

Stationary State Model in Reforming HCFC22 (CHClF₂) to Difluoromethylether (CH₃OCHF₂)

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As fluorocarbons containing chlorine atoms deplete the ozone layer, restrictions on production and consumption of chlorofluorocarbons (CFCs) were agreed in the Montreal Protocol (1987) and hydro chlorinated fluorocarbons (HCFCs) are expected to have the same fate. Massive wastes of CFCs and HCFCs will be occurring in the near future and its treatment is a serious problem. Wastes of HCFC22 are expected to be in the thousands of tonnes.

Chlorinated compounds were injected into 200 (mL) methanol or 2-propanol solvent containing 28 % CH₃ONa or NaOH, under irradiation with a 100 (W) high-pressure mercury lamp (λ max: 356 nm) or 32 W low-pressure mercury lamp (λ max: 254 nm) at room temperature and atmospheric pressure. As shown in Table 1, Nishiumi et al. (1994) found that each fluorocarbon was decomposed by low-pressure mercury lamp irradiation, and astonishingly, HCFC22 and HFC123a could be easily decomposed at room temperature in an alcoholic alkali solution without any UV irradiation

For either 254 or 185nm irradiation, using a low-pressure mercury lamp, photodecomposition experiments were carried out. The products analyzed by GC-MS were similar for the two wavelengths. The results for 254nm were shown in Table 1, which revealed mainly two kinds of products, i.e., HFCs and fluoroethers. It is interesting that the process produces either the second or the third generation refrigerant depending on conditions. Partially fluorinated ethers are now being considered as possible replacements for CFCs. It means that the photo-dechlorination process converts CFCs into useful refrigerants, which do not cause environmental problems.

Nishiumi et al. (1994) have proposed a process where chlorodifluoromethane (HCFC22) is reformed to difluoromethylether (CH₃OCHF₂) through simple contact with methanol solution containing sodium hydroxide (NaOH). Hine et al. (1957) already reported the HCFC22 decomposing reaction, although he was mainly interested in mechanism of this reaction. Lee et al. (2001) also reported synthesis of difluoromethylether from HCFC22, using alkali metal carbonate such as K₂CO₃, Na₂CO₃ and Li₂CO₃. Nishiumi et al. (2002) reported that the accumulated NaCl precipitation which disturbed liquid mixing decreased the reaction rate. Sako et al. (1998) reported the critical properties of fluorinated ethers.

In this work, measuring HCFC22 concentrations in a methanol solution by gas chromatography directly, we found that they were kept constant and smaller than the solubility. The object of this work is to set up a reaction model in which reaction rate and mass transfer rate are competitive.

To prevent the ozone layer depletion, we proposed a new dechlorination process at room temperature and atmospheric pressure. We have a strong interest in reforming reaction of chlorodifluoromethane (CHClF₂, HCFC22) to difluoromethylether (CH₃OCHF₂), because fluoroethers are expected to be the third generation refrigerants. In a previous paper, we reported that the model that NaCl precipitation, which disturbed mixing of a solution, decreased the reaction rate as the reaction proceeded. In this work, we found that the concentration of HCFC22 was kept constant and smaller than the solubility. The Reaction rate constant k_1 was estimated from NaCl production rate and volumetric coefficient $K_L a$ was estimated from material balance of HCFC22 in a solution at stationary state. Calculation results gave excellent agreement with experimental data.

Afin de prévenir la dégradation de la couche d'ozone, nous proposons un nouveau procédé de déchloration à la température ambiante et à la pression atmosphérique. Nous nous intéressons fortement à la réaction de reformage du chlorodifluorométhane (CHClF₂, HCFC22) en difluorométhyléther (CH₃OCHF₂), les fluoroéthers étant considérés comme la troisième génération de réfrigérants. Dans un article antérieur, nous avons mentionné que la précipitation de NaCl qui entrave le mélange d'une solution diminue la vitesse de réaction au cours de la réaction. Dans ce travail, nous avons trouvé que la concentration de HCFC22 demeurait constante et plus petite que la solubilité. La constante de vitesse de réaction k_1 est estimée à partir de la vitesse de production de NaCl et le coefficient volumétrique $K_L a$ à partir du bilan de matière de HCFC22 dans une solution en régime permanent. Les résultats des calculs donnent un excellent accord avec les données expérimentales.

