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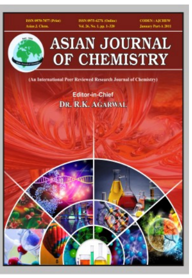

Synthesis and Characterization of Long-Chain Dialkyl Carbonate

YU FENG, JUNLING YANG* and FULONG ZHAO

School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, P.R. China

*Corresponding author: E-mail: zyy520fy@163.com; yangjunling@tjpu.edu.cn

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Dialkyl carbonate are currently of commercial interest as lubricants and additives in various industrial applications. Alcoholysis of urea is considered to be a novel and promising process during the synthesis of carbonate ester. Urea and nonanol reacted in the presence of dibutyltin oxide as the catalyst. Dialkyl carbonate was purified by Kügelrohr distillation and characterized by FTIR, MS, ^{1}H and ^{13}C NMR spectroscopy. Dibutyltin oxide catalyst system show excellent catalytic activity and got the highest dinonyl carbonate yield 53.9 %. The optimized reacted conditions of the highest yield were as follow: reaction time was 3h; reaction temperature was 473 K; molar ratio of urea to ethanol was 2; concentration of catalyst (dibutyltin oxide) was 2 wt %. Under these conditions, dialkyl carbonate with symmetrical structure can be synthesized.

Keywords: Urea, Alcoholysis, Dibutyltin oxide, NMR spectroscopy, Dialkyl carbonate.

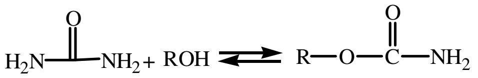
INTRODUCTION

With the development of society and economy, the environmental benign green chemical technology has received increasing attention[1], because of the serious problem of environment. Dialkyl carbonates are generally safe green noncorrosive materials employed in numerous commercial and synthetic applications. At present, short chain of double alkyl carbonate as an oxygenated additive in gasoline and diesel has reduced toxic exhaust emissions from engines[2]. Both diethyl and dimethyl carbonates are gaining popularity as non-toxic replacements for hazardous chemical reagents such as phosgene and dimethyl sulfate[3]. Recently, Rüsch gen *et al.*[4] showed that dimethyl carbonate and diethyl carbonate can be used as a reactive solvents to extract and transesterify oilseed oils simultaneously. Long chain of dialkyl carbonate not only can be used as detergent additive, surfactant and softener additive, but also they achieved the widespread application in the solvent of spinning, water-soluble coloring matter, pigment dispersant and spinning solution in the textile industry. In addition, they are wildly used in fields of producing high performance resin, flavour enhancers, food preservatives, *etc*. Especially, a kind of alkyl carbonate as the basic composition of the lubricant, alkyl group and the metal surface reaction of friction tests showed that the lubrication properties of alkyl carbonate with the same viscosity and better compatibility of sealing compared with traditional mineral oil and synthetic esters[1]. The widespread application cannot easily be coking, less carbon deposition and simple post processing[5]. The United States, Germany and Italy are studying long-chain double alkyl carbonate as lubricating oil. Italy and Japan have produced lubricating oil containing those components[6].

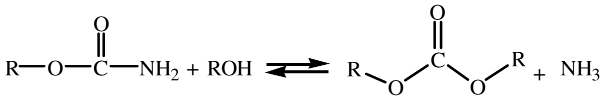
At present, alkyl carbonate synthetic methods primarily contain phosgenation and non phosgenation. Phosgenation now is cleared away gradually because of the virulent raw materials, environmental pollution and strongly corrosive. The nonphosgenation includs transesterification, electrochemical synthesis, direct oxidation of carbon dioxide, oxidative carbonylation and alcoholysis of urea. Urea alcoholysis synthesis of carbonate is a new technique of polymer synthesis and an eco-friendly process with several benefits over conventional chemical polymerization. This synthetic method has many advantages, such as easiness, low cost and the reaction without water which can avoid the problems during the process of complex azeotropic system including separation of methanol, dimethyl carbonate and water separation. The successful development of the chemical process is helpful to reduce dependence on petroleum products such as epoxy compounds in addition reactions of propylene oxide and carbon dioxide. At the same time, the by-product ammonia has very good economy benefit as industrial material. It is of most significant to the effective protection and rational exploitation resources[7]. In this paper, by the method of alcoholysis of urea, urea can reacte with long chain aliphatic alcohol in the presence of catalyst (dibutyltin oxide). The dialkyl carbonate was isolated by purification or Kügelrohr distillation from the mixture and characterized by FTIR, MS, ^{1}H and ^{13}C NMR spectroscopy. The influencing factors on the reaction were investigated under identified dibutyltin oxide catalyst system to get the appropriate conditions.

