Solvent free cycloadition of CO_2 and Propylene Oxide to Cyclic carbonates using different ligand metal complexes

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Abstract

Tetradentate ligand metal complexes salenCo(III)OBzF_5, salen-CH_3Co(III)OBzF_5, salen-CH_3Co(III)Br and salen-ClCo(III)Br have been synthesized. The complexes were used as catalyst for the chemical fixation of CO_2 and propylene oxide to cyclic carbonates. Tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium) and tetrabutyl ammonium bromide were used as co-catalysts in the reactions. Additionally, the catalytic activity of napthenCoSO_4 and salenCoSO_4 was also explored using the above co-catalysts. The conversion of propylene oxide to cyclic carbonate was found to increase with an increase in temperature and pressure of carbon dioxide. It is significant to note that cyclic carbonate product could be obtained at temperature as low as 60°C and pressure of 20 bar in just 2 h. Further, it has been observed that introduction of electron donating methyl substituent increases the nucleophilic character of the catalyst and reaction conversion. On the contrary, electron withdrawing substituent like chlorine decreased the cyclic carbonate conversion thereby making it a weaker nucleophilic catalyst.

Keywords

carbon dioxide; propylene oxide; cyclic carbonate; catalyst; co-catalysts; ligand metal complexes

INTRODUCTION

Ligand metal complexes have myriad applications in various reactions such as oxygenation, hydrolysis, electro-reduction and decomposition etc [1-3]. The metal core in the complexes can provide Lewis acid center and thus they can act as catalysts for a number of reactions. One such reaction is coupling reaction between carbon dioxide and heterocyclics such as epoxides to synthesize cyclic carbonates. Synthesis of cyclic carbonates from CO_2 has turned out to be of great interest since CO_2 is an inexpensive and greener source [4-7]. Further, there have also been continued efforts to use CO_2 as a carbon source in different organic reactions (such as synthesis of methanol, salicylalic acid, urea etc) and one such reaction is the addition of CO_2 to epoxides to produce cyclic carbonates [6-7]. Cyclic carbonates are products of great commercial importance as they are used for various purposes such as electrolytic elements of lithium secondary batteries, polar aprotic solvent and monomers for synthesis of polycarbonates and chemical intermediates for preparing medicines or agricultural chemicals [8-11].

CO_2 is a stable molecule with bond angle of 180^o and thus it becomes a challenge to use it in chemical reactions. Thus, its reaction with appropriate reactants such as reactive heterocyclics in the presence of suitable catalysts for the reaction under milder conditions (temperature, pressure and reaction time) is of great interest. Many studies have been carried out to synthesize cyclic carbonates using various ionic liquids, inorganic salts, organometallic and ligand metal complexes [12-21]. It has been observed that most of the reported studies deal with the catalyst systems which are either expensive or involves a tedious methodology to prepare. The present work is an attempt to synthesize cyclic carbonates in solvent free system by fixing CO_2 with propylene oxide in the presence of various ligand metal complexes as catalysts and different co-catalysts. Interestingly, the catalysts used in the reactions are economical, achiral and offers easy route of preparation without any further purification.

In our previous work [22], we had reported preliminary catalytic studies of two different ligand metal complexes (salenCoSO_4 and naptheCoSO_4) for cycloaddition of propylene oxide and carbon dioxide. This further motivated us to comprehensively investigate the effect of more number of new complexes with different electron densities and nucleophilic groups on this cycloaddition reaction. Additionally, the enhanced catalytic activity of the previously synthesized complexes has been observed by changing the co-catalysts ($[PPN]^+Cl^-$, tetrabutyl ammonium bromide, hexdecyltrimethyl ammonium bromide and tetradecyltrimethyl ammonium bromide). These quaternary ammonium ions were used as co-catalysts since they bear bromide ion as nucleophilic group which can open up the epoxide ring. There are number of studies available which uses different type of salen cobalt based catalysts [21, 23-24] in such CO_2 based fixation reactions. It is noteworthy that the use of co-catalysts as hexdecyltrimethyl ammonium bromide and tetradecyltrimethyl ammonium bromide has not much been explored in such reactions. As formed out of studies, the catalytic activity of different ligand metal complexes used in various type of reactions can also be controlled by simply changing the electron density around the catalyst.

Experimental

***Materials*:**

Propylene oxide, DMAP, $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium), 4-chloro-o-phenylenediamine, 4-methyl-o-phenylenediamine were purchased from Aldrich. Salicylaldehyde and o-phenylenediamine were purchased from Loba Chemicals India. Tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, tetrabutyl ammonium bromide, cobaltous acetate and cobalt sulphate were purchased from SD Fine Chemicals, India. Ethanol was purchased from E Merck (Germany) and pentaflourobenzoic acid was purchased from High Media.