Keywords: HCFC, chlorodifluoromethane, dechlorination, fluoroether, gas absorption process, precipitation

Equipment and Experimental Material and Purity

Chlorodifluoromethane (HCFC22) was supplied by Toei Chemical Industries that had a purity of 99.8%.

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Table 1. Results of dechlorination in NaOH-methanol solution Nishiumi et al. (1994).

Chlorinated compounds	Thermal at room temp.*	UV irradiation	
		High-press. mercury lamp	Low-press. mercury lamp
CFC-11	N	Y	Y
CFC-12	N	Y	Y
CFC-113	N	Y	Y
CFC-114	N	Y	Y
CFC-115	N	N	N
HCFC-22	Y	Y	Y
HCFC-123	N	N	Y
HCFC-123a	Y	Y	Y
HCFC-141b	N	N	Y

Y: dechlorinated, N: not reacted, *: without UV irradiation

Table 2. Products of chlorofluorocarbon photo-decomposition using low pressure mercury lamp (254nm) Nishiumi et al. (1994).

Chlorinated compounds	Solvent		
	Methanol +NaOH	2-Propanol +NaOH	2-Propanol
CFC11	HCFC21	HCFC31	-
CFC12	CHF ₂ OCH ₃	CHF ₂ OCH(CH ₃) ₂	HCFC22
CFC113	CCl=CClF	CClF=CClF	CHClFCHClF
	CHF=CClF	CHF=CClF	CHClFCCl ₂ F
CFC114	-	HFC124a	HFC124a
CFC115	not reacted	HFC125	not reacted
HCFC22	CHF ₂ OCH ₃	CHF ₂ OCH(CH ₃) ₂	not reacted
HCFC123	HCFC133a	HFC143a	HCFC133a
HCFC123a	CHClFCF ₂ OCH ₃	CHClFCF ₂ OCH(CH ₃) ₂	not reacted
		CHF ₂ CHFOCH(CH ₃) ₂	
		HFC143	
HCFC141b	HCFC151a	HCFC151a	not reacted

Methanol with purity over 99% and sodium hydroxide (NaOH) with purity 96% were purchased from DAN Chemical Industries and Koso Chemical Industries. All chemicals were used without further purification.

Experimental Apparatus

Reaction was carried out in a constant temperature water bath. The temperature uncertainty was ± 0.5 (K) using alcohol thermometers. The condenser was held at 273 K by a chiller to prevent solvent evaporation during reaction. Nitrogen, and HCFC22 gasses were fed into the reactor at a constant flow rate at a given ratio through the flow meters that were previously calibrated for each gas. The overall average deviations of flow meter calibrations were 2.0% for HCFC22 and 1.0% for nitrogen. Gas mixtures were fed into the solution with a sintered glass ball filter and the mixture was stirred with a magnetic stirrer. The solution was sampled from the sample port and analyzed. The reaction produced sodium chloride NaCl, and the concentration of NaCl in solution was measured using the Mohr method. The mole number of produced NaCl is equal to the amount of decomposed quantity of HCFC22. The concentration of HCFC22 in methanol solution was measured

