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A kinetic study of Zn halide/TBAB-catalysed fixation of CO_2 with styrene oxide in propylene carbonate

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Abstract: Synthesis of styrene carbonate (SC) via the fixation of CO_2 with styrene oxide (SO) has been investigated using a combination of zinc bromide ($ZnBr_2$) and tetrabutylammonium halides (TBAX) as acid-base binary homogeneous catalysts. The combination of $ZnBr_2$ and TBAB had a synergistic effect, which led to about 6-fold enhancement in the rate of SC formation as compared to using TBAB alone as a catalyst. Propylene carbonate (PC) was chosen as a green solvent for a comprehensive study of reaction kinetics. The reaction followed a first-order kinetics with respect to SO, CO_2, and TBAB, whereas a fractional order was observed for the $ZnBr_2$ when used in combination with the TBAB. Arrhenius and Eyring's expressions were applied to determine the kinetic and thermodynamic activation parameters, where activation energy (E_a) of 23.3 kJ mol^{-1} was obtained for the SC formation over the temperature range of 90-120°C. The thermodynamic analysis showed that positive values for enthalpy ($\Delta H^{\ddagger} = 18.53$ kJ mol^{-1}), Gibbs free energy ($\Delta G^{\ddagger} = 79.74$ kJ mol^{-1}), whereas a negative entropy ($\Delta S^{\ddagger} = -162.88$ J mol^{-1} K^{-1}) was obtained. These thermodynamic parameters suggest that endergonic and kinetically controlled reactions were involved in the formation of SC from SO and CO_2.

Keywords: cyclic carbonate; carbon dioxide; kinetic study; green solvent; thermodynamic parameters

1 Introduction

In recent decades, the increasing CO_2 concentration in the atmosphere has resulted in drastic changes in the climate. The anthropogenic emission of CO_2 into the atmosphere now exceeds 36 Gt, which is 43% above the level since the beginning of the industrial revolution [1]. This has necessitated some research in the industry and academia to reduce the CO_2 emission via sequestration and utilization [2,3]. Amongst the methods of CO_2 utilization, the most attractive and economically viable option is the application of CO_2 for the production of cyclic carbonates via reactions with epoxides due to its 100% atom economy [4-7]. Another advantage of CO_2 utilisation in cyclic carbonate productions is that it is a naturally abundant non-toxic and non-flammable and can be used as a sustainable alternative to toxic phosgene used in the conventional process [8,9]. Generally, cyclic carbonates are valuable chemicals which have applications as monomers for polycarbonates and polyurethanes [10,11], polar aprotic green solvents [12-14], electrolytes in Li-ion batteries [15,16], and platform chemical for other products [17,18]. However, a major challenge in CO_2 utilization as a feedstock for productions of platform chemicals is due to its high thermodynamic and kinetic stability [19]. Therefore, CO_2 utilisation for organic synthesis is recommended for formations of compounds that have relatively high free energies to provide a thermodynamically feasible process, such as reactions of CO_2 with epoxides in cyclic carbonate formations [20]. Although the reactions of CO_2 with epoxide to form cyclic carbonates was observed to be exothermic [21], such reactions require high activation energy, in the range of 209-251 kJ mol^{-1} based on nature of the epoxide [22,23]. Therefore, a highly efficient catalyst is required to overcome this kinetic barrier [24]. During the last two decades, various catalyst systems have been developed to catalyse the reaction at mild reaction conditions. These mainly include organo-catalysts such as alkylammonium/phosphonium halides [25-28], ionic liquids [29-33], and alkali and alkaline earth metals-based salen/salphen complexes [34-38]. However, there are several catalyst systems which still lack their commercial viability because of their availability, low catalytic activity, the requirement of extreme reaction conditions and complex downstream separation processes. To increase the catalytic activity, it is important to

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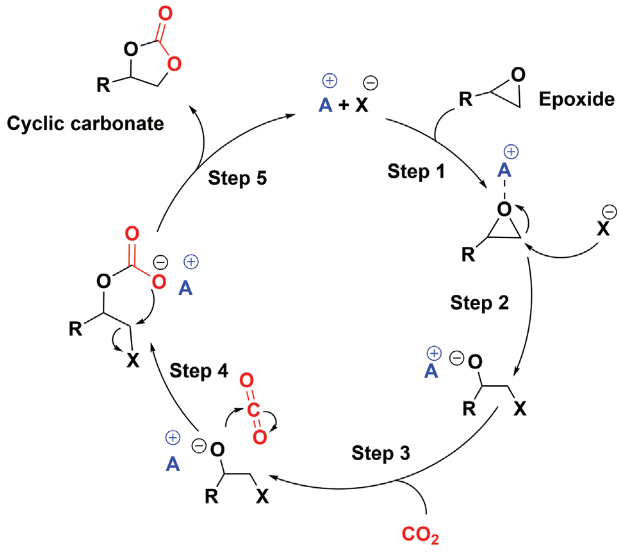

Figure 1: General mechanism of cyclic carbonate synthesis from CO_2 and epoxide using an acid-base catalyst.

understand the mechanism involved in the cycloaddition reaction. Generally, the commonly accepted mechanism for the reactions of CO_2 with epoxides under acid-base catalysis involves the following steps (Figure 1): Epoxide activation by the interaction of Lewis acid (A) with an oxygen atom of the epoxide (Step 1). Ring-opening of activated epoxide by the nucleophilic attack of halide anion (X) on the least substituted carbon (C) atom to form an alkoxide intermediate (Step 2), followed by insertion of CO_2 to the negatively charged alkoxide intermediate (Step 3). Subsequently, an intramolecular rearrangement occurs resulting in the displacement of the halide anion (X) and formation of a carbonate intermediate (Step 4), which forms a five-membered cyclic carbonate and regenerates the catalyst (Step 5) [27,39,40].

In this study, chemical fixation of CO_2 with styrene oxide (SO) was performed using a combination of zinc bromide ($ZnBr_2$) in conjunction with tetrabutylammonium halide (TBAX) as an acid-base binary homogeneous catalyst. Although cyclic carbonate synthesis via CO_2 cycloaddition to epoxides has been broadly investigated using various catalyst systems with higher conversions and yields of cyclic carbonates [21,41], comprehensive studies are required to investigate the mechanism of the reaction. This study involved the determination of reaction rate law, kinetic parameters and testing of hypothesis on the mechanism for the synergistic effect, to obtain a deep insight into the observed catalytic activity due to the synergistic effect between $ZnBr_2$ and TBAB. Arrhenius and Eyring expressions will be used to determine the effects of temperature, activation energy and thermodynamic parameters for SC formation. A reaction mechanism will be proposed based on kinetic analysis of the experimental data.

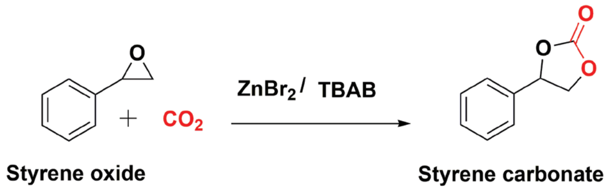

Figure 2: Styrene carbonate (SC) synthesis from styrene oxide (SO) and CO_2 catalysed by $ZnBr_2$/TBAB.

