LIQUID-PHASE CHLORINATION OF ETHYLENE AND 1,2-DICHLOROETHANE

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Liquid-phase chlorination of ethylene and 1,2-dichloroethane in a dark system was investigated, by using an agitated vessel with a flat free gas-liquid interface. The results were analysed to obtain the chemical reaction kinetics through a theoretical treatment of simultaneous absorption and reaction for gas-liquid heterogeneous systems.

The chemical reaction kinetics for chlorine addition to ethylene and for chlorine substitution to 1,2-dichloroethane showed respectively (1, 1)- and (1, 2)-order dependencies on the concentrations of ethylene and chlorine. In the absence of ethylene, however, chlorine substitution to 1,2-dichloroethane, where the reaction occurred homogeneously, obeyed (1, 1)-order dependency on the concentrations of chlorine and 1,2-dichloroethane.

It is explained by the radical chain mechanisms of chlorine substitution reaction that the presence of ethylene enhances the initiation to produce chlorine radical and that the termination step is controlled by the deactivation of 1,2-dichloroethyl radical. Without ethylene, the production of chlorine radical is so slow that the deactivation of chlorine radical controls the termination step.

Introduction

Chlorination of ethylene has been studied by many researchers for its academic and industrial interest. Earlier studies dealt with the reaction in gas phase. Rust and Vaughan[21] reported that the reaction of ethylene and chlorine in gas phase was negligibly slow at comparatively low temperature, but that at temperatures above 200°C both addition and substitution reactions took place. Stewart and Smith[22] attempted to study the vapor-phase reaction of chlorine and ethylene at ambient temperatures but found that the major portion of the reaction occurred in liquid films of product deposited on the walls of the vessel and that two reactions appeared to occur simultaneously: addition to form 1,2-dichloroethane and substitution on this product to form 1,1,2-trichloroethane.

Recently, Poutsma[17,18] stated that the chlorine substitution reaction in dark liquid phase is a free-radical process because of spontaneous initiation of radical chains by interaction between chlorine and the olefin. Nishiwaki *et al.*[16] reported that in the substitution reaction of chlorine and 1,2-dichloroethane the reaction was significantly enhanced by the presence of a small amount of ethylene.

Since liquid-phase chlorination of ethylene is a rapid reaction, i.e., the overall rate process is generally controlled by mass transfer of reacting

components, it is difficult to obtain quantitative information about chemical reaction kinetics. Balasubramanian *et al.*[2] proposed a model of absorption and reaction of ethylene and chlorine in 1,2-dichloroethane liquid, and Chua and Ratcliffe[4-6] also described an experimental investigation of the photocatalytic chlorination of ethylene. However, in their works, the liquid-phase reaction of ethylene and chlorine was assumed to be an irreversible instantaneous reaction.

The aim of the present study was to investigate the chemical reaction kinetics for the liquid-phase dark chlorination of ethylene and 1,2-dichloroethane. An agitated vessel with a flat free gas-liquid interface was used for experiments in concurrent diffusion of ethylene and chlorine into 1,2-dichloroethane liquid. Thus, through a theoretical analysis by film model, the specific interaction of ethylene with the substitution reaction was clarified. The mechanisms of elementary reactions are also discussed.

1. Modeling of the Chemical Reaction and Mass Transfer

1.1 Chemical reaction of ethylene and chlorine in 1,2-dichloroethane liquid

The reaction of ethylene and chlorine in a liquid phase of 1,2-dichloroethane involves two competing reaction pathways, addition and substitution reactions, as follows:

$$C_2H_4 + Cl_2 \xrightarrow{R_1} C_2H_4Cl_2 \qquad (1)$$

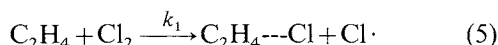$$C_2H_4Cl_2 + Cl_2 \xrightarrow{R_2} C_2H_3Cl_3 + HCl \qquad (2)$$
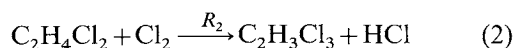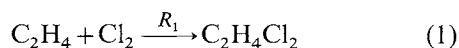
The addition reaction is explained by an ionic mechanism,[17,18] and so the chemical reaction kinetics shows presumably (1,1)-order dependency on the concentrations of ethylene, A, and chlorine, B, as:
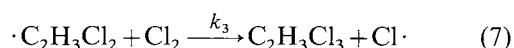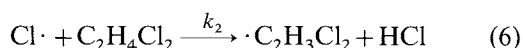
$$R_1 = k_{R1} A B \qquad (3)$$

