

Highly selective, sustainable synthesis of limonene cyclic carbonate from bio-based limonene oxide and CO₂: A kinetic study

Abdul Rehman,^{a, b, *} Ana María López Fernández,^a M.F.M. Gunam Resul^a and Adam Harvey^a

^a School of Engineering, Merz Court, Newcastle University, Newcastle Upon Tyne, NE1 7RU,
UK

^b Department of Chemical and Polymer Engineering, University of Engineering and Technology
Lahore, Faisalabad Campus, Pakistan

*a.rehman2@ncl.ac.uk

Abstract

Bio-derived cyclic carbonates are of significant research interest as building blocks for non-isocyanate polyurethanes (NIPUs). Cyclic carbonates from limonene are bio-renewable monomers for the production of fully bio-based polymers from citrus waste; however, there are currently very few reports on their synthesis. This work reports the synthesis of five-membered cyclic carbonates from bio-based limonene oxide (LO) and CO₂ catalysed by commercially available inexpensive, tetrabutylammonium halides (TBAX). The cycloaddition of CO₂ with commercial LO mixture of *cis/trans*-isomers (40:60) is highly stereoselective and the *trans*-isomer exhibits considerably higher conversion than the *cis*-isomer. Therefore, a stereoselective method of (*R*)-(+)-limonene epoxidation was performed to achieve a significantly higher yield of the *trans*-isomer (87 ± 2%) than *cis*-isomer, which leads to high conversion and yield to the corresponding cyclic carbonates. The catalytic effect of halide anions (X⁻) and the influence of operational reaction parameters such as temperature, pressure, and catalyst amount were studied. High conversion (87%) was obtained after 20 h at 120 °C, 40 bar CO₂ using 6 mol% tetrabutylammonium chloride (TBAC) catalyst. A detailed study of the reaction kinetics revealed

the reaction to be first-order in epoxide (LO), CO₂ and catalyst (TBAC) concentrations. Moreover, the temperature dependence of the reaction was studied using Arrhenius and Eyring equations. The activation energy (E_a) of the reaction was calculated to be 64 kJ mol⁻¹. The high positive value of Gibbs free energy ($\Delta G^\ddagger = 102.6$ kJ mol⁻¹) and negative value of activation entropy ($\Delta S^\ddagger = -103.6$ J mol⁻¹) obtained as result of the thermodynamic study, indicate that the reaction was endergonic and kinetically controlled in nature.

Keywords: Limonene oxide, cyclic carbonates, stereoselective epoxidation, tetrabutylammonium halide, kinetic study, activation energy

1. Introduction

Global concerns about high CO₂ levels in atmospheric concentration and dwindling supplies of fossil resources are increasing [1]. As a consequence, the utilization of CO₂ and waste biomass as renewable resources into valuable products is highly desirable as part of a sustainable future chemical process industry [2, 3]. Naturally occurring terpenes have been identified as key starting materials for the production of bio-based epoxides [4]. Limonene is a monocyclic unsaturated terpene, mainly extracted from the peel of citrus fruits (90 wt %) [5-7]. It is a principal component of many essential oils and obtained as a waste product during harvesting and orange juice production [8, 9]. Due to its abundance as a waste by-product and its suitability for organic synthesis in the presence of two double bonds, it can be used as a sustainable replacement for petrol-based epoxides without competing with food crops [10, 11]. In 2013 the global production of limonene was approximately 70,000 tonnes, which is gradually increasing every year [12, 13]. CO₂ is inexpensive, non-toxic and non-flammable; it can be potentially used as an environmentally friendly renewable source of C1 building blocks for organic synthesis. Among

various methods of CO₂ utilization, cycloaddition of epoxides and CO₂ is highly promising in terms of “green chemistry” due to its 100% atom-economical conversion [14, 15]. Five-membered cyclic carbonates have a diverse range of applications such as polar aprotic solvents [16, 17], electrolytes in Li-ion batteries [18, 19], the monomers for polycarbonates and polyurethanes synthesis [20-22], intermediates for the manufacturing of pharmaceuticals [23-25] and many other fine chemicals [26-28]. The formation of cyclic carbonates from epoxides and CO₂ involves fewer hazardous species, as it incorporates CO₂ as a C1 feedstock source rather than the conventional highly toxic and corrosive phosgene route [29, 30]. The synthesis of cyclic carbonates from limonene, in particular, is of significant interest as it is bio-renewable monomer for the production of fully bio-based polymers such as non-isocyanate polyurethanes (NIPUs), which have potential applications as thermoset materials, elastomers, or thermoplastics [11].

However, due to the high kinetic and thermodynamic stability of CO₂ (i.e. $\Delta H_f = -394 \text{ kJ mol}^{-1}$), the effective utilization of CO₂ as a C1 building block is challenging [31, 32]. Therefore, significant research has been conducted to develop homogeneous and heterogeneous catalysts to overcome this kinetic barrier. Catalysts for cyclic carbonisation of epoxides include transition metal complexes [33-36], non-metallic organic bases such as quaternary ammonium and phosphonium salts [37-39], alkali metal salts [40-42] and ionic liquids [43-47] to achieve high yield (%) of the cyclic carbonates at mild reaction conditions. However, most of these catalyst systems have a high activity for petroleum-based terminal epoxides, but little or none towards di- and tri-substituted epoxides. Bio-based limonene oxide (LO) is a tri-substituted epoxide containing an internal epoxide attached to the highly substituted, bulky structure of limonene. Due to the high steric hindrance on the internal epoxide, LO is a challenging substrate for CO₂ cycloaddition [48, 49]. Kleij and co-workers reported amino triphenolate based aluminium

complexes in combination with bis(triphenylphosphine)iminium chloride as a nucleophilic additive having activity towards di- and tri-substituted epoxides [49-51]. However, preparation of these catalysts involves several steps [52]. Alternatively, tetrabutylammonium halides (TABX) have been extensively studied as nucleophile additives for the cycloaddition of CO₂ to epoxides due to their strong nucleophilicity and commercial availability [53, 54]. Particularly, for internal epoxides where the steric hindrance plays an important role to decide the activity of the catalyst, the use of small nucleophiles is highly advantageous compared to bulky catalyst system [55, 56].

Recently, Hiroshi *et al.*, (2018) reported CO₂ cycloaddition to LO catalyzed by commercially available inexpensive tetrabutylammonium chloride (TBAC). The formation of cyclic carbonates was reported to be highly stereoselective, suggesting high reactivity of *trans*-isomer than *cis*-isomer [55]. Therefore, commercial LO which is a mixture of *cis* and *trans*-LO (40:60), is not economically feasible for this reaction as it contains approximately 40% less reactive *cis*-isomer. In this study, a stereoselective method of (*R*)-(+)-limonene epoxidation was carried out with the aim to get a higher yield of *trans*-LO. The *trans*-enriched LO was further used as a substrate for the bio-based cyclic carbonates synthesis using TBAC as a homogeneous catalyst. A detailed kinetic study of cycloaddition reaction was performed to investigate the kinetic parameters and to understand the operating mechanism. Moreover, the temperature dependence of reaction was studied to determine the activation energy (E_a) and thermodynamic activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger). As a result of the kinetic analysis, a reaction mechanism was proposed which is in agreement with the generally accepted mechanism for cyclic carbonate synthesis and highlights the importance of small nucleophiles when such reactions are performed with highly substituted epoxides.