2 Materials and methods

The styrene carbonates (SC) synthesis was carried out using a mono-substituted styrene oxide (SO) and CO_2 (Figure 2). All chemicals were obtained from Sigma Aldrich. The reaction was performed in a semi-batch operation using a high-pressure stainless steel Parr reactor (Model 4750) (Figure 3). The temperature was controlled using an automatic temperature control system (PID controller), whereas pressure inside the reactor was controlled using a 70 bar gas pressure regulator. A high-speed magnetic stirrer was used to provide agitation. For an exemplary experiment, the desired quantities of styrene oxide (SO) and homogeneous catalyst ($ZnBr_2$/TBAB) were added into the reactor and heated to the required temperature by setting the value on the temperature controller. When the temperature set point was achieved, the reactor was pressurised with CO_2 from a gas cylinder to the required pressure. The reaction starts immediately after introducing CO_2 in the reactor. A continuous supply of CO_2 was provided to the reactor to maintain the constant pressure during the reaction. The progress of the reaction was examined by withdrawing a very small volume of aliquots (200 µL) from a large volume of the reaction mixture (40 mL) at regular intervals. These samples were immediately analysed by IR analysis. The IR spectra showed an increase in the intensity at 1800 cm^{-1} due to carbonyl peak of SC formation (Figure 4), and peaks at 1065 and 1159 cm^{-1} corresponding to asymmetric (C–O) stretching vibrations of SC [42-44]. However, the carbonyl absorption peaks of solvent (PC) and product (SC) were overlapped at 1800 cm^{-1} and no changes in the intensity were observed during kinetic experiments using PC as a solvent (Figure 5). Therefore, the progress of the reaction was monitored by the decrease in the intensity of the peak at 876 cm^{-1} assigned to C–O stretch mode in SO, which was clearly

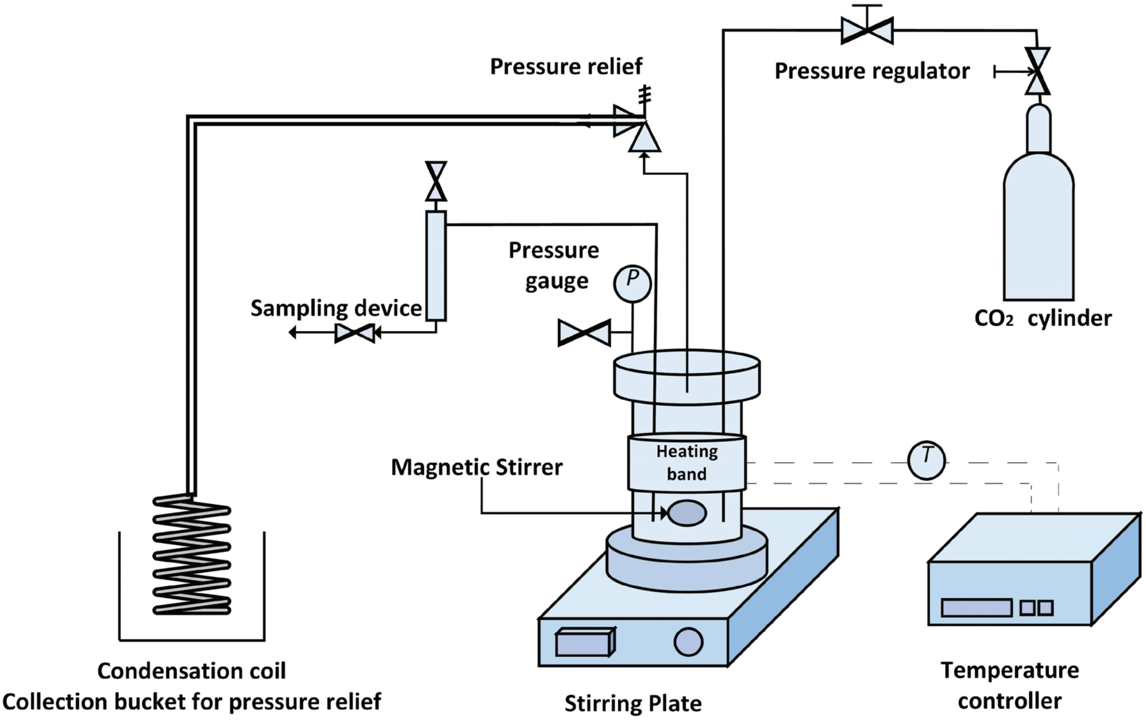

Figure 3: Schematic diagram of the semi-batch reactor used for styrene carbonate (SC) formation.

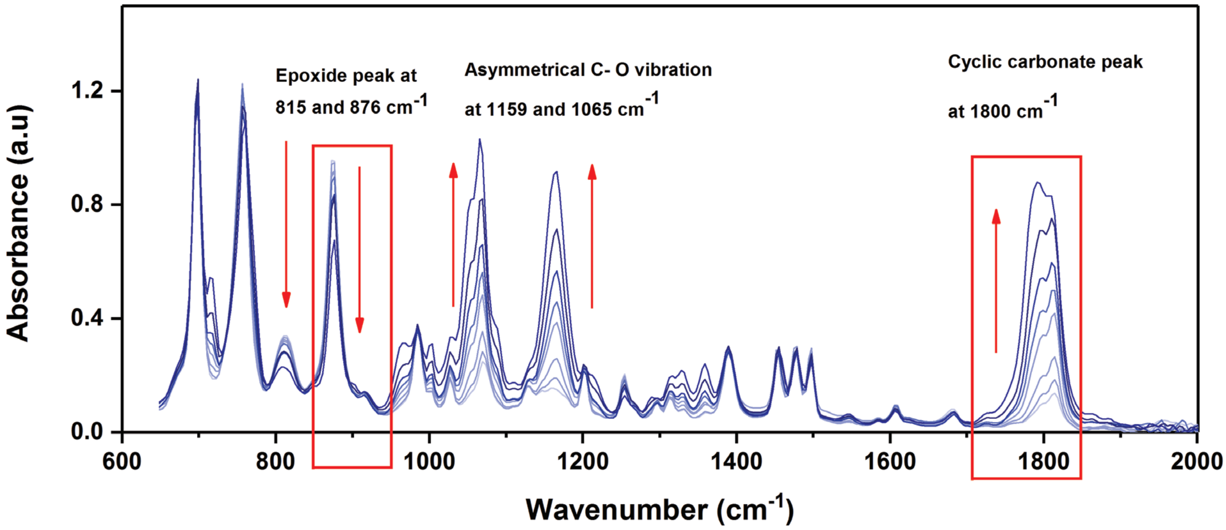

Figure 4: FTIR spectroscopic-monitoring of styrene carbonate (SC) formation.

not masked by the PC absorption. The rate at which the SO epoxide peak at 876 cm^{-1} diminished was directly proportional to SC formation as there was no by-product formation was observed. The conversion (%) was determined based on the decrease in SO peak intensity at 876 cm^{-1} after calibration against known concentrations of SO and was also validated using a 5890 Series II Hewlett Packard gas chromatograph.

