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Chemical Absorption of Carbon Dioxide into Glycidyl Methacrylate Solution with Tetrabutylammonium Bromide

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Chemical Absorption of Carbon Dioxide into Glycidyl Methacrylate Solution with Tetrabutylammonium Bromide

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Abstract: Absorption of carbon dioxide was carried out in a semi-batch stirred tank of glycidyl methacrylate solution with tetrabutylammonium bromide as a catalyst at 101.3 kPa. The measured rate of absorption of carbon dioxide was used to obtain the reaction kinetics by the mass transfer mechanism accompanied by the chemical reaction, which was consisted of two elementary reactions. An empirical correlation formula between the reaction rate constants and the solubility parameters of the solvents, such as toluene, *N*-methyl-2-pirrolidinone, and dimethyl sulfoxide, was presented.

Keywords: Absorption, carbon dioxide, glycidyl methacrylate, tetrabutylammonium bromide

INTRODUCTION

Recently, the chemistry of carbon dioxide has received much attention (1); its reactions with oxiranes, leading to five-membered cyclic carbonate, are well-known among many examples (2, 3). In the oxirane-CO_2 reaction, a high pressure (5–50 atm) of CO_2 was known to be necessary (2), but recently

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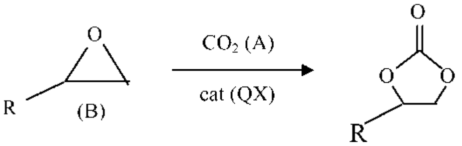
oxirane-CO_2 reactions that occur at atmospheric pressure have been reported (4). Many organic and inorganic compounds, including amines, phosphines, quaternary ammonium salts, and alkali metal salts, are known to catalyze the reaction of CO_2 with oxirane (3). Most of these papers (1–4) have focused on the reaction mechanism, the pseudo-first-order reaction rate constant with respect to the concentration of oxirane, and the effect of the catalyst on the conversion.

In mass transfer processes that accompany chemical reactions, the diffusion may have an effect on the reaction kinetics (5). We believe that it is worthwhile to investigate the effect that diffusion has on the reaction kinetics of the gas-liquid heterogeneous reaction such as the oxirane-CO_2 reaction.

In this study, we measured the absorption rates of carbon dioxide into the solution of glycidyl methacrylate (GMA) as a reactant and tetrabutylammonium bromide (TBAB) as a catalyst in organic solvents such as toluene, *N*-methyl–2-pirrolidinone, and dimethyl sulfoxide to determine the pseudo-first-order reaction constant, which we used to obtain the elementary reaction rate constants.

THEORY

To determine the reaction kinetics between an oxirane and carbon dioxide using a catalyst, such as a quaternary onium salts it is necessary to understand the reaction mechanism. Although the reaction mechanism shown in Eq. (1) have been proposed by many researchers for the oxirane-CO_2 reaction (3, 6–9), no reliable evidence has yet been reported. It has been found that the rate-determining step is the attack of the anion part of the catalyst to the oxirane. The importance of the anion part of the catalyst can be explained by this mechanism. That is, the overall reaction between CO_2 and GMA to form five-membered cyclic carbonate is as follows:



(1)

The overall reaction (1) in this study is assumed to consist of two steps:

(i) A reversible reaction between GMA(B) and TBAB(QX) to form an intermediate complex (C_1),
(ii) An irreversible reaction between C_1 and carbon dioxide(A) to form QX and five-membered cyclic carbonate(C).

$$B + QX \underset{k_2}{\overset{k_1}{\longleftrightarrow}} C_1 \tag{2}$$

$$A + C_1 \xrightarrow{k_3} C + QX \tag{3}$$

The reaction rate of CO_2 under the condition of a steady-state approximation to formation of C_1 is presented as follows:

$$r_A = \frac{k_1 k_3 C_A C_B Q_o}{k_2 + k_3 C_A + k_1 C_B} = \frac{C_B Q_o}{1/k_1 + k_2/k_1 k_3 C_A + C_B/k_3 C_A} \tag{4}$$

