Coupling Reactions of Carbon Dioxide with Epoxides Catalyzed by Vanadium Aminophenolate Complexes

Ali I. Elkurtehi and Francesca M. Kerton*

Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, A1B 3X7, Canada

fkerton@mun.ca

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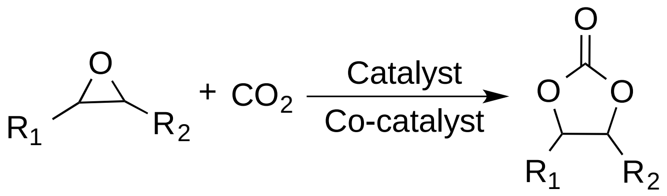
Abstract

A series of vanadium compounds supported by tetradentate amino-bis(phenolate) ligands were screened for catalytic reactivity in the reaction of propylene oxide (PO) with carbon dioxide, [VO(OMe)($O_2NO^{BuMeMeth}$)] (**1**), [VO(OMe)(ON_2O^{BuMe})] (**2**), [VO(OMe)(O_2NN^{BuBuPy})] (**3**), and [VO(OMe)($O_2NO^{BuBuFurf}$)] (**4**) (where ($O_2NO^{BuMeMeth}$) = $MeOCH_2CH_2N(CH_2ArO^-)_2$, Ar = 3,5-$C_6H_2$-Me, *t*Bu]; ($ON_2O^{BuMe}$) = $^-OArCH_2NMeCH_2CH_2NMeCH_2ArO^-$, Ar = 3,5-$C_6H_2$-Me, *t*Bu; ($O_2NN^{BuBuPy}$) = $C_5H_4NCH_2N(CH_2ArO^-)_2$, Ar = 3,5-$C_6H_2$-*t*$Bu_2$; ($O_2NO^{BuBuFurf}$) = $C_4H_3OCH_2N(CH_2ArO^-)_2$, Ar = 3,5-$C_6H_2$-*t*$Bu_2$). They showed similar reactivities but reaction rates were greater for **2**, which was studied in more detail. TOF for conversion of PO over 500 h^{-1} were observed. Activation energies were determined experimentally via *in situ* IR spectroscopy for propylene carbonate (48.2 kJ mol^{-1}), styrene carbonate (45.6 kJ mol^{-1}) and cyclohexene carbonate (54.7 kJ mol^{-1}) formation.

Introduction

Carbon dioxide (CO_2) chemistry and the development of reactions utilizing CO_2 as a C1 feedstock have drawn significant attention because CO_2 is not only an abundant, inexpensive and non-toxic carbon source but also a major contributor to climate change.[1-11] One of the most promising reactions for using CO_2 is its transformation with epoxides to yield cyclic carbonates (Scheme 1). Cyclic carbonates can be used as synthetic intermediates in the synthesis of fine or bulk chemicals. They have been used as a raw material for the synthesis of polycarbonates,[12] and can be found as components in other carbonate-containing materials and composites.[13-16] Cyclic carbonates can also be used as intermediates in the synthesis of other small molecules such as dimethylcarbonate.[17] It is also worth noting that carbonate structural motifs are also found in natural products.[18-20] An application of cyclic carbonates, which has grown significantly in recent years, is as green polar aprotic solvents,[21-31] because of their excellent solubilizing properties and relatively low toxicities. This has also led to their use as electrolyte solvents in lithium-ion batteries.[32-35]



propylene oxide, PO: $R_1 = CH_3$, $R_2 = H$ PC
styrene oxide, SO: $R_1 = Ph$, $R_2 = H$ SC
cyclohexene oxide, CHO: $R_1,R_2 = -(CH_2)_4-$ CHC

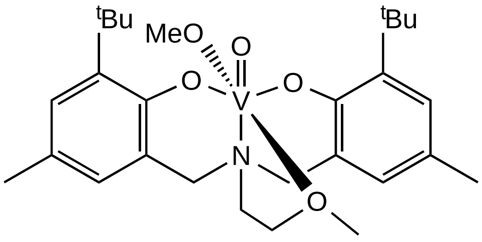
Scheme 1. General scheme for conversion of carbon dioxide to propylene carbonate (PC), styrene carbonate (SC), or cyclohexene carbonate (CHC) via reaction with the corresponding epoxides.

