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Original article

A catalyst-free novel synthesis of diethyl carbonate from ethyl carbamate in supercritical ethanol

Li-Cai Zhao, Zhi-Qiang Hou, Chun-Ze Liu, Yuan-Yuan Wang *, Li-Yi Dai *

Department of Chemistry, East China Normal University, Shanghai 200241, China

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ABSTRACT

Diethyl carbonate has been synthesized *via* the alcoholysis of ethyl carbamate in supercritical ethanol under catalyst-free conditions. The influences of various parameters such as reaction temperature, reaction time, reaction pressure, ethanol/ethyl molar ratios and reaction loading volume on the yield of DEC were studied systematically. The experimental results indicated that the alcoholysis of ethyl carbamate was greatly improved in supercritical ethanol. The optimal reaction conditions were as follows: a reaction temperature of 573 K, a reaction time of 30 min, a reaction pressure of 13.2 MPa, an ethanol/ethyl carbamate molar ratio of 10 and a reactor loading volume of 285 μL respectively. The optimal yield of DEC was 22.9%.

1. Introduction

As a biodegradable compound, diethyl carbonate (DEC) has attracted much attention in recent years and has been widely used in organic synthesis, electrical chemistry, and fuel additives [1–3]. Currently, the existing methods for preparing DEC mainly include phosgenation of ethanol, oxidative carbonylation of ethanol, transesterification of carbonate and ethanolysis of CO_2 [4–6]. However, these methods suffer from drawbacks such as high toxicity, inconvenient operations, complicated processes and poor yields, which were undesirable for industrial productions [7].

Recently, a new process for preparing DEC from urea and ethanol described in Scheme 1 becomes more attractive. The raw materials are low in price and the byproduct ammonia can be used as a recycled material for urea production [8]. This reaction proceeds in two steps: ethyl carbamate (EC) is formed as an intermediate initially and then it can be further converted to DEC. The first step is fast and EC can be easily obtained even without a catalyst. However, the subsequent EC ethanolysis in the second step is difficult to perform [9]. And until now, this process was usually conducted in the presence of catalysts such as organotin compounds, alkali metal compounds and metal oxides [10]. Wang *et al.* [11] conducted the urea ethanolysis over a series of metal oxides at 463 K in 5 h. The highest yield of DEC 14.2% was achieved using ZnO as a catalyst, while in the absence of catalysts the yield of DEC was 0%. Zhao *et al.* [12] reported that with PbO as catalyst, the highest yield of DEC was 16.2% with 44.0% selectivity at 463 K in 7 h. Compared to the single metal oxide catalysts, An *et al.* [13] provided insights into double metal oxide for the reaction of ethyl carbamate and ethanol, a higher yield of DEC of 20.6% was achieved over ZnO–PbO but DEC selectivity was only 41.0% at 463 K in 7 h. So, in previous studies, expensive catalysts were indispensable and the reaction equilibrating time was very long. Accordingly, it is vital to identify new methods to promote the reaction in a more environmentally benign and commercially viable way.

Supercritical fluids (SCFs) technology has attracted increasing attention in recent years. SCFs have been widely used in organic syntheses [14], biodiesel production [15] and chemical degradation [16]. The superiorities of SCFs are summarized as the follows: (1) They are green and catalyst-free; (2) High yield and selectivity are always achieved by manipulating reaction temperature and pressure of SCFs [17]. Supercritical ethanol is one of the most promising SCFs because of its milder critical conditions (243.1 °C, 6.38 MPa), non-toxicity and high activity. To the best of our knowledge, there have been no report on the synthesis of DEC from EC in supercritical ethanol. Based on the unique properties of supercritical ethanol, we expected its good performance in the ethanolysis reaction.

2. Experimental

Ethyl carbamate (A.R.), ethanol (A.R.), diethyl carbonate (A.R.), acetone (A.R.), dodecane (A.R.) were commercially available from Sinopharm Chemical Reagent and were used as received.

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* Corresponding authors.
E-mail addresses: 48387162@qq.com (Y.-Y. Wang), lydai@chem.ecnu.edu.cn (L.-Y. Dai).

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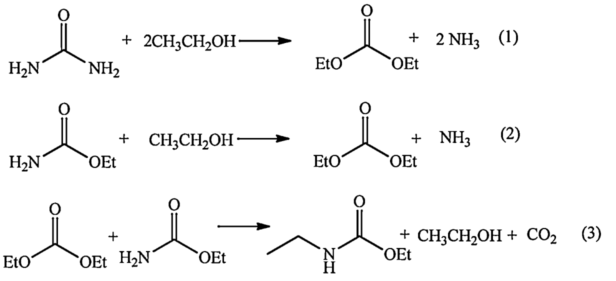

Scheme 1. The reaction equation between urea and ethanol (1), ethyl carbamate and ethanol (2) and the side reaction of NEEC and diethyl carbonate.

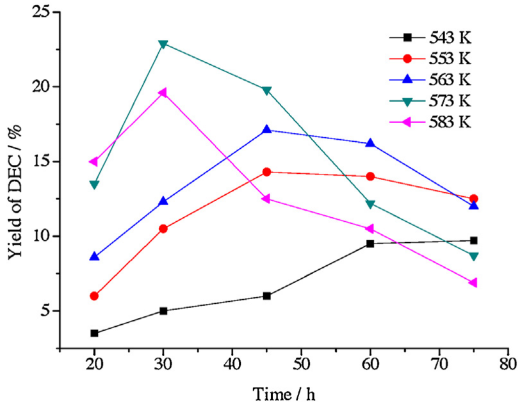

Fig. 1. The effects of reaction temperature and time on the yield of DEC. The molar ratio of ethanol/EC: 10.

