Carbonation of Epoxidized Methyl Soyates in Tetrabutylammonium Bromide-Based Deep Eutectic Solvents

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Abstract: Carbonated methyl soyates have been successfully prepared by cycloaddition of carbon dioxide (CO₂) to epoxidized methyl soyates in tetrabutylammonium bromide (TBAB)-based deep eutectic solvents (DES). Experimental parameters, i.e., reaction temperature, reaction time, CO₂ pressure and TBAB concentration were evaluated. The different reaction conditions have a significant influence on the yields of carbonated methyl soyates. The use of TBAB-based DES (tetrabutylammonium bromide/triethylene glycol) significantly shortened the reaction time of the cycloaddition of CO₂ to epoxidized methyl soyates. FT-IR and NMR analysis indicated that 95% of the yield of the five-membered cyclic carbonated methyl soyates were obtained at 120°C with 1.0 MPa pressure of CO₂.

Key words: cycloaddition, CO₂, deep eutectic solvents, TBAB, epoxidized methyl soyates

1 Introduction

Cyclic carbonates are one of the useful fine chemical products. Because of their advantages of high boiling point, excellent biodegradability and solubility, cyclic carbonates are widely used as a kind of main raw material for polycarbonates¹ and other plastics industries, such as non-isocyanate polyurethanes². Five-membered cyclic carbonates, as a member of the cyclic carbonates, are often used as electrolyte solvents for lithium-ion batteries³, plasticizers⁴, environmentally friendly aprotic polar organic solvent⁵, fuel additive⁶, starting materials and intermediates in the manufacture of fine chemicals⁷.

Carbon dioxide (CO₂) is an economical, renewable, environmentally friendly and not extensively widely used carbon source in chemical industry⁸⁻¹⁰. And CO₂ is a major greenhouse gas, its excessive presence in the air is unfavourable. Up to present, the effective pathway to chemical fixation of CO₂ is conducted by the synthesis of five-membered cyclic carbonates through cycloaddition of CO₂ to epoxides, which has become one of the most promising synthesis routes for the utilization of CO₂¹¹.

The cycloaddition of CO₂ to epoxides is a catalyst reaction, which depends on the type of catalysts. Therefore, the biggest challenge is to develop efficient catalyst that promote the cycloaddition reaction under moderate reaction conditions. Over the past decades, a lot of researchers

have focused on development of efficient catalyst system for these reactions¹². Due to high catalytic activity, homogeneous catalysts, such as quaternary ammonium salts^{13, 14}, metal complexes^{15, 16} and ionic liquids¹⁷, organocatalysts¹⁸, crown ether complexes¹⁹, polyethylene glycol²⁰, have received many attentions. Therefore, it is highly desirable to explore a simple and efficient catalyst system for this important transformation.

Deep eutectic solvents (DESs) was first proposed by Abbott in 2003, which aroused the interest of the scientific community immediately. DESs can be obtained by simply mixing together two safe components (e.g. choline chloride and urea), which are capable of forming a eutectic mixture through hydrogen bond interactions²¹. DESs are widely used as extraction solvents^{22, 23}, reaction medium²⁴ and catalysts²⁵. Additionally, DESs can be also used to separate and capture of acidic gases, such as CO₂²⁶.

As we all known, the methyl soyate is one of the typical vegetable oil fatty acid methyl esters prepared from soybean oil. In addition, carbonated methyl soyates represents a useful and sustainable biobased chemical intermediate for the preparation of functional fluids, fuel additives, and other bio-based products. Up to now, there are limited examples to investigate carbonation of epoxidized methyl soyates in deep eutectic solvents. In the present work, we explored the catalytic performance of TBAB-based DESs

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for cycloaddition of CO₂ to epoxidized methyl soyates to produce the carbonated methyl soyates. In particular, the TBAB-based DES play the role of both solvent and promoter, which can efficiently mediated the cycloaddition. And the product of carbonated methyl soyates was confirmed by FT-IR and NMR.

2 Materials and methods

2.1 Materials

CO₂ (99.995%) was supplied by Dumaoai Purge Gas Co. (Shanghai, China). Epoxidized soybean oil (CP) was purchased from Aladdin (Shanghai, China). Tetrabutylammonium bromide (TBAB, 99.0%), triethylene glycol (99.0%), levulinic acid (99.0%) and decanoic acid (99.0%) were obtained from Macklin Bio-Chem Technology Co. (Shanghai, China). Tetrabutylammonium chloride (TBAC, AR), 1,2-propanediol (AR), oleic acid (AR) and ethylene glycol (AR) were purchased from Kermel Chemical Reagent Co. (Tianjin, China).