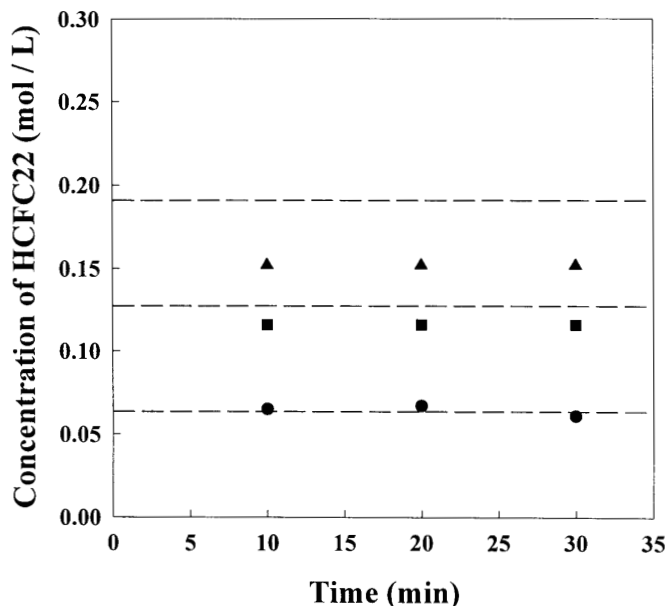


Figure 1. Effect of partial pressure of HCFC22 on concentration of HCFC22 in 0.5 (mol/L) NaOH-methanol solution at 303 K: partial pressure of HCFC22 ●, 5, ■; 10, ▲; 15 (kPa), ----; Saturated solubility.

by gas chromatography equipped by thermal conductivity detector (TCD). The overall average deviation of the calibration for HCFC22 was 1.3 %.

Analytical Method

Concentrations of NaCl of liquid samples were analyzed by a precipitation analysis. The Mohr method is a titration analysis by silver nitrate AgNO_3 with 5 wt % potassium chromate K_2CrO_4 in water as an indicator. 2 mL of reaction solution was diluted by 25 mL of pure water. 5 mL of the dilution solution was poured into a beaker. Neutralization of the solution by 2 N nitric acid HNO_3 with 1 wt% phenolphthalein in ethanol as an indicator was done before analysis. Two or three drops of K_2CrO_4 were added to the solution, when the color of the solution changed to yellow. The addition of 0.1 N- AgNO_3 caused clouding of the solution due to silver chloride AgCl precipitation as:



Reddish-brown silver chromate (Ag_2CrO_4) precipitated when all of the NaCl was consumed by the above reaction. The operation was carried out less than 6.5 ~10.5 in pH because acidic condition dissolves silver chromate:



And alkaline conditions precipitate silver oxide Ag_2O .

Reaction Rate

In this work, all the experiments were carried out at 303 K and total flow rates were maintained at $2.0 \text{ L}\cdot\text{min}^{-1}$. The reaction

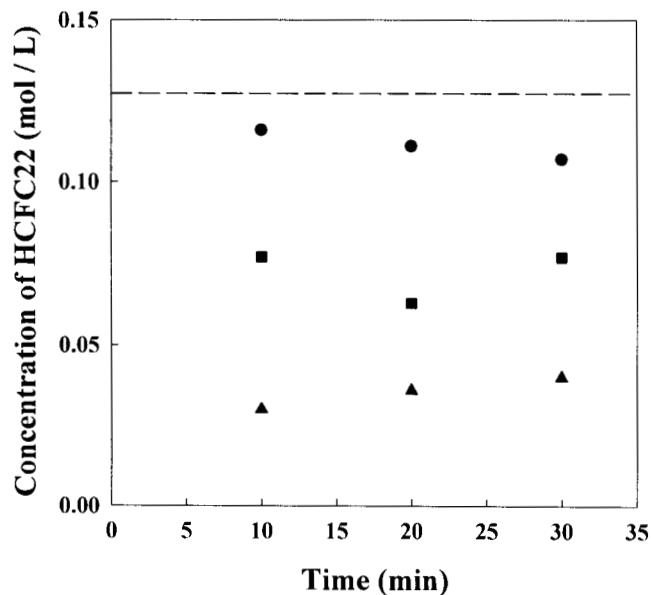


Figure 2. Effect of initial concentration of NaOH on concentration of HCFC22 in reacted solution at 303 K and 10 (kPa) of HCFC22 partial pressure. Initial concentration of NaOH ●; 0.5, ■; 1.0, ▲; 2.0 (mol/L), ----; Saturated solubility.

