SYNTHESIS OF CARBONATE BY REACTION OF CARBON DIOXIDE WITH PGE

Sang-Wook Park[a], Dae-Won Park, Tae-Young Kim, Mi-Young Park, and Kwang-Joung Oh

[a]Division of Chemical Engineering, Pusan National University, Pusan 609-735, Korea

Introduction

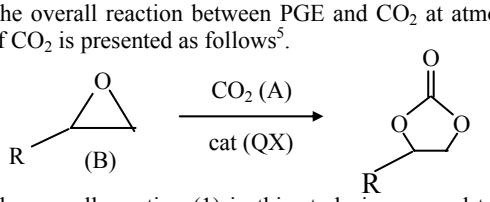
Recently, the chemistry of carbon dioxide has received much attention[1], and its reaction with oxiranes leading to five-membered cyclic carbonate (oxirane-CO_2 reaction) is well-known among many examples[2,3]. These carbonates can be used as aprotic polar solvent and sources for polymer synthesis[4]. In the oxirane-CO_2 reaction, high pressure (5-50 atm) of CO_2 has been thought to be necessary[2]. The oxirane-CO_2 reactions under atmospheric pressure have been reported[4] only recently. Many organic and inorganic compounds including ammines, phosphines, quaternary ammonium salts, and alkali metal salts are known to catalyze the oxirane-CO_2 reaction[3]. Most purpose of these papers have been to show the reaction mechanism, the pseudo-first-order reaction rate constant with respect to the concentration of oxirane, and the catalyst dependence of its conversion.

In the mass transfer accompanied by a chemical reaction, the diffusion may have an effect on the reaction kinetics. It is considered worthwhile to investigate the reaction kinetics of the gas-liquid heterogeneous reaction such as the oxirane-CO_2 reaction.

In this study, a chemical absorption mechanism of carbon dioxide into the toluene solution of phenyl glycidyl ether(PGE) and Aliquat 336(QX), and the experimental value of the equilibrium reaction constant between PGE and Aliquat 336 were presented, from which the reaction rate constant of reaction of CO_2 was obtained using the measured molar flux and liquid-side mass transfer coefficient of CO_2 at 85°C and 1 atm.

Theory

The overall reaction between PGE and CO_2 at atmospheric pressure of CO_2 is presented as follows[5].



(1)

The overall reaction (1) in this study is assumed to consist of three steps as follows[5];

The three steps are (i) a reversible reaction of PGE and QX to form complex, C_1, (ii) reaction of C_1 and carbon dioxide to form complex,C_2, and (iii) dissociation reversible reaction of C_2 to form QX and five-membered cyclic carbonate.

$$B + QX \rightleftharpoons C_1 \quad \text{(i)}$$

$$A + C_1 \longrightarrow C_2 \quad \text{(ii)}$$

$$C_2 \rightleftharpoons QX + C \quad \text{(iii)}$$

The mass balances accompanied by the overall reaction $(A + B \xrightarrow{k_c} P)$, which consists of reaction(i)-(iii), and initial and boundary conditions are presented as follows,

$$D_A \frac{\partial^2[A]}{\partial z^2} = \frac{\partial[A]}{\partial t} + k_c[A][B] \quad (2)$$

$$D_{C1} \frac{\partial^2[B]}{\partial z^2} = \frac{\partial[B]}{\partial t} + \nu k_c[A][B] \quad (3)$$

$$t = 0, z > 0; [A] = 0, [B] = [B]_o \quad (4)$$

$$t > 0, z = 0; [A] = [A]_i, \frac{\partial[B]}{\partial z} = 0 \quad (5)$$

$$t > 0, z = \infty; [A] = 0, [B] = [B]_o \quad (6)$$

The mass balances, (2) and (3), and the conditions, (4)-(6) are rearranged the dimensionless forms as follows;

$$\frac{\partial^2 a}{\partial x^2} = \frac{\pi}{4}\frac{\partial a}{\partial \theta} + m\,a\,b \quad (7)$$

