparing synthetic quantities of trimethylene carbonate, where maximum conversion is desired in a batch reaction, using a non-coordinating cosolvent, toluene, and longer reaction time led to approximately 100% yield and selectivity of the product (see entries 7–9). The oxetane derivatives, 3-ethyl-3-oxetanemethanol (**1**) and 3,3-dimethyloxetane (**2**), provided 100% selectivity for cyclic carbonate production upon coupling with CO_2 under similar reaction conditions. Nevertheless, presumably due to steric inhibition these reactions occur at a much slower rate than those involving oxetane and CO_2. More detailed studies of substituted oxetanes and CO_2 coupling reactions are currently underway.



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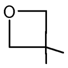

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In an effort to examine this CO_2 coupling reaction in more quantitative detail, we have monitored the progress of the process by *in situ* infrared spectroscopy.[16] This was accomplished employing the reaction conditions (entry 9) which provided a nearly quantitative yield of trimethylene carbonate. Fig. 1 contains the infrared traces for trimethylene carbonate formation as a function of time, along with the reaction profile for TMC production as monitored by the infrared absorption in the ν_{CO_3} region at 1770–1750 cm^{-1}. Since the ν_{CO_3} bands in TMC and poly(TMC) are grossly overlapped at 1770 and 1750 cm^{-1} in toluene solution, it is important to point out here that the infrared band monitored in Fig. 1 is exclusively that of TMC as verified by ^{1}H NMR spectroscopy. Fig. 2 illustrates the linear plot obtained from the data in Fig. 1 of ln($A_\infty - A_t$), where A is the absorbance of TMC, *vs.* time. This provides a pseudo-first order rate constant of about 10^{-4} s^{-1} for a reaction involving a catalyst loading of 5 mol% VO(acac)$_2$ at 60 °C and 3.5 MPa CO$_2$ pressure. Further detailed studies of this kinetically well-behaved reaction will be forthcoming from our laboratories.

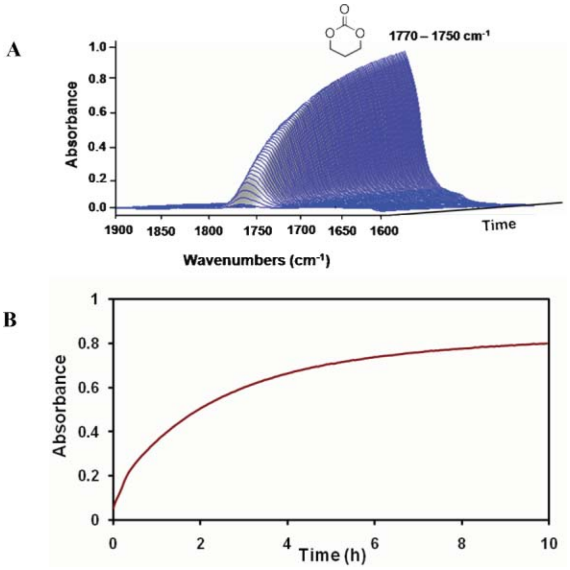

Fig. 1 (A) Three-dimensional stack plot of IR spectra collected every 3 min during the coupling reaction of oxetane and CO$_2$. (B) Reaction profile indicating trimethylene carbonate formation with time. Reaction carried out at 60 °C in toluene in the presence of 5 mol% of VO(acac)$_2$ and 1 equiv. of *n*-Bu$_4$NBr at 3.5 MPa of CO$_2$ pressure.

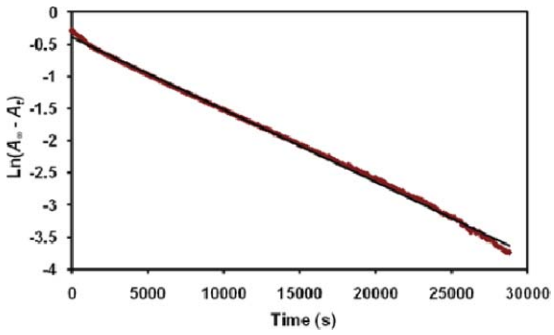

Fig. 2 Plot of ln($A_\infty - A_t$) *vs.* time, where A_∞ and A_t are the infrared absorbances for trimethylene carbonate (1765 cm^{-1}) at time = infinitive and time = t, respectively. Slope = 1.0 × 10^{-4} s^{-1} with an R^2 value of 0.9985.

In an attempt to gain evidence in support of the suggested reaction pathway outlined in eqn (5), we have examined the competitive binding ability of oxetane *vs.* the anion provided by the cocatalyst *n*-Bu$_4$NX. In order to accomplish this we have employed the anion X = azide because of its strong, isolated band in the infrared. Upon addition of one equivalent of *n*-Bu$_4$NN$_3$ to VO(acac)$_2$ in CH$_2$Cl$_2$ two ν_{N_3} infrared absorptions are observed at 2062 and 2005 cm^{-1}, where the former is due to VO(acac)$_2$N$_3^-$ and the later to free azide ion.[3] Subsequent addition of 100 equivalents of oxetane resulted in an increase in the quantity of free azide with a concomitant decrease in the quantity of vanadium bound azide. That is, azide is a much better ligand for VO(acac)$_2$ than oxetane. It would be anticipated that oxetane would be more competitive with the anion bromide used in our synthetic procedure. Nevertheless as we have observed, the use of excessive quantities of *n*-Bu$_4$NBr greatly inhibits the reaction's progress. At this point in our studies we do not have a solid state structure of the adduct formed between VO(acac)$_2$ and azide or oxetane. However, there are structures in the literature between VO(acac)$_2$ and a good base such as DMAP (4-dimethylaminopyridine) which exhibit a *cis*-coordination geometry.[17] Endeavours to obtain crystals of an oxetane derivative of VO(acac)$_2$ have led to isolation of X-ray quality crystals of VO(acac)$_2$ with no oxetane bound to vanadium or found anywhere in the crystal lattice.[18,19]

Future investigations from our laboratory will be directed at more comprehensive mechanistic studies of the selective coupling reaction of various oxetanes and CO$_2$ to provide six-membered cyclic carbonates employing a variety of vanadium catalysts, *e.g.*, in addition to VO(acac)$_2$, VO(salen) was found to catalyze this coupling process.

We gratefully acknowledge the financial support from the National Science Foundation (CHE 05–43133) and the Robert A. Welch Foundation (A-0923). Professor Adolfo Horn also gratefully acknowledges funds for a sabbatical leave from CAPES (Brazil).

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