If the value of k_1 is very large, such that $1/k_1$ approaches to 0, Eq. (4) is arranged to

$$r_A = \frac{C_A C_B Q_o}{k_2/k_1 k_3 + C_B/k_3} \tag{5}$$

Species B is a nonvolatile solute, which has been dissolved in the liquid phase prior to its introduction into the gas absorber. It is assumed that gas phase resistance to absorption is negligible by using pure species A, and, thus, the concentration of species A at the gas-liquid interface corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

Under the assumptions mentioned above, the mass balances of species A and B, using film theory accompanied by a chemical reaction, and the boundary conditions are given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = \frac{C_A C_B Q_o}{k_2/k_1 k_3 + C_B/k_3} \tag{6}$$

$$D_B \frac{d^2 C_B}{dz^2} = \frac{C_A C_B Q_o}{k_2/k_1 k_3 + C_B/k_3} \tag{7}$$

$$z = 0; \quad C_A = C_{Ai}; \quad \frac{dC_B}{dz} = 0 \tag{8}$$

$$z = z_L; \quad C_A = 0; \quad C_B = C_{B0} \tag{9}$$

The enhancement factor of CO_2, defined as ratio of the flux of CO_2 with chemical reaction to that without chemical reaction, is shown as follows:

$$\beta = -\left.\frac{da}{dx}\right|_{x=0} \tag{10}$$

where $a = C_A/C_{Ai}$, $x = z/z_L$.

The value of β can be obtained from the numerical solution of the simultaneous differential Eqs. (6) and (7) using FEMLAB program and Eq. (10), by applying the known values of D_A, D_B, k_1, k_2 and k_3, and given values of C_{Bo} and Q_o.

The absorption rate of CO_2 can be estimated as follows:

$$R_A = \beta k_L C_{Ai} S \tag{11}$$

where β is obtained from Eq. (10), D_A, D_B, k_L and C_{Ai} from Table 1.

Table 1. Physicochemical properties of CO_2/GMA system

Temp (°C)	Solvent	μ (cp)	C_{Ai} (kmol/m^3)	$D_A \times 10^9$ (m^2/s)	$D_B \times 10^9$ (m^2/s)	$k_L \times 10^5$ (m/s)
80	Toluene	0.322	0.0783	9.379	3.665	1.268
	NMP	0.848	0.0711	3.694	1.444	1.204
	DMSO	0.857	0.0612	3.245	1.268	2.595
85	Toluene	0.307	0.0727	9.977	3.898	1.472
	NMP	0.797	0.0679	3.986	1.558	2.285
	DMSO	0.808	0.0576	3.490	1.364	2.864
90	Toluene	0.294	0.0698	10.563	4.128	1.946
	NMP	0.750	0.0629	4.295	1.678	1.998
	DMSO	0.764	0.0544	3.743	1.463	3.110

It is impossible to solve the non-linear differential Eqs. (6) and (7) if the reaction rate constants such as k_1, k_2, and k_3 are not known. But the pseudo-first-order reaction method (10) can be used to obtain the reaction rate constants as following situation.

If the concentration of B is constant (C_{Bo}), the reaction between CO_2 and GMA is assumed to be pseudo-first-order reaction with respect to the concentration of CO_2, and r_A in Eq. (5) is shown as

$$r_A = k_o C_A \tag{12}$$

where,

$$k_o = \frac{C_{Bo} Q_o}{k_2/k_1 k_3 + C_{Bo}/k_3} \tag{13}$$

Eq. (13) is rearranged as follows:

$$\frac{Q_o C_{Bo}}{k_o} = \frac{k_2}{k_1 k_3} + \frac{C_{Bo}}{k_3} \tag{14}$$

The mass balance of species A with the film theory accompanied by a pseudo-first-order reaction is given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = k_o C_A \tag{15}$$

From the exact solution of Eq. (15), β is presented as follows:

$$\beta = \frac{Ha}{\tanh Ha} \tag{16}$$

where Ha is called as Hatta number, $\sqrt{k_o D_A}/k_L$.