2.2 Preparation of epoxidized methyl soyates

Epoxidized methyl soyates were prepared as described in the literature²⁷. Briefly, 200.0 g epoxidized soybean oil was loaded into a 1000-mL three-necked round-bottom flasks along with a mechanical stirrer. Sodium methoxide catalyst, 2.0 g (1 wt%), was dissolved in 60 mL methanol and then added to the epoxidized soybean oil in the reactor. The transesterification reaction was performed at 50°C for 2 h with suitable speed. After the reaction was completed, the epoxidized methyl soyates were obtained by static separation, water washing and drying treatment. Finally, solvent and trace water were removed with the rotary evaporator. The purity of the epoxidized methyl soyates was determined and analyzed by gas chromatography (Agilent 7890B) equipped with a DB-1HT capillary column (29.0 m × 250 μm × 0.1 μm) and a flame ionization detector (FID). Finally, the purity of the reaction substrate (epoxidized methyl soyates) reached above 98.0%.

2.3 Synthesis of DESs

In this work, 11 kinds of binary DESs, which were composed of a hydrogen bond acceptor (tetrabutylammonium bromide or tetrabutylammonium chloride) and hydrogen bond donors (ethylene glycol, 1,2-propanediol, triethylene glycol, levulinic acid, decanoic acid and oleic acid) were obtained through a mixing-heating step at 80°C in an oil bath until a homogeneous and stable liquid was formed (Table 1). In particular, when the molar ratio of tetrabutylammonium bromide (TBAB) and ethylene glycol was 1:1, the appearance of the mixture was white solid and opaque when it was cooled to room temperature. In other words, the mixture of TBAB-ethylene glycol with molar ratio of 1:1 is

Table 1 The compositions of binary TBAB-based DESs.

Abbreviation	Salt	HBD	Ratio (mol/mol)
DES-1	TBAB	Ethylene glycol	1:2
DES-2	TBAB	Ethylene glycol	1:4
DES-3	TBAB	Ethylene glycol	1:6
DES-4	TBAB	1,2-Propanediol	1:2
DES-5	TBAB	1,2-Propanediol	1:4
DES-6	TBAB	1,2-Propanediol	1:6
DES-7	TBAB	Triethylene glycol	1:1
DES-8	TBAC	Triethylene glycol	1:1
DES-9	TBAB	Levulinic acid	1:3
DES-10	TBAB	Decanoic acid	1:2
DES-11	TBAB	Oleic acid	1:2

unable to form DES. Thus, the molar ratio of TBAB and ethylene glycol used in this experiment are 1:2, 1:4 and 1:6.

2.4 Synthesis of carbonated methyl soyates

5.0 g of epoxidized methyl soyates (epoxide number = 6.20, i.e. 0.01938 mol epoxides) and TBAB-based DESs were added to the Parr stainless steel autoclave equipped with gas inlet tube and outlet, and the autoclave was sealed. Before the reaction was started, the air in the autoclave was replaced by carbon dioxide (CO₂) three times in order to clean out the air completely. Then the autoclave was heated to the desired reaction temperature and maintained for 10 min. At the moment, the reaction mixture was pressured with CO₂ to a definite value at a specific stirring speed, and kept for different reaction time. At the end of the reaction, the autoclave was cooled to room temperature and the unreacted CO₂ was vented out. The DES was completely removed by dissolving the reaction mixture in ethyl acetate and washing the reaction mixture three times with water. The organic layer was dried with anhydrous sodium sulfate. The solvent and trace water in the organic layer was then distilled under reduced pressure with the rotary evaporator.

2.5 Characterization of the product

The addition of CO₂ to the epoxidized group to form the five-membered cyclic carbonate group was confirmed by React IRTM. Characteristic epoxide peaks of epoxidized methyl soyates are noted at 842–822 cm⁻¹. As expected, the React IRTM spectrum of carbonated methyl soyates lacks these epoxide peaks, while the appearance of an strong absorption peak at 1,800–1,804 cm⁻¹ (C=O bond) is carbonate. Formation of the carbonate and the disappearance of the epoxide structures were also confirmed by ¹H-NMR and ¹³C-NMR analysis. ¹H-NMR inspection and ¹³C-NMR inspection, samples were prepared by dissolving a

certain amount of products in CDCl_3 . Both of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis were recorded using a Bruker Avance III HD 500 NMR spectrometer (Swiss) operating at a frequency of 500 MHz with tetramethylsilane (TMS) as the internal standard.