Many homogeneous catalysts using a wide variety of ligand classes have been examined for the transformation of CO_2 to cyclic carbonates using epoxides. For porphyrin species, chromium,[36] manganese,[37, 38] copper,[37] iron,[38] cobalt,[38-40] and zinc,[41] have all been investigated. In most cases, these complexes are combined with a nucleophilic co-catalyst, such as tetrabutylammonium bromide (TBAB), bis(triphenylphosphine)iminium chloride (PPNCl) or 4-dimethylaminopyridine (DMAP). At Memorial University, Kozak and co-workers have been investigating chromium complexes of amino-bis(phenolate) ligands as homogeneous catalysts for CO_2/epoxide copolymerization.[42-46] However, cobalt(II) and cobalt(III) complexes of these ligands were shown to couple CO_2 with propylene oxide under neat conditions to give propylene carbonate and not polymer,[47] but when closely related complexes were studied more recently poly(cyclohexene)carbonate was produced in the presence of DMAP.[48] Iron has also been studied with this class of ligand and such complexes have shown excellent reactivity for either cyclic carbonate or polycarbonate formation.[49-51] The use of the aminophenolate ligand class, as exemplified by the above examples, presents a number of advantages for homogeneous catalyst development among which are their ease of synthesis, simple electronic and steric variation, and tuneable complexation modes achieved by changing the substituents on the phenolate groups, the amine or any pendant donors.[52]

In the current study, vanadium was chosen because it is an abundant and relatively non-toxic metal. In the first study including vanadium species for the coupling of CO_2 and epoxides, VCl_3 and other Lewis acids were examined as catalysts.[53] More recently, complexes containing vanadium(IV) metal centres involving a variety of ligand classes including salphen and salen,[54] and porphyrins,[55] have shown excellent activity towards cyclic carbonate synthesis. Herein, several oxo vanadium(V) amino-bis(phenolate) complexes (Figure 1) in conjunction with co-catalysts were screened in the hope of finding an efficient catalyst system for cycloaddition of epoxides and CO_2 to synthesize cyclic carbonates. We have recently reported the synthesis and characterization of these complexes, and their reactivity as oxidation catalysts.[56] Furthermore, as far as we are aware, this is the first report on the reactivity of a vanadium aminophenolate complex in these reactions and activity of vanadium(V) complexes in such reactions is currently unknown.

Results and Discussion

Catalysts **1-4** (Figure 1) were prepared as previously described.[56] They were previously studied in oxidation catalysis and add to the literature there.[57-61] Aminophenolate vanadium complexes have also been studied in olefin polymerization and copolymerization reactions.[62-66] They have also recently found application as anti-tumor agents. [67] In **1-4**, the electronic properties of the phenolate donors are all similar, as there is little difference in the electronic parameters associated with ^{t}Bu and Me groups. [68] Furthermore, their steric influence around the active metal centre is identical, as in all cases the phenolates bear *ortho* ^{t}Bu groups. The current study seeks to address the way in which the neutral donor groups within the amino-phenolate ligands affects their reactivity and potential as catalysts. For example, **1** and **3** both contain pendant *O*-ether donors, whereas **2** and **4** contain amine and pyridyl-donors. Furthermore, **1**, **3** and **4** are tripodal ligands whereas **2** belongs to the salan-ligand family.