The value of k_o is obtained from the experimental value of equation (16) at given values of C_{Bo} and Q_o. The values of k_3 and k_2/k_1 can be evaluated from the slope and intercept of plots against C_{Bo}.

EXPERIMENTAL

All chemicals in this study were reagent grade, and used without further purification. Purity of both CO_2 and N_2 was more than 99.9%. GMA and TBAB were used as reagent grade supplied by Aldrich chemical company, USA without purification.

The gas-liquid contactor used was a stirred tank made of glass (7.5 cm inside diameter, 13 cm in height) having a planar unbroken gas-liquid interface; it was operated continuously with respect to the gas and batchwise with respect to the liquid phase. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The contact area between the gas and the liquid was measured as $4.286 \times 10^{-3}\,m^2$. The liquid phase was agitated using an agitator driven by a 1/4 Hp variable speed motor without agitation in gas phase, because it was pure CO_2 gas. A straight impeller (3.4 cm length, 1.7 cm width, and 0.5 cm thickness) was used as the liquid phase agitator; it was located at the middle position of the liquid phase of $0.3\ dm^3$. The solute gas, carbon dioxide, was saturated with solvent vapor, and fed into the absorber. The absorber and saturator were maintained at a constant given temperature in a water bath and the gas flow meters were maintained at the same temperature in an air bath. The gas flow rate was maintained at $50\,cm^3/min$. The flow rate of outlet gas was measured using a mass flow meter (Brook Instrument, USA). The absorption rate was calculated from the difference between the inlet and outlet flow rates of CO_2 in the concentrations of GMA ranging from 0.5 to $3\,kmol/m^3$ and catalyst of $0.05\,kmol/m^3$, and at reaction temperature in range of 80–90°C. The experimental procedure used to obtain the absorption rate duplicated in detain the reported approach (11).

The viscosity of solvent was measured with a Cannon-Fenske viscometer. The solubility of CO_2 in organic solvents such as toluene, *N*-methyl-2-pirrolidinone, and dimethyl sulfoxide at 101.3 kPa was obtained by measuring the pressure difference of CO_2 between before and after equilibrium between gas and liquid phase similar to the procedure reported elsewhere (12). The mass transfer coefficient (k_L) of CO_2 was calculated using the measured rate of absorption of CO_2 and solubility of CO_2 at an impeller speed of 50 rev/min. The diffusivity of CO_2 and GMA in solvent was estimated from the Wilke-Chang equation (10). Because the difference between a solvent and its solution of GMA was not large, the physico-chemical properties such as C_{Ai}, D_A and D_B might to be assumed to be independent of C_{Bo}, and these values was ones obtained in the pure solvents. The viscosity of solvent, solubility, mass transfer coefficient, diffusivities of CO_2 and GMA are given in Table 1.

Analysis of the Five-Membered Cyclic Carbonate and Physicochemical Properties of CO_2 and GMA

The presence of (2-oxo-1,3-dioxolan-4-yl)methacrylate (DOMA), which was produced from the reaction between CO_2 and GMA, was confirmed by the instrumental analysis, such as FT-IR (cyclic carbonate C=O peak at $1800\,cm^{-1}$) and ^{13}C-NMR (cyclic carbonate C=O at 160 ppm) spectra.

RESULTS AND DISCUSSION

To get the pseudo-first-order reaction constant (k_o), we measured the absorption rates (R_{Aexp}) of CO_2 in toluene, *N*-methyl-2-pirrolidinone (NMP), and dimethyl sulfoxide (DMSO), respectively, at GMA concentration ranging from 0.5 to $3\,kmol/m^3$. Figure 1 shows typical plots of R_{Aexp} against the concentration of GMA at a TBAB concentration of $0.05\,kmol/m^3$. The solid line in Fig. 1 is the absorption rate calculated from Eq. (11) using the known values of k_3 and k_2/k_1, which are obtained by following the procedure mentioned below. As shown in Fig. 1, R_{Aexp} increase gradually with increasing GMA concentration, and increase in order toluene, NMP, and DMSO.