3 Results and discussion

3.1 Effect of halide anion on SC formation

Formation of SC was carried out using various TBAX (where X = I$^-$, Br$^-$, Cl$^-$, F$^-$) in combination with $ZnBr_2$ (Figure 6). The results indicate that the order of halide

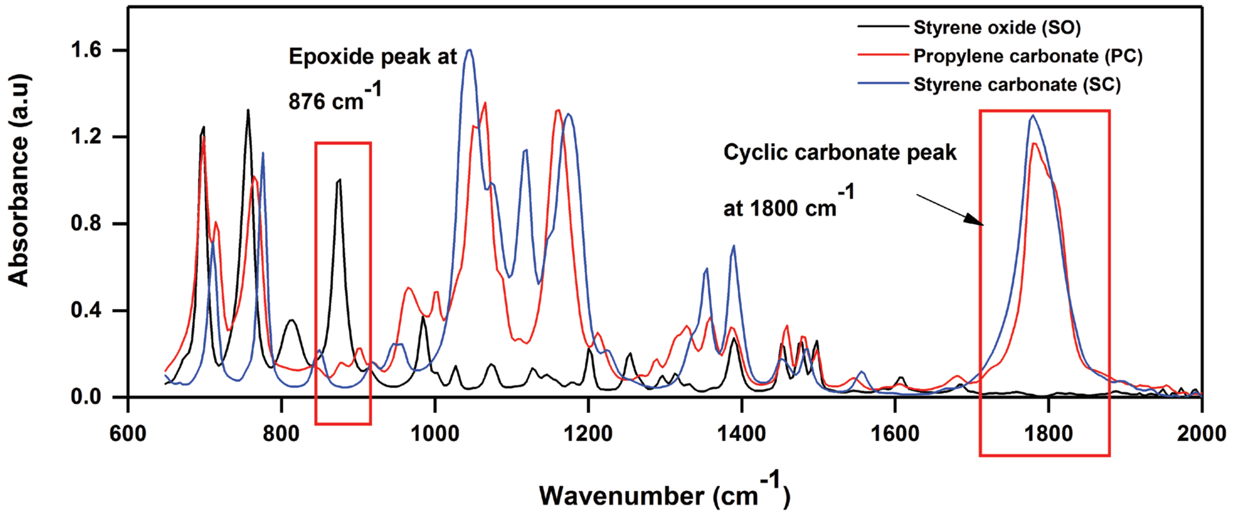

Figure 5: FTIR spectra showing the overlapping of propylene carbonate (PC) and styrene carbonate (SC) peaks at 1800 cm^{-1}.

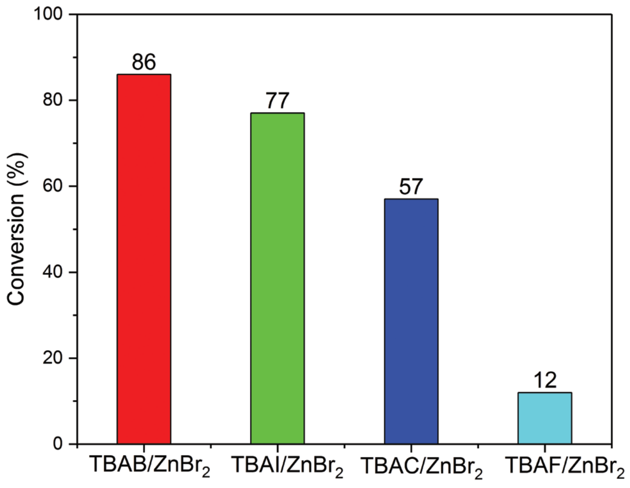

Figure 6: Catalytic activity of tetrabutylammonium halides (TBAX) in combination with $ZnBr_2$ (reaction conditions: Solvent-free SO 35 mmol, 0.4 mmol TBAB, 0.1 mmol $ZnBr_2$ 100°C and 6 bar $p(CO_2)$, 1 h).

anions activity was $Br^- > I^- > Cl^- > F^-$, in agreement with the order of leaving group ability of the halide anions i.e. $I^- > Br^- > Cl^- > F^-$, except for Br^- which exhibited greater activity due to its optimum balance between nucleophilicity and leaving group ability [45]. The activity of halide anion in a binary catalyst system is strongly influenced by the presence of a second catalyst [46]. The order of halide anions activity also varies depending upon the type of epoxide and second catalyst used for cycloaddition reaction [47-50]. A similar order of catalytic activity for SC formation from SO and CO_2 was observed previously when TBAB was used as a co-catalyst with bimetallic aluminium-salen complex [43].

3.2 Kinetic study of SC formation

A detailed study of reaction kinetics was performed to investigate the mechanism associated with SC formation catalysed by a homogeneous binary catalyst ($ZnBr_2$/TBAB). This requires the use of a reaction solvent in order to vary the concentration of SO, and these were selected from commonly used organic solvents such as toluene and polar aprotic solvents: N,N-dimethylformamide (DMF), acetonitrile (CH_3CN) and propylene carbonate (PC) (Table 1). From the results obtained, the use of CH_3CN has exhibited a higher reaction rate and turnover frequency (TOF) than other solvents under these set of reaction conditions. However, PC was selected as it is a 'green' solvent. PC is a high boiling point, biodegradable and non-toxic polar aprotic solvent, which has been commonly used a replacement for toxic solvents such as acetonitrile, DMF and DMSO that are expected to be restricted due to SO_x and NO_x emission when incinerated [39,51]. Another advantage of PC is that its density (1.2 g/cm^3) is close to that of SO (1.05 g/cm^3), which results in a reaction medium with mass transfer properties and miscibility that do not vary considerably from solvent-free reaction conditions. PC can also be prepared by the CO_2 cycloaddition to propylene oxide (PO) using the same catalytic system i.e. $ZnBr_2$/TBAB. Therefore, it will clearly not inhibit the catalyst.

Prior to the detailed kinetic study, the catalytic activity of TBAB with and without $ZnBr_2$ was investigated. Figure 7 shows the significant increase in reaction rate (~6-fold) when TBAB was used in combination with $ZnBr_2$, rather than as TBAB alone. These results clearly

Table 1: Effect of solvent on styrene carbonate (SC) formation catalysed by $ZnBr_2$/TBAB catalyst.*

Solvent	Conversion (%)	TOF (h^{-1})**
Toluene	67	466.7
DMF	55	394.6
Acetonitrile	81	550.4
Propylene carbonate	73	487.5

* Reaction conditions: 4.5 M SO in PC, TBAB (0.1 M), $ZnBr_2$ (6.5 mM) at 100°C and 6 bar CO_2.

** Turnover frequency = TOF = (moles of product) / (moles of catalyst · time).

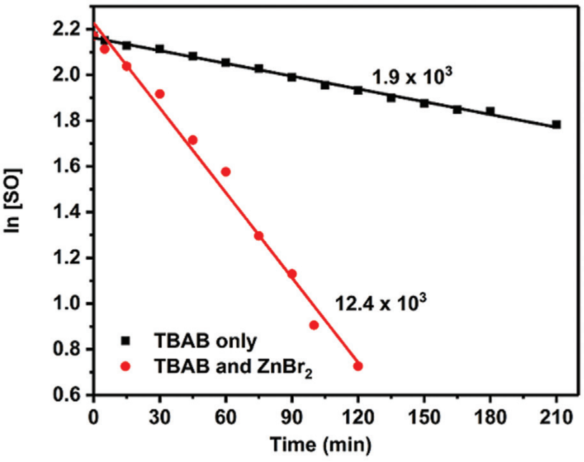

Figure 7: Rate of styrene carbonate (SC) formation catalysed by TBAB with and without $ZnBr_2$ (reaction conditions: Solvent-free SO, $ZnBr_2$/TBAB (1:4), 100°C and 6 bar $p(CO_2)$).

exhibit the synergetic catalytic effect of using $ZnBr_2$ in combination TBAB. Here, the Lewis acidic Zn site caused the SO activation, which undergoes attack by the Br^- anion acting as a nucleophile provided by the TBAB.