The epoxidized oxygen group content (EOC) of epoxidized methyl soyates determination was carried out by the direct method with hydrobromic acid solution in acetic acid²⁸⁾.

3 Results and discussions

As we all known, the cycloaddition reaction of epoxides and carbon dioxide is a gas-liquid two-phase reaction. Since the solubility of carbon dioxide in epoxides is not very well, many reaction systems used organic solvents or additives to improve the mass transfer of the reaction, thus enhancing the efficiency of the reaction^{13, 29)}. However, the use of organic solvents is not environmentally friendly and increases the production costs. To the best of our knowledge, tetrabutylammonium bromide (TBAB) is one of the most widely used catalysts for chemical fixation of CO_2 to epoxides to form cyclic carbonate^{30–34)}. Therefore, in this work, cycloaddition reaction of CO_2 with epoxidized methyl soyates was performed in the presence of TBAB-based DESs.

The proposed scheme for cycloaddition reaction of CO_2 and epoxidized methyl soyates mediated by TBAB-based DESs is shown in Scheme 1.

3.1 Selection of the TBAB-based DESs

DESs are now widely acknowledged as a new kind of ionic liquid (IL) analogues. Due to their biocompatibility, renewability, biodegradability and easy synthesis, DESs are often presented as a more economical and eco-friendly alternative to ionic liquid³⁵⁾. DESs are usually obtained by the complexation of a quaternary ammonium salt with metal salt or hydrogen bond donor (HBD)²¹⁾. In this work, six types of HBD (ethylene glycol, 1,2-propanediol, triethylene glycol, levulinic acid, decanoic acid and oleic acid) were used to combine with TBAB to prepare TBAB-based DESs. Then the TBAB-based DESs were used as the catalyst for the chemical fixation of CO_2 to epoxidized methyl

Scheme 1 Reaction scheme of cycloaddition of CO_2 to epoxides.

Fig. 1 The effect of different TBAB-based DESs on cycloaddition reaction of epoxidized methyl soyates with CO_2 . Reaction conditions: reaction temperature: 100°C ; reaction time: 10 h; CO_2 pressure: 1.0 MPa; stirring speed: 400 rpm; catalyst concentration: 0.04 mol TBAB per mol of epoxidized group.

soyates to prepare the corresponding five-membered cyclic carbonates, carbonated methyl soyates. The catalytic effect of different TBAB-based DESs was shown in Fig. 1.

The different kinds of HBDs lead to differences in physicochemical properties of the formed TBAB-based DESs³⁶⁾, such as viscosity, polarity, melting point and solubility, etc. The experimental results shown in Fig. 1 demonstrated that DES-7 (TBAB/TEG) has the best catalytic activity for the cycloaddition reaction of the epoxidized methyl soyates with CO_2 under the identical reaction conditions, compared with other examined DESs. When the DES-7 was replaced with DES-8 (TBAC/TEG), the cycloaddition reaction afforded lower yield (49%). The obtained results suggested that bromide ion indeed played crucial role in the catalytic process³⁷⁾. Therefore, DES-7 (TBAB/TEG) was selected as the best solvent to promote the cycloaddition reaction of epoxidized methyl soyates with CO_2 in the following experiments.

3.2 Effect of the concentration of DES

In the present work, the DES-7 acted as both a solvent and a promotor. Since the reaction is a gas-liquid two-phase reaction, the contact area between gaseous CO_2 and the substrate is the key to the promote this reaction. Many studies have shown that DES has the ability to capture and separate acidic gases^{26, 38)}. When CO_2 was dissolved into DES, the DES was blended with epoxidized methyl soyates at a suitable stirring rate, thereby increasing the contact area with the epoxidized methyl soyates. Therefore, different concentrations of TBAB-based DES would lead to dif-

Fig. 2 The effect of TBAB concentration on cycloaddition reaction of epoxidized methyl soyates with CO₂. Reaction conditions: reaction temperature: 100°C; reaction time: 10 h; CO₂ pressure: 1.0 MPa; stirring speed: 400 rpm.

ferent absorption amounts of CO₂, which affected the reaction rate of cycloaddition reaction obviously (Fig. 2).

A set of experiments were performed and the results were shown in Fig. 2. The experimental results demonstrated that the yields of carbonated methyl soyates increased sharply with the molar amount of the catalyst before it reached 0.08 times the molar amount of epoxidized group. Further increasing the molar amount of the catalyst after it reached 0.12 times that of epoxidized group, the reaction rate increased slowly, and gradually approaching 0 (as shown in Fig. 2B). When the catalyst concentration was 0.12, the yield of carbonated methyl soyates could reach 88%. Therefore, the optimum DES amount was 0.12 times the molar amount of epoxidized group, and was used in the following experiments.