On the other hand, the substitution reaction of chlorine and 1,2-dichloroethane is accommodated by a radical chain mechanism. Photochemical or thermal initiation of chlorine radical is usually considered as:

$$Cl_2 \xrightarrow{k_1} 2Cl \cdot \qquad (4)$$

However, in the case of liquid-phase dark chlorination, Poutsma[17,18] proposed the spontaneous initiation of radical chains by interactions between chlorine and ethylene as:

$$C_2H_4 + Cl_2 \xrightarrow{k_1} C_2H_4\text{---}Cl + Cl \cdot \qquad (5)$$

Propagation steps are usually considered as:

$$Cl \cdot + C_2H_4Cl_2 \xrightarrow{k_2} \cdot C_2H_3Cl_2 + HCl \qquad (6)$$

$$\cdot C_2H_3Cl_2 + Cl_2 \xrightarrow{k_3} C_2H_3Cl_3 + Cl \cdot \qquad (7)$$

As for termination steps, the probability of coupling between low concentration radicals should not be so large, but radical deactivation by collision between surrounding molecules should be rather important, as reported by Franklin et al.[7] and by Knox and Waugh.[15] Then, the deactivations of dichloroethylene and chlorine radicals are respectively given by Eqs. (8) and (9).

$$\cdot C_2H_3Cl_2 + M_i \xrightarrow{k_4} \text{deactivated} \qquad (8)$$

$$\cdot Cl + M_i \xrightarrow{k_4} \text{deactivated} \qquad (9)$$
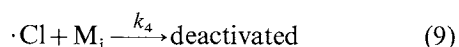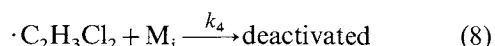
where M_i represents the surrounding molecules.

Since production of chlorine radical is significantly enhanced by the existence of ethylene, the termination step may be controlled by the deactivation of 1,2-dichloroethyl radical. Hence, according to the usual assumption of steady state for radical concentrations, the mechanisms of Eqs. (5) to (8) lead to the overall 1,1,2-trichloroethane formation rate equation with (1,2)-order dependency on the concentrations of ethylene and chlorine as:

$$R_2 = \left\{ \frac{k_1 k_2 [C_2H_4Cl_2]}{k_4[M_i]} - k_1 \right\} \cdot [C_2H_4] \cdot [Cl_2]^2$$

$$= k_{R2} \cdot [C_2H_4] \cdot [Cl_2]^2 \qquad (10)$$

If the termination step is controlled by deactivation of chlorine radical, the same derivation of Eqs. (5), (6), (7) and (9) gives the overall rate equation with (1,1)-order dependency on the concentrations of ethylene and chlorine as:

$$R_2 = \left\{ \frac{k_1 k_2 [C_2H_4Cl_2]}{k_4[M_i]} \right\} \cdot [C_2H_4] \cdot [Cl_2]$$

$$= k_{R2} \cdot [C_2H_4] \cdot [Cl_2] \qquad (11)$$

In the operation without olefin, where the initiation step of Eq. (4) is slower than that of Eq. (5), the overall rate equation of chlorine substitution reaction may be considered from Eqs. (4), (6), (7) and (9), which leads to:

$$R_2' = \left\{ \frac{k_1 k_2}{k_4[M_i]} \right\} \cdot [Cl_2] \cdot [C_2H_4Cl_2]$$

$$= k_{R2}' \cdot [Cl_2] \cdot [C_2H_4Cl_2] \qquad (12)$$

1.2 Mass transfer of ethylene and chlorine in 1,2-dichloroethane liquid

To obtain information about rapid chemical reaction rates in a gas-liquid heterogeneous system, the method of concurrent diffusion of two reactants was proposed by Roper et al.[20] and has been developed to cover a wide range of conditions, including experimental procedures.[12,23,24]

