Chinese Chemical Letters Vol. 11, No. 7, pp. 589–592, 2000

Catalytic Formation of Propylene Carbonate from Supercritical Carbon Dioxide/Propylene Oxide Mixture

Xiao Bing LU, Yu Zhen PAN, Dong Feng JI, Ren HE*

Laboratory of Comprehensive utilization for carbonaceous resources, Dalian University of Technology, Dalian 116012

Abstract: Propylene carbonate was synthesized from supercritical carbon dioxide (SC-CO_2)/ propylene oxide mixture with phthalocyaninatoaluminium chloride (ClAlPc)/ tetrabutylammon-ium bromide (n-Bu_4NBr) as catalyst. The high rate of reaction was attributed to rapid diffusion and the high miscibility of propylene oxide in SC-CO_2 under employed conditions. Various reaction periods present different formation rate of propylene carbonate, mainly due to the existence of phase change during the reaction. The experimental results demonstrate that SC-CO_2 could be used as not only an environmentally benign solvent but also a carbon precursor in synthesis.

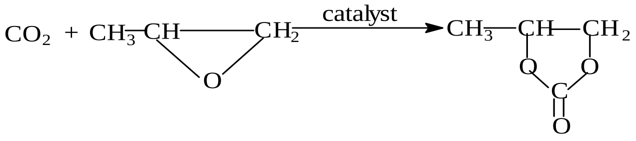
Keywords: Supercritical carbon dioxide, propylene oxide, propylene carbonate, cycloaddition reaction.

The use of supercritical carbon dioxide as a substitute solvent for chemical synthesis is a very attractive area in view of resource utilization and environmental problems[1,2,3,4]. Since CO_2, which has an easily accessible critical point with a Tc of 31.1°C and a Pc of 7.3MPa, is nontoxic, nonflammable and inexpensive, it can replace hazardous organic solvent and thereby provide a valuable pollution prevention tool. As similar to other supercritical fluids, SC-CO_2 has gaslike diffusitivity and liquidlike density, and changing pressure and temperature can vary its physical properties[5]. Furthermore, SC-CO_2 may be a particularly advantageous reaction medium when CO_2 serves as a reagent and a solvent. The improved rates for catalytic hydrogenation of CO_2 to formic acid in supercritical conditions provided support for this approach[6].

This paper reports on the catalytic production of propylene carbonate from supercritical CO_2/propylene oxide mixture utilizing phthalocyaninatoaluminium chloride/ tetrabutylammonium bromide as catalyst.(**Scheme 1**)

The catalytic reaction was carried out in a 100 ml 50 MPa autoclave with magnetic stirrer (**Figure 1**). The autoclave with weighted catalyst was sealed and purged with CO_2 for three times. Propylene oxide and liquid CO_2 (CO_2 was purified by passing through a column packed with 4A molecular sieves before use) were charged into the autoclave and then it was heated to the desired temperature under continuous stirring.

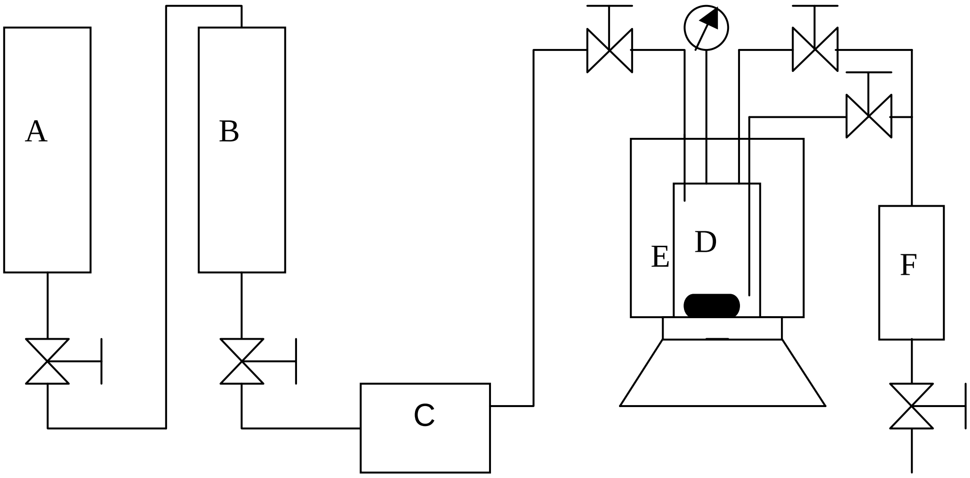
Scheme 1



When the reaction finished, the autoclave was cooled to room temperature and the excess gases were vented. The remainder mixture was distilled in vacuum(88-90°C/2mmHg), in order to obtain pure propylene carbonate. The spectra data were listed as follows:
IR: $\nu_{C=O}$ 1793cm^{-1}; ν_{C-O} 1183, 1052cm^{-1}; ^{1}H-NMR($CDCl_3$/TMS): $\delta_{1.4}$(d); $\delta_{3.9-4.1}$(t); $\delta_{4.4-4.6}$(t); $\delta_{4.7-4.9}$(m).