$$\frac{\partial^2 b}{\partial x^2} = \frac{\pi}{4} r \frac{\partial b}{\partial \theta} + \nu\, r\, q\, m\, a\, b \quad (8)$$

$$\theta = 0, x > 0; a = 0, b = 1 \quad (9)$$

$$\theta > 0, x = 0; a = 1, \frac{\partial b}{\partial x} = 0 \quad (10)$$

$$\theta > 0, x = \infty; a = 0, b = 1 \quad (11)$$

where,

$$a = \frac{[A]}{[A]_i},\ b = \frac{[B]}{[B]_o},\ x = \frac{z}{\delta},\ \theta = \frac{t}{t_o},\ \delta = \frac{D_A}{k_L},\ q = \frac{[A]_i}{[B]_o}$$

$$t_o = \frac{4D_A}{\pi k_L^2},\ m = \frac{k_c[B]_o D_A}{k_L^2},\ r = \frac{D_A}{D_{BI}},$$

The enhancement factor(β), which is defined as ratio of absorption rate of CO_2 with chemical reaction to that without the chemical reaction, is presented as follow;

$$\beta = -\left.\frac{\partial a}{\partial x}\right|_{x=0} \quad (12)$$

The measured enhancement factor, which is obtained under the given experimental condition such as concentration of PGE, Aliquat336, and the agitation speed of the impeller, is used to get the reaction rate constant by the comparison of its value with the value estimated from Eq.(12).

Experimental

Absorption experiments were carried out in a semi-batch flat-stirred agitated vessel constructed of pyrex glass of 0.075 m inside diameter and of 0.13 m in height. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. A straight impeller with 0.034 m in length, 0.017 m in width and 0.005 m in thickness was used as the liquid phase agitator and located at the middle position of the liquid phase of 0.3 dm^3. The absorption rates of CO_2 were obtained from the difference of the flow rate of CO_2 between inlet and outlet of the vessel at 85°C. The molar flux of CO_2 absorbed into the liquid was obtained from the measured rate of absorption.

Results and Discussion

The concentration profiles of components A and B can be obtained by the numerical analysis (FEMLAB) of the equations (7) and (8). The estimated values concentration of component A and B are shown in **Fig.1** under the typical reaction condition such as [PGE]= 0.1 kmol/m^3, [QX]= 0.05 kmol/m^3, T= 85°C. As shown in **Fig.1**, the concentration of CO_2 decreases and that of B increases as the depth of the liquid increases. Using the measured molar flux of CO_2 according to the change of fed concentrations of component, PGE and QX, the reaction rate constant of the reaction (1), which can be obtained under the boundary condition such as [A]=0 at z=0, is 0.53 m^3/kmol·s at 85°C.

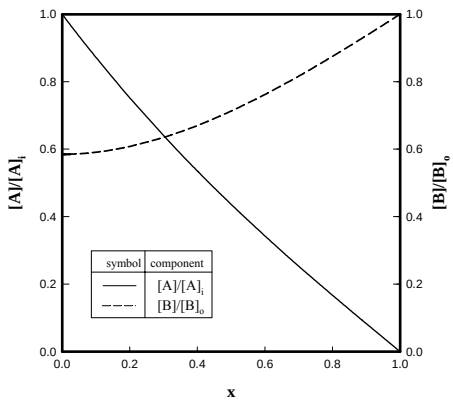


Figure.1. Concentration profile of A and C1. ($[B]_o$=0.1 kmol/m^3, $[QX]_o$=0.05 kmol/m^3, T=85°C)

The measured value of absorption rate of CO_2 at the concentration of PGE in the range of 0.1~2.0 kmol/m^3, that of Aliquat336 of 0.05 kmol/m^3, and the agitation speed of impeller of 50 rev/min are plotted against the concentration of PGE in **Fig. 2**. As shown in **Fig.2**, the absorption rate of CO_2 increased as increasing of PGE concentrations. The reaction rate constant(k_2) was estimated by comparison of enhancement factor obtained from the measured absorption rate of CO_2 in **Fig.2** with the value in Eq.(12).