A steady-state mass balance of concurrent diffusion of ethylene and chlorine within a liquid film of 1,2-dichloroethane accompanied by chemical reactions gives the following equations and boundary conditions according to the film model:

$$D_A(d^2A/dx^2) = R_1 \qquad (13)$$

$$D_B(d^2B/dx^2) = R_1 + R_2 \qquad (14)$$

at gas-liquid interface:

$$x = 0 \quad A = A_i, \ B = B_i \qquad (15)$$

at the edge of bulk liquid:

$$x = x_f \quad A = 0, \ B = B_0 \qquad (16)$$

Film thickness, x_f, is related to mass transfer coefficient and diffusion coefficient as follows:

$$x_f = D/k_L^* \qquad (17)$$

Liquid-phase concentrations of ethylene and chlorine at the interface are determined by the equilibrium concentrations of gas phase. The absorption rates of the two gases through gas-liquid interface are given as:

$$N_A = -D_A(dA/dx)_{x=0} \qquad (18)$$

$$N_B = -D_B(dB/dx)_{x=0} \qquad (19)$$

To obtain the solution of Eqs. (13) to (16), the finite difference method was used with the modification

proposed by Brian and Beaverstock.[3] Then, theoretical values of the gas absorption rate are calculated by numerical differentiations of Eqs. (18) and (19).

2. Experimental

2.1 Experimental apparatus

The agitated vessel used in this study was of the same size as the vessel of which the mass transfer character was clarified by Hikita et al.[8] The vessel, shown in **Fig. 1**, was a cylindrical glass separable flask, 12 cm in inner diameter and 20 cm in height. Four vertical baffle plates, made of Teflon and 1 cm in width, were provided around the inside wall of the vessel at equal intervals. Glass paddle agitators were located at the center of each phase. Two flat blades of 1.5 cm height and 5 cm diameter were prepared for the liquid phase, and six flat blades of 2 cm height and 8 cm diameter for the gas phase. Each agitator could be driven individually at different speed. An electric heater was attached around the outside of the vessel. A glass cooling tube was set in the liquid phase. Temperature was detected by C.A. thermocouples at the bottom and top of the liquid phase and in the gas phase, and was controlled within ±0.5°C difference. The interior of the vessel and connecting pipes were kept dark.

2.2 Reagent

A sample of industrially distilled 1,2-dichloroethane was shaken out thoroughly with concentrated sulfuric acid and distilled water. After drying with sodium sulfate, it was distilled to obtain 1,2-dichloroethane more than 99.99% pure by gas chromatographic analysis. Purified material was treated under a nitrogen atmosphere. Ethylene (Seitetsu Chemical Ind. Co.) was more than 99.9% pure. Pure chlorine (Kanegafuchi Chemical Ind. Co.) and 5% chlorine diluted by nitrogen (Takachiho) were used. Nitrogen (Nihon Sanso) was more than 99.9995% pure and contained less than 1 ppm oxygen.

2.3 Experimental procedure of physical absorption

Physical absorptions of ethylene into 1,2-dichloroethane liquid and that of oxygen into water were observed to determine liquid-side mass transfer coefficients of the apparatus. Under nitrogen atmosphere, 1500 ml of 1,2-dichloroethane or water was introduced into the vessel, and then temperature and agitation speed were set constant at 20–30°C and 57–240 rpm, respectively. The gas-phase agitator was driven at 500 rpm. Then, ethylene gas or air was caused to flow through the gas phase in the vessel at a rate of about 2000 ml/min, and the time course of the dissolving concentration was measured. Dissolving ethylene in 1,2-dichloroethane liquid was analyzed by gas chromatography. Oxygen concentration in water was continuously measured by D.O. meter (Beck-man).
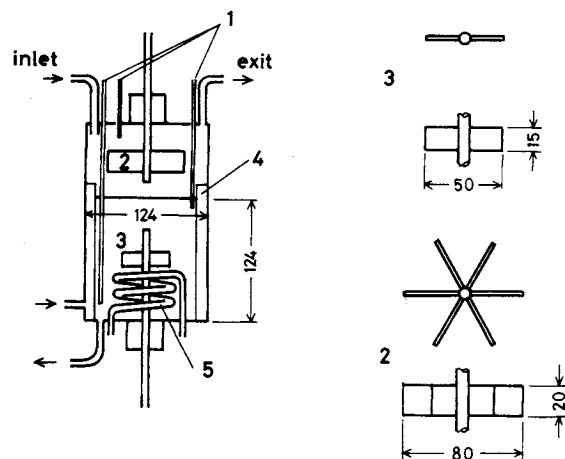

Fig. 1. Agitated vessel and stirrers: 1, thermocouple; 2, gas-phase stirrer; 3, liquid-phase stirrer; 4, baffle plate; 5, cooling tube.