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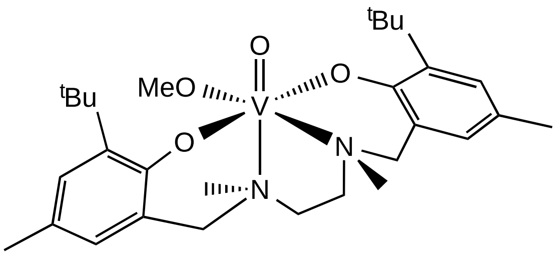

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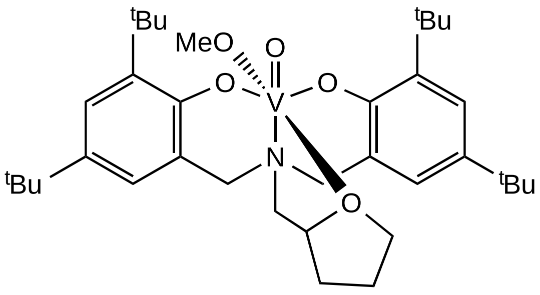

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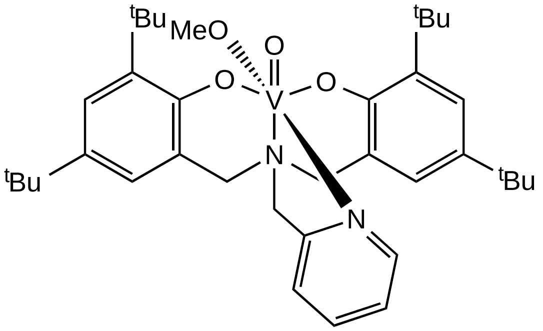

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Figure 1. Homogeneous catalysts tested in this work.

As **1-4** are soluble in the epoxides studied, the reactions were carried out without the addition of any organic co-solvent. The catalytic performance of complexes **1–4** in the cycloaddition of CO_2 to epoxides was initially investigated using PO as the model substrate. Reactions were performed in neat propylene oxide at 80 to 120 °C and under 20 or 40 bar of CO_2 pressure. They were monitored via *in situ* IR spectroscopy and Figure 2 displays a typical reaction profile, where a strong absorption just above 1800 cm^{-1} [ν(C= O) propylene carbonate] was observed for all catalyst systems**,** and no sign of a polycarbonate peak at 1750 cm^{-1} was seen. **1**-**4** were studied under identical conditions in order to determine if any of them showed superior reactivity towards propylene carbonate formation, PC (Figures 3 and 4). Using TBAB as the co-catalyst at 120 °C and 20 bar CO_2, **2** and **4** appear to show an induction period of around 10 minutes whereas **1** and **3** immediately form PC. Induction periods were also observed using **2** and **4** when either styrene oxide or cyclohexene oxide were studied in this way.

We note that **1** and **3** both contain neutral *O*-ether donor groups within their tetradentate ligand framework whereas **2** and **4** contain *N*-donor groups alongside the anionic phenolate donors. We postulate that the induction period observed using **2** and **4** is due to the stronger coordination of the *N*-donors to the vanadium. In **1** and **3**, the methoxy- and furfuryl-donors are less strongly bound to the vanadium and are immediately displaced by the epoxide upon dissolution in this solvent thus forming the catalytically active species immediately. However, the *N*-donors in **2** and **4** remain bound upon initial dissolution at room temperature in the epoxide and it takes some time under the reaction conditions for the *N*-donors to dissociate and provide a vacant site for the epoxide to coordinate and generate the active catalytic species. Similar differences in reactivity have been observed recently in chromium amino-phenolate complexes used for copolymerization of cyclohexene oxide and CO_2.[45]

However, once the reaction started the rate of PC formation was significantly greater for **2** compared with the other 3 catalysts studied and was therefore chosen as the starting point for further investigations. It is worth noting that **2** has two amine donors in the backbone of the ligand and no pendant ligand group unlike **1**, **3** and **4**, and this might be the reason for the increased reaction rate observed for **2**. However further studies would be needed to confirm this hypothesis.