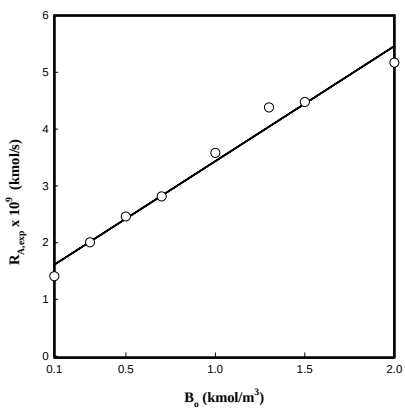


Figure. 2. Effect of PGE concentration on flux of CO_2.

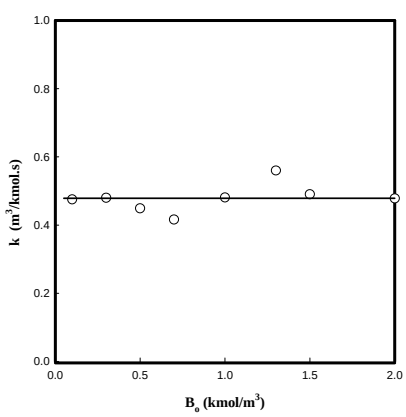


Figure. 3. Effect of PGE concentration on reaction rate constant.

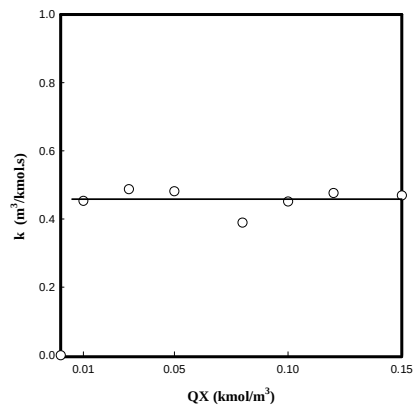


Figure. 4. Effect of QCl concentration on reaction rate constant.

The values of k_2 are plotted against the concentration of PGE in **Fig.3**. As shown in **Fig.3**, the reaction rate constants are constant as 0.434-0.592 m^3/kmol.s at the PGE concentration in the range of 0.5-2.0 kmol/m^3. Also the values of k_2, which are estimated by using the experiments at the concentration of PGE of 1.0 kmol/m^3 and those of Aliquat336 in the range of 0.01-0.15 kmol/m^3, are plotted against the concentration of Aliquat336 in **Fig.4**. As shown in **Fig.4**, the reaction rate constants were constant in the range of Aliquat 336 concentrations.

Conclusion

Carbon dioxide was absorbed into the toluene solution of phenyl glycidyl ether(PGE) as a oxirane and tricaprylylmethylammonium chloride (Aliquat 336, QX) as a catalyst using a semi-batch flat-stirred absorber at 85°C and 1atm to obtain a five-membered cyclic carbonate, phenoxy methyl ethylene carbonate. The reaction mechanism of oxirane – CO_2 reaction divided into three steps was used to obtain the reaction kinetics using the mass balance equations. The reaction rate constant in the overall reaction between CO_2 and PGE was obtained by the numerical solution of the mass balance equation using the measured molar flux of CO_2 and the liquid-side mass transfer coefficient of CO_2 at given concentration of PGE and QX.

Acknowledgement

This work was supported by KOSEF (Grant No : R01-2003-000-100200-0), the Brain Korea 21 project in 2003, and Brain Busan 21 program.

References

1. Inoue, S., In organic and bioorganic chemistry of carbon dioxide ; Inoue, S., N. Yamazaki, Eds., Kodansha Ltd., Tokyo, 1982.
2. Peppel, W.J., *Ind. Eng. Chem.*, 50(5), 767-770 (1958).
3. Kihara, N., Hara, N., and Endo, T., *J. Org. Chem.*, 58, 6198-6202 (1993).
4. Rokicki, G., *Makromol. Chem.* 186, 331-337 (1985).
5. Aida, T. and S. Inoue, *J. Am. Chem. Soc.*, 105, 1304-1309 (1983).