The general rate equation for the SC formation by the cycloaddition of CO_2 to SO can be written as Eq. 1. The catalyst concentration was constant throughout the reaction, while the CO_2 was maintained in excess through continuous supply in a semi-batch operation. Therefore, it can be assumed that CO_2 concentration was constant throughout the reaction [20,44]. Hence, Eq. 1 can be simplified as Eq. 2, and taking the natural logarithm of both sides of Eq. 3 gives Eq. 4. Assuming a pseudo-first-order reaction, Eq. 5 applies and this can be integrated to obtain Eq. 6, which can be used to determine the order of reaction of the SO [44].

$$rate = k\,[SO]^a[CO_2]^b[TBAB]^c[ZnBr_2]^d \tag{1}$$

$$rate = k_{obs}\,[SO]^a \tag{2}$$

where

$$k_{obs} = k\,[CO_2]^b[TBAB]^c[ZnBr_2]^d \tag{3}$$

$$ln\,k_{obs} = \ln k + b\,ln\,[CO_2] + c\ln\,[TBAB] + d\,ln\,[ZnBr_2] \tag{4}$$

$$rate = -\frac{d[SO]}{dt} = k_{obs}\,[SO]^a \tag{5}$$

$$-\ln\,[SO] = k_{obs}.\mathrm{t} \tag{6}$$

The order of the reaction with respect to epoxide was determined using SO in the range of 2.5-5.5 M concentrations. The experimental data showed a good fit to first-order kinetics using a plot of ln [SO] against reaction time (min) (Figure 8a). The values of the observed rate constants (k_{obs}) were obtained from the gradients of the first-order plot. Moreover, a linear graph was also obtained between initial concentrations of epoxide against initial reaction rate (mol L^{-1} min^{-1}) (Figure 8b), which confirms a first-order (a = 1) reaction kinetics for the SO [52-54].

The order of the reaction with respect to CO_2 was also studied by varying the pressure over the range 2-8 bar at otherwise constant reaction parameters. Increasing pressure caused the increase in CO_2 concentration in the liquid phase and thereby the increase in reaction rate. The order of the reaction was observed to be first-order as experimentally obtained data exhibit a good fit in first-order kinetics (Figure 9a). There was a linear correlation between the graphs of initial reaction rate against CO_2 pressure (Figure 9b). This shows that the reaction was first-order (b = 1) with respect to CO_2, an indication that one molecule of CO_2 was involved in catalytic cycles [28,55,56].

Reaction order with respect to TBAB was investigated using TBAB concentrations in the range of 0.2-0.5 M, while the other parameters were kept constant. The rate of reaction increased with TBAB concentration (Figure 10a), as would be expected, and all of the data points exhibited good fit to first-order kinetics. Moreover, the reaction was found to be first-order from the gradient (i.e. 1.08) of the double logarithmic graph between (k_{obs}) and [TBAB] (c = 1) (Figure 10b). The role of tetrabutylammonium halides (TBAX) as nucleophile additive to CO_2 cycloaddition reactions is generally well accepted [25,57,58]. These essentially provide a halide anion (X) for epoxide ring-opening by the nucleophilic attack on the least substituted carbon atom of epoxide and also facilitate ring-closing in the final step of the catalytic cycle to form corresponding cyclic carbonate due to its good leaving group abilities.

The order of reaction with respect to $ZnBr_2$ (in combination with TBAB) was also observed by changing the concentration of $ZnBr_2$ over the range of 0.0325-0.25 M

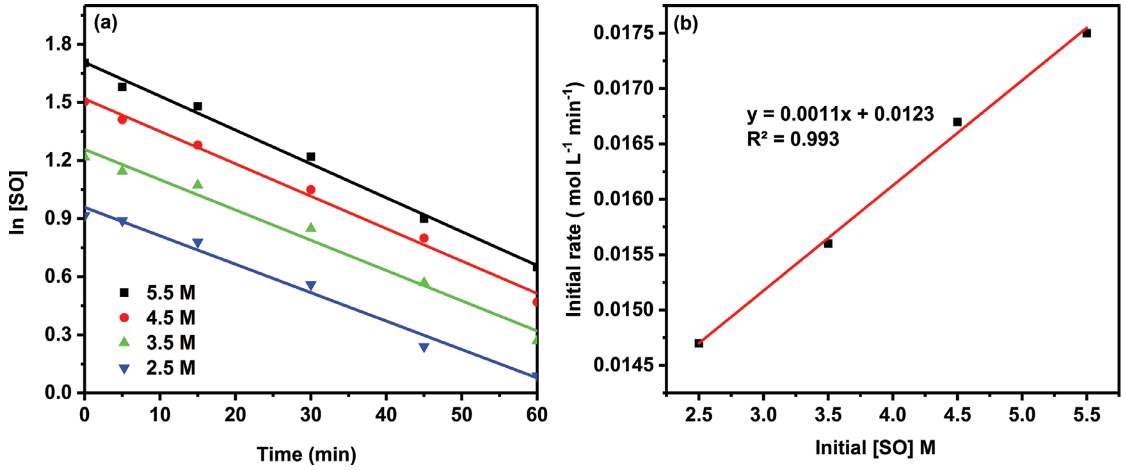

Figure 8: (a) Curve fittings of ln [SO] as a function of time (min) over the range of SO (2.5-5.5) M (b) Plot showing a linear dependence of initial reaction rate (mol L^{-1} min^{-1}) against initial epoxide concentrations [SO] M (reaction conditions: 6.5 mM $ZnBr_2$, 0.1 M TBAB at 100°C and 6 bar p (CO_2)).

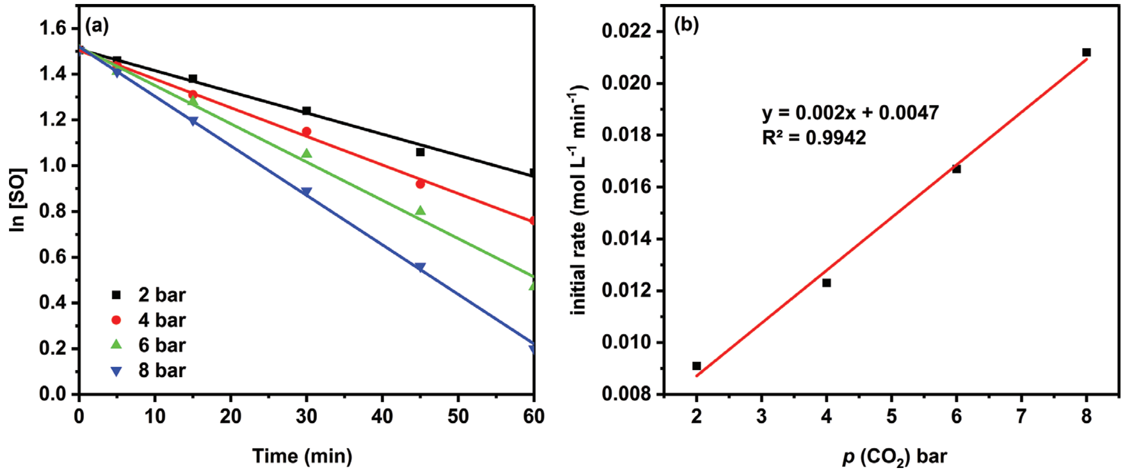

Figure 9: (a) Curve fittings of ln [SO] as a function of time (min) over the range of 2-8 bar $p(CO_2)$; (b) Plot showing a linear dependence of initial reaction rate (mol·L^{-1}·min^{-1}) on CO_2 pressure (reaction conditions: SO 4.5 M in PC, 6.5 mM $ZnBr_2$, 0.1 M TBAB at 100°C).