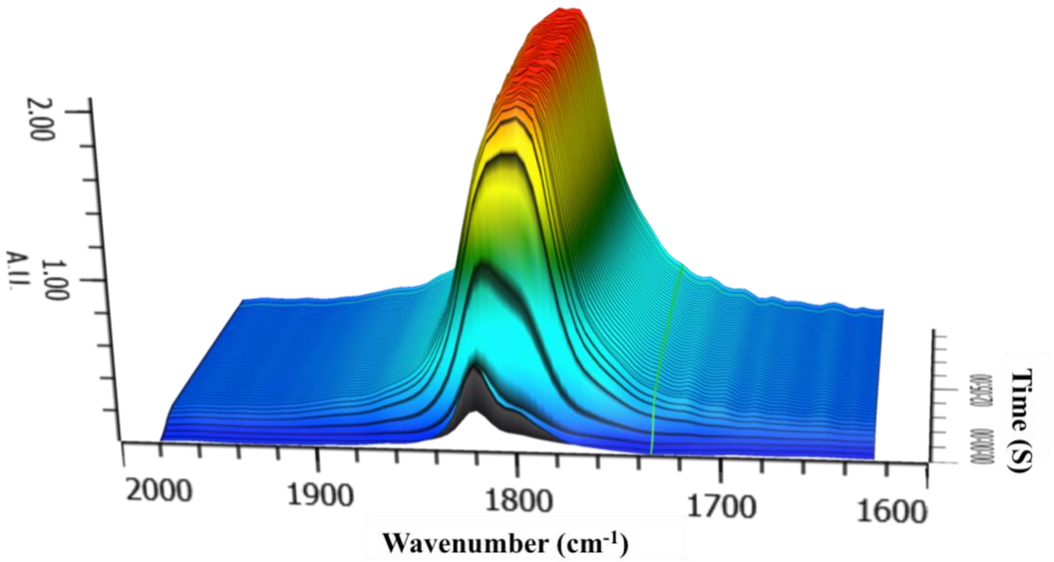

Figure 2 **S**urface diagram showing the growth of the cyclic carbonate group peak for propylene carbonate over time using **1**. No sign of polycarbonate peak at 1750 cm^{-1}. Reaction conditions: 20 bar CO_2, 120 °C, [V]:[PO]:[TBAB] = 1:500:2

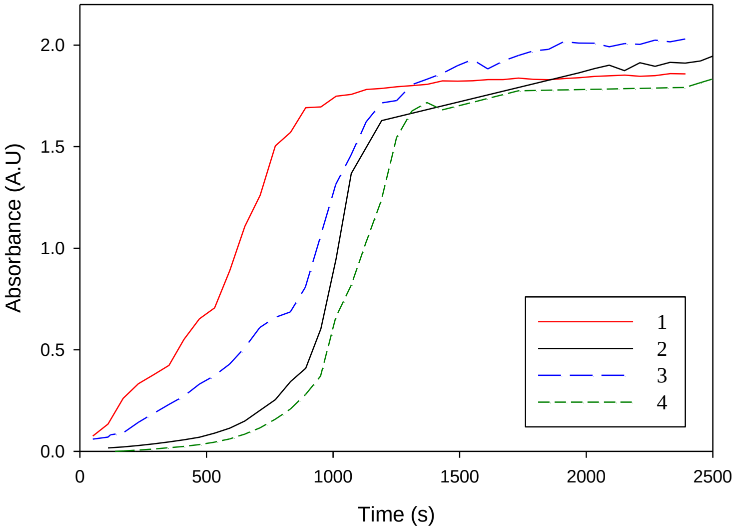

Figure 3 First hour of the reaction profiles showing the absorbance of the cyclic carbonate C=O band at 1810 cm^{-1} catalyzed by **1** (solid red line), **2** (solid black line), **3** (long dashed blue line), **4** (dashed green line). Reaction conditions: 20 bar CO_2, 120 °C, [V]:[PO]:[TBAB] = 1:500:2, 70 mmol PO