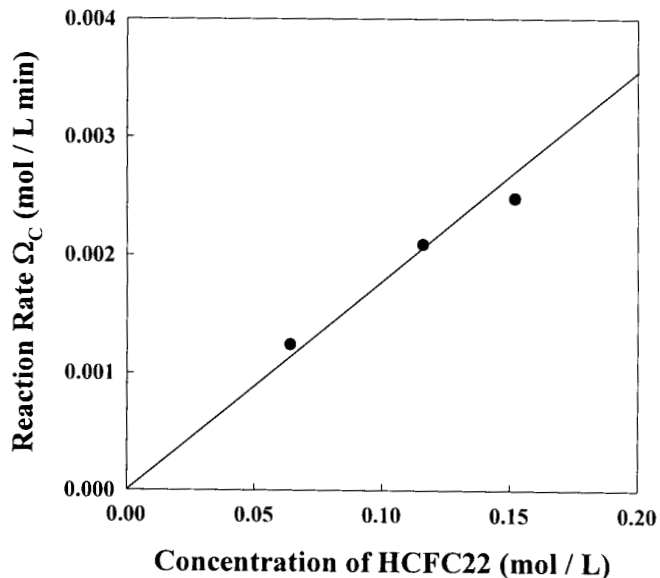


Figure 4. Relationship between reaction rate and concentration of HCFC22 in 0.5 (mol/L) NaOH-methanol solution at 303 (K). ●; experimental data, — correlation.

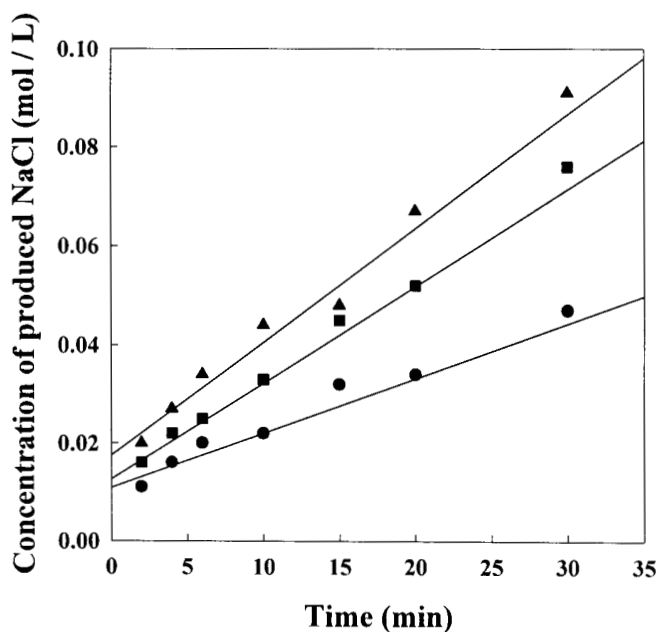
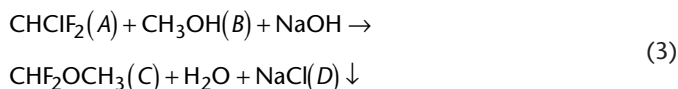


Figure 3. Effect of partial pressure of HCFC22 on reaction in 0.5 (mol/L) NaOH-methanol solution at 303K. partial pressure of HCFC22 ●; 5, ■; 10, ▲; 15 (kPa), —; correlations.

was carried out at partial pressures of HCFC22 ranging from 5 to 15 kPa and initial concentrations of NaOH ranging from 0.5 to 2.0 mol/L. Stoichiometry of this reaction in a solution is:



Simply, it can be rewritten as follows:

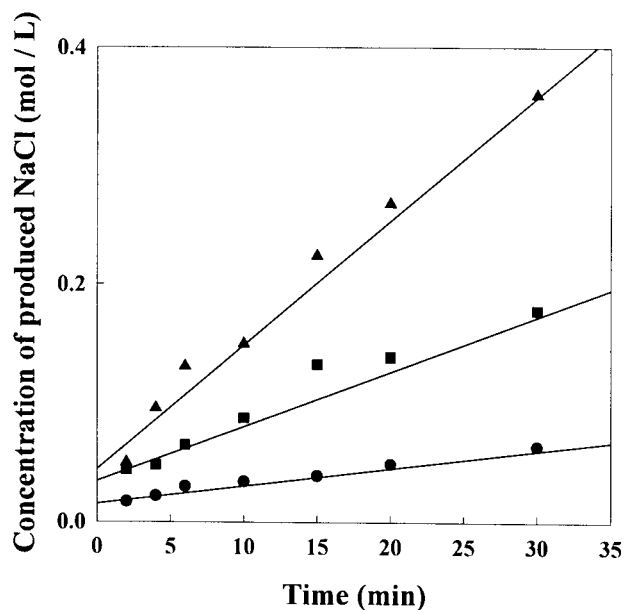


Figure 5. Effect of concentration of NaOH on reaction at 303 K and 10 kPa of partial pressure of HCFC22. Initial concentration of NaOH ●; experimental data, ●; 0.5, ■; 1.0, ▲; 2.0 (mol/L), — correlation.