The values of k_o were obtained from R_{Aexp} and Eq. (16) using the physicochemical properties in Table 1; they are plotted in Fig. 2. The solid

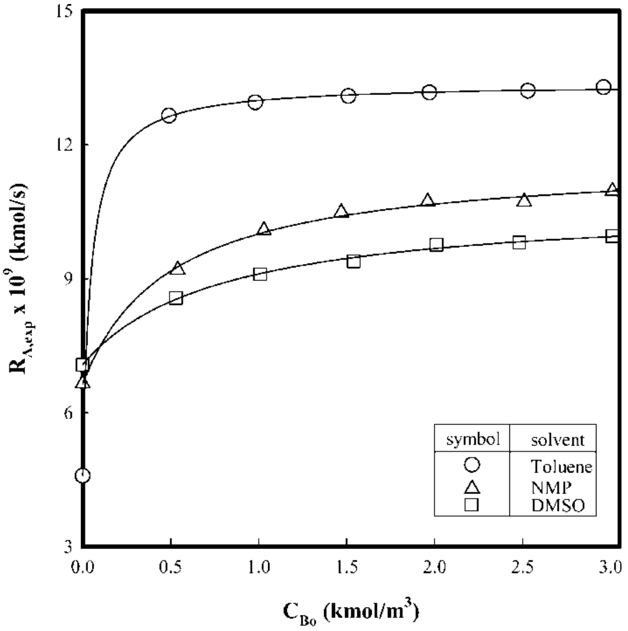


Figure 1. Absorption rates of carbon dioxide into various solvents in the reaction of CO_2 with GMA using TBAB at 85°C.

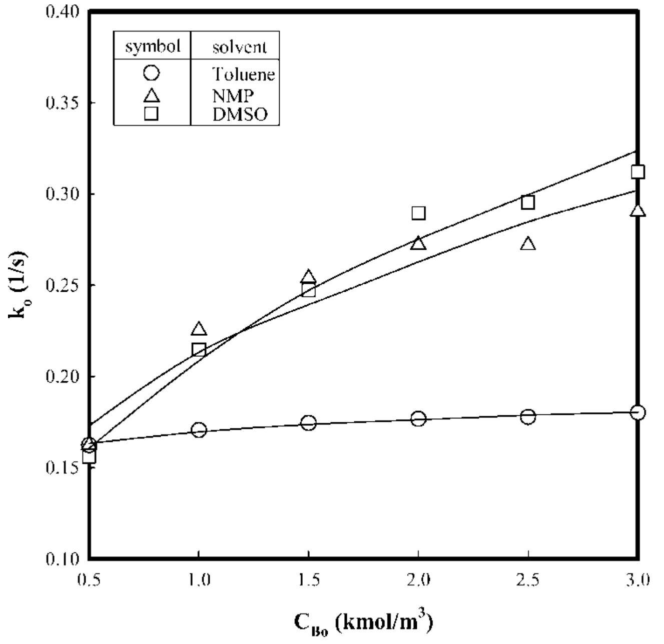


Figure 2. Pseudo-first-order reaction rate constant for various solvents in reaction of CO_2 and GMA with TBAB of 0.05 kmol at 85°C.

line in Fig. 2 is the value calculated from Eq. (13) using the known values of k_3 and k_2/k_1, which are obtained by following the procedure mentioned below. As shown in Fig. 2, k_o increased gradually with increasing GMA concentration. Figure 3 shows plots of Q_o C_{Bo}/k_o against C_{Bo}; and these plots satisfy straight lines. The reaction between CO_2 and GMA might be assumed to be a pseudo-first-order reaction with respect to the concentration of CO_2 in the concentration range of GMA of 0.5–3 kmol/m^3 from the experimental results of the linear relationship of the plots as shown in Fig. 3. The values of k_3 and k_2/k_1 were obtained from the slopes and intercepts of these straight lines. The values of k_3 and k_2/k_1 were used to estimate R_A and k_o, which were then presented as solid lines in Figs. 1 and 2.