***Measurements**:*

^{1}HNMR was also used for the identification and quantification of the obtained crude product. Both ^{1}HNMR and ^{13}C NMR spectra were recorded using $CDCl_3$ as solvent and tetramethysilane as an internal standard on Jeol ECS-400 Spectrophotometer. FTIR measurements were carried out using Agilant Cary-660 spectrophotometer from 650 to 4000 cm^{-1}. ATR mode was used for all the measurements. CHNS analysis was carried on Thermo Scientific Flash 2000 Organic Elemental Analyzer equipped with Themal conductivity detector.

Experimental

Procedure for the Synthesis of catalysts:

One equivalent of R-phenylenediamine (R=H, CH_3 and Cl) and two equivalents of salicylaldehyde or napthaldehyde were dissolved in ethanol. The refluxing and stirring of the reaction was carried for 3-4 hours and then the mixture was cooled to room temperature. The precipitate thus obtained were filtered, washed with cold ethanol and finally dried in oven. The corresponding reaction scheme is shown in Figure 1. Complexation of the ligand was carried out separately with cobalt by refluxing with continuous stirring a 1:1 molar mixture of the synthesized ligand and the corresponding salt dissolved in methanol for 3 h. The solid products thus obtained were filtered using vacuum filtration. In order to bind pentafluorobenzoate or bromine to the metal axial site, one equivalent of ligand cobalt complex and one equivalent of pentafluorobenzoic acid/lithium bromide were taken and stirred open to air (for 18 h) using toluene as solvent. The obtained products were analysed using ^{1}HNMR, ^{13}C NMR, CHNS and FTIR.

***^{1}H NMR, ^{13}C NMR and CHNS analysis of the Ligands**:*

N,N′-bis-(salicylaldehyde)-4-methyl-o-phenylenediamine (salen-CH$_3$)

Salicylaldehyde (0.86 ml, 0.008 mol) with 3,4-diaminotoluene (0.5g, 0.004 mol) were used for synthesizing this ligand by employing the general procedure.

Bright orange precipitates. **(^{1}H NMR, 400 MHz, CDCl$_3$):** δ 8.61(s, CH=N); 6.88-7.38 (m, Ar-H); 11.01 (s, OH), 2.42 (s, 3H, CH$_3$) **(^{13}C NMR, 100 MHz, CDCl$_3$):** 163.67, 161.42, 142.56, 139.99, 133.38, 132.26, 128.40, 120.46, 119.03, 117.63, 21.23 **CHNS:** Calculated for $C_{21}H_{18}N_2O_2$: **C**: 75.4; **H**: 5.38; **N**: 8.38 Found: **C**:75.8; **H**: 5.49; **N**: 8.49

N,N′-bis-(salicylaldehyde)-4-chloro-o-phenylenediamine (salen-Cl)

For synthesizing this catalyst salicylaldehyde (0.86 ml, 0.008 mol) and 4-chloro-o-phenylenediamine (0.568g, 0.004 mol) were taken and the general procedure as mentioned above was followed.

Brown coloured product. **(^{1}H NMR, 400 MHz, DMSO):** δ 12.7 (s, CH=N); 7.0-8.06 (m, Ar-H); 13.3 (s, 1H, OH) **(^{13}C NMR, 100 MHz, DMSO):** 157.97, 152.96, 131.76, 126.31, 123.05, 122.49, 118.96, 117.34, 112.54, 111.14 **CHNS:** Calculated for $C_{20}H_{15}N_2O_2$: **C**:67.3; **H**: 4.2; **N**: 7.85, Found: **C**:65.8; **H**:3.88; **N**: 8.04.

N,N′-bis-(2-hydroxy-1-naphthyldehyde)-o-phenyleneldiamine (napthen)

The precursors 2-hydroxy-1-naphthaldehyde (1g, 0.0058 mol) and o-phenylenediamine (0.313g, 0.0029 mol) were taken for the synthesis of the ligand using the general procedure.