As a reaction proceeds, precipitation of NaCl occurred and increased. We measured the concentration of NaCl and HCFC22 in a solution during the reaction. Figure 1 shows that the measured concentrations of HCFC22 decreased from solubility and reached steady state as a reaction proceeded at 15 kPa, although at lower partial pressure we could not observe decrease because of small reaction rate Ω_C . The saturated

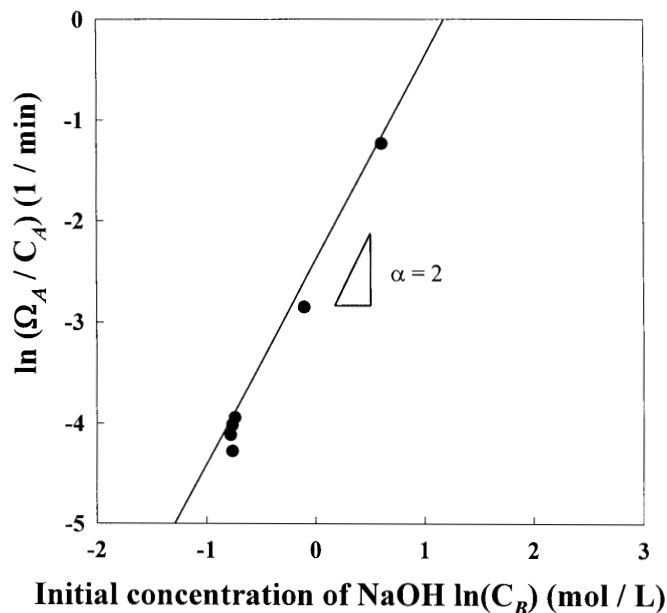


Figure 6. Relationship between reaction rate and initial concentration of NaOH at 303 K. ●, experimental data, — correlation.

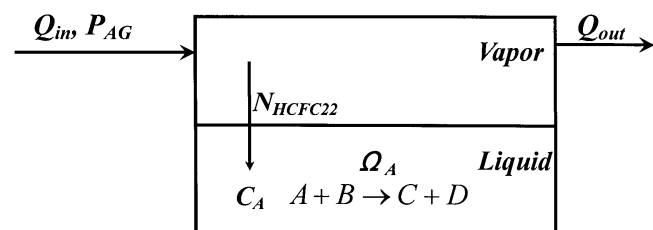


Figure 7. Schematic diagram of reaction process.

solubility of HCFC22 was obtained by Henry's law constant measured by Takenouchi et al. (2001).

$$p_{HCFC22} = H C_A^S \quad (5)$$

where p_{HCFC22} is partial pressure of HCFC22, C_A^S is saturated concentration of HCFC22 and H is the Henry's law constant of HCFC22 in a methanol solution. Figure 2 also shows that concentration of HCFC22 decreased with an increase in the initial concentration of NaOH. Figure 3 together with Figure 1 show the effect of partial pressure of HCFC22 on reactions, as initial concentration of NaOH was 0.5 mol/L. As shown in Figure 3, reaction rate Ω_C was estimated as a slope of the experimental data because of constant concentrations of HCFC22 as shown in Figure 1. Figure 4 shows that the reaction rate is proportional to concentrations of HCFC22 in a liquid solution, C_A . Figures 2 and 5 show the effect of initial concentration of NaOH, C_B^0 , on the reaction, as partial pressure of HCFC22 was 10 kPa.