At steady states of dissolving concentration, following the transient periods of physical absorption, the equilibrium solubility of ethylene into 1,2-dichloroethane liquid was determined from the concentrations in gas and liquid phases.

2.4 Experimental procedure for reacting system

Concurrent diffusion of ethylene and chlorine was examined in the experimental vessel at a temperature of 30°C.

Under nitrogen atmosphere, 1500 ml of 1,2-dichloroethane was introduced into the vessel. The liquid-phase agitator was driven at a constant speed of 57–240 rpm, and the agitating speed of the gas phase was 500 rpm. A mixture of ethylene, chlorine and nitrogen gases was caused to flow through the gas phase of the vessel at atmospheric pressure. Gas samples were taken at the inlet and exit of the vessel (see Fig. 1). Ethylene flow rate was determined, based on the known flow rate of nitrogen, by a gas chromatograph after absorption of chlorine and hydrogen chloride into sodium hydroxide aqueous solution. Flow rate of chlorine and by-product hydrogen chloride were determined by potassium iodide absorption followed by titrations with sodium thiosulfate and sodium hydroxide, respectively. The concentration of chlorine dissolving in the liquid phase was continuously observed by a spectrophotometer of 370 nm visible absorbance, using a flow-type cell.

Chlorination of 1,2-dichloroethane was also examined in the absence of ethylene at the temperatures of 45, 60 and 75°C. Chlorine gas was diluted with nitrogen, and was supplied into 1,2-dichloroethane liquid. Then, time courses of dissolving chlorine and 1,1,2-trichloroethane produced were observed.

3. Results and Discussion

3.1 Mass transfer coefficient in the experimental apparatus

The mass transfer coefficient was determined from the slope of $\ln(1 - C/C^*)$ vs. $(S/V)t$ plot. Experimentally obtained mass transfer coefficients are plotted in **Fig. 2** as the relation of $Re(=d_L^2 N_t \rho_L/\mu_L)$ vs. $Sh/Sc^{1/3}(=(k_L^* l/D)/(\mu_L/\rho_L D)^{1/3})$, where liquid-phase molecular diffusion coefficients were calculated by the estimation method of Wilke and Chang.[25] The solid line in Fig. 2 shows the empirical correlation of Eq. (20) presented by Hikita and Ishikawa.[8]

$$Sh = 0.322 \, Re^{0.7} \, Sc^{1/3} \tag{20}$$

Measured mass transfer coefficients are well correlated by Eq. (20). In the following analysis, the values of liquid-phase mass transfer coefficient were determined by Eq. (20).

Gas-phase resistance to mass transfer was estimated by using the empirical equation presented by Hikita et al.,[11] and was found to be negligible (less than 2%) compared to the overall resistance for ethylene or chlorine under the present experimental conditions.

Hikita et al.[9] recommended that the Leveque model best describes the liquid-phase mass transfer in this kind of apparatus. The theoretical value of reaction factor by the Leveque model lies in between those by the film model and the penetration model.[10] If the two absorbing species have similar values of molecular diffusivity, the difference between the film model and the penetration model is small in the reaction factor of concurrent diffusion.[12] Liquid-phase molecular diffusivities of ethylene and chlorine are respectively $3.05 \times 10^{-9} \, (\mathrm{m^2 \, s^{-1}})$ and 2.90×10^{-9} $(\mathrm{m^2 \, s^{-1}})$ at 30°C, and thus the film model was adopted in the analysis of this study.