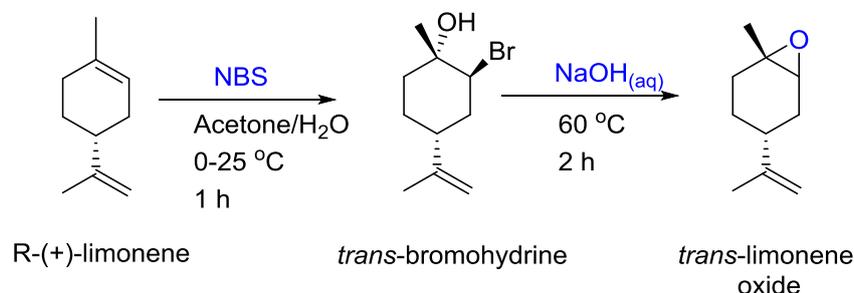
2. Experimental

2.1 Material and methods

The chemicals required for cyclic carbonate synthesis and study of the reaction kinetics were purchased from Sigma Aldrich. The following reagents were used: (*R*)-(+)-limonene (97%), (+)-limonene oxide (a mixture of *cis* and *trans*) ($\geq 97.0\%$), *N*-bromosuccinimide (NBS) (99%), acetone anhydrous HPLC grade ($\geq 99.9\%$), sodium hydroxide, diethyl ether anhydrous ($\geq 97.0\%$), tetrabutylammonium bromide (TBAB) ($\geq 98\%$), tetrabutylammonium chloride (TBAC) ($\geq 97.0\%$), tetrabutylammonium iodide (TBAI) (98%), tetrabutylammonium fluoride trihydrate (TBAF·3H₂O) ($\geq 97.0\%$), propylene carbonate anhydrous (99.7%), toluene anhydrous (99.8%), *N,N*-dimethylformamide anhydrous (99.8%), and CO₂ gas (99.9%) was supplied by BOC Gases.

2.2 Stereoselective epoxidation of limonene

Briefly, the method involves bromination of (*R*)-(+)-limonene with *N*-bromosuccinimide (NBS) as a source of bromine. The reaction was performed in an aqueous solution of acetone at 0–25 °C for 1 h. This results in the formation of endo-cyclic *trans*-bromohydrin which was readily epoxidised into subsequent *trans*-LO using aqueous sodium hydroxide solution at 60 °C for 2 h (Scheme 1). The conversions and yields of (*R*)-(+)-limonene into *cis* and *trans*-LO were obtained using gas chromatography (GC), with naphthalene as an internal standard (Fig. S1).



Scheme 1 Stereoselective epoxidation of (*R*)-(+)-limonene using NBS as bromination source[57].

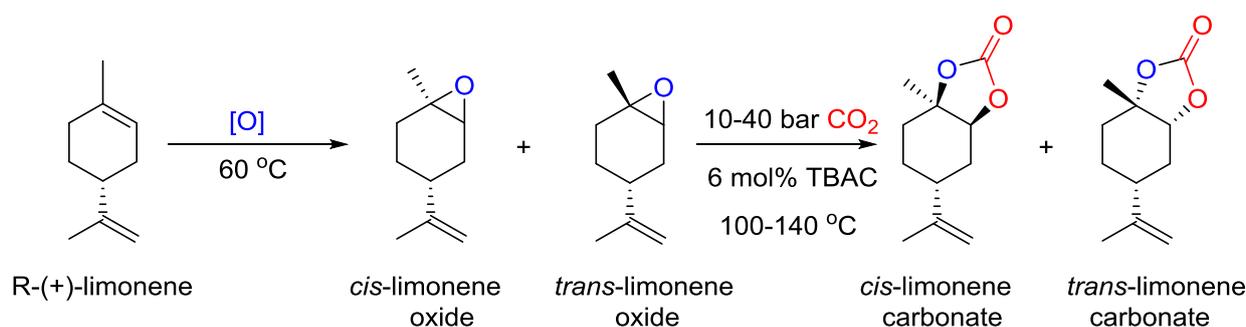
2.3 Cyclic carbonate formation

Cyclic carbonates synthesis (LC) from CO₂ and LO was performed in a 100 ml high-pressure stainless steel Parr reactor (Model 4750) in semi-batch operation. In a typical experiment for cyclic carbonate synthesis, the desired amounts of LO (44 mmol) and homogeneous TBAC catalyst (6 mol%) were charged into the reactor. The reactor was heated to the required temperature set point (100–140 °C). The temperature inside the reactor was controlled by an automatic control system (Elmatic heating controller). After achieving the desired temperature, the reactor was pressurised to the required pressure (10–40 bar) with CO₂ from a gas cylinder. The flow rate to and pressure inside the reactor were controlled by a high-pressure (70 bar) CO₂ gas regulator connected to the outlet of the CO₂ gas cylinder. A pressure gauge was installed on the top of the reactor to measure the pressure inside. The reaction mixture was agitated by a magnetic stirrer. After the completion of the reaction, the reactor was allowed to cool down to room temperature and slowly depressurized to atmospheric pressure. The product of the reaction was analysed by FTIR and ¹H-NMR spectroscopy. For kinetic study experiments, the progress of the reaction was monitored by taking aliquots from the reaction mixture at regular intervals with immediate FTIR analysis, by following the decrease in the intensity of the epoxide peak (C–O stretch) at 841 cm⁻¹. The reduction in this absorbance is consistent with an increase in the intensity of the peak at 1800 cm⁻¹ (carbonyl stretch vibration) corresponds to cyclic carbonate formation (Fig. S2). Similarly, the increase in the intensity of the peak at 1065 cm⁻¹ (asymmetrical C–O vibration) also relates to the formation of cyclic carbonate. To determine the conversion of LO to LC, a calibration curve was drawn by collecting the FTIR epoxide peak area at 841 cm⁻¹ for known concentrations of LO (Table S1, Fig. S6). The conversion and yield of the product can also be determined using ¹H-NMR spectroscopy (Fig. S3). As a result of cyclic carbonate formation, new signals at 4.4 ppm start appearing and the intensity of signals at 2.9 ppm which relate to the

epoxide group starts decreasing [11, 55]. The signals between 0.9 and 2.5 ppm correspond to methyl and methylene protons of LO and LC. The triplet at 3.4 ppm is because of the methylene protons of tetrabutylammonium halide used as a catalyst. The purification of the crude LC was carried out by silica column chromatography using a mixture of ethyl acetate and n-hexane to determine the isolated yield (~ 54%).

3. Results and Discussion

The direct epoxidation of (*R*)-(+)-limonene in the presence of a diverse range of oxidants results in the formation of two diastereomers (a mixture of *cis* and *trans*-LO nearly 1:1) [58]. This stereochemical information obtained from epoxidation was retained in the CO₂ cycloaddition step with formal retention of configuration i.e. *cis* and *trans*-LC (Scheme 2) [49]. The cycloaddition of CO₂ to commercially available LO, which is a mixture of the *cis* and *trans*-isomers (40:60), exhibits a significantly higher conversion of the *trans*-isomer than the *cis*-isomer (Fig. S4), as reported previously [55]. The low reactivity of *cis*-LO versus *trans*-LO was due to its higher energy transition state, owing to its ‘boat-like’ structure [59].



Scheme 2 Epoxidation of (*R*)-(+)-limonene and cyclic carbonate synthesis via CO₂ cycloaddition.