The rate constants in organic reaction in a solvent generally reflect the solvent effect. Various empirical measures of the solvent effect have been proposed to correlate with the reaction rate constant (13). Of these, some measures have a linear relation to the solubility parameter of the solvent. Using the data for k_3, k_2/k_1 and solvent parameter (14) of toluene, NMP, and DMSO of 18.2, 23.1, and 24.6 $(J/m^3)^{0.5}$, respectively, the logarithms of k_3 and k_2/k_1 were plotted against the solubility parameter of the solvent. Figure 4 demonstrates this relationship; the plots satisfy the linear relationship between the reaction rate constant and solubility parameter

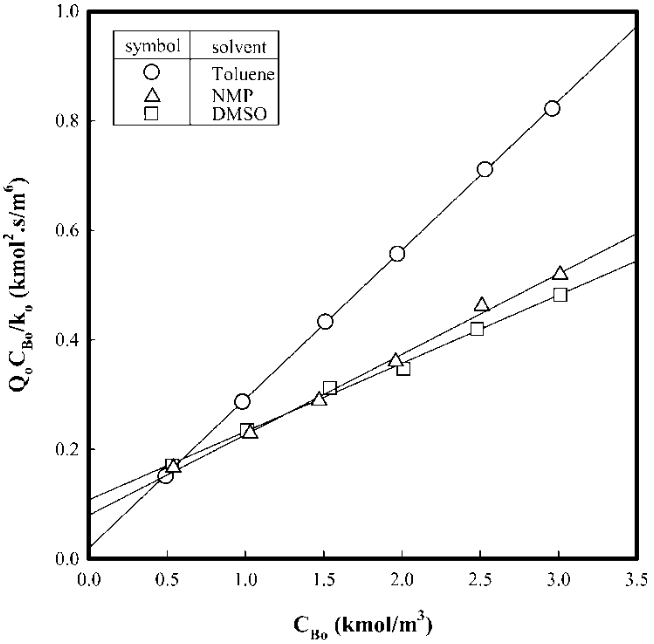


Figure 3. Q_oC_{Bo}/k_o vs. C_{Bo} for various solvents in the reaction of CO_2 with GMA using TBAB at 85°C.

of the solvent. The solvent polarity is increased when increasing the solubility parameter of the solvent. It may be assumed that the increased instability and solvation of C_1 arising from the increased solvent polarity enhance the dissociation reaction of C_1 and the reaction between C_1 and CO_2, such as SN_1 by solvation (15), respectively; thus, the values of k_2/k_1 and k_3 increase upon increasing the solubility parameter as shown in Fig. 4.

To observe the effect that the reaction temperature has on the reaction rate constants, k_3 and k_2/k_1, absorption rates of CO_2 were measured according to changes reaction temperature over the range of 80–90°C in a particular solvent, e.g., DMSO, to obtain to these reaction rate constants. Figure 5 shows plots of the reaction rate constants against $1/T$ in a semi-logarithm scale; the plots satisfy straight lines. The activation energy in the reaction (3) for k_3 was obtained from the slope of the line for k_3; its value is 13.87 kcal/mol.