Reactions in supercritical fluids are strongly affected by phase changes[7]. For this reason, quantitative measurement of the concentration of propylene oxide was also performed. Samples from the uppermost and lowermost phase of the autoclave were transferred into the vessel for the measurement of propylene oxide. The results showed that 35 g propylene oxide was completely miscible with 54 g CO_2 in the 100 ml autoclave above 35.0MPa at 110°C. At the same temperature, the uppermost phase mainly comprised CO_2, propylene oxide and trace propylene carbonate, and the lowermost phase comprised mainly propylene carbonate in the autoclave (10 g propylene carbonate, 18 g propylene oxide, and 60 g CO_2 were added). These experimental results indicated that phase change must occur during the cycloaddition reaction of SC-CO_2 and propylene oxide, thus may affect the reaction rate significantly. The typical reaction process was present as follows: before the reaction, the reactants were present only one phase (namely supercritical phase) , but as the reaction proceeded, produced propylene carbonate precipitated on the bottom of the autoclave and the phase separation arose. Because the catalyst was concentrated in the liquid phase of propylene carbonate, the catalytic reaction at the latter period mainly occurred in propylene carbonate phase, in which the concentration of CO_2 and propylene oxide was small. The process can be

Figure 1. Equipment used for the reaction in supercritical carbon dioxide



A: CO_2 tank; B: drying columns; C: pump; D: autoclave; E: oven; F: analytic system confirmed by the formation rates of propylene carbonate in various reaction periods, as shown in **Table 1**. The fastest reaction with an average rate of 6.9 mole product/mole ClAlPc•min^{-1} was in the first hour. The average rate decreased to 3.5 in the second hour and 2.9 in the third hour.

Table 1. The average formation rates of propylene carbonate in various reaction periods[a]

Reaction period	1h	2h	3h
Rate[b] (mol/mol·min^{-1})	6.9	3.5	2.9

a: reaction condition: ClAlPc/n-Bu_4NBr/Propylene oxide = 1:1:1500(mole ratio); CO_2/propylene oxide = 5 (mol/mol); density of reactants in the autoclave is 0.75g/ml; reaction temperature, 110°C.

b: average rate = mol of product(propylene carbonate)/mol of ClAlPc per minute.

Table 2 The average formation rates of propylene carbonate from SC-CO_2/propylene oxide under various conditions[a]

No	CO_2/PO[b] (mol/mol)	n-BuNBr/ClAlPc (mol/mol)	Temperature (°C)	Rate[c] (mol/mol·min^{-1})
1	5	0	110	<0.1
2	5	∞	110	1.3
3	5	0.5	110	3.1
4	5	1	110	6.1
5	5	2	110	7.8
6	5	1	100	3.6
7	5	1	120	8.3
8	4	1	110	6.4
9	3	1	110	6.8
10	2	1	110	7.4
11[d]	5	1	110	3.1

a: reaction condition: ClAlPc/PO = 1:1000 (mol/mol); time, 1hour; density of reactants in the autoclave is 0.75-0.80g/ml;

b: PO = propylene oxide;

c: average rate = mol of product(propylene carbonate)/mol of ClAlPc per minute.

d: propylene carbonate of 10 g was also charged into the autoclave together with propylene oxide and CO_2.

In previous paper[8], we reported that ClAlPc could effectively catalyze the reaction of CO_2 and epoxyethane to synthesize ethylene carbonate only at high temperature (180°C). Tetraalkylammonium halides such as n-Bu_4NBr could promote the conversion of the epoxide to cyclic carbonate at relative low temperature(110°C), although ClAlPc or n-Bu_4NBr itself showed low catalytic activity under employed condition (**Table 2**). However, the synergistic catalytic mechanism of the binary catalyst was not clear.

In **Table 2** shown, the reaction temperature had a great effect on the catalytic activity. The formation rate of propylene carbonate increased remarkably with the enhancement of reaction temperature. The molar ratio of CO_2 to propylene oxide also affected the reaction rate. From **Table 2** it can be observed that the formation rate of propylene carbonate decreased with the increase of the molar ratio of CO_2 to propylene oxide, when the ratio was higher than 2.

The process described in this report demonstrated that SC-CO_2 could be used as not only an environmentally benign solvent but also a carbon precursor in organic synthesis. This fact is valuable for environment protection.

References

1. C. A. Eckert, B. L. Knutson, P. G. Debenedetti, *Nature*, **1996**, *383*, 313.
2. M. J. Burk, S. G. Feng, M. F. Gross, W. Tumas, *J. Am. Chem. Soc.*, **1995,** *117*, 8277.
3. J. M. Desimone, Z. Guan, C. S. Elbernd, *Science*, **1992**,*257*,945.
4. S. Hadida, M. S. Super, E. J. Beckman, D. P. Curran, *J. Am. Chem. Soc.*, **1997**, *119*, 7406.
5. M. E. Paulaitis, G. C. Alexander, *Pure & Appl. Chem.*, **1987**, *59*(1), 61.
6. P. G. Jessop, T. Ikariya, R. Noyori, *Nature*, **1993**,*363*,685.
7. J. A. Darr, M. Poliakoff, *Chem. Rev.*, **1999**,*99*,498.
8. D. F. Ji, H. R. Do, X. B. Lu, R. He, *Chinese J. Mol. Cat.*, **1999**, *13*(2), 140.

Received 6 December 1999
Revised 10 April 2000