

CYCLOADDITION OF OXIRANE WITH CARBON DIOXIDE IN THE SUPERCRITICAL HOMOGENEOUS STATE

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Reaction of carbon dioxide with 2-methyloxirane was carried out in both supercritical homogeneous and vapor-liquid coexisting regions to produce a cyclic carbonate compound of 4-methyl-1,3-dioxolan-2-one. The yield of the cyclic carbonate exceeded 95%, when the reaction proceeded at the supercritical uniform condition. On the other hand, the yield was less than 5%, when the reaction occurred in the two-phase region. While almost all kinds of alkali metal halides exhibited the high catalytic activity in a polar liquid solvent, limited numbers of halides were found to have large activity in supercritical carbon dioxide. The kinetics was studied based on the first-order reaction model with respect to the oxirane concentration. The activation energy and volume were determined from the experimental data in the pressure range from 10 to 30 MPa at 70-100 °C.

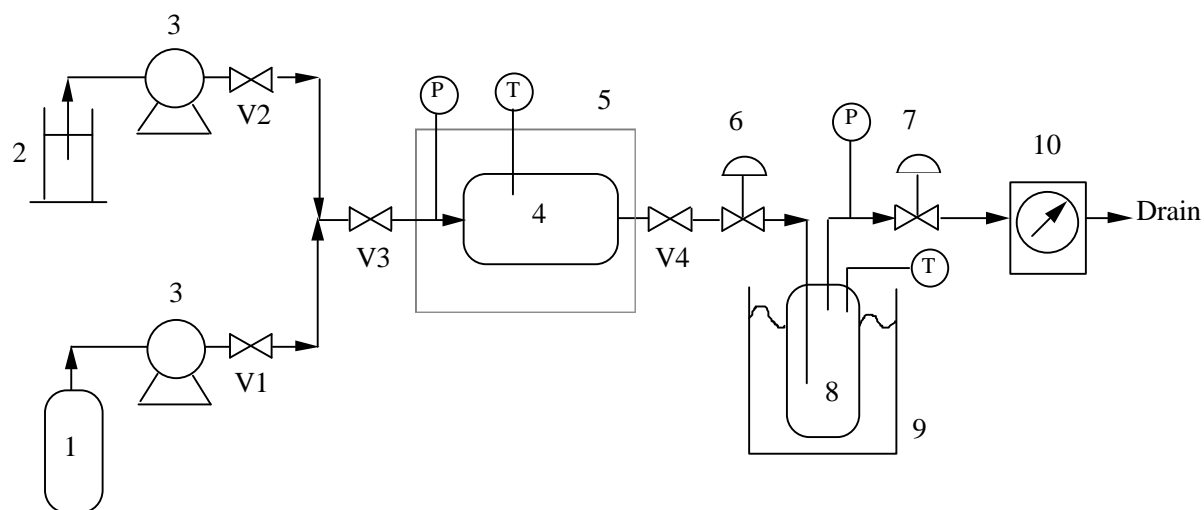
INTRODUCTION

Cyclic carbonates have a lot of promising applications to an environmentally friendly organic solvent, electrolyte solution of lithium ion battery, monomers of polymeric materials and others. The synthesis from the oxirane and carbon dioxide represents one of the typical examples of successful utilization and chemical fixation of carbon dioxide. The reactions using gaseous carbon dioxide have been investigated in a polar aprotic liquid solvent such as dimethylformamide and N-methylpyrrolidone so far. A variety of substances from alkali metal salts to classical organometallic complexes were found to catalyze the formation of cyclic carbonates and polycarbonates [1-3]. The selectivity was more than 90% in many cases. However, the reaction was slow and more than 10 hours were often required to complete the reaction.

The purpose of this work is to develop a new synthesis of cyclic carbonates using supercritical carbon dioxide as both reactant and solvent. This operation makes use of the excellent properties of supercritical carbon dioxide that may enhance the reaction rate by changing the reaction field from vapor-liquid coexisting to supercritical uniform phase and separate the carbonate selectively from the reaction mixture by adjusting the dissolution power. The effects of the operation variables such as the temperature, pressure, kind of catalyst and phase condition on the reaction rate and the desired product selectivity and yield were examined and discussed. Furthermore the kinetic analysis was carried out using a flow reactor in the wide temperature and pressure regions.