3.2 Solubility of ethylene and chlorine in 1,2-dichloroethane liquid

Henry's solubility constants, defined as Eq (21), were calculated from the experimental values of equilibrium concentrations in gas and liquid phases, which are plotted in **Fig. 3**.

$$H = y/C^* \tag{21}$$

In the measurement of chlorine solubility, ferric chloride was added into 1,2-dichloroethane liquid (200 wt ppm). Thus, the effect of chemical reaction on the measurement of solubility was negligible, since the reaction rate of chlorine substitution in the presence of this amount of ferric chloride significantly decreased to about 3% of that in the absence of ferric chloride.

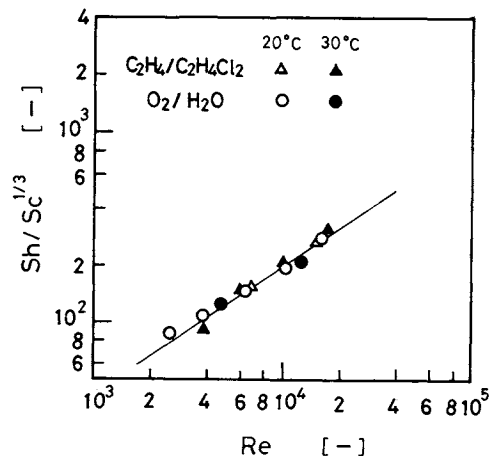Prausnitz and Shair[19] presented a thermodynamic relation of the solubility as:

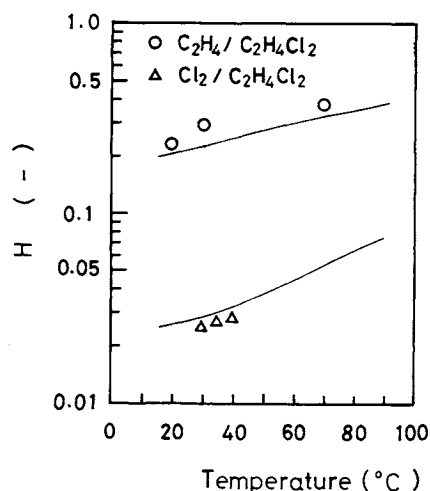**Fig. 2.** Correlation of mass transfer coefficient.

Fig. 3. Henry's solubility constant.

$$1/x_2 = (f_2^L/f_2^0)\exp\{V_2^L(\delta_1 - \delta_2)^2 \phi_1^2/(RT)\} \tag{22}$$

Liquid-phase hypothetical fugacity, f^L, was experimentally given for ethylene and chlorine,[19] and the values of molecular volume, V^L, and solubility parameter, δ, were given by Hildebrand and Scott.[13,14] Solid lines in Fig. 3 are the calculated results of Eq. (22) for ethylene and chlorine. Since the experimental data are almost described by the calculated lines, liquid-phase interfacial equilibrium concentrations were determined by using Eq. (22).
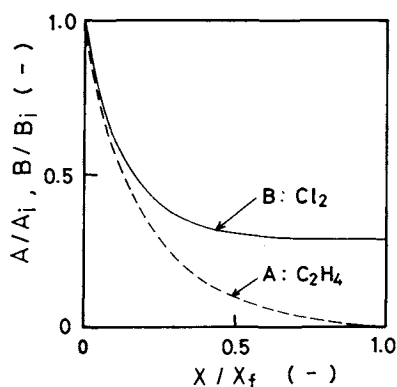
3.3 Chlorination of ethylene and 1,2-dichloroethane

Experimental conditions of the concurrent diffusion system and measured results are shown in **Table 1**. For the analysis of reaction kinetics, Eqs. (10) and (11) are respectively adopted in case 1 and case 2. Then, the values of reaction rate constants k_{R1} and k_{R2} were determined so that the theoretical calculation of both Eqs. (18) and (19) agree with the experimental values, as shown in **Table 2**. Typical concentration profiles within the liquid film are shown in **Fig. 4**, which is calculated by the kinetic model of case 1 at the condition of Run 1. This figure suggests that diffusion of the reactants into the main body of