The production rate of the ether, Ω_C , is equal to production rate of NaCl, D :

$$\frac{dC_D}{dt} = \Omega_C \quad (6)$$

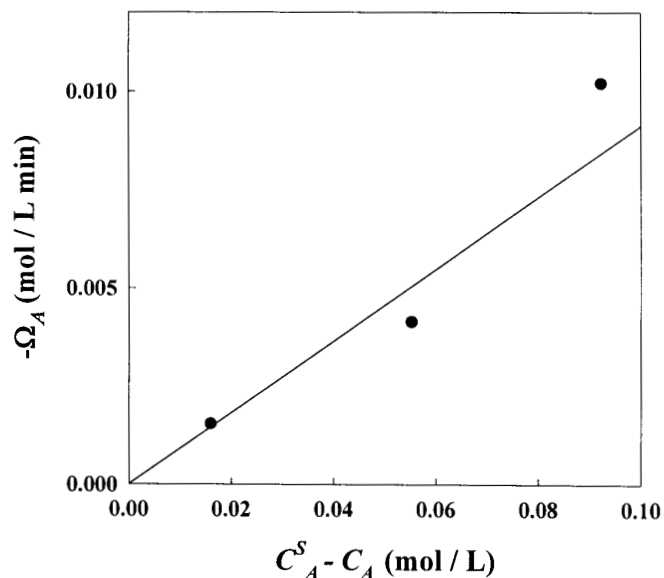


Figure 8. Relationship between reaction rate $-\Omega_A$ and concentration difference $C_A^S - C_A$ (mol/L). ● experimental data, — correlation.

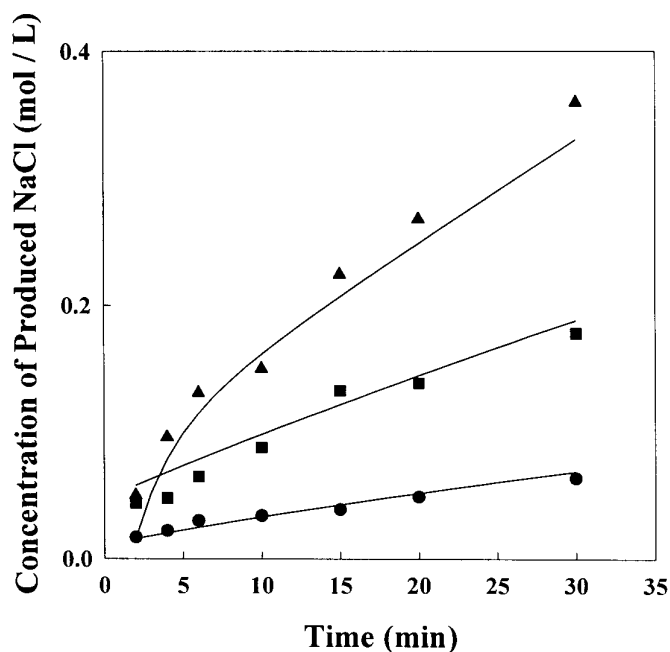


Figure 9. Comparison between calculated NaCl concentration and experimental data at 303 K and 10 kPa of HCFC22 partial pressure in methanol-NaOH solution: Initial concentration of NaOH ●; 0.5, ■; 1.0, ▲; 2.0 mol/L —; calculation with stationary state model.

At a constant temperature, Ω_C is expected to be a function of C_A and C_B . Considering the above-mentioned experimental results, the following reaction effect of initial concentration of NaOH seems to be more complex. The Ω_C expression may be written:

$$\Omega_C = \frac{dC_D}{dt} = k_1 (C_B^0)^\alpha C_A \quad (7)$$

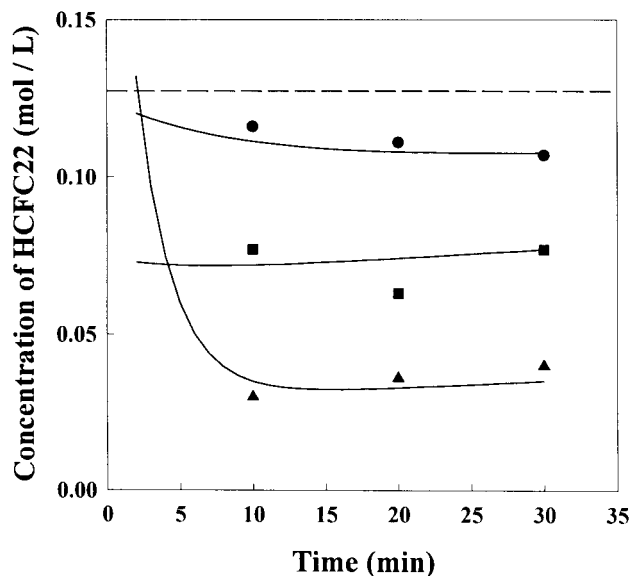


Figure 10. Comparison between calculated HCFC22 concentration and experimental data at 303 K and 10 (kPa) of HCFC22 partial pressure in methanol-NaOH solution: Initial concentration of NaOH ●; 0.5, ■; 1.0, ▲; 2.0 (mol/L) — calculation with stationary state model, ---- saturated solubility.

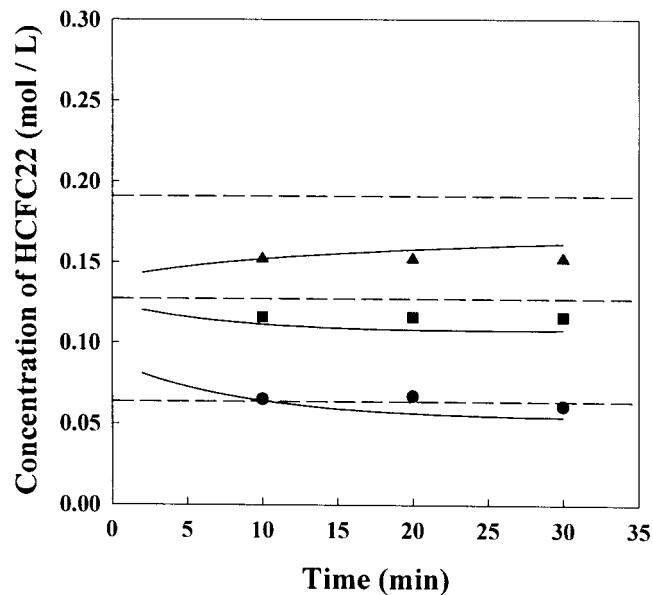


Figure 12. Comparison between calculated HCFC22 concentration and experimental data at 303 K and 0.5 mol/L of NaOH in methanol solution: Partial pressure of HCFC22 ●; 5, ■; 10, ▲; 15 (kPa) — calculation with stationary state model, ---- Saturated solubility.

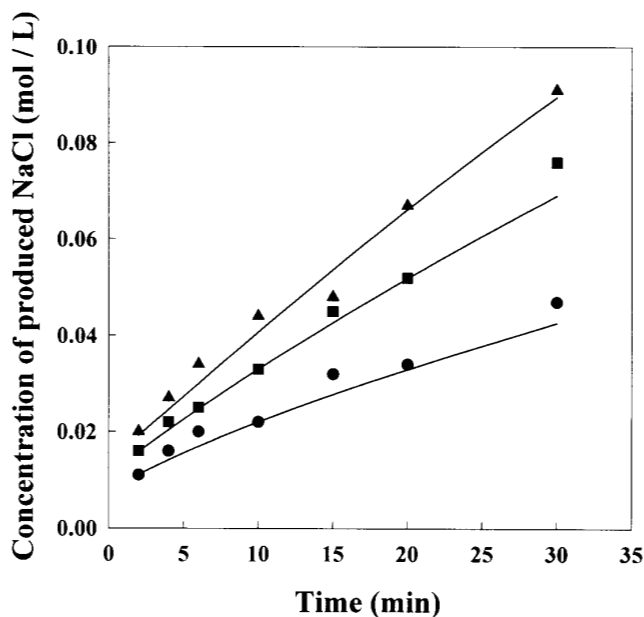


Figure 11. Comparison between calculated NaCl concentration and experimental data at 303 (K) and 0.5 () of NaOH in methanol solution: Partial pressure of HCFC22 ●; 5, ■; 10, ▲; 15 (kPa) — calculation with stationary state model.

where C_B^0 is initial concentration of NaOH in a methanol solution and C_A is average concentrations of HCFC22 estimated from the Figure 2. Equation (7) can be written as:

$$\frac{\Omega_C}{C_A} = k_1 (C_B^0)^\alpha \quad (8)$$

$$\ln\left(\frac{\Omega_C}{C_A}\right) = \ln(k_1) + \alpha \ln(C_B^0) \quad (9)$$

The value of power α of Equation (9) estimated from Figure 6 was 2. The reaction rate constant k_1 was estimated to be $0.0823 \text{ L}^2/\text{mol}^2 \cdot \text{min}$ from experimental data with a least squares method.