EXPERIMENTAL SECTION

The experimental apparatus used for batch and flow reactions under a high pressure condition is illustrated in Figure 1. A reactor (4) was the stainless steel 316 vessel having 50 cm³ in volume. It was placed in a temperature controlled air bath (5). The maximum working temperature and pressure were 200 °C. and 40MPa, respectively.



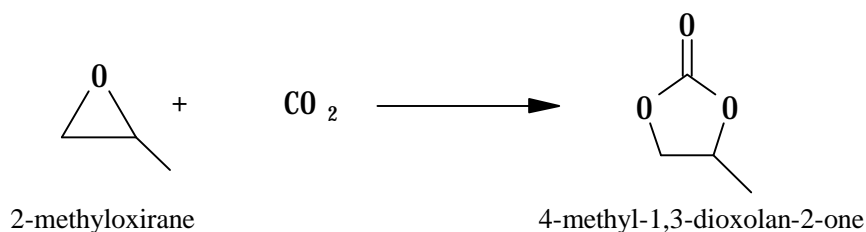
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|-----------------------------|-------------------------------|--------------------|
| 1. CO ₂ cylinder | 6, 7. Back pressure regulator | P. Pressure gauge |
| 2. Oxirane compound | 8. Product separation vessel | T. Thermometer |
| 3. High pressure pump | 9. Water bath | V1-V4. Stop valves |
| 4. Reactor | 10. Gas meter | |
| 5. Air bath | | |

Figure 1 Experimental apparatus used for batch and flow reactions at supercritical condition

The batch-mode operation was employed for the reaction analysis to investigate the effect of the operating variables such as the temperature, pressure and existing phase in the reaction field on the oxirane conversion and the carbonate yield. The flow-mode operation was used for the solubility test of the catalyst and the kinetic analysis in the supercritical condition.

RESULTS AND DISCUSSION

For the synthesis of a cyclic carbonate from carbon dioxide and an oxirane compound in N-methylpyrrolidone under atmospheric pressure, Kihara et al. indicated that the reaction proceeded with high yield in the presence of an alkali metal halide as catalyst [3]. In this work, the same catalyst was used for the cycloaddition of an oxirane compound with carbon dioxide



Scheme 1

at the supercritical condition. The product yield was defined as the molar ratio of the product to the fed oxirane compound, and the product selectivity was defined as the molar ratio of the product to the reacted oxirane compound, respectively.

2-Methyloxirane of 10g (172 mmol) was reacted with carbon dioxide using lithium bromide of 0.15g at various temperatures from 50 to 100 °C for the pressures of 6, 8, 10 MPa and the reaction time of 2 hours in a batch reactor. Lithium bromide was a catalyst and the amount corresponding to 1 mole% of 2-methyloxirane was used.

Figure 2 shows the temperature dependence of the yield of the desired product 4-methyl-1,3-dioxolan-2-one at various pressure conditions. The product yield of each isobaric line increased steeply from less than 5% to more than 95% in a narrow temperature region. The rising temperature moved to a lower side when the pressure increased. The main reason for this phenomenon might be a change of the surrounding environment of the catalyst. As seen through the view window, there was a dramatic change of the phase surrounding the catalyst from the vapor-liquid coexisting to supercritical homogeneous state, when the reaction temperature increased under a constant pressure condition: that is, the critical locus existed near the yield-rising temperature for each isobaric line.