Bright Yellow precipitates. **(^{1}H NMR, 400 MHz, DMSO):** δ 9.5 (s, CH=N); 6.86-8.9 (m, Ar-H); 15.1 (s, OH) **(^{13}C NMR, 100 MHz, DMSO):** 168.54, 157.22, 138.51, 136.65, 132.99, 128.92, 127.28, 126.84, 123.50, 121.42, 120.47, 119.61, 109.20 **Napthen**: Calculated for $C_{28}H_{20}N_2O_2$: **C**: 80.0; **H**: 4.76; **N**: 6.66 Found: **C**: 81.8; **H**: 4.86; **N**: 6.83.

FTIR spectra of the catalysts:

The FTIR spectra of the SalenCoOBzF_5 catalyst are shown in Figure 2. The band around 1275 cm^{-1} attributed to C−O stretch in salen shifted to higher frequency by about 30−40 cm^{-1} (around 1310 cm^{-1}) which confirms the participation of oxygen in the C−O−M bond. The band for the ligand at 1616 cm^{-1} due to C=N stretching shifted to a lower frequency of 1572 cm^{-1} and the band due to C-N at 1480 cm^{-1} shifted to a lower frequency by about 20 cm^{-1} (around 1460 cm^{-1}) further confirming the coordination of nitrogen with the metal.

In case of FTIR spectra of Salen-CH_3 CoBr and Salen-CH_3 CoOBzF_5 (Figure 3) the band around 1268 cm^{-1} attributed to C−O in Salen-CH_3 shifted to higher frequency by about 30−40 cm^{-1} (around 1305 cm^{-1}) confirming the participation of oxygen in the C−O−M bond. The band for the ligand around 1613 cm^{-1} corresponding to C=N stretching shifted to a lower frequency of 1597 cm^{-1} and the band due to C-N at 1484 cm^{-1} shifted to a lower frequency by about 20 cm^{-1} (around 1457 cm^{-1}) further confirming the coordination of nitrogen with the metal.

FTIR spectra of Salen-Cl Co(III)Br catalyst (Figure 4) also shows band around 1245 cm^{-1} attributed to C−O stretch in Salen-Cl which shifted to higher frequency around 1260 cm^{-1} on binding to cobalt metal confirming the formation of C−O−M bond. The band due to C=N strech in the ligand around 1635 cm^{-1} shifted to a lower frequency of 1610 cm^{-1} and the band corresponding to C-N stretch about 1480 cm^{-1} shifted to a lower frequency around 1460 cm^{-1} thereby confirming the coordination of nitrogen atom of the ligand with the metal. Similar pattern was observed in case of Salen $CoSO_4$ and Napthen $CoSO_4$ spectra (Figure 5) [19].

These results indicate that Salen Co(III)$OBzF_5$, Salen-CH_3 Co(III)$OBzF_5$, Salen Co(III)Br and Salen-Cl Co(III)Br catalysts have been successfully synthesized.

Procedure for the Synthesis of cyclic carbonates :

A mixture of catalyst and co-catalyst was dispersed in propylene oxide (25 ml) and added to 100 ml reactor. The reaction was then carried out at the desired temperature and CO_2 pressure of 20 bar. The mixture was stirred for a desired period of time with an overhead mechanical stirrer. After a predetermined time, the reactor was cooled and the remaining CO_2 was vented in a fume hood. Finally, a small aliquot of the resultant product was taken from the reactor for ^1H NMR analysis. The obtained product can be purified by dissolving it in dichloromethane and washing with aqueous HCl. The corresponding reaction and reactor setup for the reaction are given in Figure 6 & 7.

The proposed mechanism for the chemical fixation of propylene oxide and CO_2 is shown in Figure 8 and is close agreement with the literature [24]. It is supposed that the metal ion in the salen/napthen metal complexes acts as electrophilic metal center which coordinates to propylene oxide units. Further, the ring opening of epoxide ring is assisted by nucleophile (Br^- or Cl^-) of the catalyst or the co-catalyst. It is supposed that the electropositive part of the co-catalyst reacts with CO_2 molecule to form carbamate salt which on further forms cyclic carbonate.