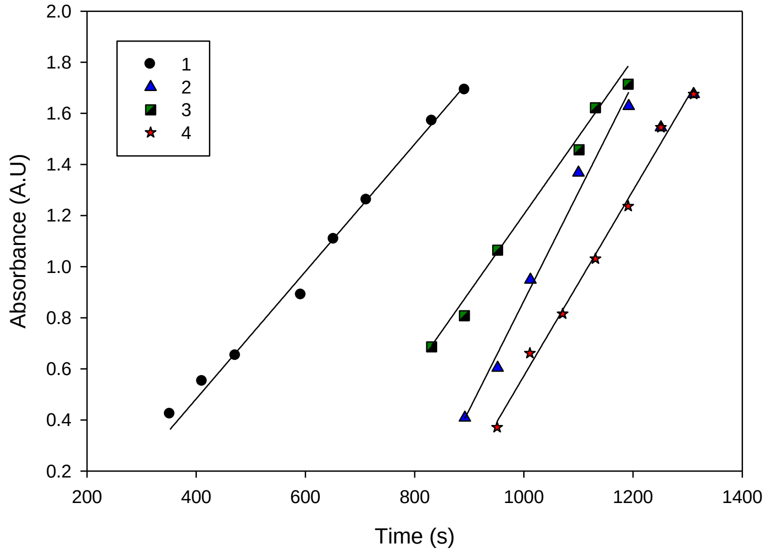

Figure 4. Initial rates of reactions during the first hour based on C=O absorbance of propylene carbonate. **1**(●)(y = 0.0025x - 0.5144, R^2 = 0.9835), **2** (▲)(y = 0.0043x – 3.39, R^2 = 0.9874), **3** (□) (y = 0.0030x – 1.8365, R^2 = 0.9822), **4** (★) (y = 0.0036x – 3.0600, R^2 = 0.9934) Lines represent best fits of a linear model to the observed data.

Table 1. Optimal reaction condition screening study for cyclic carbonate synthesis catalyzed by **2**.[a]

Entry	Epoxide	Co-catalyst	[V]:[Epoxide]:[Co-cat]	P_{CO2} [bar]	T [°C]	time (h)	Conv. [%]	TON	TOF [h^{-1}]
1	PO	TBAB	0:500:1	40	80 or 100	18	0	0	0
2	PO	DMAP	1:500:1	40	80 or 100	18	0	0	0
3	PO	PPNCl	1:500:1	40	80	18	42	210	11.6
4	PO	TBAB	1:500:1	40	80	18	79	395	22
5	PO	TBAB	1:500:1	20	100	18	85	425	23.6
6	PO	TBAB	1:500:1	20	120	5	87	435	87
7	PO	TBAB	1:500:2	20	120	5	>99	>495	>99
8	PO	TBAB	1:500:3	20	120	5	85	425	23.6
9	PO	TBAB	1:2000:2	20	120	5	74	1480	296
10	PO	TBAB	1:4000:2	20	120	5	66	2640	528
11	PO	TBAB	1:4000:2	20	120	10	75	3000	300
12	PO	TBAB	1:4000:2	20	120	20	91	3640	182
13	PO	TBAB	1:4000:2	20	120	25	>99	>3960	>158
14	SO	TBAB	1:500:2	20	120	7	>99	>495	>71
15	CHO	TBAB	1:500:2	20	120	18	87	435	24.2

[a] Reaction conditions: 100 mL reactor volume, 50 mmol epoxide. (PO, propylene oxide, SO, styrene oxide and CHO, cyclohexene oxide). Conversions determined by ^{1}H NMR spectroscopy. TON = overall turnover number ($mol_{Epoxide\ converted}/mol_{Vanadium}$). TOF = overall turnover frequency (TON/reaction time).