EXPERIMENTAL

Dialkyl carbonate was synthesized through two steps reaction by urea and long chain aliphatic alcohol with the help of catalyst. The reaction equation is described as follows:

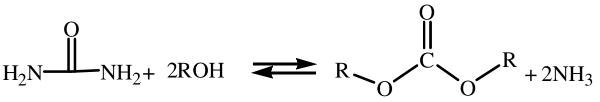


$$H_2N-C(=O)-NH_2 + ROH \rightleftharpoons R-O-C(=O)-NH_2 \quad (1)$$



$$R-O-C(=O)-NH_2 + ROH \rightleftharpoons R-O-C(=O)-O-R + NH_3 \quad (2)$$

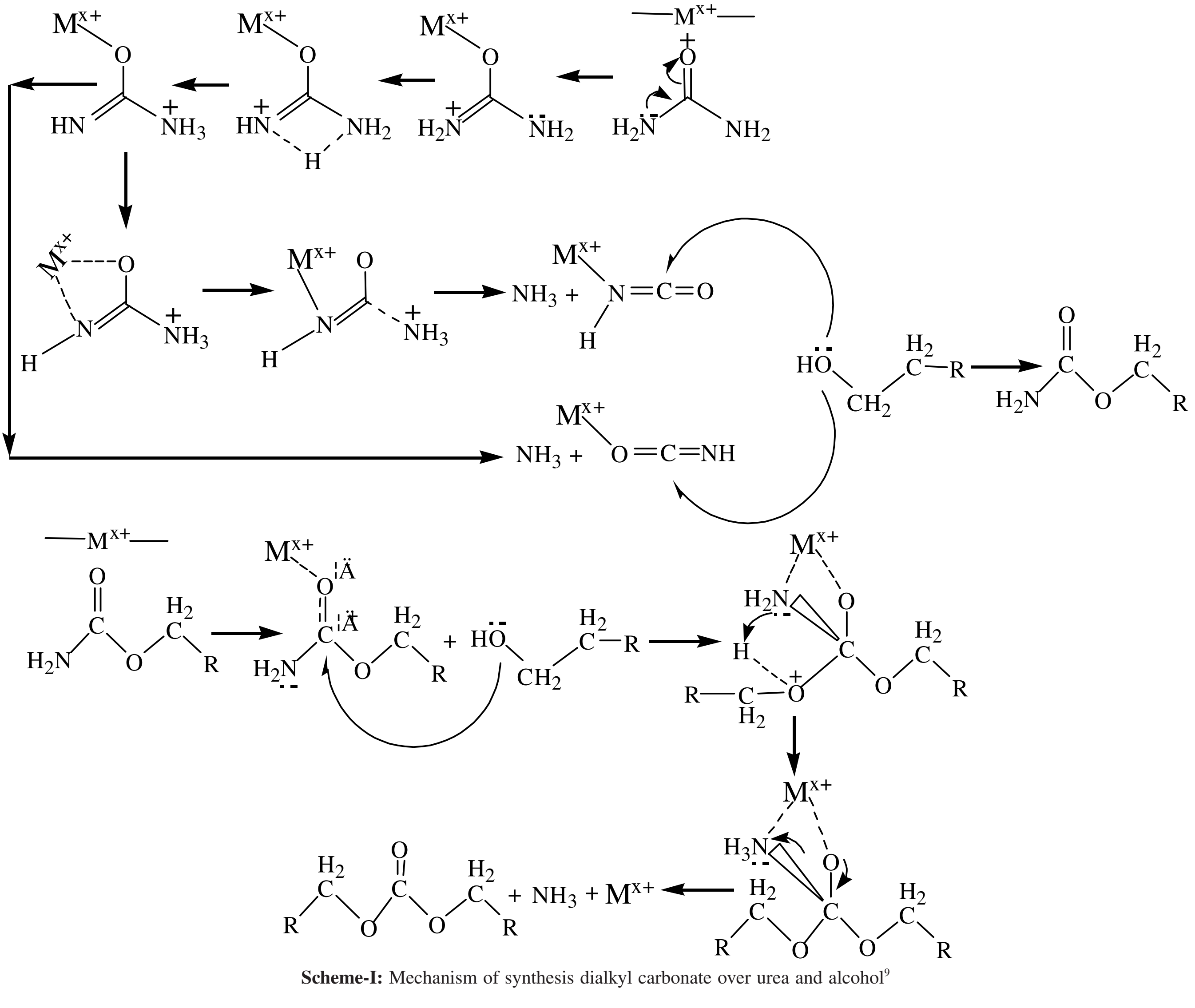
The chemical overall reaction equations as follows