Therefore, previously reported stereoselective method of (*R*)-(+)-limonene epoxidation was performed to gain an advantageous high yield of reactive *trans*-isomer ($87 \pm 2\%$) [57, 60]. To investigate the catalytic effect of halide anions (X^-) on LC synthesis, experiments were carried

out using commercial LO in the presence of different tetrabutylammonium halides (Table 1). The catalytic activity of the halide anions was found to be TBAC > TBAB > TBAI, similar to the previous report [55]. The literature precedent shows the order of catalytic activity of halide anions for CO₂ cycloaddition to terminal epoxides is I⁻ > Br⁻ > Cl⁻ > F⁻, which is in agreement with the nucleophilicity and leaving group ability of halide anions [61-63]. However, LO is an internal epoxide causing a high degree of a steric hindrance due to the presence of two rings in its molecular structure [64]. The steric hindrance of the molecule should obstruct and retard nucleophilic attack of halide anions to ring-open the epoxide. Therefore, in the case of CO₂ cycloaddition to LO, the steric hindrance seems to be a more important factor than the nucleophilicity of the halide anions [34]. Therefore, Cl⁻, having a smaller size than Br⁻ and I⁻ and as a better leaving group than F⁻ exhibits greater catalytic activity. Moreover, the experiments were also performed using both commercial and *trans*-enriched LO to compare the observed rate (k_{obs}) for cyclic carbonate synthesis at different reaction temperatures (i.e. 120 °C and 140 °C), whilst keeping the other reaction parameters constant (Fig. 1 a, b). From the results obtained, the rate of reaction was found to be significantly higher (more than 3-fold) using *trans*-enriched LO. The metallic halide salts (e.g. LiBr, LiCl, ZnBr₂, and ZnCl₂) acting as Lewis acids are commonly used as cocatalysts with alkyl ammonium halides to increase the rate by the activation of the epoxides [61, 65]. However, in the case of LO, no increase in rate was observed due to the metallic salts used in combination with tetrabutylammonium salts. This is was probably due to poor solubility of the metallic salts in the solvent-free reaction mixture [55].

Table 1 Catalytic effect of quaternary alkyl ammonium salts on limonene carbonate synthesis from commercially available LO and CO₂ (Reaction condition: 6 mol% TBAX, 120 °C, p (CO₂) = 40 bar, 10 h).

Entry	Catalyst	Conversion		
		LO (<i>cis</i> + <i>trans</i>)	<i>trans</i> -LO	<i>cis</i> -LO
1	TBAC	71	55.4	15.6
2	TBAB	55	40.2	14.8
3	TBAI	18	13.7	4.3
4	TBAF	18	14.9	3.1

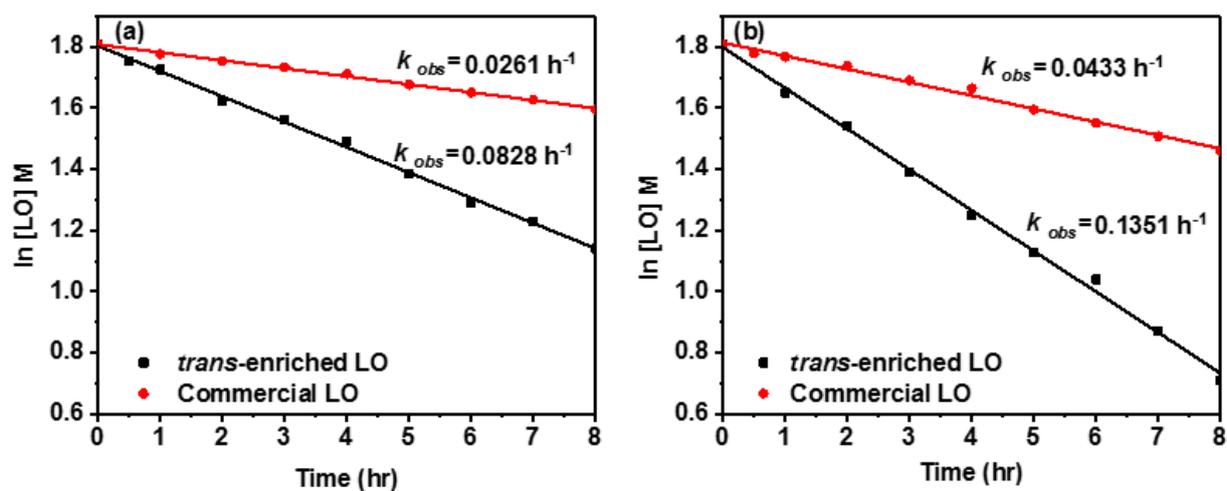


Fig. 1 Comparison of the rate constants for limonene cyclic carbonate synthesis using commercial and *trans*-enriched limonene oxide determined at (a) 120 °C and (b) 140 °C, Reaction conditions: solvent-free LO, 6 mol % TBAC and 40 bar p (CO₂).

3.1 Kinetic Study

A detailed study of reaction kinetics was performed to investigate the mechanism involved and to establish a general rate law equation for cyclic carbonate synthesis from LO and CO₂ in the presence of homogeneous TBAC catalyst. Only the initial experiments for catalyst screening were performed using commercial LO (40:60 mixture of *cis/trans*-isomers) which demonstrated the higher reactivity of *trans*-isomer. Based on these results, *trans*-enriched LO obtained from our stereoselective epoxidation of limonene was used for the further kinetic studies. A series of experiments were performed to determine the order of the reaction with respect to epoxide (LO), catalyst (TBAC) and CO₂ in the presence of a reaction solvent. To find a suitable solvent, the experiments were performed in the presence of commonly used solvents for cycloaddition reactions, such as toluene, N, N-dimethylformamide (DMF), acetonitrile (CH₃CN) and propylene carbonate (PC) [66-68]. The reaction rate of LC formation was determined in the presence of these solvents (Fig. 2a). The results indicate that the reaction rate is higher (0.1769 h⁻¹) in the presence of DMF as a solvent than toluene, CH₃CN, and PC (Table 2). The enhanced reaction rate in the presence of DMF solvent was probably due to nucleophilic activation of the CO₂ by an amide. This catalytic role of DMF in cycloaddition reaction was reported previously [69-72]. Moreover, the yield (%) of LC has been also plotted against the reaction time (Fig. 2b). The results indicate the higher yield of LC was obtained using polar aprotic solvents such as DMF, PC, and CH₃CN compared to a non-polar solvent such as toluene. Due to their high dielectric constants (>20) and large dipole moments, polar aprotic solvents have a high affinity for dissolution of charged species such as various anions used as nucleophiles (catalyst) compared to other non-polar solvents such as toluene [73]. However, PC is being increasingly used as 'greener' alternative to traditionally used toxic, polar aprotic solvents such as DMF, dimethyl sulfoxide (DMSO), and acetonitrile, which are likely to be banned due to their associated SO_x and NO_x emission [74, 75]. PC has low

toxicity, is biodegradable and economical, allowing its large-scale use [76]. Therefore, the PC was chosen as the most advantageous ‘green’ reaction solvent to study the reaction kinetics.

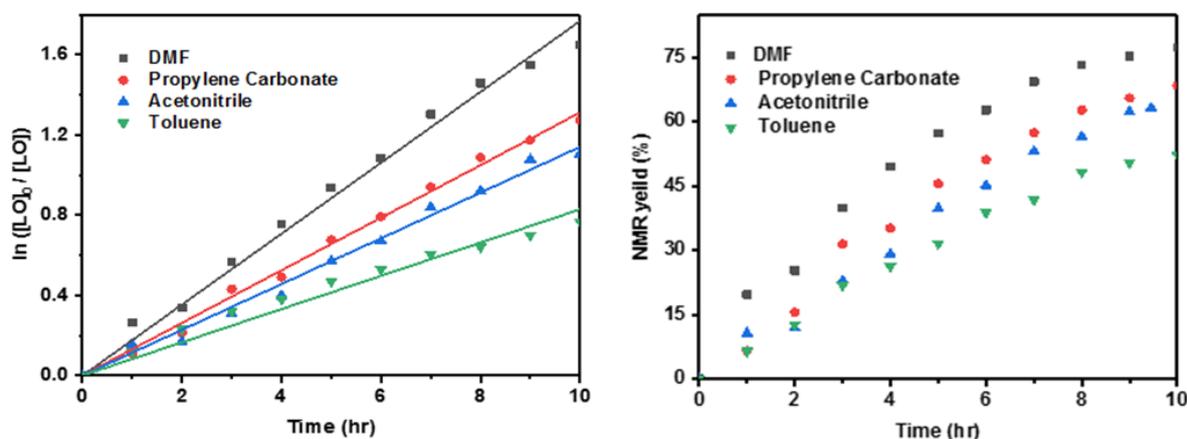


Fig. 2 (a) Plot of $\ln ([LO]_0/[LO])$ against time showing the change in the rate of reaction using different reaction solvents, (b) Plot of NMR yield (%) against the reaction time using different reaction solvents (Reaction conditions: 4.5 M LO, 120 °C, p (CO₂) = 40 bar, 6 mol% TBAC catalyst).