An assembled stainless-steel reactor with a volume of 500 μL served as the batch-type reactor. Before it use, the reactor should be cleaned at 573 K for 8 h with 300 μL of deionized water.

The reaction solution was prepared by dissolving EC in ethanol with the aid of ultrasound at room temperature. An exact amount of reactant was fed to the stainless-steel reactor by a microliter syringe. Reactant volumes at different temperature were as follows: 315 μL at 543 K, 305 μL at 553 K, 295 μL at 563 K, 285 μL at 573 K and 275 μL at 583 K. After loading, the reactor was sealed and immersed into a molten-salt bath (consisted of 40 wt% $NaNO_2$, 7 wt% $NaNO_3$ and 53 wt% KNO_3) that has been preheated to the required temperature. The temperature was controlled at ±2 K by an Omega temperature controller. After a desired reaction time, the reactor was placed into ice water for about 10 min to quench the reaction. The liquid reactant mixture was taken out by microliter syringe. Then the reactor was treated with acetone for three times to ensure that the reaction mixture was completely transferred.

The liquid reaction contents were analyzed quantitatively by gas chromatograph (SHIMADZU GC-2014) equipped with an RT-10223 capillary column (30 m × 0.25 mm × 0.25 μm). The analytical conditions were: injector temperature 553 K, column temperature program-raised from 313 K to 523 K at a rate of 15 K/min, nitrogen at a flow rate of 3 mL/min served as the carrier gas. N-dodecane was selected as an internal standard.

The products were identified by GC–MS (Varian Saturn 3900/2100) equipped with a VF-5MS non-polar column (30 m × 0.25 mm × 0.25 μm). The analytical conditions were: injector temperature 523 K, column temperature was settled at 333 K for 3 min, then program-raised to 523 K at a rate of 15 K/min, helium gas at a flow rate of 1 mL/min served as the carrier gas. The product DEC was verified by the fragment ion peaks of m/z 18, 29, 45, 63, 75, 91, 118. The fragment peaks of N-EEC were m/z18, 28 44, 58, 72, 88, 102, 117. These mass data matched exactly with the standard chromatograms in mass spectral library.

The yield and selectivity in this work were defined as the follows:

$$\text{Yield}(\text{DEC}, \%) = \frac{\text{moles of DEC}}{\text{moles of EC added}} \times 100\%$$

$$\text{Selectivity}(\text{DEC}, \%) = \frac{\text{Yield of DEC}}{\text{Conversion of EC}} \times 100\%$$

3. Results and discussion

3.1. Effect of reaction temperature and reaction time on the yield of DEC

Figs. 1 and 2 depict the effects of reaction temperature (543–583 K) and time (20–75 min) on the conversion of EC and the yield of DEC. It is observed that the conversion of EC and the yield of DEC were both enhanced as the temperature increased from 543 K to 573 K and the yield of DEC reached its maximum of 22.9% with an EC conversion of 48.3% at 573 K. This revealed that synthesis of DEC in supercritical ethanol was greatly affected by temperature. The effect of temperature lied in two aspects: On one hand, as reported in the literature, the reaction was endothermic, so elevated temperatures are favorable according to the laws of thermodynamics [12,13]; On the other hand, the temperature played a decisive role on the properties of supercritical ethanol [18–20]. As we know, ethanol under supercritical conditions mainly exists in the form of small oligomers instead of H-bonded aggregates in the liquid. Monomers dominated in these small oligomers and its percentage (ranging from 35.2% to 92.2%) rises as temperature increases. As a result, at higher temperatures, more monomers of ethanol were directly exposed to EC, which increased the chance of collisions of molecules and promoted the reaction. This hypothesis was consistent with our experimental results. However, when the temperature exceeded 573 K, the conversion of EC increased but the yield of DEC decreased. Meanwhile, we also found that the major by-product N-EEC increased significantly, which suggested that at higher temperatures the side reaction described in Eq. (3) by consuming DEC and EC became more significant, which leads to higher conversion of EC and lower yield of DEC. Therefore, the optimum reaction temperature was 573 K for the synthesis of DEC. The effect of temperature on the yield of DEC agreed with the findings in the literature [13].

The influence of reaction time on the DEC synthesis was also described in Figs. 1 and 2. The yield of DEC and conversion of EC

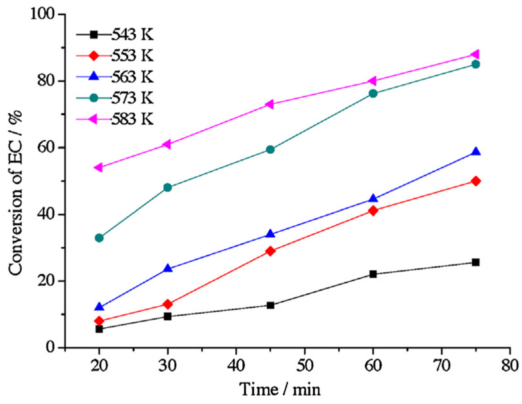

Fig. 2. The effects of reaction temperature and time on the conversion of EC. The molar ratio of ethanol/EC: 10.