Table 1. Experimental conditions and results of absorption and reaction

Run No.	N_L [s^{-1}]	$k_{LA}^* \times 10^5$ [m/s]	$k_{LB}^* \times 10^5$ [m/s]	A_i [mol/m^3]	B_i [mol/m^3]	B_0 [mol/m^3]	$N_A \times 10^4$ [mol/(s·m^2)]	$N_B \times 10^4$ [mol/(s·m^2)]	β_A [—]	β_B [—]	HCl production/ethylene consumption [—]
1	0.95	1.32	1.28	6.51	24.9	7.28	5.19	21.2	6.06	9.41	3.02
2	1.52	2.17	2.10	6.45	25.6	11.3	5.27	21.0	3.77	6.99	2.78
3	2.50	3.14	3.04	6.42	23.6	8.09	5.60	21.3	2.78	4.65	2.70
4	4.00	5.09	4.92	6.32	22.8	2.27	6.02	22.5	1.87	2.12	2.66
5	0.95	1.32	1.28	14.9	15.4	4.82	8.32	16.8	4.23	12.40	1.02
6	1.52	2.17	2.10	14.7	15.2	4.01	8.65	16.9	2.71	7.17	0.89
7	2.50	3.14	3.04	14.6	15.0	2.98	9.17	17.1	1.99	4.69	0.80
8	4.00	5.09	4.92	14.2	14.1	2.01	10.8	17.6	1.49	2.94	0.65

Table 2. Calculated results of chemical reaction rate constants

Run No.	Case 1		Case 2	
	k_{R1} [m^3/(mol·s)]	k_{R2} [m^6/(mol^2·s)]	k_{R1} [m^3/(mol·s)]	k_{R2} [m^3/(mol·s)]
1	0.120	0.0227	0.126	0.395
2	0.115	0.0215	0.122	0.411
3	0.143	0.0296	0.149	0.524
4	0.157	0.0250	0.162	0.447
5	0.122	0.0177	0.134	0.173
6	0.124	0.0199	0.134	0.202
7	0.125	0.0225	0.130	0.236
8	0.146	0.0297	0.147	0.307

Fig. 4. Concentration profiles within liquid film; calculated by kinetic model of case 1 at the condition of Run 1.

the liquid phase is negligibly small, and so most reaction occurs within the liquid film.

It can be seen from the results of case 2 in Table 2 that the values of chemical reaction rate constant, k_{R2}, in the range of relatively large chlorine concentrations (Runs 1–4) are significantly greater than those in the range of Runs 5–8. This suggests that the kinetic dependency of chlorine substitution upon chlorine concentration should be more significant than that given by the kinetic model of case 2, whereas the calculated results of all runs in case 1 show relatively small deviation compared to those in case 2. Then, in the calculation of case 1, mean values of the chemical reaction rate constant were obtained

as $k_{R1} = 0.132$ (m^3 mol^{-1} s^{-1}) and $k_{R2} = 0.0239$ (m^6 mol^{-2} s^{-1}). Theoretical values of the reaction factor were calculated by using these mean values of k_{R1} and k_{R2}, which are shown in Fig. 5 in comparison with experimental data. The values of the reaction factor are well predicted by the calculation of case 1 with maximum deviation of 10%. This supports the chemical reaction rate equations, Eqs. (3) and (10).

Selectivity of the substitution reaction based on the addition reaction can be considered in a homogeneous system as:

$$R_2/R_1 = \{k_{R2}[C_2H_4][Cl_2]^2\}/\{k_{R1}[C_2H_4][Cl_2]\}$$

$$= \{k_{R2}/k_{R1}\}[Cl_2] \tag{23}$$

In the last column of Table 1, considerably large ratios of hydrogen chloride production by substitution reaction are observed at the large chlorine concentrations of Runs 1–4 in comparison with Runs 5–8. This is reasonably explained by Eq. (23).

3.4 Chlorination of 1,2-dichloroethane

Figure 6 shows 1,1,2-trichloroethane formation rates in dark chlorination of 1,2-dichloroethane without ethylene at 60°C. The reaction rate shows first-order dependency on chlorine concentration:

$$d[C_2H_3Cl_3]/dt = k_R[Cl_2] \tag{24}$$

$$k_R = 7.5 \times 10^{-5} \quad [s^{-1}] \tag{25}$$

Temperature dependency of this reaction rate constant gave the value of activation energy as 20.1 [kJ·mol^{-1}].