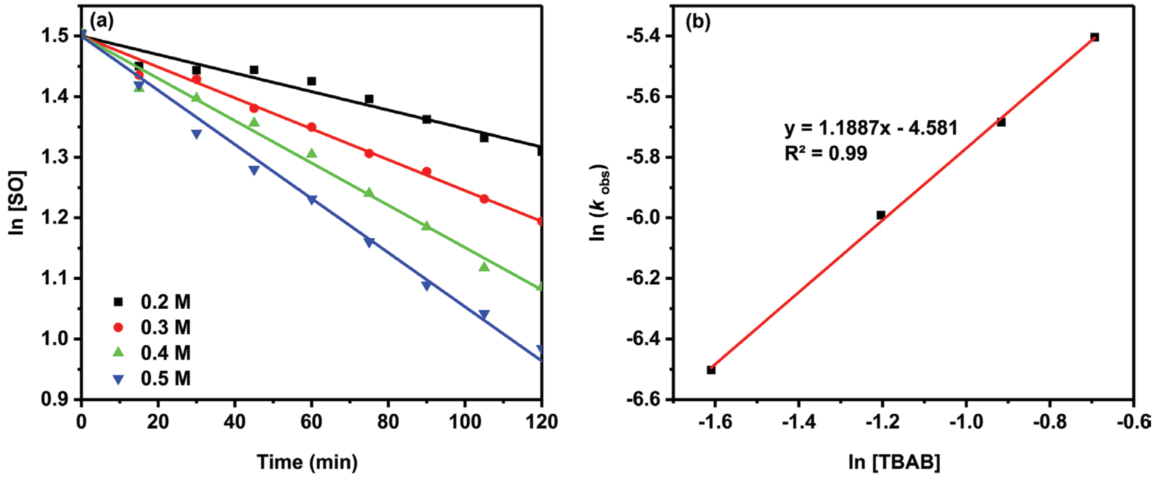

Figure 10: (a) Curve fittings of ln [SO] as a function of time (min) over the range of TBAB (0.2-0.5) M (b) Plot showing a linear dependence of ln (k_{obs}) vs ln [TBAB] (reaction conditions: SO 4.5 M in PC at 100°C and 6 bar p (CO_2)).

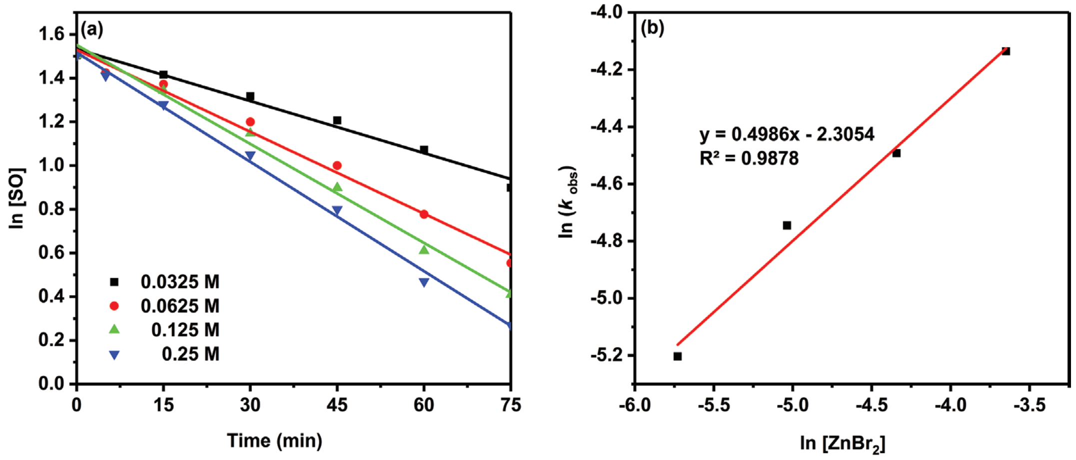

Figure 11: (a) The curve fittings of ln [SO] as a function of time (min) over the range of $ZnBr_2$ (0.0325-0.25) M (b) Double natural logarithmic graph between (k_{obs}) and ($ZnBr_2$) concentrations (reaction conditions: SO 4.5 M in PC, 0.1 M TBAB at 100°C and 6 bar p (CO_2)).

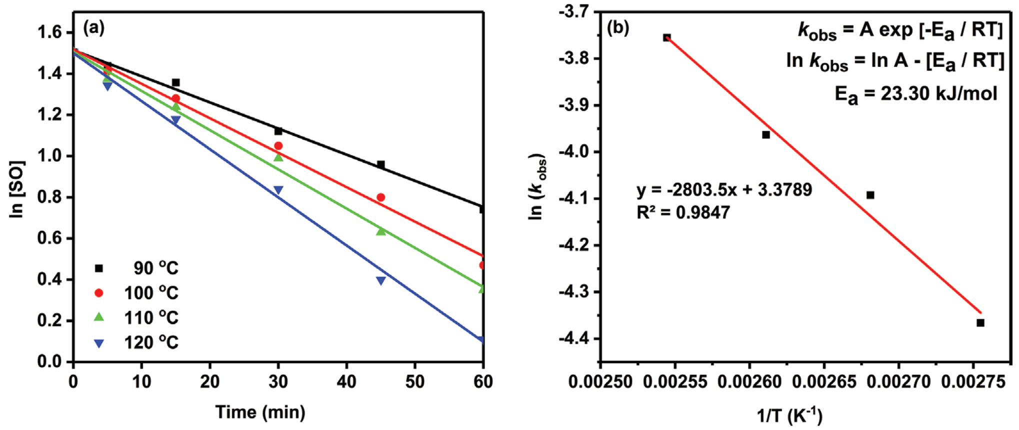

Figure 12: (a) The curve fittings of ln [SO] as a function of time (min) over the temperature range (90-120)°C; (b) Determination of activation energy from Arrhenius plot (ln k_{obs} vs. 1/T) (reaction conditions: SO 4.5 M in PC, 6.5 mM $ZnBr_2$ and 0.1 M TBAB at 6 bar $p(CO_2)$).

(Figure 11a). As mentioned earlier, the reaction rate significantly enhanced due to the synergetic effect of $ZnBr_2$ in combination with TBAB. However, reaction order with respect to $ZnBr_2$ was not first-order. The gradient was instead found to be ~0.5 (Figure 11b). A fractional order (d = 0.5) is normally an indication of the complex reaction. Herein, the proposed reaction mechanism includes a pre-dissociation step. This was probably due to active complex formation consisting of one molecule of $ZnBr_2$ and two molecules of epoxide (Step 2, Figure 14). The metallic salt ($ZnBr_2$) provides a Lewis acidic site in the catalytic cycle for epoxide activation. The activated epoxide then undergoes a nucleophilic attack by halide anion on the less substituted carbon (C) atom of epoxide to open the ring [59,60].