Table 2 Rate constants of limonene carbonate synthesis in the presence of different solvents.

Solvent	Rate constant (h ⁻¹)
DMF	0.1769
Propylene carbonate	0.1312
Acetonitrile	0.1157
Toluene	0.0753

The general form of the rate equation for LO/CO₂ cycloaddition catalyzed by TBAC can be shown as:

$$rate = \frac{-d[LO]}{dt} = k [LO]^a [CO_2]^b [TBAC]^c \quad (1)$$

Where [LO], [CO₂], and [TBAC] are limonene oxide, carbon dioxide, and tetrabutylammonium

chloride concentrations, respectively. As CO₂ was present in large excess due to the semi-batch operation, we assume that the concentration of CO₂ remains unchanged throughout the reaction. Similarly, (TBAC) acts as a catalyst; therefore its concentration can be assumed to be constant during the reaction. Therefore Eq. (1) can be simplified as (Eq.2):

$$\frac{-d[LO]}{dt} = k_{obs} [LO]^a \quad (2)$$

Where

$$k_{obs} = k [CO_2]^b [TBAC]^c$$

Here, k_{obs} is the pseudo-first-order observed rate constant for LO concentration and a, b and c are the order of the reactions with respect to epoxide [LO], catalyst [TBAC] and [CO₂] concentrations. Assuming the first-order reaction and by integration of both sides, Equation 2 can be written as (Eq. 3):

$$-\ln [LO] = k_{obs} \cdot t \quad (3)$$

3.1.1 Reaction order in [LO]

To find the reaction order with respect to epoxide, experiments were performed by changing the initial concentration of LO from 1.5–5.5 M using PC as a reaction solvent at 120 °C and 40 bar CO₂ pressure in the presence of 6 mol% TBAC catalyst. The decrease in the epoxide concentration [LO] was monitored by following the decrease in the intensity of epoxide peak area (C–O stretch i.e. 841 cm⁻¹) using ATR-IR spectroscopy. The graph of experimentally determined values of ln [LO] against time shows a linear-correlation as all the data points obtained were found to fit first-order kinetic plots (Fig. 3a), Eq. 3. Moreover, the order of the reaction was determined from the

slope of the double logarithmic plot of observed reaction rates (k_{obs}) against [LO] i.e. 0.81~ 1, suggesting a first-order reaction in LO concentration ($a = 1$), (Fig. 3b). This was further confirmed from by the plot of k_{obs} against the initial concentration of epoxide [LO] showing a good fit to the straight line ($R^2 = 0.99$), (Fig. S8). This result was found to be consistent with previously reported studies for CO_2 cycloaddition to terminal epoxides [68, 77, 78].

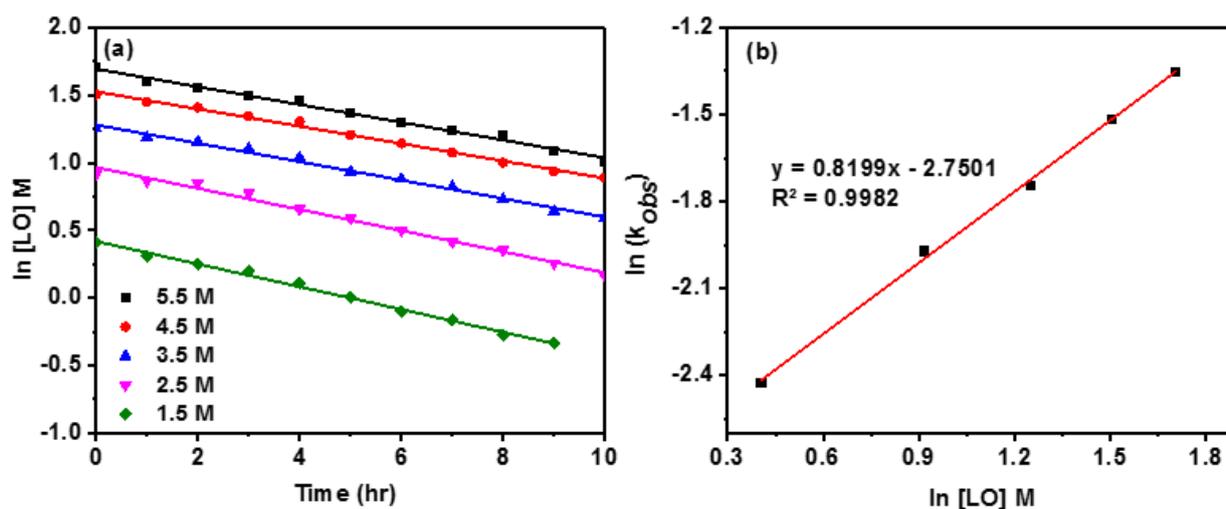


Fig. 3 a) Plot of $\ln [LO]$ against reaction time (h) showing all the data points fits into first-order kinetics for five different LO initial concentrations (1.5–5.5 M) **b)** Plot of $\ln(k_{obs})$ against $\ln(LO)$ showing the first-order dependence of the reaction rate with respect to LO (Reaction conditions: 120 °C, $p(CO_2) = 40$ bar and 6 mol% TBAC catalyst).

3.1.2 Reaction order in $[CO_2]$

The order of the reaction with respect to CO_2 concentration was investigated by changing the CO_2 pressure from 10–40 bar whilst keeping all other reaction parameters constant (i.e. 4.5 M LO, 120 °C and 6 mol% TBAC). The rate of CO_2 dissolution in the reaction solvent (PC) is well known and is considerably higher than the rate of the cycloaddition reaction [79]. Hence, the CO_2 in the gas and liquid phases will quickly reach equilibrium. The data obtained from the kinetic experiments were found to be fit in first-order kinetics (Fig. 4a). The order of the reaction was

determined from the slope of the double logarithmic graph of k_{obs} vs. CO_2 pressure i.e. 0.86 (Fig. 4b) indicating a first-order dependence of reaction in CO_2 concentration ($b=1$) over the range of 10–40 bar CO_2 pressure. These results were consistent with the previously reported study of CO_2 cycloaddition to LO where the conversion of both *cis* and *trans*-isomers increased with the increase in CO_2 pressure up to 50 bar. However, a slight decrease in conversion was reported when the pressure was further increased to > 50 bar [55]. The first-order dependence of the reaction with respect to CO_2 concentration suggests the involvement of one molecule of CO_2 in the catalytic cycle [80, 81].