$$H_2N-C(=O)-NH_2 + 2ROH \rightleftharpoons R-O-C(=O)-O-R + 2NH_3 \quad (3)$$

This reaction is reversible reaction, the characteristics of catalyst and the selection of reaction conditions have important influence on the yield of product and the properties of the product. The first step reaction is more easily, while the second step reaction is more difficult from the point of view of thermodynamics. In order to make the overall reaction to the direction of the products to improve the selectivity and conversion, so as to increase the yield of product, by some physico-chemical methods, such as adding appropriate high performance catalyst was applied.

Herein, we demonstrated a synthetic mechanism for synthesis of dialkyl carbonate by alcoholysis of urea process as shown in **Scheme-I**. As for the methods, first of all, the decomposition of urea into ammonia and isocyanate species, in the catalytic conditions, but it is well known that urea directly decomposed into isocyanate base species is difficult due to the structure resonance stability. By the addition of amphoteric oxide or alkaline oxide into the reaction system, with urea promoted the electronic transformation of urea, the coordinating role of oxide cations decreased the stability of the urea to form isocyanate species and released the ammonia. Then, aliphatic alcohol reacts with isocyanate species to generate



Scheme-I: Mechanism of synthesis dialkyl carbonate over urea and alcohol[9] intermediate product unbranched ester carbamate. Under the action of catalyzer, carrying out reaction between unbranched ester carbamate and another molecular aliphatic alcohol to form dialkyl carbonate and release ammonia again.

Urea (industrial grade, tianjin deson fertilizer Co., LTD); dibutyltin oxide (Laboratory preparation); Nonanol (AR, Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd.); Concentrated sulfuric acid (AR, Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd.); potassium bromide (Spectrography, Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd.); deuterated chloroform ($CDCl_3$, AR, Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd.). All chemicals used without further purification unless otherwise noted.

Synthesis of dinonyl carbonate: In a three-necked round-bottomed flask equipped with a magnetic stir bar and reflux condenser, a mixture of nonanol and dibutyltin oxide was slowly heated to 378 K, when reactants were well mixed, urea was added. And then began to reflux reaction after heating up to 473 k. After 3 h the reaction was completed, the exhaust gas (ammonia) generated in the reaction with dilute sulfuric acid to absorb. When deemed complete, the reaction mixture was taken up in $CHCl_3$. The reaction mixtures were separated and purified by purification or Kügelrohr distillation. The crude product was then placed under vacuum overnight at 298 K and obtainin dinonyl carbonate.

IR spectroscopy was obtained using a FTIR-650 (Tianjin Gangdong Sci. & Tech. development Co., Ltd.). Resolution of 1.5 cm^{-1}, spectral range 4000-400 cm^{-1}, Spectrum system as either a film on NaCl plates (liquids) or in a KBr matrix (solids). Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS), Waters Corporation, electrospray ionization (ESI), negative ion scanning mode, scan range is 150-2000 (m/e). ^1H and ^{13}C NMR spectra were recorded using a Bruker ARX 400 spectrometer with a 5 mm dual proton/carbon probe (400 MHz 1H/100.61 MHz ^{13}C) using $CDCl_3$ as the solvent in all experiments.