The effect of temperature on SC formation was also studied by varying temperature over the range of 90-120°C. As expected, the reaction rate of CO_2 cycloaddition to SO increases significantly with temperature. The experimental data obtained was found to be fitted well with first-order kinetics (Figure 12a). Furthermore, the Arrhenius activation energy (E_a) was determined by plotting ln (k_{obs}) against reciprocal of absolute temperature (1/T) (Figure 12b). From the results obtained, the activation energy (E_a) for SC formation was determined to be 23.3 kJ mol^{-1}, which is lower than most of the catalyst systems reported previously [53,61]. Moreover, the thermodynamic activation parameters were studied using the Eyring equation (Eq. 7) [62].

$$\ln\left(\frac{k_{obs}}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} \tag{7}$$

where h (6.62608×10^{34} J s) and k_B (1.38065×10^{-23} J K^{-1}) are the Planck's and Boltzmann constants, respectively. The values of enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were determined from the Eyring

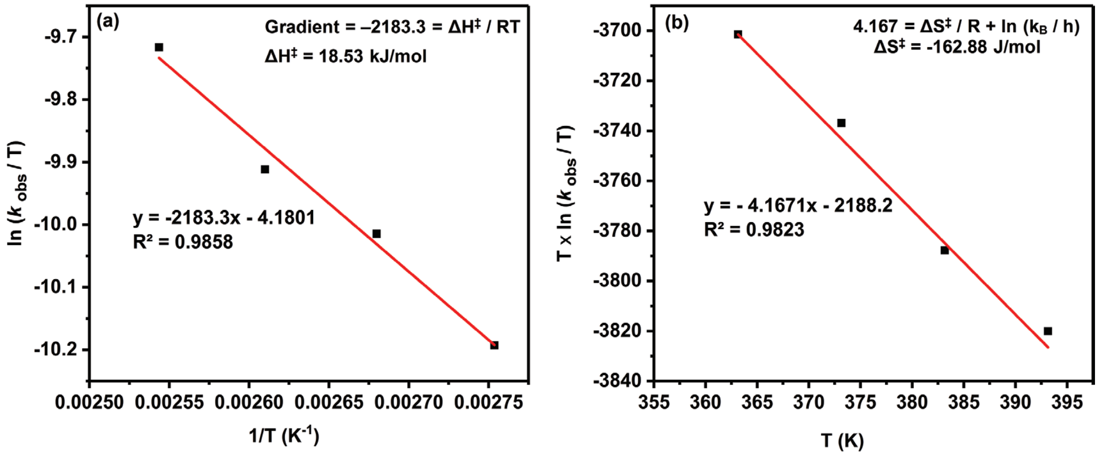

Figure 13: Eyring plots to determine the thermodynamic activation parameters of the reaction according to Eq. 7: (a) enthalpy of activation ($\Delta H^{\ddagger}$); (b) entropy of activation ($\Delta S^{\ddagger}$).

Table 2: Summary of thermodynamic activation parameters of styrene carbonate (SC) formation according to Eyring Equation.

$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T.\,\Delta S^{\ddagger}$ (kJ/mol)			
(kJ/mol)	(J/mol)	363 K	373 K	383 K	393 K
18.53	−162.88	77.3	78.93	80.56	82.19

plots (Figures 13a and 13b). Similarly, the values of Gibb's free energy of activation ($\Delta G^{\ddagger}$) were determined for all temperatures using fundamental thermodynamics equation (Table 2). The values of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ were positive, an indication that the formation of SC via reactions of CO_2 and SO was endergonic and kinetically controlled. However, the low value of $\Delta S^{\ddagger}$ indicates that there is an associative mechanism involved in using the binary catalytic system, as the activated complex has a tendency to become more ordered [63].

3.3 Proposed reaction mechanism

A reaction mechanism was proposed based on the kinetic analysis of SC formation by the reactions of CO_2 and SO catalysed by $ZnBr_2$/TBAB (Figure 14). Initially, the activation of SO takes place by the interaction of Zn-site (Lewis acidic) with the oxygen atom (Step 1). The activated SO undergoes nucleophilic attack by the bromide anion (Br^-) on least substituted carbon (C) atom resulting in a bromo-alkoxide intermediate. This intermediate was stabilised by the tetrabutylammonium cation (TBA^+) to facilitate rapid CO_2-insertion (Step 2). Subsequently, CO_2-insertion takes place by the nucleophilic attack of the negatively charged oxygen of alkoxide intermediate on the electrophilic C atom of CO_2 (Step 3). Lastly, a five-membered ring of styrene carbonate (SC) was formed due to cleavage of Zn–O bond and intramolecular displacement of bromide anion (Br^-) owing to its high leaving group ability (Step 4).

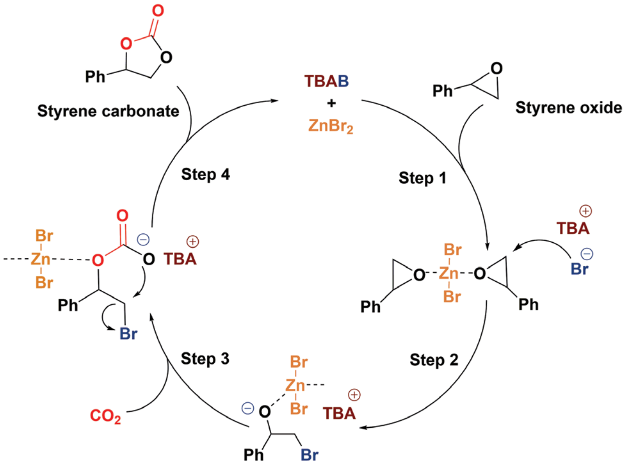

Figure 14: Proposed mechanism of styrene carbonate (SC) formation from styrene oxide (SO) and CO_2 catalysed by $ZnBr_2$/TBAB.

4 Conclusions

Synthesis of styrene carbonate (SC) via the chemical fixation of CO_2 with styrene oxide (SO) was carried out using a combination of cheaply available $ZnBr_2$ and tetrabutylammonium halides (TBAX), as an acid-base binary homogeneous catalyst. Propylene carbonate (PC) was used, as it is considered to be a 'green' solvent. The order of halide anion activity on SC formation was found to be $Br^- > I^- > Cl^- > F^-$, in agreement with the order of leaving group ability of the halide anions, apart from Br^-, which exhibited higher activity due to an optimum balance between nucleophilicity and leaving group ability. The $ZnBr_2$/TBAB combination achieved the highest catalytic activity due to the synergistic effect, increasing the rate 6-fold, compared to TBAB alone. The SC formation reaction was found to be first-order with respect to SO, CO_2 and TBAB, whereas non-first-order kinetics was observed for the $ZnBr_2$. The Arrhenius activation energy (E_a) for the SC formation was 23.3 kJ mol^{-1} at temperatures of 90-120°C. The values of $\Delta H^\ddagger$ and $\Delta G^\ddagger$ determined from the Eyring equation were both positive, suggesting that the SC formation was endergonic and controlled by reaction kinetics. However, the SC formation had a negative $\Delta S^\ddagger$, an indication that the associative mechanism was involved in the binary catalytic system. A reaction mechanism for the SC formation was proposed, explaining the *modus operandi* of the binary homogeneous catalyst.