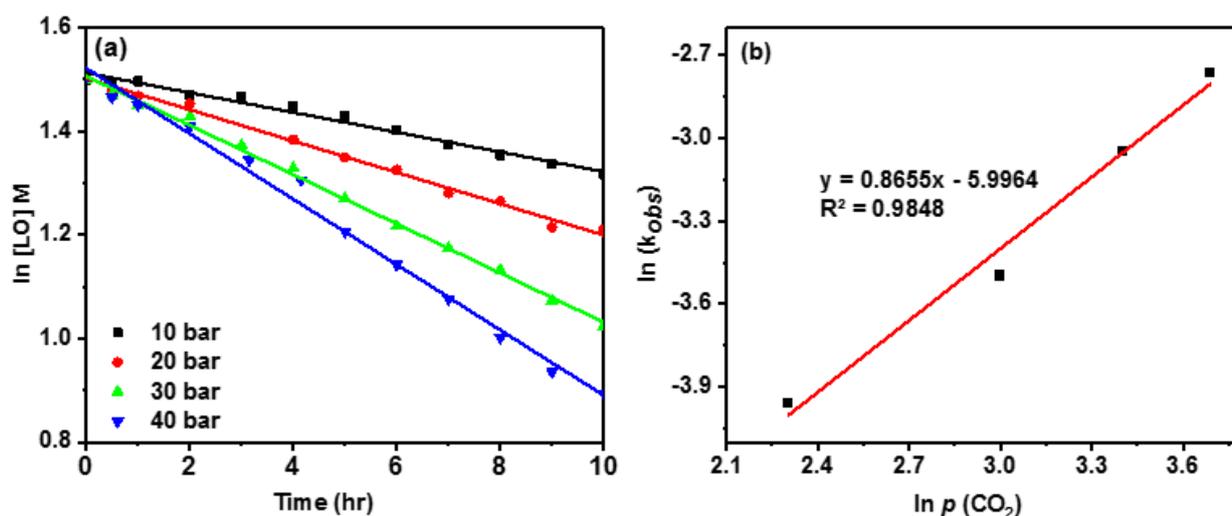


Fig. 4 a) Plot showing the decrease in LO concentration [M] against time at different CO_2 pressures ranging from 10–40 bar b) The fitting curve of $\ln (k_{obs})$ against the $\ln p (\text{CO}_2)$ showing linear dependence of reaction rate (Reaction condition: 4.5 M LO in PC 120 °C and $p (\text{CO}_2) = 10\text{--}40$ bar).

3.1.3 Reaction order in [TBAC]

The order of the reaction with respect to catalyst (TBAC) was determined using five different concentrations of TBAC from 1.5–7.5 mol%, whilst keeping other reaction parameters constant. The results indicate that the rate of the reaction increases with the catalyst amount, and a linear

relation between $\ln [\text{LO}]$ and time (hr) was obtained (Fig. 5a), which is in agreement with the previous report where a gradual increase in conversion was reported over the range of 1–40 mol% TBAC [55]. The double logarithmic graph between k_{obs} and $[\text{TBAC}]$ had a slope of 1.07 clearly indicating first-order dependence with respect to catalyst concentration ($c=1$), (Fig. 5b). This was further confirmed by the plot of k_{obs} against $[\text{TBAC}]$ showing a good fit to the straight line ($R^2 = 0.99$) (Fig. S10). Recently, a similar order of the reaction has been reported for epoxide/ CO_2 cycloaddition reaction in the presence of tetrabutylammonium halide as a monofunctional catalyst [82]. The role of the halide anion (X^-) in the catalytic cycle of cyclic carbonate formation has been well-established and is determined by the balance of its nucleophilicity and leaving group ability [83-86]. Here, the chloride anion (Cl^-) of the TBAC catalyst opens the ring of epoxide by the nucleophilic attack to form a chloro-alkoxide intermediate. This chloro-alkoxide further incorporates CO_2 to form carbonate anion, which then undergoes intramolecular formation of the five-membered cyclic carbonate by the elimination of Cl^- ion acting as a leaving group.

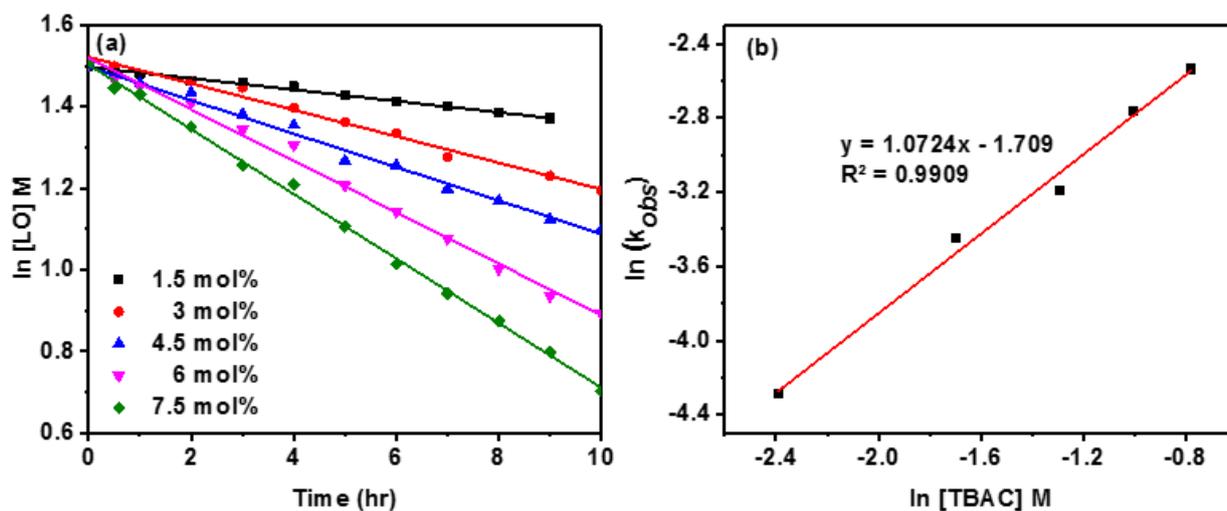


Fig. 5 a) Plot of $\ln [\text{LO}]$ vs. time (h) for five concentrations of TBAC (1.5–7.5 mol%) indicating first-order kinetics **b)** Plot of $\ln (k_{\text{obs}})$ vs. $\ln [\text{TBAC}]$ showing a linear correlation having slope= 1.07 (Reaction condition: 4.5 M LO in PC 120 °C and $p(\text{CO}_2) = 40$ bar).

In summary, on the basis of the experimental results of the kinetic study, the orders of reaction with respect to [LO], [TBAC] and [CO₂] were determined. The rate law of LC synthesis from LO and CO₂ in the presence of TBAC as a catalyst can be written as (Eq. 4):

$$rate = k [LO]^1 [TBAC]^1 [CO_2]^1 \quad (4)$$

Where k is the rate constant and the reaction is first-order in [LO] and [TBAC] and [CO₂] over the range of pressure from 10–40 bar.

3.1.4 Activation Energy

To calculate the activation energy (E_a) for LC formation, the dependence of the reaction rate was studied over a temperature range of 100–140 °C at 40 bar CO₂ pressure using 6 mol% of TBAC catalyst (Fig. 6a). As expected, the reaction rate increased with the increase in temperature due to increased catalytic activity at higher temperatures. The activation energy (E_a) can be calculated from the plot of ($\ln k_{obs}$) against the reciprocal of the absolute reaction temperature ($1/T$) using the Arrhenius equation i.e. $k_{obs} = A \cdot \exp(-E_a/RT)$, (Fig. 6b). As a result, the activation energy was calculated to be 63.90 kJ mol⁻¹ over a temperature range of 100–140 °C. The activation energy for cyclic carbonate synthesis from internal epoxides such as cyclohexene oxide catalyzed by dizinc and trizinc complexes was determined as 137.5 and 83.1 kJ mol⁻¹ respectively [87, 88]. These high values of a kinetic barrier for cyclic carbonate synthesis from internal epoxides show the challenging nature of internal epoxides. Moreover, the activation parameters of the reaction were also determined using the Eyring equation (Eq. 5–6, Fig. 7) [89]. This involves calculations of activation enthalpy (ΔH^\ddagger), activation entropy (ΔS^\ddagger) and Gibbs free activation energy (ΔG^\ddagger) as

listed in Table 3. The value of activation energy (E_a) obtained from the Eyring plot (i.e. 63.74 kJ mol⁻¹) was found to be in close agreement with the value obtained from the Arrhenius plot.

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{k_B T}{h} \exp\left(-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \quad (5)$$

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT} + \left(\frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h}\right) \quad (6)$$

Where h is Planck constant (6.6261×10^{-34} Js) and k_B is Boltzmann constant (1.3807×10^{-23} J K⁻¹).