RESULTS AND DISCUSSION

FTIR spectroscopy, NMR and MS were used to confirm the formation of the dinonyl carbonate. Fig. 1 shows the FTIR spectra of urea, nonanol and dinonyl carbonate. Two reactants have a big difference with product form FTIR spectra. The characteristic absorption peaks of samples are assigned to their monomer functional groups, according to their monomer structure. The spectra of $-NH_2$ antisymmetric and symmetric stretching vibrations absorption in 3429 cm^{-1} and 3331 cm^{-1}, the combined absorption peaks of C=O stretching vibration and $-NH_2$ bending vibration in 1620 cm^{-1}, -C-N stretching vibration absorption peak in 1155 cm^{-1} (Fig.1a). The FTIR spectra of nonanol shows in Fig. 1b. -O-H stretching vibration absorption peak in 3338 cm^{-1}, absorptions in 2928 and 2844 cm^{-1}, corresponding to the stretching vibration of $-CH_3$ and $-CH_2$, the combined absorption peaks of $-CH_3$ antisymmetric bending vibration and $-CH_2$ scissoring vibration absorption in 1467 cm^{-1} and the symmetric bending vibration of $-CH_2$ in 1377 cm^{-1}, C=O stretching vibration of nonanol in 1056 cm^{-1}, in addition, due to the continuous methylene number of nonanol is greater than 4, so in 724 cm^{-1} has a corresponding in-plane rocking vibration absorption peak. The FTIR spectra of this product shows in Fig. 1c. Compared to the reactants urea and nonanol infrared spectrum, the infrared absorption peaks of $-NH_2$ and -O-H has been remarkably weakened until no absorption in specific location, but a group of new strong absorption peak appeared in 1744 cm^{-1} that the location belongs to ester compounds specific functional group (C=O) infrared absorption area, meanwhile, in 1263 cm^{-1}, appeared a strong and wide absorption peak too, corresponding to the stretching vibration of -C-O-C and there is a similar absorption peak with nonanol in 722 cm^{-1}, proof that the continuous methylene number of this ester compound product is greater than four.

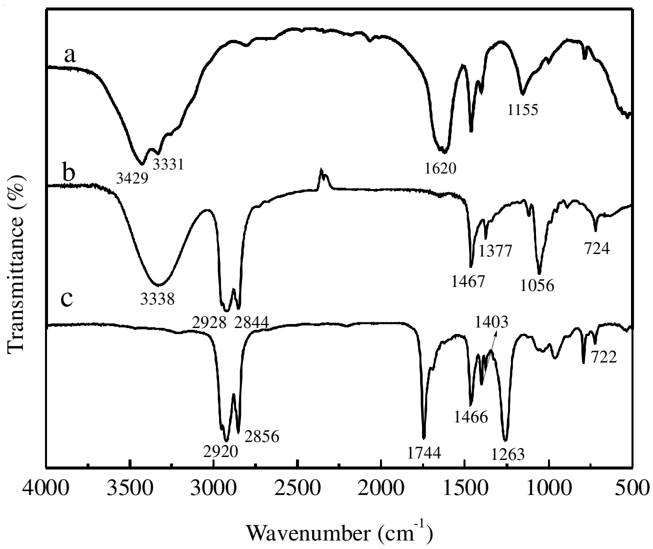


Fig. 1. FTIR spectra of raw materials and product; Notes: (a) urea, (b) nonanol, (c) dinonyl carbonate

The ^1H and ^{13}C NMR data for the dinonyl carbonate synthesized are presented in Table-1, Fig. 2. In ^1H NMR spectroscopy (Fig. 2), there is an absorption peak that caused by $CDCl_3$ solvent residual hydrogen nuclei in 7.27 ppm, the ^1H NMR show the expected CH_2 and CH_3 peaks and their integration corresponds to the expected number of hydrogens, respectively in 0.6-1.0 and 1.0-1.4 ppm. In the structure of the nonanol, there are two methylenes directly and indirectly connected, respectively with oxygen atoms, because of its high electronegativity of oxygen, which results in the decrease of the density of electron cloud around the hydrogen nuclei, shielding effect shall be weakened, eventually lead to hydrogen nuclei will appear in the lower field. Peak D and peak E correspond, respectively to the methylene which is connected with oxygen atom indirectly and directly, single peak C corresponds to the hydrogen atom which is belongs to the hydroxyl in nonanol. Fig. 2 clearly showed the ^1H NMR spectra of dinonyl carbonate. Peak A and peak B correspond, respectively to methyl terminated and methylene, meanwhile, peak C and peak D correspond, respectively to the methylene which is connected with oxygen atom indirectly and directly. In ^1H NMR spectra, the integral area of peak corresponds to the number of hydrogens.