CONCLUSIONS

The overall reaction between CO_2 and GMA, using TBAB as a catalyst, was assumed to consist of two elementary reactions: the reversible

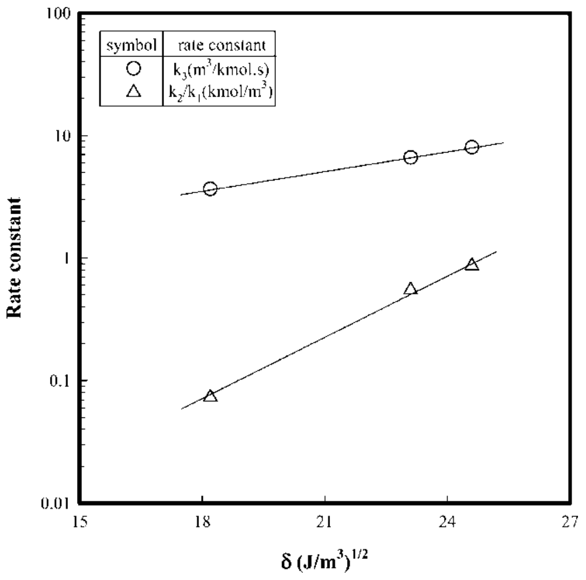


Figure 4. Relationship between reaction rate constant and solubility parameter of solvent in the reaction of CO_2 with GMA using TBAB at 85°C.

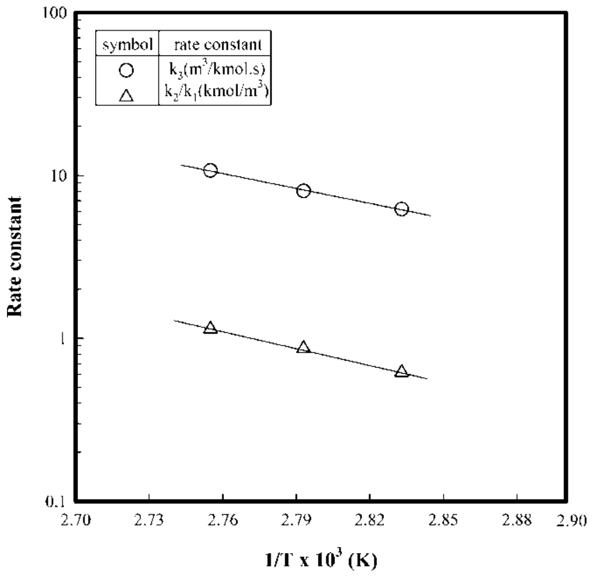


Figure 5. Dependence of reaction temperature on reaction rate constant in the reaction of CO_2 with GMA using TBAB and DMSO.

reaction of GMA and catalyst to form an intermediate, and an irreversible reaction of this intermediate and carbon dioxide to form five-membered cyclic carbonate. Absorption data for CO_2 in the solution at 101.3 kPa were interpreted to obtain pseudo-first-order reaction rate constant, which was used to obtain the elementary reaction rate constants. The effect that the solubility parameters of toluene, *N*-methyl-2-pirrolidinone, and dimethyl sulfoxide have on the rate constant was determined.

NOMENCLATURE

C_{Ai}	Solubility of CO_2 in absorbent ($kmol/m^3$)
C_i	Concentration of component, i ($kmol/m^3$)
D_i	Diffusivity of component, i (m^2/s)
k_o	Pseudo-first-order reaction constant (1/s)
k_3	Reaction rate constant in reaction (3) ($m^3/kmol\ s$)
k_L	Mass transfer coefficient of CO_2 in absorbent (m/s)
k_1	Forward reaction rate constant in reaction (2) ($m^3/kmol\ s$)
k_2	Backward reaction rate constant in reaction (2) (1/s)
r_A	Reaction rate of CO_2 ($kmol/m^3s$)
R_A	Absorption rate of CO_2 (kmol/s)
R_{Aexp}	Measured absorption rate of CO_2 (kmol/s)
Q_o	Total concentration of catalyst ($kmol/m^3$)
S	Contact area of gas-liquid interface (m^2)
z	Distance (m)
z_L	Film thickness (m)

Greek Letters

β	Enhancement factor of CO_2
δ	Solvent parameter $(J/m^3)^{1/2}$
μ	Viscosity of solvent (cP)

Subscripts

A	CO_2
B	GMA
C_1	Intermediate complex
QX	TBAB
i	Gas-liquid interface
o	Feed

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