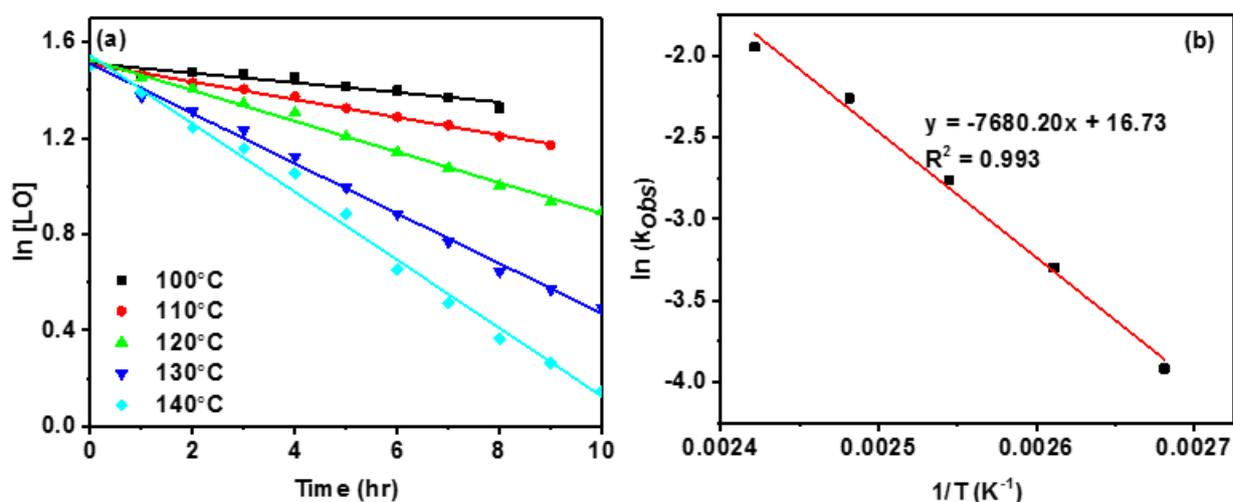


Fig. 6 a) Decrease in LO mole concentration ($[LO] = 4.5$ M) with time over the temperature range of 100–140 °C **b)** Curve fitting of $\ln k_{obs}$ against the reciprocal absolute temperature (Reaction conditions: 4.5 M LO in PC at $p(\text{CO}_2) = 40$ bar and 6 mol% TBAC catalyst).

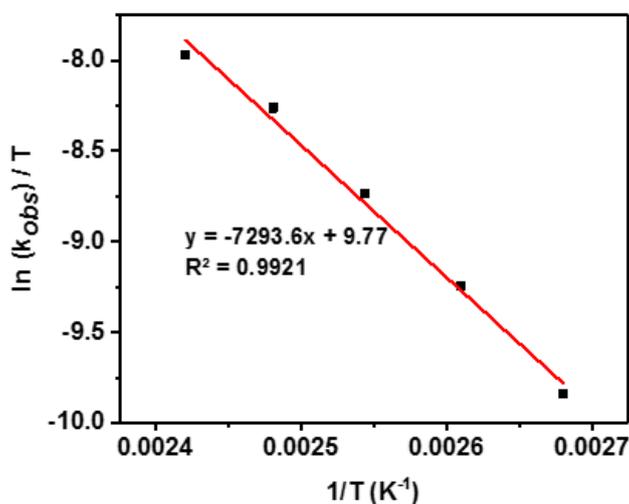


Fig. 7 Eyring plot of $\ln(k_{obs}) / T$ against the reciprocal of absolute reaction temperatures ($1/T$) over a temperature range of 100–140 °C.

Table 3 Activation parameters for LC synthesis calculated using Eyring equation.

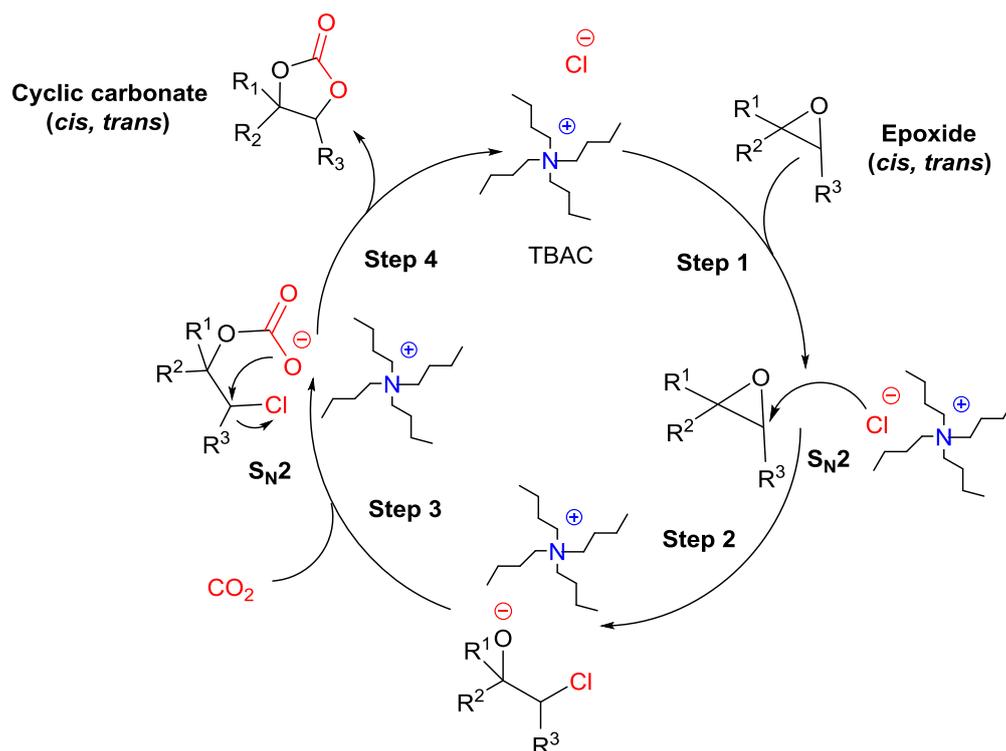
Activation enthalpy	Activation entropy	Gibbs free energy	Activation energy
ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	E_a
kJ mol^{-1}	$\text{J mol}^{-1}\text{K}^{-1}$	kJ mol^{-1}	kJ mol^{-1}
60.64 ^a	-103.59 ^a	102.55 ^b	63.74 ^c

^aAccording to Eq. 6, ^b $\Delta G^\ddagger = \Delta H - T \cdot \Delta S$ at 373 K, ^c $E_a = \Delta H + RT$

3.1.5 Proposed reaction mechanism

On the basis of the detailed kinetic study, a reaction mechanism for cyclic carbonate from tri-substituted epoxide has been proposed (Scheme 3) that is consistent with the observations here. In the first step, the halide anion (Cl^-) of tetrabutylammonium chloride (TBAC) undergoes a nucleophilic attack on the least hindered carbon atom to ring-open the epoxide. In the absence of Lewis acid catalyst, there was no partial positive charge on any carbon atom and the 2 C atoms in the epoxide ring have the same electrophilicity. Therefore, the nucleophilic attack takes place on the least sterically hindered carbon atom due to its higher accessibility. This results in the formation of a highly reactive chloro-alkoxide intermediate which is stabilized by the counter cations (TBA^+) (step 2). This ring-opened epoxide further coordinates with a carbon atom of CO_2 to give carbonate anion (step 3). Finally, the carbonate anion goes through intramolecular cyclic elimination to give a five-membered cyclic carbonate (*cis* and *trans*-isomer) and the catalyst is regenerated (step 4). The reported observations are in agreement with the accepted mechanism for cyclic carbonate formation and highlight the importance of small nucleophiles like chloride when such reactions are performed with highly substituted epoxides. Moreover, the overall

stereochemical information was retained due to two consecutive S_N2 reactions at the same carbon center as shown in ring opening and ring closure steps of the mechanism. This retention in the overall configuration was suggested for cyclic carbonate synthesis from internal epoxide using a relatively high concentration of halide anion in the reaction mixture [90].