Acknowledgments

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References

[1] Kleij A.W., North M., Urakawa A., CO_2 catalysis. ChemSusChem, 2017, 10, 1036-1038.

[2] Aresta M., Dibenedetto A., Utilisation of CO_2 as a chemical feedstock: opportunities and challenges. Dalton Transactions, 2007, 2975-2992.

[3] Omae I., Aspects of carbon dioxide utilization. Catal. Today, 2006, 115, 33-52.

[4] Trost B.M., On inventing reactions for atom economy. Acc. Chem. Res., 2002, 35, 695-705.

[5] Sakakura T., Kohno K., The synthesis of organic carbonates from carbon dioxide. Chem. Commun., 2009, 1312-1330.

[6] Yoshida M., Ihara M., Novel Methodologies for the Synthesis of Cyclic Carbonates. Chem.-Eur. J., 2004, 10, 2886-2893.

[7] Kurisingal J.F., Rachuri Y., Gu Y., Kim G.-H., Park D.-W., Binary metal-organic frameworks: Catalysts for the efficient solvent-free CO2 fixation reaction via cyclic carbonates synthesis. Appl. Catal. A-Gen., 2019, 571, 1-11.

[8] Sakakura T., Choi J.-C., Yasuda H., Transformation of carbon dioxide. Chem. Rev., 2007, 107, 2365-2387.

[9] Aresta M., Dibenedetto A., Angelini A., Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. Technological use of CO_2. Chem. Rev., 2013, 114, 1709-1742.

[10] Fukuoka S., Fukawa I., Tojo M., Oonishi K., Hachiya H., Aminaka M., et al., A novel non-phosgene process for polycarbonate production from CO_2: green and sustainable chemistry in practice. Catal. Surv. Asia, 2010, 14, 146-163.

[11] Nohra B., Candy L., Blanco J.-F.O., Guerin C., Raoul Y., Mouloungui Z., From petrochemical polyurethanes to biobased polyhydroxyurethanes. Macromolecules, 2013, 46, 3771-3792.

[12] Schaffner B., Schaffner F., Verevkin S.P., Borner A., Organic carbonates as solvents in synthesis and catalysis. Chem. Rev., 2010, 110, 4554-4581.

[13] North M., Pizzato F., Villuendas P., Organocatalytic, asymmetric aldol reactions with a sustainable catalyst in a green solvent. ChemSusChem, 2009, 2, 862-865.

[14] Lang X.-D., Li Z.-M., He L.-N., Protic ionic liquid-catalyzed synthesis of oxazolidinones using cyclic carbonates as both CO_2 surrogate and sustainable solvent. Catal. Today, 2019, 324, 167-173.

[15] Xu K., Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. Chem. Rev., 2004, 104, 4303-4418.

[16] Scrosati B., Hassoun J., Sun Y.-K., Lithium-ion batteries. A look into the future. Energy Environ. Sci., 2011, 4, 3287-3295.

[17] Shaikh A.-A.G., Sivaram S., Organic carbonates. Chem. Rev., 1996, 96, 951-976.

[18] Clements J.H., Reactive applications of cyclic alkylene carbonates. Ind. Eng. Chem. Res., 2003, 42, 663-674.

[19] Castro-Osma J.A., Alonso-Moreno C., Lara-Sánchez A., Martínez J., North M., Otero A., Synthesis of cyclic carbonates catalysed by aluminium heteroscorpionate complexes. Catal. Sci. Technol., 2014, 4, 1674-1684.

[20] Castro-Osma J.A., Lamb K.J., North M., Cr (salophen) complex catalyzed cyclic carbonate synthesis at ambient temperature and pressure. ACS Catal., 2016, 6, 5012-5025.

[21] North M., Pasquale R., Young C., Synthesis of cyclic carbonates from epoxides and CO_2. Green Chem., 2010, 12, 1514-1539.

[22] Castro-Gómez F., Salassa G., Kleij A.W., Bo C., A DFT study on the mechanism of the cycloaddition reaction of CO_2 to epoxides catalyzed by Zn (Salphen) complexes. Chem. - Eur. J., 2013, 19, 6289-6298.

[23] Wang J.-Q., Dong K., Cheng W.-G., Sun J., Zhang S.-J., Insights into quaternary ammonium salts-catalyzed fixation carbon dioxide with epoxides. Catal. Sci. Technol., 2012, 2, 1480-1484.

[24] Martin R., Kleij A.W., Myth or reality? Fixation of carbon dioxide into complex organic matter under mild conditions. ChemSusChem, 2011, 4, 1259-1263.

[25] Calo V., Nacci A., Monopoli A., Fanizzi A., Cyclic carbonate formation from carbon dioxide and oxiranes in tetrabutylammonium halides as solvents and catalysts. Org. Lett., 2002, 4, 2561-2563.

[26] Sun J., Ren J., Zhang S., Cheng W., Water as an efficient medium for the synthesis of cyclic carbonate. Tetrahedron Lett., 2009, 50, 423-426.

[27] Cokoja M., Wilhelm M.E., Anthofer M.H., Herrmann W.A., Kuehn F.E., Synthesis of cyclic carbonates from epoxides and carbon dioxide by using organocatalysts. ChemSusChem, 2015, 8, 2436-2454.

[28] Rehman A., Fernández A.M.L., Resul M.F.M.G., Harvey A., Highly selective, sustainable synthesis of limonene cyclic carbonate from bio-based limonene oxide and CO_2: A kinetic study. J. CO2 Util., 2019, 29, 126-133.

[29] Peng J., Deng Y., Cycloaddition of carbon dioxide to propylene oxide catalyzed by ionic liquids. New J. Chem., 2001, 25, 639-641.

[30] Kim H.S., Kim J.J., Kim H., Jang H.G., Imidazolium zinc tetrahalide-catalyzed coupling reaction of CO_2 and ethylene oxide or propylene oxide. J. Catal., 2003, 220, 44-46.

[31] Bobbink F.D., Dyson P.J., Synthesis of carbonates and related compounds incorporating CO_2 using ionic liquid-type catalysts: State-of-the-art and beyond. J. Catal., 2016, 343, 52-61.

[32] Kim D., Ji H., Hur M.Y., Lee W., Kim T.S., Cho D.-H., Polymer-supported Zn-containing imidazolium salt ionic liquids as sustainable catalysts for the cycloaddition of CO_2: A kinetic study and response surface methodology. ACS Sustain. Chem. Eng., 2018, 6, 14743-14750.

[33] Li W., Cheng W., Yang X., Su Q., Dong L., Zhang P., et al., Synthesis of Cyclic Carbonate Catalyzed by DBU Derived Basic Ionic Liquids. Chin. J. Chem . 2018, 36, 293-298.

[34] Büttner H., Longwitz L., Steinbauer J., Wulf C., Werner T., Recent developments in the synthesis of cyclic carbonates from epoxides and CO_2. Top. Curr. Chem., 2017, 375, 50.

[35] Martin C., Fiorani G., Kleij A.W., Recent advances in the catalytic preparation of cyclic organic carbonates. ACS Catal., 2015, 5, 1353-1370.