3.3 Effect of the reaction temperature

The reaction temperature was one of the critical factors for this cycloaddition reaction. Since the epoxidized groups of epoxidized methyl soyates are located in the middle of the molecular chain rather than in terminal position, and the steric hindrance exists in the substrates led to higher reaction temperature. Therefore, the effect of reaction temperature (60°C, 80°C, 100°C, 120°C and 140°C) on the cycloaddition reaction of epoxidized methyl soyates with CO₂ was investigated (Fig. 3). At 60°C, no cycloaddition reaction was detected. When the reaction temperature was increased from 80°C to 120°C, the product yield was increased from 40% to 93%. However, the yield of carbonated methyl soyates was decreased with further increasing of the reaction temperature (140°C). This is because that the TBAB can readily decompose into volatile compounds such as hydrogen bromide, which is highly reactive with epoxidized groups. Zheng and his co-workers³⁹⁾ have demon-

Fig. 3 The effect of reaction temperature on cycloaddition reaction of epoxidized methyl soyates with CO₂. Reaction conditions: the TBAB concentration of 0.12; reaction time: 10 h; CO₂ pressure: 1.0 MPa; stirring speed: 400 rpm.

strated that the maximum reaction temperature should not exceed 130°C during the TBAB catalyzed cycloaddition of CO₂ to epoxidized vegetable oils. Therefore, an operation temperature of 120°C was chosen as the optimum reaction temperature.

3.4 Effect of the reaction time

The effect of reaction time on cycloaddition reaction of epoxidized methyl soyate was also investigated and the experimental results were shown in Fig. 4. The experiments

Fig. 4 The effect of reaction time on cycloaddition reaction of epoxidized methyl soyates with CO₂. Reaction conditions: the TBAB concentration of 0.12; reaction temperature: 120°C; CO₂ pressure: 1.0 MPa; stirring speed: 400 rpm.

were performed under a CO₂ atmosphere with 1.0 MPa pressure using DES-7 as the promotor/solvent to investigate the effect of different reaction time on the cycloaddition process.

The yield of carbonated methyl soyates were increased rapidly with the reaction time before it reached 6 h. The rate of the cycloaddition reaction shows a first-order dependence with respect to the EMSs concentration and the rate constants was 0.0070 min⁻¹. However, further increasing the reaction time (10–14 h), the rate of cycloaddition reaction was increased slowly, and gradually became horizontal eventually. When the reaction time was reached 10 h, the yield of carbonated methyl soyates was 95%. The result was similar with the results of much longer reaction time (14 h) and it was not necessary to prolong the reaction time. Therefore, an operation time of 10 h was chosen as the optimum reaction time.

3.5 Effect of the CO₂ pressure

The CO₂ pressure was one of the key factors for this cycloaddition of CO₂ to epoxidized methyl soyates. This is due to the solubility of CO₂ in DES and epoxidized methyl soyates has a great relationship with pressure^{26, 40}. The difference in pressure caused the amount of carbon dioxide to dissolve in the reaction mixture. In order to investigate the relationship between CO₂ pressure and product yield, a set of experiments were conducted under different CO₂ pressure (0.1 MPa, 0.5 MPa and 1.0 MPa). The experimental results were presented in Fig. 5.

It is obvious that the CO₂ pressure has a relatively high impact on the yield of carbonated methyl soyates. It can be seen that the CO₂ pressure was 0.1 MPa, the yield of the

Fig. 5 The effect of CO₂ pressure on cycloaddition reaction of epoxidized methyl soyates with CO₂. Reaction conditions: the TBAB concentration of 0.12; reaction temperature: 120°C; stirring speed: 400 rpm.

product was 73%. When the CO₂ pressure was increased to 0.5 MPa, 80% yield of carbonated methyl soyates was obtained. Increasing the CO₂ pressure to 1.0 MPa, the yield of carbonated methyl soyates was increased to 95%. In addition, prolonging this cycloaddition reaction time from 12 h to 24 h on the conditions of 0.1 MPa pressure of CO₂, the yield of carbonated methyl soyates was 89%. Considering the yield and time cost, 1.0 MPa pressure of CO₂ was selected as the optimum operation pressure.