RESULTS AND DISCUSSION

Table 1 gives conversion of propylene oxide and CO_2 to cyclic carbonate using various catalyst/co-catalyst systems. The actual state of monomers under high pressure and temperature conditions should be known before attempting to analyse the reaction data. Using the Clausius-Clapeyron equation, it can be easily shown that at CO_2 pressure of 20 bar and temperature of 100^oC, the boiling point of propylene oxide is more than 200^oC which is nearly two times higher than the reaction temperature hence propylene oxide must exist in liquid state though its boiling point at atmospheric pressure is 35^oC. Thus, it is expected that at polymerization temperatures of 60, 80 and 100^oC, propylene oxide will exist in liquid state under high pressure. The reaction between propylene oxide and CO_2 with salenCoSO_4/$Bu_4^+Br^-$ and napthenCoSO_4/$[PPN]^+Cl^-$ as catalyst systems (Table 1, Entry 1,2, 15 & 16) shows that on increasing the temperature the conversion to cyclic carbonate increases. It has been observed that DMAP as a co-catalyst does not give any conversion with either salenCoSO_4 or napthenCoSO_4 (Table 1, Entry 3, 4 and 14). Among the explored catalysts salen-CH_3CoBr/$[PPN]^+$Cl was found to be the most active catalyst (Table 1, Entry 17). It was observed that the conversion value increased from 40% to around 50% on increasing the pressure from 10 to 20 bar keeping the reaction time constant (Table 1, Entry 11 and 12). Respective conversions with salen CoOBzF_5/$Bu_4^+Br^-$ were found to increase with an increase in reaction time from 56.8% in 2 h to 67.3% conversion in 4 h (Table 1, Entry 8 and 9).

In order to study the steric effect on the catalyst, electron donating group was introduced on the catalyst salen-CH_3 Co(III)$OBzF_5$ and its effect on the reaction was investigated. It is thought that methyl substituent will increase the electron density on the ligand and thereby will decrease the Lewis acid character of the Co(III) metal center by making the lone pair of electrons on nitrogen more available to cobalt and thus enhance the Lewis base or nucleophilic character of the pentafluorobenzoate group. Thus, it was observed that salen-CH_3CoBr bearing electron donating methyl group and relatively strong nucleophile as bromide ion was able to enhance activity of the catalyst and gave 67.0% conversion with $[PPN]^+Cl^-$ as co-catalyst (Table 1, Entry 17). The obtained conversion was found to be significant in comparison to the conversion obtained with salenCo(III)$OBzF_5$ catalyst for the same reaction time of 2h (Table 1, Entry 13). Further, introduction of electron withdrawing group decreased the electron density on the ligand by making the lone pairs of electrons on nitrogen of diamine moiety less available to cobalt metal center. This turns cobalt metal into a strong Lewis acid metal center and its conjugate bromide into a relatively weak nucleophile and thus decreases the conversion of propylene carbonate (Table 1, S.No. 18 and 19).

^{1}H NMR, ^{13}C NMR , HSQC and FTIR of cyclic carbonates:

^{1}H NMR spectra of propylene carbonate confirms the formation of cyclic carbonates in all the samples (Figure 9). A doublet around 1.49 ppm corresponds to methyl protons, triplet around 4.0 and 4.5 ppm corresponds to CH_2 protons, and multiplet about 4.8 ppm refers to CH protons. The multiplet at 4.8 ppm confirms the coupling of CH with both methyl and methylene hydrogens.

^{13}C NMR spectra of propylene carbonate (Figure 10). The chemical shift around19 ppm corresponds to primary carbon and that around 70 ppm and 73 ppm corresponds to secondary and tertiary carbons respectively. The shift due to carbonyl carbon appears around 155 ppm. HSQC spectrum further clearly confirms the formation of propylene carbonate (Figure 11). The shift around1.5 ppm corresponds to primary carbon at 19 ppm. The shift around 4.2 and 4.5 ppm corresponds to secondary carbon at 70 ppm and the one around 4.8 ppm corresponds to tertiary carbon around 73 ppm.

The obtained propylene carbonate was also characterized by FTIR giving bands due to C=O at around 1790 cm^{-1} and C−O stretching at about 1180 cm^{-1} which are the characteristic bands of propylene carbonate and thereby confirm the formation of the product (Figure 12).

CONCLUSION

Cyclic carbonate was successfully synthesized from propylene oxide and CO_2 using Salen CoX, Napthen CoX (X=SO_4, $OBzF_5$) and Salen-CH_3 CoBr and Salen-Cl CoBr as catalyst. Tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, $[PPN]^+Cl^-$ and tetrabutyl ammonium bromide and DMAP (dimethylaminopyridine) were used as co-catalysts in the reaction. It was observed that % conversion of propylene oxide to cyclic carbonates increases with an increase in temperature and pressure. Higher monomer to catalyst ratio does not give any homoether linkages and led to an increase in conversion in same reaction time. It was observed that introduction of electron donating group such as methyl substituent will increase the electron density on the ligand and will thereby increase the propylene carbonate conversion by increasing the nucleophilic activity of the catalyst. On the other hand, introduction of electron withdrawing group on the ligand will decrease the nucleophilic activity of the catalyst and thus will decrease the propylene carbonate conversion. Thus the best activity was achieved using Salen-CH_3 CoBr/$[PPN]^+$Cl catalyst systems and least catalytic activity was achieved by Salen-Cl CoBr/$[PPN]^+Cl^-$.