The contribution of mass transfer resistance is roughly evaluated by the method of Astarita[1] as:

$$\frac{\text{Maximum reaction rate}}{\text{Maximum diffusion rate}} = \frac{k_R[Cl_2]_i x_f}{k_L^*([Cl_2]_i - 0)}$$

$$= (k_R D)/(k_L^*)^2 \tag{26}$$

Since the values of Eq. (26) for the present experimental conditions are very small (less than 0.002), the effect of mass transfer resistance is negligible, and the chemical reaction occurs homogeneously and slowly. The effect of this homogeneous reaction on the
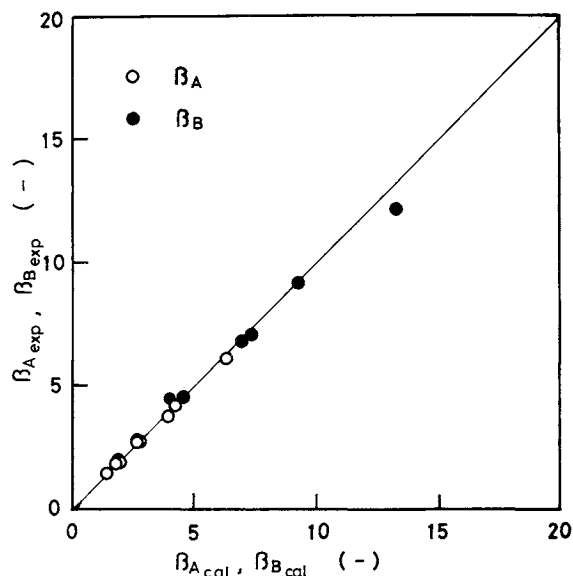
Fig. 5. Comparison of experimental reaction factors with theoretical prediction of case 1, where $k_{R1} = 0.132$ [$m^3 \cdot mol^{-1} \cdot s^{-1}$] and $k_{R2} = 0.0239$ [$m^6 \cdot mol^{-2} \cdot s^{-1}$].
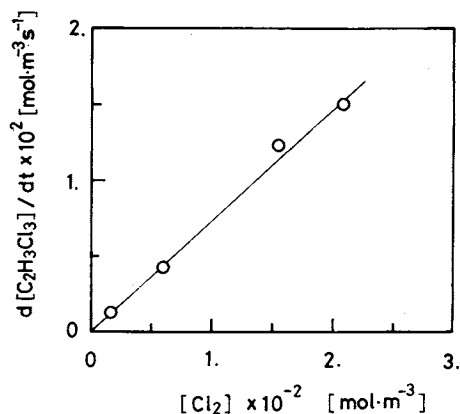

Fig. 6. Effect of chlorine concentration on the rate of 1,1,2-trichloroethane formation.

heterogeneous reaction with ethylene was evaluated as at most 2%.

The effect of 1,2-dichloroethane concentration was examined by diluting the reaction solvent with carbon tetrachloride. The reaction rate, shown in **Fig. 7**, indicates first-order dependency on 1,2-dichloroethane concentration as:

$$d[C_2H_3Cl_3]/dt = k'_{R2}[Cl_2][C_2H_4Cl_2] \qquad (27)$$

$$k'_{R2} = 6.12 \times 10^{-9} \qquad [m^3 \, mol^{-1} \, s^{-1}] \qquad (28)$$

This experimental result supports the kinetic mechanism of Eq. (12).

Conclusion

The chlorine substitution reaction to 1,2-dichloro-ethane in dark liquid phase is significantly en-hanced by the presence of ethylene. The chemical reaction kinetics for chlorine addition to ethylene
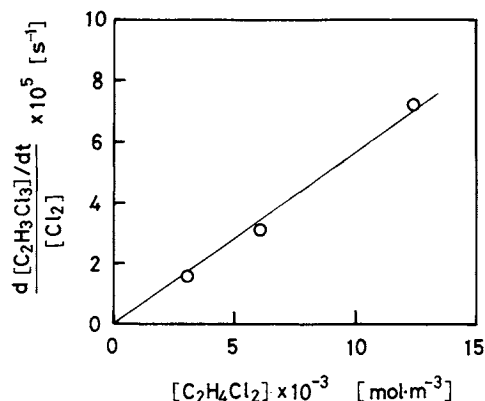