[36] Shaikh R.R., Pornpraprom S., D'Elia V., Catalytic strategies for the cycloaddition of pure, diluted, and waste CO_2 to epoxides under ambient conditions. ACS Catal., 2017, 8, 419-450.

[37] Martínez J., de la Cruz-Martínez F., Gaona M.A., Pinilla-Peñalver E., Fernández-Baeza J., Rodríguez A.M., et al., Influence of the Counterion on the Synthesis of Cyclic Carbonates Catalyzed by Bifunctional Aluminum Complexes. Inorg. Chem., 2019.

[38] Della Monica F., Leone M., Buonerba A., Grassi A., Milione S., Capacchione C., CO_2 cycloaddition to epoxides promoted by bis-thioether-phenolate Fe(II) and Fe(III) complexes. Molecular Catalysis, 2018, 460, 46-52.

[39] Comerford J.W., Ingram I.D.V., North M., Wu X., Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings. Green Chem., 2015, 17, 1966-1987.

[40] Laugel G., Rocha C.C., Massiani P., Onfroy T., Launay F., Homogeneous and Heterogeneous Catalysis for the Synthesis of Cyclic and Polymeric Carbonates from CO_2 and Epoxides: A Mechanistic Overview. Adv. Chem. Lett., 2013, 1, 195-214.

[41] Sun J., Fujita S.-I., Zhao F., Arai M., A highly efficient catalyst system of $ZnBr_2/n\text{-}Bu_4NI$ for the synthesis of styrene carbonate from styrene oxide and supercritical carbon dioxide. Appl. Catal. A-Gen., 2005, 287, 221-226.

[42] Jutz F., Grunwaldt J.-D., Baiker A., Mn (III)(salen)-catalyzed synthesis of cyclic organic carbonates from propylene and styrene oxide in “supercritical” CO_2. J. Mol. Catal. A-Chem., 2008, 279, 94-103.

[43] Clegg W., Harrington R.W., North M., Pasquale R., Cyclic carbonate synthesis catalysed by bimetallic aluminium–salen complexes. Chem.-Eur. J., 2010, 16, 6828-6843.

[44] Luo R., Zhang W., Yang Z., Zhou X., Ji H., Synthesis of cyclic carbonates from epoxides over bifunctional salen aluminum oligomers as a CO_2-philic catalyst: Catalytic and kinetic investigation. J. CO2 Util., 2017, 19, 257-265.

[45] Langanke J., Greiner L., Leitner W., Substrate dependent synergetic and antagonistic interaction of ammonium halide and polyoxometalate catalysts in the synthesis of cyclic carbonates from oleochemical epoxides and CO_2. Green Chem., 2013, 15, 1173-1182.

[46] Steinbauer J., Kubis C., Ludwig R., Werner T., Mechanistic Study on the Addition of CO_2 to Epoxides Catalyzed by Ammonium and Phosphonium Salts: A Combined Spectroscopic and Kinetic Approach. ACS Sustain. Chem. Eng., 2018, 6, 10778-10788.

[47] Büttner H., Lau K., Spannenberg A., Werner T., Bifunctional one-component catalysts for the addition of carbon dioxide to epoxides. ChemCatChem, 2015, 7, 459-467.

[48] Werner T., Buettner H., Phosphorus-based Bifunctional Organocatalysts for the Addition of Carbon Dioxide and Epoxides. ChemSusChem, 2014, 7, 3268-3271.

[49] Büttner H., Steinbauer J., Werner T., Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Bifunctional One-Component Phosphorus-Based Organocatalysts. ChemSusChem, 2015, 8, 2655-2669.

[50] Bobbink F.D., Vasilyev D., Hulla M., Chamam S., Menoud F., Laurenczy G.b., et al., Intricacies of Cation–Anion Combinations in Imidazolium Salt-Catalyzed Cycloaddition of CO_2 Into Epoxides. ACS Catal., 2018, 8, 2589-2594.

[51] Bello Forero J.S., Hernández Muñoz J.A., Jones Junior J., da Silva F.M., Propylene Carbonate in Organic Synthesis: Exploring its Potential as a Green Solvent. Curr. Org. Synth., 2016, 13, 834-846.

[52] Jutz F., Buchard A., Kember M.R., Fredriksen S.B., Williams C.K., Mechanistic investigation and reaction kinetics of the low-pressure copolymerization of cyclohexene oxide and carbon dioxide catalyzed by a dizinc complex. J. Am. Chem. Soc., 2011, 133, 17395-17405.

[53] Liu M., Liu B., Zhong S., Shi L., Liang L., Sun J., Kinetics and mechanistic insight into efficient fixation of CO_2 to epoxides

over N-heterocyclic compound/$ZnBr_2$ catalysts. Ind. Eng. Chem. Res., 2015, 54, 633-640.

[54] Rehman A., Eze V.C., Resul M.F.M.G., Harvey A., Kinetics and mechanistic investigation of epoxide/CO_2 cycloaddition by a synergistic catalytic effect of pyrrolidinopyridinium iodide and zinc halides. J. Energy Chem., 2019, 37, 35-42.

[55] North M., Pasquale R., Mechanism of cyclic carbonate synthesis from epoxides and CO_2. Angew. Chem., 2009, 121, 2990-2992.

[56] Cuesta-Aluja L., Castilla J., Masdeu-Bultó A.M., Aluminium salabza complexes for fixation of CO_2 to organic carbonates. Dalton T., 2016, 45, 14658-14667.

[57] Jutz F., Grunwaldt J.-D., Baiker A., Mn (III)(salen)-catalyzed synthesis of cyclic organic carbonates from propylene and styrene oxide in “supercritical” CO_2. J. Mol. Catal. A-Chem., 2008, 279, 94-103.

[58] Jutz F., Grunwaldt J.-D., Baiker A., In situ XAS study of the Mn (III) (salen) Br catalyzed synthesis of cyclic organic carbonates from epoxides and CO_2. J. Mol. Catal. A-Chem., 2009, 297, 63-72.

[59] Sun J., Fujita S.-I., Zhao F., Arai M., A highly efficient catalyst system of $ZnBr_2$/*n*-Bu_4NI for the synthesis of styrene carbonate from styrene oxide and supercritical carbon dioxide. Appl. Catal. A-Gen., 2005, 287, 221-226.

[60] Xiao L.-F., Li F.-W., Peng J.-J., Xia C.-G., Immobilized ionic liquid/zinc chloride: Heterogeneous catalyst for synthesis of cyclic carbonates from carbon dioxide and epoxides. J. Mol. Catal. A-Chem., 2006, 253, 265-269.

[61] Supasitmongkol S., Styring P., A single centre aluminium (III) catalyst and TBAB as an ionic organo-catalyst for the homogeneous catalytic synthesis of styrene carbonate. Catal. Sci. Technol., 2014, 4, 1622-1630.

[62] Lente G., Fábián I., Poë A.J., A common misconception about the Eyring equation. New J. Chem., 2005, 29, 759-760.

[63] Ghodsi F., Habibi-Khorassani S.M., Shahraki M., Kinetic Spectrophotometric Method for the 1,4-Diionic Organophosphorus Formation in the Presence of Meldrum′ s Acid: Stopped-Flow Approach. Molecules, 2016, 21, 1514.