Notes

The author declares no financial interest.

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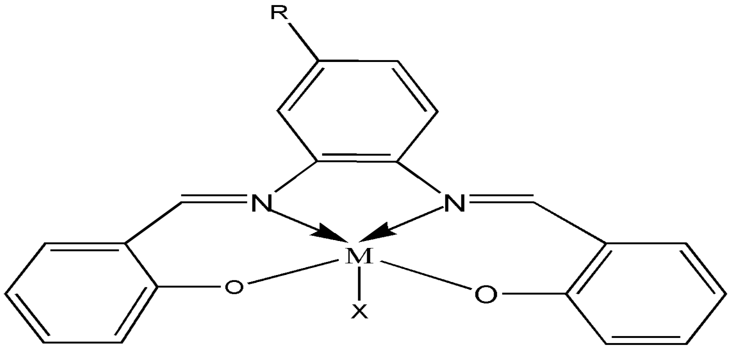
Table 1: Reactions between Propyleneoxide and CO_2 using different catalyst/co-catalyst systems

Entry	**Catalyst/Co-catalyst**	**Temperature (^oC)**	**Reaction Time (h)**	**% Conversion**
1.	$SalenCoSO_4/\ Bu_4N^+Br^-$	60	2	24.4
2.	$SalenCoSO_4/\ Bu_4N^+Br^-$	100	2	50.7
3.	$SalenCoSO_4$/DMAP	60	2	No conversion
4.	$SalenCoSO_4$/DMAP	80	2	No conversion
5.	$SalenCoSO_4/[PPN]^+Cl^-$	60	2	13.6
6.	$SalenCH_3\text{-}CoSO_4/[PPN]^+Cl^-$	100	2	19.1
7.	$SalenCoSO_4$/Hexadecyl ammonium bromide	80	2	50.0
8.	$SalenCo(III)OBzF_5/\ Bu_4N^+Br^-$	80	2	56.8
9.	$SalenCo(III)OBzF_5/\ Bu_4N^+Br^-$	80	4	67.3
10.	$SalenCo(III)OBzF_5$/Tetradecyltri methylammonium bromide	80	2	36.3
11.	$SalenCo(III)OBzF_5/[PPN]^+Cl^-$	80	2	50.2
12.	#$SalenCo(III)OBzF_5/[PPN]^+Cl^-$	80	2	40.9
13.	$SalenCo(III)OBzF_5/[PPN]^+Cl^-$	100	2	55.6
14.	$NapthenCoSO_4$/DMAP	60	2	No conversion
15.	$NapthenCoSO_4/[PPN]^+Cl^-$	60	2	No Conversion
16.	$NapthenCoSO_4/\ [PPN]^+Cl^-$	100	2	51.8
17.	$SalenCH_3\text{-}Co(III)Br\ /[PPN]^+Cl^-$	100	2	67.0

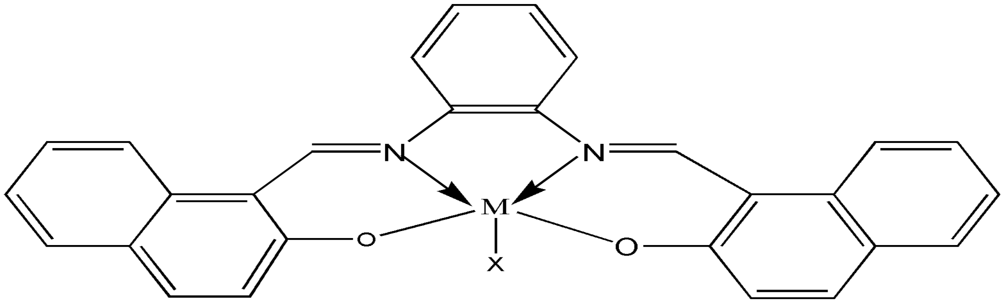
18.	SalenCl-Co(III)Br/[PPN]$^+$Cl$^-$	100	2	20.0
19.	SalenCl- Co(III)Br/ Bu$_4$N$^+$Br$^-$	100	2	23.0

M_o/I_o =2000:1, Pressure=20 bar, % Conversion has been calculated through ^{1}HNMR.