Fig. 7. Effect of 1,2-dichloroethane concentration on the rate of 1,1,2-trichloroethane formation.

and for chlorine substitution to 1,2-dichloroethane showed respectively (1,1)- and (1,2)-order depen-dencies on the concentrations of ethylene and chlo-rine. In the absence of ethylene, however, chlorine substitution to 1,2-dichloroethane obeyed (1,1)-order dependency on the concentrations of chlorine and 1,2-dichloroethane.

Nomenclature

A, B	= concentrations of A (ethylene) and B (chlorine), respectively	[$mol \cdot m^{-3}$]
A_i, B_i	= interfacial concentrations of A and B, respectively	[$mol \cdot m^{-3}$]
B_0	= concentration of B in liquid bulk	[$mol \cdot m^{-3}$]
C	= concentration of ethylene or chlorine in bulk liquid phase	[$mol \cdot m^{-3}$]
C^*	= liquid-phase concentration of ethylene or chlorine equilibrium to gas phase	[$mol \cdot m^{-3}$]
d_L	= diameter of stirrer	[m]
D	= molecular diffusivity in liquid phase	[$m^2 \cdot s^{-1}$]
f^L	= fugacity in liquid phase	[Pa]
f^0	= fugacity in gas phase	[Pa]
H	= Henry's solubility constant	[—]
k_L^*	= liquid-phase mass transfer coefficient	[$m \cdot s^{-1}$]
k_{R1}	= chemical reaction rate constant of addition chlorination in Eq. (3)	[$m^3 \cdot mol^{-1} \cdot s^{-1}$]
k_{R2}	= chemical reaction rate constant of chlorine substitution in Eq. (10) or (11)	[$m^6 \cdot mol^{-2} \cdot s^{-1}$] or [$m^3 \cdot mol^{-1} \cdot s^{-1}$]
k_R	= chemical reaction rate constant of chlorine substitution in Eq. (12) or (27)	[$m^3 \cdot mol^{-1} \cdot s^{-1}$]
k'_{R2}	= chemical reaction rate constant of chlorine sustitution in Eq. (12) or (27)	[$m^3 \cdot mol^{-1} \cdot s^{-1}$]
k_{1-4}	= elementary reaction rate constant	[$m^3 \cdot mol^{-1} \cdot s^{-1}$] or [$s^{-1}$]
l	= diameter of vessel	[m]
N_A, N_B	= absorption fluxes of A and B, respectively	[$mol \cdot m^{-2} \cdot s^{-1}$]

N_L	= speed of stirrer		$[\mathrm{s}^{-1}]$
R	= gas constant		$[\mathrm{J \cdot K^{-1} \cdot mol^{-1}}]$
Re	= Reynolds number		$[-]$
R_1, R_2	= chemical reaction rates of addition and substitution chlorinations, respectively		$[\mathrm{mol \cdot m^{-3} \cdot s^{-1}}]$
Sc	= Schmidt number		$[-]$
Sh	= Sherwood number		$[-]$
S	= gas-liquid interfacial area		$[\mathrm{m^2}]$
T	= temperature		$[\mathrm{K}]$
t	= time		$[\mathrm{s}]$
V	= volume of liquid		$[\mathrm{m^3}]$
V^L	= molecular volume		$[\mathrm{m^3 \cdot mol^{-1}}]$
x	= distance from gas-liquid interface		$[\mathrm{m}]$
x_f	= thickness of liquid film		$[\mathrm{m}]$
x_2	= mole fraction in liquid phase		$[-]$
y	= concentration in gas phase		$[\mathrm{mol \cdot m^{-3}}]$
β_A, β_B	= reaction factors of A and B, respectively		$[-]$
δ	= solubility parameter		$[\mathrm{J^{1/2} \cdot m^{-3/2}}]$
μ_L	= viscosity of liquid		$[\mathrm{Pa \cdot s}]$
ρ	= density		$[\mathrm{kg \cdot m^{-3}}]$
ϕ	= volume fraction		$[-]$

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