Reaction Model Considering Stationary State of HCFC22 Concentration in Methanol Solution

Figure 7 shows the schematic diagram of this reaction process. In this process, HCFC22 fed as a mixture gas is absorbed into methanol and reaction proceeds in a liquid phase. As shown in Figure 2, HCFC22 concentration in a methanol solution was kept constant. Assuming stationary state, the HCFC22 gas absorption rate into methanol N_{HCFC22} is equivalent to the reaction rate of HCFC22 Ω :

$$\frac{dC_A}{dt} = K_L a (C_A^S - C_A) + \Omega_A = 0 \quad (10)$$

$$\Omega_A = -\Omega_C = -k_1 C_A C_B^2 \quad (11)$$

where $K_L a$ is volumetric coefficient, k_1 is reaction rate constant, C_A^S is saturated solubility obtained from Equation (5), C_A is HCFC22 concentration in a solution, C_B is NaOH concentration. The first term on the left-hand side of Equation (10) is the HCFC22 gas absorption rate into a methanol solution, and the second term is the reaction rate of HCFC22, Ω_A which is equal to $-\Omega_C$, according to stoichiometry expressed by Equation (3). So, Equation (10) can be written as:

$$\Omega_A = -K_L a (C_A^S - C_A) \quad (12)$$

Figure 8 shows the relationship between reaction rate $-\Omega_A$ and concentration difference $(C_A^S - C_A)$. The value of $K_L a$ is estimated to be 0.0911 min^{-1} from a slope of Figure 8 using the least squares method. The coefficients k_1 and $K_L a$ estimated above were substituted into Equations (7) and (10). Initial conditions were set to be:

$$t^0 = 10[\text{min}], \quad C_D^0 = C_D|_{t=10}, \quad C_A^0 = C_A \quad (13)$$

t^0 was set to 10 min because at the initial period of reaction the concentration of HCFC22 and temperature of the solution were not under stationary state. As shown in Figures 9 to 12, the calculation results for NaCl and HCFC22 concentration in a methanol solution showed excellent agreement with experimental data at all reaction conditions.

Conclusions

We carried out vapor-liquid reaction experiments on production of fluoroether CH_3OCHF_2 from chlorodifluoromethane CHClF_2 (HCFC22 or R22). The stoichiometry of reaction was found to be simple with negligible side reactions as Equation (3). The reaction rate was proportional to the concentration of dissolved HCFC22. It reached a stationary state at the mixing conditions of this experiment. The production rate of the ether Ω_C was estimated from the amount of NaCl. The volumetric coefficient $K_L a$ was estimated from the material balance of HCFC22 at the stationary state. The calculated results were in excellent agreement with the experimental data.

Nomenclature

C_A	concentration of HCFC22, (mol/L)
C_A^S	saturated solubility of HCFC22, (mol/L)
C_B	concentration of NaOH, (mol/L)
C_D	concentration of NaCl, (mol/L)
C_A^0	initial concentration of HCFC22, (mol/L)
C_D^0	initial concentration of NaCl, (mol/L)

C_B^0	initial concentration of NaOH, (mol/L)
H	Henry's law constant of HCFC22, (MPa/L-mol)
k_1	reaction rate constant, ($\text{L}^q/\text{mol}^q \cdot \text{min}$)
$K_L a$	volumetric coefficient, (1/min)
N_{HCFC22}	mass transfer rate of HCFC22 into methanol, (mol/L-min)
P_{HCFC22}	Partial pressure of HCFC22, (MPa)
t^0	Initial reaction time for starting calculation, (min)

Greek Symbols

α	Power of concentration of NaOH in Eq.(7)
Ω_A	reaction rate of HCFC22, (mol/L-min)
Ω_C	production rate of difluoromethylether, (mol/L-min)

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