 # Pressure= 10 bar,*M_o/I_o =1000:1



Salen
M=Co, Fe X=SO_4, $OBzF_5$, Br
R=H, CH_3, Cl
(A)



Napthen
M=Co X=SO_4
(B)

Figure 1: Ligand used for the synthesis of cyclic carbonates. **(A)** [N,N′-bis-(salicylaldehyde)-o-phenylenediamine] (salen), [N,N′-bis-(salicylaldehyde)-4-methyl-o-phenylenediamine] (salen-CH_3) and [N,N′-bis-(salicylaldehyde)-4-chloro-o-phenylenediamine] (Salen-Cl) **(B) [**N,N′-bis-(2-hydroxy-1-naphthyldehyde)-o-phenyleneldiamine] (Naphthen)

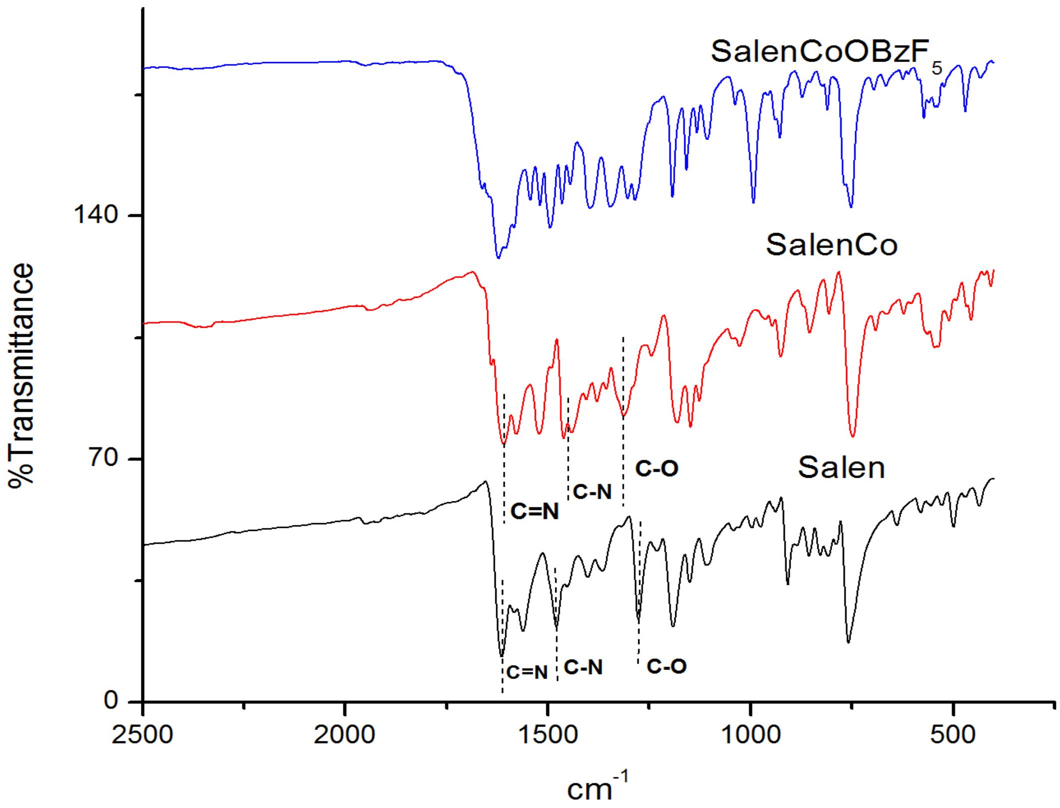


Figure 2: FTIR analysis of Salen, SalenCo and SalenCoOBzF$_5$

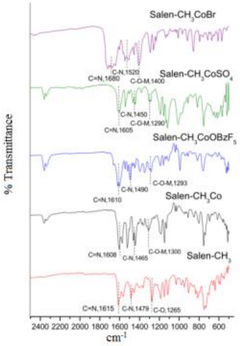


Figure 3: FTIR spectra of Salen-CH_3, Salen-CH_3Co, Salen-CH_3Co(III)OBzF_5, Salen-CH_3 CoSO_4 and Salen-CH_3CoBr