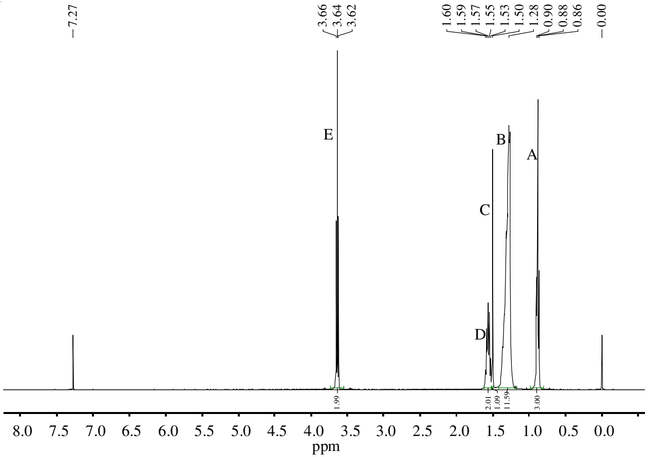


Fig. 2. ^{1}H NMR spectrum of dinonyl carbonate

TABLE-1
^{1}H NMR/^{13}C NMR DATA OF NONANOL AND DINONYL CARBONATE

	^{1}H NMR	^{13}C NMR
Nonanol	δ 3.64 (t, *J* = 6.7 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.50 (s, 1H), 1.28 (s, 12H), 0.88 (t, *J* = 6.7 Hz, 3H)	63.02, 33.27, 32.51,30.56, 30.38, 30.02, 26.39, 23.14, 14.05
Dinonyl carbonate	δ 4.12 (t, *J* = 6.7 Hz, 4H), 1.72–1.55 (m, 4H), 1.26 (s, 24H), 0.88 (t, *J* = 6.8 Hz, 6H)	155.46, 77.02, 31.89, 29.52, 29.30, 25.71, 22.68, 14.11

The structure of the nonanol and the dinonyl carbonate with assignments of characteristic ^{13}C signal are given in Table-1. The ^{13}C NMR spectra of the dinonyl carbonate display the signal of the carbonate carbons at 155-156 ppm. At the same time, the product was characterized by electrospray ionization time-of-flight mass spectrometry, dinonyl carbonate gave a M$^+$ molecular ion at *m/z* 340. Through qualitative characterization of product can determine the product synthesized is dinonyl carbonate of this paper.

Effect of reaction time on the yield of dinonyl carbonate: Fig. 3 showed the effect of reaction time on the yield of dinonyl carbonate. It can be observed that reaction is not sufficient, the yield of dinonyl carbonate is low at the beginning of the reaction, the dinonyl carbonate yield increases rapidly as the reaction time increase and reaches a maximum of 53.9 % after 3 h. Then, the dinonyl carbonate yield gradually decreases. The reason is the synthesis reaction is a reversible reaction, due to the dinonyl carbonate decomposition may occur and the adverse reactions will happen with biuret obtained from urea by self polymerization and cyanate that from the decomposition of urea, which reduces the yield as well as reaction time too long will cause a waste of energy, So for dinonyl carbonate synthesis, 3 h of reaction time is more appropriate.