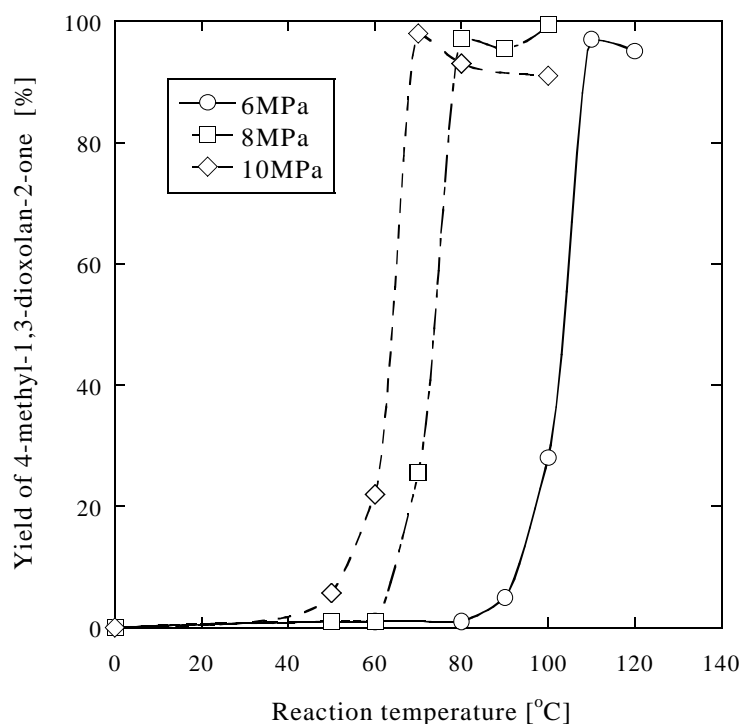


Figure 2 Temperature dependence of yield of 4-methyl-1,3-dioxolan-2-one using lithium bromide catalyst

This result clearly stated that the supercritical homogeneous region could accelerate the reaction so much. This might be owing to the disappearance of the diffusion barrier between a vapor and liquid interface, the high diffusivity of the reactants in the supercritical phase and the increase in the collision probability of the reactants and catalyst. The similar acceleration of the reaction was observed for the hydrogenation of carbon dioxide in the supercritical state [4].

The catalytic activity was compared among nine kinds of alkali metal halides at 100 °C. and 14MPa for the reaction time of 2 hours in a batch reactor. The phase in the reactor remained homogeneous during the reaction, even when the reaction proceeded and the composition changed. The experimental results are given in Table 1. Kihara et al. reported that almost all alkali metal halides had a large catalytic activity in a polar aprotic liquid solvent such as N,N-dimethylformamide or N-methylpyrrolidone and the order was lithium salt> sodium salt> potassium salt for catalyst cations and chloride> bromide> iodide for halides. However, only four halides were found to have a high performance at supercritical condition and the order of the catalytic activity was lithium bromide> lithium iodide> sodium iodide> potassium iodide, indicating that the alkali metal halides composing of the halogen anion with the large ionic diameter and the metal cation with the small ionic diameter would work well in the supercritical state. The difference of the catalytic activity between in the liquid and supercritical solvents might be owing to the difference of the solvent properties such as the polarity and the dissolution power to the catalyst in both solvents.

Table 1 Comparison of catalytic activity at supercritical condition

Metal halide	Conversion
LiCl	0
LiBr	97
LiI	94
NaCl	0
NaBr	0
NaI	63
KCl	0
KBr	0
KI	11

(100 °C, 14MPa, 2 hours, 2-methyloxirane 172mmol, catalyst 1mol% of 2-methyloxirane)

The reaction rate was measured using a continuous stirred tank reactor shown in Figure 1. The kinetic data were analyzed based on the first-order reaction model with respect to the oxirane concentration. Judging from the products, there were three main reactions: a desired reaction to produce the cyclic carbonate and two side reactions to produce 1-bromo-2-propanol and 1,2-propanedial. Figure 3 shows the temperature dependence of the rate constants of three reactions at 30MPa. The activation energy of each reaction was determined from the slope of the straight line and is given in Table 2. Figure 4 shows the pressure dependence of the rate constants at 80°C. The maximum rate constants existed around 20MPa for all reactions.