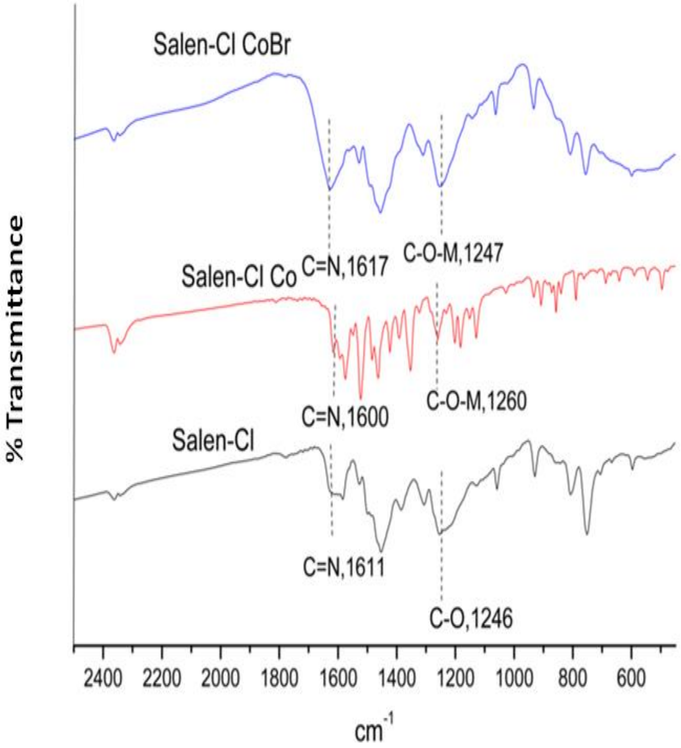


Figure 4: FTIR spectra of Salen-Cl, Salen-Cl Co and Salen-Cl CoBr

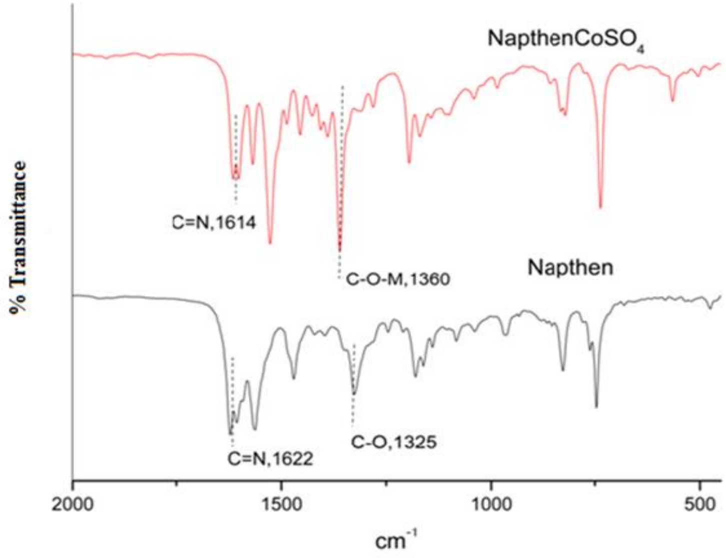


Figure 5: FTIR Spectra of Napthen and NapthenCoSO$_4$

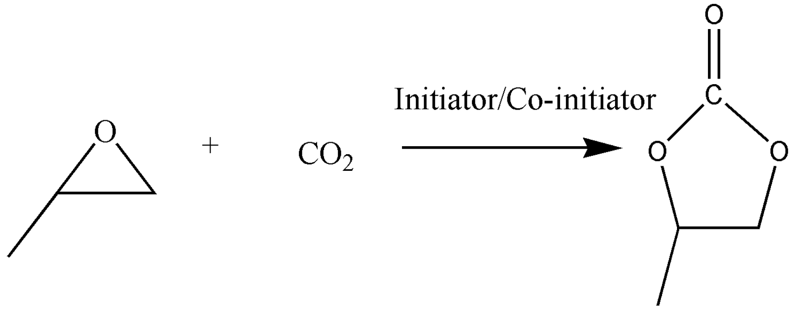


Figure 6: Formation of Cyclic carbonate from Propylene Oxide and CO_2

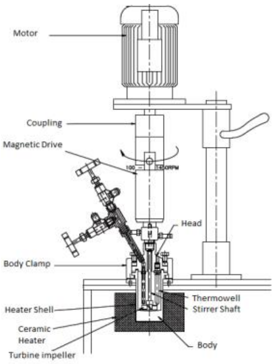


Figure 7: Diagram of reactor used to carry out synthesis of cyclic carbonates