Effect of Reaction Parameters on Conversion of PO

Results for reactions performed using **2** are summarized in Table 1 alongside a control reaction using TBAB and no catalyst (entry 1). Reactions were attempted at lower CO_2 pressures (1 bar and 10 bar) at 120 °C but no conversion was observed over an 18 h period. Reactions could be performed at lower temperatures (30 °C) using 20-40 bar CO_2 and proceeded slowly according to Arrhenius' principles (see discussion of kinetics below). Among the different co-catalysts, TBAB showed greater activity compared with DMAP and PPNCl (entries 2-4). It is worth noting that an ionic co-catalyst was critical in obtaining catalytic turnovers, as no conversion was observed when DMAP was employed as the co-catalyst. The conversion of PO decreased if the **2**:TBAB mole ratio was increased or decreased from the optimum 1:2 ratio (Table 1, entries 6–8). Similar trends were noted for the other vanadium catalysts studied.[55] Although PPNCl also functioned as an ionic co-catalyst for the cycloaddition of PO and CO_2, the PO conversion was lower than when TBAB was used (Table 1, entry 3 versus 4–13). This is due to the fact that although chloride is a better nucleophile than bromide in aprotic solvents such as epoxides, bromide is a better leaving group and therefore the rate-determining step in the reaction may be the ring-closing step that occurs with concomitant loss of a bromide ion.[55] Further studies would be needed to confirm that the cation associated with the co-catalyst (TBA *vs*. PPN) does not affect the resulting activity of the catalyst system significantly. Catalyst loading was also varied (1:500 - 1:4000) and the binary catalyst system could achieve high conversions after longer reaction times indicating that the catalysts are stable and can achieve high TON (Table 1, entries 9-13).

Cycloaddition Reaction of Styrene Oxide or Cyclohexene Oxide with CO_2 Catalyzed by 2/TBAB

The cycloaddition of CO_2 with other epoxides (styrene oxide, SO; cyclohexene oxide, CHO) using **2**/TBAB was examined at 120 °C and 20 bar (initial CO_2 pressure). Table 1 shows that the catalyst is active for all the selected substrates under the adopted conditions. For SO, the catalyst system is active and achieves 100% conversion to the corresponding cyclic carbonate within 7 h, (Table 1, entry 14). Reactivity towards CHO was also good; however, much longer reaction times were needed compared with PO and SO (Table 1, entry 15), which could be rationalized by the known lower rate of epoxide ring-opening for CHO due to its bicyclic nature which hinders the nucleophilic attack.

Kinetic Measurements

It is well known that cyclic carbonate is produced with increased selectivity over polycarbonate at elevated temperatures in the coupling reaction of PO and CO_2.[4] The formation of cyclic carbonate is believed to occur via a backbiting mechanism from either an alkoxide or a carbonate group during the coupling reaction.[4, 69] In order to develop a better understanding the of the mechanistic aspects of the formation of PC, the effect of reaction temperature on PC formation catalyzed by V/TBAB system was monitored by *in situ* infrared spectroscopy. At room temperature, no PC formation was observed. By increasing the temperature to 30 °C, the absorbance at 1815 cm^{-1} which corresponds to the cyclic carbonate carbonyl group started to slowly grow. The rate of formation of PC increases significantly as expected with increases in temperature (Figure 5). Overall, it is clear that the activity of the catalyst is extremely sensitive to reaction temperature. From the kinetic data at variable temperatures as illustrated in Figure 6 the activation energy for the PC formation can be obtained (Figure 6). The activation energy for PC formation in the **2**/TBAB catalyst system is 48.2 ± 0.16 kJ mol^{-1} at 20 bar of CO_2 pressure. This result under the present conditions was analogous with those reported in the literature for the cycloaddition reaction using different catalysts, in which the range of about 35-70 kJ mol^{-1} for a range of other metals: Zn(II)[70, 71], Al(III) [72], Co(III),[73] and Li.[74] However, there are examples where higher activation energies are reported around 100 kJ mol^{-1},[50, 75, 76] and this might be indicative of different rate determining steps between the catalytic systems being studied. Also, from the kinetic data at variable temperatures for SO and CHO conversions as illustrated in Figures S1 and S3 the activation energies for the SC and CHC formations can be obtained (Figures S2 and S4) The activation energy for SC formation using the **2**/TBAB catalyst system was 45.6 ± 0.21 kJ mol^{-1}. The activation energy under the present conditions was in good agreement with those reported in the literature (35–70 kJ mol^{-1}) for this cycloaddition reaction using different catalysts.[72] [71] For CHC formation using the **2**/TBAB catalyst system, the activation energy was 54.7 ± 0.22 kJ mol^{-1} at 20 bar of CO_2 pressure. This is higher than those for PC and SC formation and suggests that the rate-determining step for these reactions is dependent on the nature of the epoxide and steric hindrance caused by using a non-terminal epoxide.