Effect of reaction temperature on the yield of dinonyl carbonate: Fig. 4 showed the effect of reaction temperature on the yield of dinonyl carbonate. The dinonyl carbonate yield sharply increases in the temperature range of 420-470 K and decreases significantly when the reaction temperature exceeds 480 K. Urea alcoholysis reaction is a endothermic process, the dinonyl carbonate synthesis is sensitive to the reaction temperature. It is beneficial for the synthesis of dinonyl carbonate in a higher reaction temperature range from the thermodynamics viewpoint. But the higher temperature will result in intermediate unbranched ester carbamate decomposition and the adverse reactions will increase. Although the conversion rate of urea will increase, but the product selectivity and yield of dinonyl carbonate will be greatly reduced. At the same time, biuret was prepared from the auto polymerization of urea, ammonia and cyanic acid was prepared from the urea decomposition, cyanate is polymerized cyanuric acid when reaction temperature is too high, reduces the conversion rate of urea. So for urea alcoholysis reaction, 470 K of reaction temperature is more appropriate.

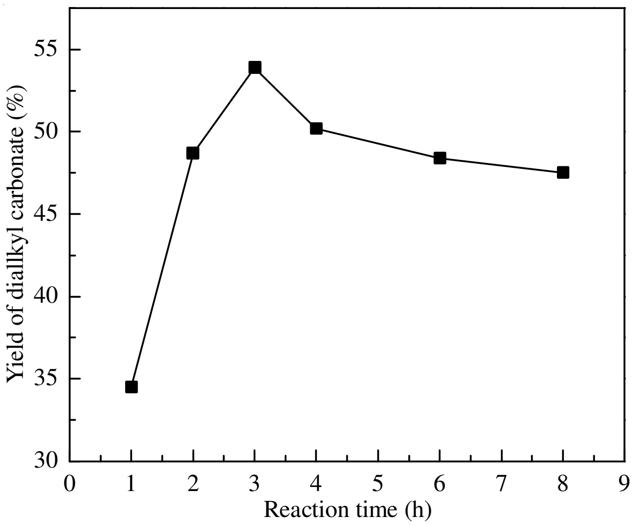


Fig. 3. Effect of reaction time on the yield of dinonyl carbonate

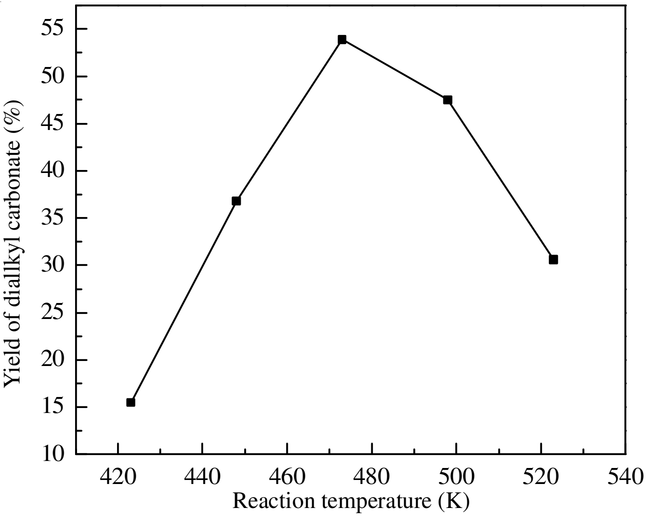


Fig. 4. Effect of reaction temperature on the yield of dinonyl carbonate

Effect of molar ratio on the yield of dinonyl carbonate: Fig. 5 showed the effect of molar ratio on the yield of dinonyl carbonate. It can be determined from this figure that the dinonyl carbonate yield increases with the increase of molar ratio of urea/nonanol until it reaches the maximum yield at 53.9 % and then declines subsequently.

The molar ratio of urea/nonyl alcohol should be 1:2 in theory for the urea alcoholysis reaction. But according to the mechanism of alcoholysis reaction, first of all, the decomposition of urea into ammonia and isocyanate species and then, aliphatic alcohol reacts with isocyanate species to generate intermediate product unbranched ester carbamate, finally to form dialkyl carbonate. Since urea is cheaper and easier to afford relative to the nonanol, so the amounts of urea is more favorable for the synthesis reaction. The whole processes gives another principal product, ammonia, which can be used to produce urea. Therefore, it has better economical benefit. It is showed that the conversion ratio of urea and the selectivity of producing dialkyl carbonate are slightly decreased with increasing molar ratio of urea to nonanol, respectively, from the Fig. 5. Meanwhile, active sites on the catalyst surface surrounded by urea and isocyanate species, it is very uneconomical to improve the yield of dialkyl carbonate. So for dinonyl carbonate synthesis, the molar ratio of urea/nonanol is 2, which is ideal!