3.6 Comparison the effects of TBAB and TBAB-based DES

In order to compare the effects of TBAB and TBAB-based DES (TBAB/TEG) on the cycloaddition of CO₂ to epoxidized methyl soyates, a control experiment was conducted (Fig. 6).

Figure 6 clearly indicated that the effect of TBAB-based DES (TBAB/TEG) on the yield of product was better than the use of TBAB alone, which suggested that the catalytic effect of DES (TBAB/TEG) on cycloaddition reaction of epoxidized methyl soyates and CO₂ is obviously better than the effect of using TBAB alone. The reason for this result was that the DES (TBAB/TEG) has certain capability to capture CO₂³⁸, thus the DES roled both as a promotor and a solvent. The properties of TBAB-based DES are helpful to the mass transfer between gas and liquid, which is beneficial to promote progress of this cycloaddition reaction. Furthermore, when the reaction time was between 0 and 2 h, the rate constants of the cycloaddition reaction mediated by TBAB and the DES (TBAB/TEG) were 0.0066 min⁻¹ and 0.011 min⁻¹, respectively. In addition, Fig. 6 showed that the yield of carbonated methyl soyates was increased rapidly and then the reaction rate became slower with prolonging of the reaction time. This is because the absorption rate of CO₂ increases in the following order: epoxidized

Fig. 6 Comparison the effects of TBAB and DES (TBAB/TEG).

vegetable oils > carbonated vegetable oils⁴⁰⁾. As the cycloaddition reaction proceeded, the epoxidized methyl soyates were consumed, and the carbonated methyl soyates were increased, which led to a slower absorption rate of CO₂. Therefore, the yield of the product increased rapidly and then increased slowly.

3.7 Characterization of product

The product of carbonated methyl soyates was characterized by FT-IR, ¹H-NMR and ¹³C-NMR. Firstly, from FT-IR spectroscopy, we can clearly observe the substrate after and before the cycloaddition reaction is different (Fig. 7). The FT-IR spectra clearly showed the generation of a new bond at 1,801 cm⁻¹ (C=O stretching), associating with the five-membered cyclic carbonates formation, which was larger than the carbonyl bond of the triglyceride backbone at 1,730 cm⁻¹ (C=O stretching). The carbonyl bonds (1,730 cm⁻¹) of ester bond are present in both the raw material (epoxidized methyl soyates) and the product (carbonated methyl soyates) without any change.

Subsequently, ¹H-NMR was used to further determine the cycloaddition reaction of epoxidized methyl soyates with CO₂. The ¹H-NMR spectra of epoxidized methyl

Fig. 7 FT-IR spectra after (A) and before (B) the cycloaddition reaction.

soyates and carbonated methyl soyates clearly indicated the occurrence of the cycloaddition reaction of epoxidized methyl soyates with CO₂, which was shown in Fig. 8. The ¹H-NMR signals of the epoxide moiety (at 2.85 ppm and 3.15 ppm) disappeared. New ¹H-NMR signals associated

Fig. 8 ¹H-NMR spectra after (A) and before (B) the cycloaddition reaction and ¹³C-NMR spectra (C) of carbonated methyl soyates.

with the carbonate moiety appeared between 4.20-4.95 ppm.

Finally, the cycloaddition product was also identified by ^{13}C -NMR spectroscopy. **Figure 8(c)** showed that the ^{13}C -NMR spectra of carbonated methyl soyates obtained under the reaction conditions of 120°C , 0.12 of TBAB concentration, 1.0 MPa pressure of CO_2 and 10 h. It became obviously that a new peak appeared at 154 ppm, which was associated with carbonate moiety in the five-membered cyclic group in the product.

4 Conclusions

Carbonated methyl soyates can be obtained by cycloaddition of CO_2 to epoxidized methyl soyate in excellent yield in the presence of TBAB-based DES at 120°C and 1.0 MPa pressure of CO_2 . The control experiments indicated that the DES (TBAB-TEG) acted both as a solvent and a promoter, which showed better activity than the TBAB alone. The TBAB-based DESs possess the characteristic of environmental friendly, cheap, greener, simple preparation, CO_2 capture capability and biodegradable compared to conventional catalysts and solvents. The use of TBAB-based DES significantly shortened the reaction time of the cycloaddition of CO_2 to epoxidized methyl soyates. And the TBAB-based DES (TBAB/TEG) will provide a potential method to promote the cycloaddition reaction of epoxidized compounds with CO_2 to form five-membered cyclic carbonated compounds without any co-solvents.

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Conflict of interest

The authors declare no competing financial interest.

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