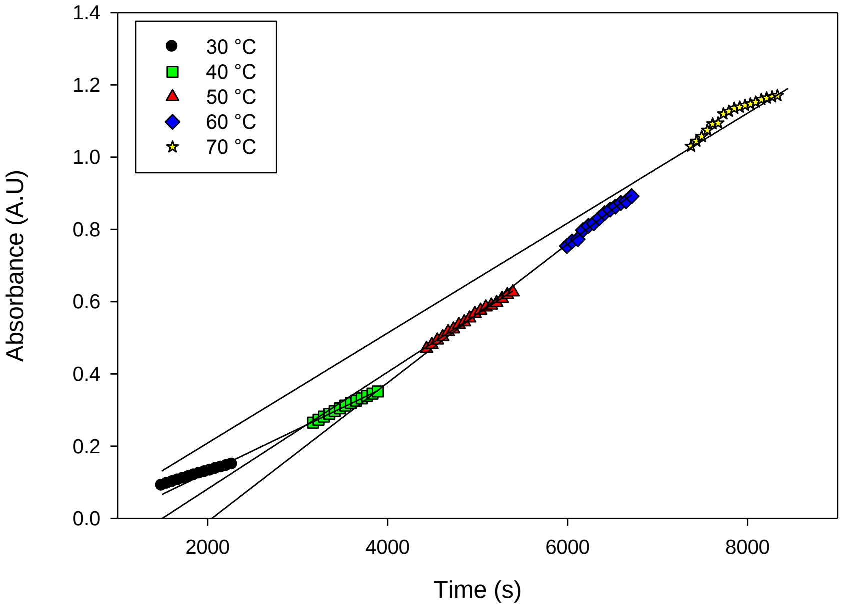

Figure 5. Temperature dependence of the initial rates of reaction based on the absorbance of the ν(C=O) of propylene carbonate (PC). Using **2** at 20 bar and [V]:[PO]:[Co-cat] 1:500:2, at 30 °C ● (y = 0.000039865x – 0.0200, R^2 = 0.9992), at 40 °C □ (y = 0.00008028x – 0.1128, R^2 = 0.9977), at 50 °C ♦ (y = 0.0001x - 0.2421, R^2 = 0.9960), at 60 °C ♦ (y = 0.0001994x – 0.1128, R^2 = 0.9977), at 70 °C 😐 (y = 0.00040163x – 0.0200, R^2 = 0.9992).

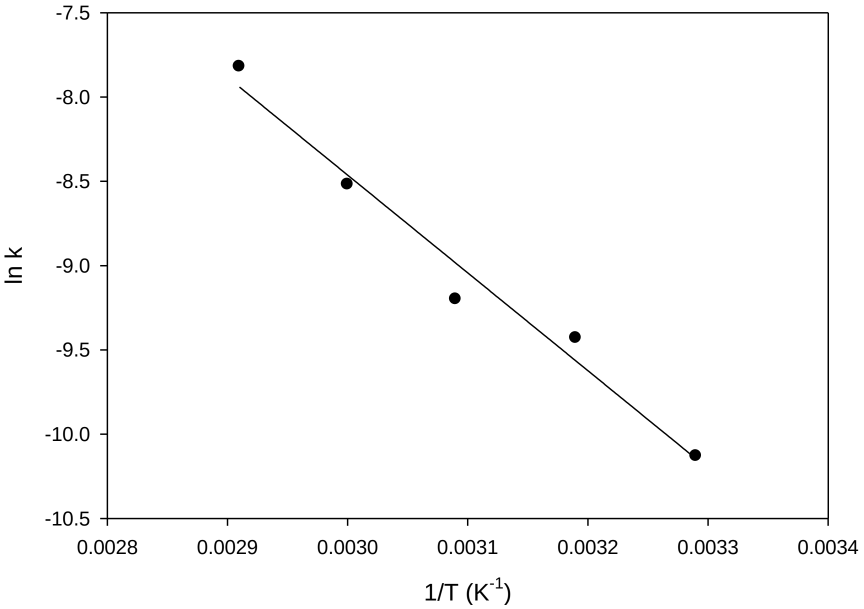

Figure 6. Arrhenius plot for the formation of propylene carbonate using variable temperature data presented in Figure 5. Straight line: $y = -5801.59x + 8.94$, $R^2 = 0.9736$