Scheme 3 Proposed reaction mechanism of cyclic carbonate synthesis from tri-substituted epoxide and CO₂.

4. Conclusions

In conclusion, a 100% selective synthesis of sustainable cyclic carbonates from bio-based LO and CO₂ was carried out using a commercially available, inexpensive TBAC as an effective homogeneous catalyst. The initial studies of cycloaddition from a commercially available LO (a mixture of *cis* and *trans*-LO) revealed that the reaction was stereoselective and the *trans*-isomer was found to be more reactive than the *cis*-isomer similar to the previous report. A stereoselective

method of (*R*)-(+)-limonene epoxidation was carried out following the reported protocols to achieve a high yield of the more reactive *trans*-isomer ($87 \pm 2\%$). Moreover, a detailed kinetic study of CO₂ cycloaddition to LO was carried out in the presence of propylene carbonate as a greener polar aprotic solvent. The results indicate a first-order dependence of the reaction with respect to LO, TBAC and CO₂ concentrations. The temperature dependence of the reaction rate was also studied over a range of 100–140 °C to determine the activation parameters, via Arrhenius and Eyring plots. The activation energy (E_a) calculated for LC synthesis was found to be 64 kJ mol⁻¹. The high positive value of free energy ($\Delta G^\ddagger = 102.55$ kJ mol⁻¹) and negative value of activation entropy ($\Delta S^\ddagger = -103.59$ J mol⁻¹) obtained from Eyring plot, indicate that the reaction was endergonic and kinetically controlled. Furthermore, a general reaction mechanism of cyclic carbonate synthesis from tri-substituted epoxides and carbon dioxide (CO₂) in the presence of TBAC catalyst was proposed.

Acknowledgments

This work is supported by the Engineering and Physical Science Research Council (EPSRC) funding for Sustainable Polymers (Project reference EP/L017393/1). We are also grateful to the support of the University of Engineering and Technology, Lahore in providing the scholarship to one of the authors.

References

- [1] IPCC, <https://www.co2.earth/global-co2-emissions> (2018).
- [2] C.O. Tuck, E. Pérez, I.T. Horváth, R.A. Sheldon, M. Poliakoff, *Science* 337 (2012) 695-699.
- [3] C. Ampelli, S. Perathoner, G. Centi, *Phil. Trans. R. Soc. A* 373 (2015) 20140177.
- [4] A.L. Villa de P, B.F. Sels, D.E. De Vos, P.A. Jacobs, *Am. J. Org. Chem.* 64 (1999) 7267-7270.
- [5] M. Firdaus, L. Montero de Espinosa, M.A.R. Meier, *Macromolecules* 44 (2011) 7253-7262.
- [6] G.P. Blanch, G.J. Nicholson, *J. Chromatogr. Sci.* 36 (1998) 37-43.
- [7] E.A. Nonino, *Perfumer & flavorist* 22 (1997) 53-58.
- [8] R. Ciriminna, M. Lomeli-Rodriguez, P.D. Cara, J.A. Lopez-Sanchez, M. Pagliaro, *Chem. Commun.* 50 (2014) 15288-15296.
- [9] A.M. Balu, V. Budarin, P.S. Shuttleworth, L.A. Pfaltzgraff, K. Waldron, R. Luque, J.H. Clark, *ChemSusChem* 5 (2012) 1694-1697.
- [10] C.M. Byrne, S.D. Allen, E.B. Lobkovsky, G.W. Coates, *J. Am. Chem. Soc.* 126 (2004) 11404-11405.
- [11] M. Bähr, A. Bitto, R. Mülhaupt, *Green Chem.* 14 (2012) 1447-1454.
- [12] R. Ciriminna, M. Lomeli-Rodriguez, P.D. Carà, J.A. Lopez-Sanchez, M. Pagliaro, *Chem. Commun.* 50 (2014) 15288-15296.
- [13] M. Firdaus, M.A.R. Meier, *Green Chem.* 15 (2013) 370-380.
- [14] B.M. Trost, *Acc. Chem. Res.* 35 (2002) 695-705.
- [15] M. Aresta, A. Dibenedetto, *Dalton Transactions* (2007) 2975-2992.
- [16] J.H. Clements, *Ind. Eng. Chem. Res.* 42 (2003) 663-674.
- [17] B. Schöffner, F. Schöffner, S.P. Verevkin, A. Börner, *Chem. Rev.* 110 (2010) 4554-4581.

- [18] K. Xu, *Chem. Rev.* 104 (2004) 4303-4418.
- [19] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* 4 (2011) 3243-3262.
- [20] O. Hauenstein, S. Agarwal, A. Greiner, *Nat. Commun.* 7 (2016).
- [21] M. Unverferth, O. Kreye, A. Prohammer, M.A.R. Meier, *Macromol. Rapid Commun.* 34 (2013) 1569-1574.
- [22] B. Ochiai, T. Endo, *Prog. Polym. Sci.* 30 (2005) 183-215.
- [23] C. Murugan, H.C. Bajaj, R.V. Jasra, *Catal. Lett.* 137 (2010) 224-231.
- [24] H. Yue, Y. Zhao, X. Ma, J. Gong, *Chem. Soc. Rev.* 41 (2012) 4218-4244.
- [25] Y. Li, K. Junge, M. Beller, M. Cui, Z. Chen, C.-Y. Cao, W.-G. Song and L. Jiang, *Chem. Commun* 49 (2013) 6093-6095.
- [26] G. Cascio, E. Manghisi, R. Porta, G. Fregnan, *J. Med. Chem.* 28 (1985) 815-818.
- [27] H. Kawai, F. Sakamoto, M. Taguchi, M. Kitamura, M. Sotomura, G. Tsukamoto, *Chem. Pharm. Bull.* 39 (1991) 1422-1425.
- [28] D.J. Carini, R.J. Ardecky, C.L. Ensinger, J.R. Pruitt, R.R. Wexler, P.C. Wong, S.-M. Huang, B.J. Aungst, P.B. Timmermans, *Bioorg. Med. Chem. Lett.* 4 (1994) 63-68.
- [29] R. Martin, A.W. Kleij, *ChemSusChem* 4 (2011) 1259-1263.
- [30] C. Martin, G. Fiorani, A.W. Kleij, *ACS Catal.* 5 (2015) 1353-1370.
- [31] Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* 6 (2015) 5933.
- [32] J.A. Castro-Osma, C. Alonso-Moreno, A. Lara-Sánchez, J. Martínez, M. North, A. Otero, *Catalysis Science & Technology* 4 (2014) 1674-1684.
- [33] M. Cokoja, C. Bruckmeier, B. Rieger, W.A. Herrmann, F.E. Kühn, *Angew. Chem. Int. Ed.* 50 (2011) 8510-8537.
- [34] C.J. Whiteoak, E. Martin, M.M. Belmonte, J. Benet-Buchholz, A.W. Kleij, *Adv. Synth. Catal.*

354 (2012) 469-476.

[35] M. Taherimehr, S.M. Al-Amsyar, C.J. Whiteoak, A.W. Kleij, P.P. Pescarmona, *Green Chem.* 15 (2013) 3083-3090.

[36] M.A. Fuchs, T.A. Zevaco, E. Ember, O. Walter, I. Held, E. Dinjus, M. Döring, *Dalton Transactions* 42 (2013) 5322-5329.

[37] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* 4 (2002) 2561-2563.

[38] M. Mamone, T. Milcent, B. Crousse, *Chem. Commun.* 51 (2015) 12736-12739.

[39] A. Mirabaud, J.-C. Mulatier, A. Martinez, J.-P. Dutasta, V.r. Dufaud, *ACS Catal.* 5 (2015) 6748-6752.