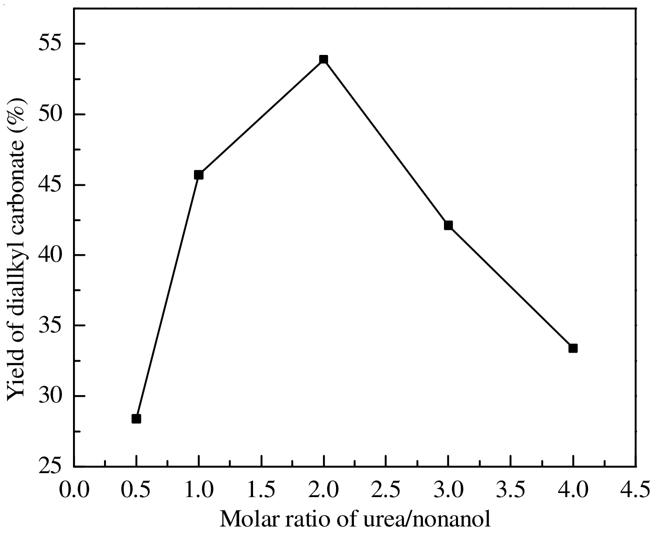


Fig. 5. Effect of molar ratio on the yield of dinonyl carbonate

Effect of catalyst concentration (relative to the mass of urea) on the yield of dinonyl carbonate: The effect of catalyst concentration (relative to the mass of urea) on dinonyl carbonate yield is shown in Fig. 6. It can be seen that dinonyl carbonate yield increases with the increase of catalyst loading. The reason is that the number of catalytic active sites in the reaction system was increased and the reaction rate was accelerated. However, when the catalyst concentration was 2 %, the dinonyl carbonate yield reached the maximum value of 53.9 % and the dinonyl carbonate yield declined with the increase of catalyst loading. For dinonyl carbonate synthesis reaction, the higher catalyst concentration caused the great consumption of dinonyl carbonate by side reactions. So for this synthesis reaction system, the best catalyst concentration in experiment is 2 % (relative to the mass of urea).

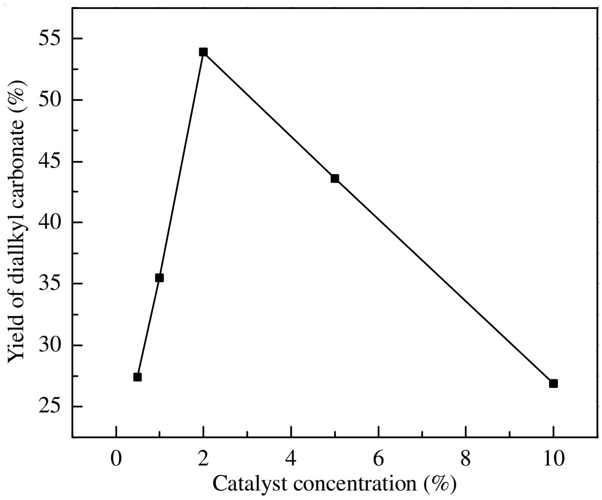


Fig. 7. Effect of catalyst concentration (relative to the mass of urea) on the yield of dinonyl carbonate

Conclusion

In summary, dinonyl carbonate was prepared by alcoholysis of urea, dibutyltin oxide catalyst system has good catalytic activity. Reaction time of 3 h, reaction temperature of 473 K, urea/nonanol molar ratio of 2, catalyst concentration of 2 % (relative to the mass of urea), under these conditions, symmetrical structure of the dinonyl carbonate can be synthesized, the highest dinonyl carbonate yield was 53.9 %.

In this process, the development of the catalysts is a key problem. dibutyltin oxide catalyst system has good catalytic activity in many kinds of catalyst. However, the uniformity of organotin compounds catalyst brought some problems, such as separation and deactivation and the toxicity of organic tin compounds slightly restricted the development of this method[9]. Subsequent work will focus on changes of the catalyst types, characteristics, load, mixed catalyst and other aspects.

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