Conclusions

Vanadium amino-bis(phenolate) complexes **1–4** show very good catalytic performance for the selective coupling of epoxides and CO_2 in the presence of ionic co-catalysts (TBAB and PPNCl) to give cyclic carbonate with no evidence of any polymer formation. Under optimized conditions (120 °C and 20 bar CO_2), **2** could achieve a TOF of over 500 h^{-1} and a TON close to 4000 for propylene carbonate formation. Activation energies for the formation of PC, SC and CHC were determined. CHC formation had a significantly greater activation energy than PC and SC formation, which suggests that the rate determining step in these reactions is epoxide dependent, e.g. ring-opening of the epoxide, for this and related catalyst systems. However, we also note that reactions using other catalysts have reported significantly higher activation energies,[50, 75, 76] which implies that not all seemingly identical reactions progress with an identical rate determining step. Further studies, including computational efforts, are needed to fully understand the reaction mechanisms and rate-determining steps in these and related reactions.

Experimental Section

Materials

1-4 were prepared according to previously reported procedures.[56] PO, SO and CHO were purchased from Aldrich and used as received. CO_2 was supplied from Praxair in a high-pressure cylinder equipped with a liquid dip tube. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc.

Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 300 MHz NMR spectrometer. All coupling reactions, unless monitored *in situ* using a ReactIR system, were carried out in a 100 mL stainless steel Parr autoclave reactor (Parr Instrument Company) equipped with a motorized mechanical stirrer and a heating mantle. For IR-monitored reactions, the pressure vessel was additionally equipped with a silicon ATR sensor (SiComp Sentinel). The ATR sensor was connected to a ReactIR 15 base unit (Mettler-Toledo) via a DS silver-halide Fiber-to-Sentinel conduit. Similar reaction monitoring systems have been described previously.[76] For monitored reactions, It is important to note that caution should be taken when operating high-pressure equipment.

Typical procedure for catalytic coupling reaction of epoxides and CO_2

A solution of the catalyst and co-catalyst in the epoxide (50 mmol) was prepared and added *via* a long-needled syringe to a 100-mL Parr autoclave, which was pre-dried under vacuum overnight at 80 °C. The appropriate pressure of CO_2 was then dosed into the reactor and heating and stirring were started to achieve the desired temperature (Table 1). After the desired time, the autoclave was cooled in an ice bath until the temperature probe read $T < 20$ ºC and vented in a fume hood. This decompression was carried out very slowly, in order to allow the liquid phase to degas properly and to avoid loss of the reaction mixture. After this, the autoclave was opened and a sample was taken immediately for the determination of conversion by NMR spectroscopy.

Acknowledgements

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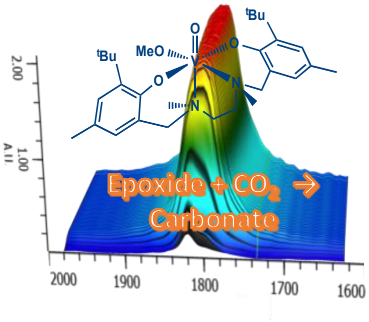
Table of Contents

Four epoxide-soluble vanadium(V) complexes with ionic co-catalysts convert epoxides to carbonates. For propylene oxide, TON up to 4000 and TOF over 500 h^{-1}. *In situ* IR spectroscopic monitoring of carbonate formation allowed activation energies to be determined (45.6-54.7 kJ mol^{-1})



Keywords

Carbon dioxide, Homogeneous catalysis, Kinetics, Vanadium