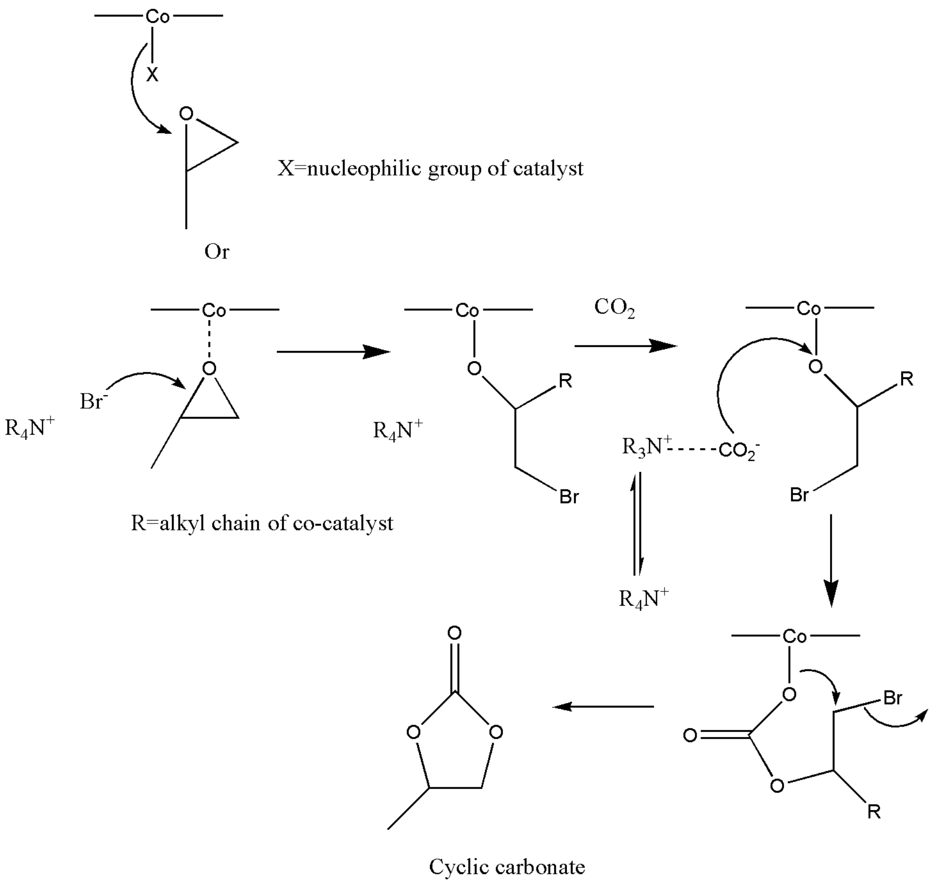


Figure 8: Probable mechanism for the formation of Cyclic carbonate

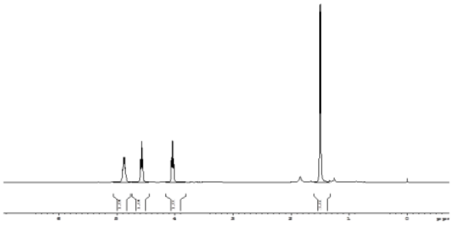


Figure 9: ^{1}HNMR of cyclic carbonate

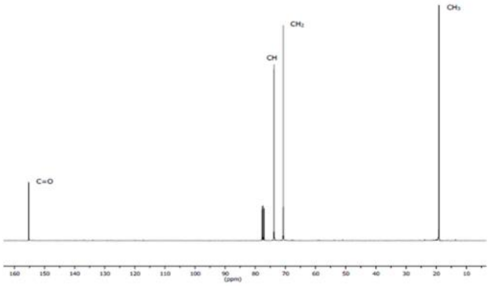


Figure 10: ^{13}C NMR spectra of cyclic carbonate

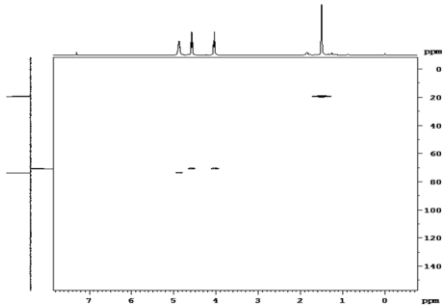


Figure 11: HSQC spectra of cyclic carbonate

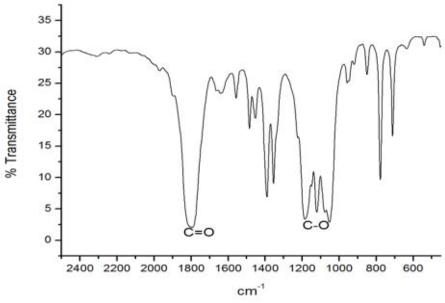


Figure 12: FTIR spectra of pure cyclic carbonate