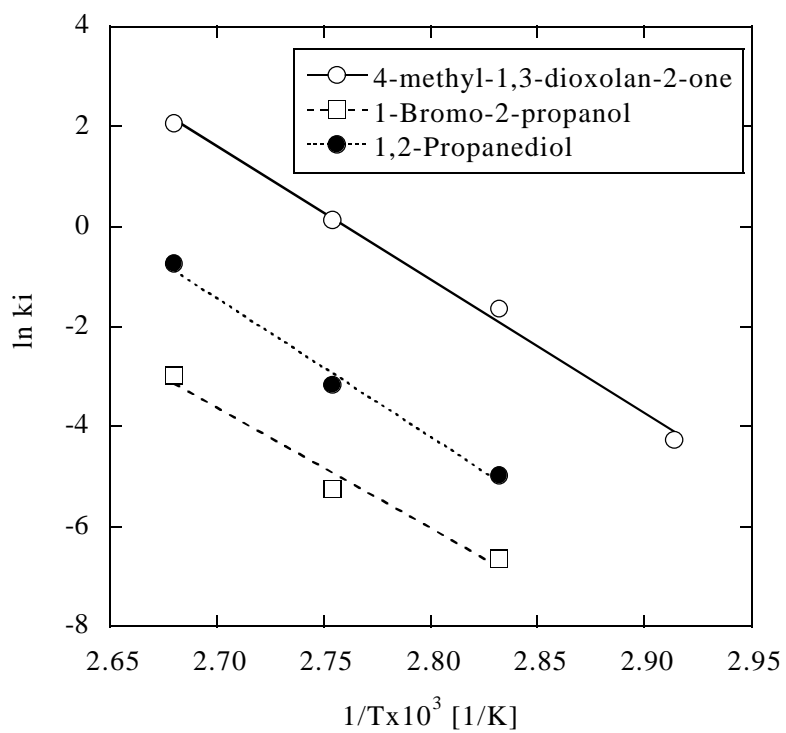


Figure 3 Temperature dependence of rate constants at 30MPa

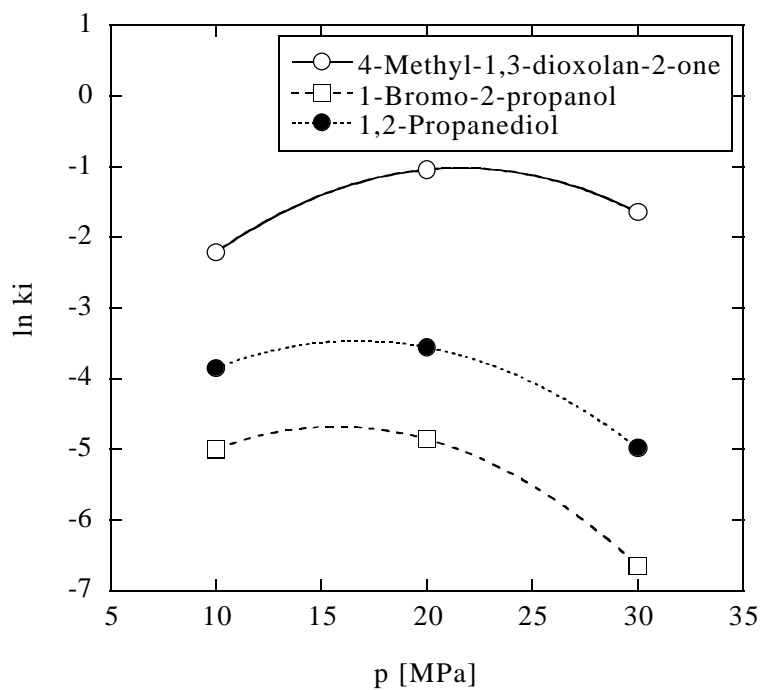


Figure 4 Pressure dependence of rate constants at 80 °C

Table 2 Activation energies of three main reactions at 30MPa

Product	Activation energy [kJ/mol]
4-Methyl-1,3-dioxolan-2-one	221.6
1-Bromo-2-propanol	200.6
1,2-Propanediol	231.6

CONCLUSIONS

Cycloaddition of 2-methyloxirane with carbon dioxide proceeded completely and rapidly in the supercritical homogeneous state, while it hardly occurred in the vapor-liquid coexisting state. Among the alkali metal halides with the excellent catalytic activity in a polar liquid solvent, some halides exhibited the high catalytic activity even at the supercritical condition. The first-order reaction model for the oxirane concentration represented the experimental kinetic data well.

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