[40] W. Desens, C. Kohrt, M. Frank, T. Werner, *ChemSusChem* 8 (2015) 3815-3822.

[41] Y. Song, C. Cheng, H. Jing, *Chemistry-A European Journal* 20 (2014) 12894-12900.

[42] X. Liu, S. Zhang, Q.-W. Song, X.-F. Liu, R. Ma, L.-N. He, *Green Chem.* 18 (2016) 2871-2876.

[43] G. Fiorani, W. Guo, A.W. Kleij, *Green Chem.* 17 (2015) 1375-1389.

[44] J. Sun, S. Zhang, W. Cheng, J. Ren, *Tetrahedron Lett.* 49 (2008) 3588-3591.

[45] B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, *Green Chem.* 17 (2015) 108-122.

[46] W. Cheng, Q. Su, J. Wang, J. Sun, F.T.T. Ng, *Catalysts* 3 (2013) 878-901.

[47] Q. He, J.W. O'Brien, K.A. Kitselman, L.E. Tompkins, G.C.T. Curtis, F.M. Kerton, *Catalysis Science & Technology* 4 (2014) 1513-1528.

[48] L. Pena Carrodeguas, J. González-Fabra, F. Castro-Gómez, C. Bo, A.W. Kleij, *Chemistry-A European Journal* 21 (2015) 6115-6122.

[49] G. Fiorani, M. Stuck, C. Martín, M.M. Belmonte, E. Martin, E.C. Escudero-Adán, A.W. Kleij, *ChemSusChem* 9 (2016) 1304-1311.

- [50] C.J. Whiteoak, N. Kielland, V. Laserna, E.C. Escudero-Adán, E. Martin, A.W. Kleij, *J. Am. Chem. Soc.* 135 (2013) 1228-1231.
- [51] V. Laserna, G. Fiorani, C.J. Whiteoak, E. Martin, E. Escudero-Adán, A.W. Kleij, *Angew. Chem. Int. Ed.* 53 (2014) 10416-10419.
- [52] C.J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E.C. Escudero-Adán, C. Bo, A.W. Kleij, *Chemistry—A European Journal* 20 (2014) 2264-2275.
- [53] H. Buettner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem.* 375 (2017) 50.
- [54] M. Cokoja, M.E. Wilhelm, M.H. Anthofer, W.A. Herrmann, F.E. Kuehn, *ChemSusChem* 8 (2015) 2436-2454.
- [55] M. Hiroshi, M. Masato, G. Yuuta, Y. Jun-ichi, M. Hisatoyo, M. Suguru, *Bull. Chem. Soc. Jpn.* 91 (2018) 92-94.
- [56] J. Martínez, J. Fernández-Baeza, L.F. Sánchez-Barba, J.A. Castro-Osma, A. Lara-Sánchez, A. Otero, *ChemSusChem* 10 (2017) 2886-2890.
- [57] O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger, A. Greiner, *Green Chem.* 18 (2016) 760-770.
- [58] A.F. Thomas, Y. Bessiere, *Natural Product Reports* 6 (1989) 291-309.
- [59] D. Steiner, L. Ivison, C.T. Goralski, R.B. Appell, J.R. Gojkovic, B. Singaram, *Tetrahedron: Asymmetry* 13 (2002) 2359-2363.
- [60] K.N. Gurudutt, S. Rao, P. Srinivas, *Flavour and fragrance journal* 7 (1992) 343-345.
- [61] J. Sun, S.-I. Fujita, F. Zhao, M. Arai, *Applied Catalysis A: General* 287 (2005) 221-226.
- [62] H. Xie, S. Li, S. Zhang, *J. Mol. Catal. A: Chem.* 250 (2006) 30-34.
- [63] Y. Zhao, J.-S. Tian, X.-H. Qi, Z.-N. Han, Y.-Y. Zhuang, L.-N. He, *J. Mol. Catal. A: Chem.* 271 (2007) 284-289.
- [64] A. Otero, J. Martínez, J. Fernández-Baeza, L.F. Sánchez-Barba, J.A. Castro-Osma, A. Lara-

Sanchez, ChemSusChem (2017).

[65] L.-F. Xiao, F.-W. Li, J.-J. Peng, C.-G. Xia, J. Mol. Catal. A: Chem. 253 (2006) 265-269.

[66] J. Martínez, J.A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North, A. Rodríguez-Diéguez, Chemistry-A European Journal 21 (2015) 9850-9862.

[67] R. Luo, W. Zhang, Z. Yang, X. Zhou, H. Ji, J. CO2 Util. 19 (2017) 257-265.

[68] W. Clegg, R.W. Harrington, M. North, R. Pasquale, Chemistry-A European Journal 16 (2010) 6828-6843.

[69] H. Kawanami, Y. Ikushima, Chem. Commun. (2000) 2089-2090.

[70] L. Wang, L. Lin, G. Zhang, K. Kodama, M. Yasutake, T. Hirose, Chem. Commun. 50 (2014) 14813-14816.

[71] J.L. Jiang, R. Hua, Synth. Commun. 36 (2006) 3141-3148.

[72] J.A. Kozak, J. Wu, X. Su, F. Simeon, T.A. Hatton, T.F. Jamison, J. Am. Chem. Soc. 135 (2013) 18497-18501.

[73] G.R. Pazuki, H. Pahlavanzadeh, Theor. Found. Chem. Eng. 39 (2005) 240-245.

[74] J.W. Comerford, I.D.V. Ingram, M. North, X. Wu, Green Chem. 17 (2015) 1966-1987.

[75] H.L. Parker, J. Sherwood, A.J. Hunt, J.H. Clark, ACS Sustainable Chemistry & Engineering 2 (2014) 1739-1742.

[76] J. S Bello Forero, J. A Hernández Muñoz, J. Jones Junior, F. M da Silva, Current Organic Synthesis 13 (2016) 834-846.

[77] R. Luo, W. Zhang, Z. Yang, X. Zhou, H. Ji, J. CO2 Util. 19 (2017) 257-265.

[78] J. Martinez, J.A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North, A. Rodríguez-Diéguez, Chemistry-A European Journal 21 (2015) 9850-9862.

[79] R. Pohorecki, C. Možeński, Chemical Engineering and Processing: Process Intensification 37 (1998) 69-78.

- [80] L. Cuesta-Aluja, J. Castilla, A.M. Masdeu-Bultó, Dalton Transactions 45 (2016) 14658-14667.
- [81] M. North, R. Pasquale, Angew. Chem. 121 (2009) 2990-2992.
- [82] J. Steinbauer, C. Kubis, R. Ludwig, T. Werner, ACS Sustainable Chemistry & Engineering (2018).
- [83] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, Chem. Commun. (2006) 1664-1666.
- [84] J. Sun, S. Zhang, W. Cheng, J. Ren, Tetrahedron Lett. 49 (2008) 3588-3591.
- [85] J. Sun, S.-i. Fujita, F. Zhao, M. Arai, Green Chem. 6 (2004) 613-616.
- [86] A. Rehman, A.M.L. Fernandez, M.F.M.G. Resul, A. Harvey, J. CO2 Util. 24 (2018) 341-349.
- [87] F. Jutz, A. Buchard, M.R. Kember, S.B. Fredriksen, C.K. Williams, J. Am. Chem. Soc. 133 (2011) 17395-17405.
- [88] Y. Xu, L. Lin, C.-T. He, J. Qin, Z. Li, S. Wang, M. Xiao, Y. Meng, Polymer Chemistry 8 (2017) 3632-3640.
- [89] G. Lente, I. Fábrián, A.J. Poë, New J. Chem. 29 (2005) 759-760.
- [90] C.J. Whiteoak, E. Martin, E. Escudero-Adán, A.W. Kleij, Adv. Synth. Catal. 355 (2013) 2233-2239.