Study of the Reaction of Dichloromethane with Hydrogen Fluoride in the Presence of Antimony Chlorofluorides

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Abstract—The reaction of dichloromethane with hydrogen fluoride in the presence of antimony chlorofluorides is studied in the setup for liquid-phase synthesis. The reaction type, orders with respect to reactants and the catalyst, and Arrhenius parameters are determined. The elemental composition of the catalyst for liquidphase fluorination in the considered process is found. The dynamics of the catalyst activity is studied.

INTRODUCTION

Ozone depletion by chlorofluorocarbons [1] motivates their replacement by other substances that do not affect the ozone layer. Of these substances, most promising are chlorine-free compounds, including difluoromethane, which can be used as a coolant in composition with other compounds.

In [1, 2], the process for the preparation of chlorofluorocarbons and fluorinated hydrocarbons, including difluoromethane, was described. This process is based on the reaction of chlorinated hydrocarbons with chlorofluorides and fluorides of variable-valence metals, including antimony chlorofluorides (Swarts reaction). A number of commercial organofluorine products are synthesized by the reaction of chlorinated hydrocarbons with hydrogen fluoride in the presence of antimony chlorofluorides, which are in turn synthesized in the reaction zone from SbCl₅ and HF [3]. The goal of this work was to study the formation of difluoromethane by the reaction of dichloromethane with hydrogen fluoride in the presence of antimony chlorofluorides.

EXPERIMENTAL

Difluoromethane was synthesized by the reaction of dichloromethane with hydrogen fluoride in the presence of antimony chlorofluorides (Swarts reaction) in the setup of liquid-phase synthesis. This setup included a stainless steel reactor (volume, 2 l; diameter, 76 mm), a distillation column attached to the top of the reactor, reactant dosing units, and a system for the purification of the final products. The reactor had a sight glass made of transparent crystalline alumina, which enabled the visual control of the level of the reactor jacket from the circulation thermostat. The working volume, i.e., the volume of the liquid phase in the reactor, was 1.3 1. During the process, temperature and pressure inside the reactor were continuously measured. Dichloromethane was supplied into the reactor with a pump. Hydrogen fluoride was fed under the action of nitrogen pressure from a cylinder installed on a balance. This enabled the control of hydrogen fluoride consumption. The packed distillation column on the top of the reactor had a packing length of 400 mm and an inner diameter of 30 mm. The column was equipped with a reflux condenser, which was a heat exchanger of the tube-in-tube type. The heat-exchange area was 170 cm². The space between the tubes was filled with a coolant from the circulation thermostat. Gaseous products leaving the reflux condenser were transported into the water system for neutralization, where hydrogen chloride was separated from hydrogen fluoride. Then, the products were dried and sent to a flowmeter.

The concentrations of chloride and fluoride ions in the neutralization system were measured by potentiometric titration with silver nitrate and lanthanum nitrate, respectively. The liquid and gaseous products from dichloromethane fluorination were purified from HCl and HF and then analyzed by GLC.

The construction of the setup made it possible to withdraw samples for the analysis of gaseous products in the reactor that were in equilibrium with the gas phase. Gaseous products were collected by passing them through a water reservoir and analyzed as described above.

The composition of the catalyst for liquid-phase fluorination, which consisted of antimony chlorofluorides, was determined by potentiometric titration. To determine antimony, the solution of potassium permanganate was used. The contents of chloride and fluoride ions were determined as described above. Titration by a solution of KMnO₄ allowed us to determine the content of Sb(III). To determine Sb(V), it was transformed into Sb(III) using a Na₂SO₃ solution. The amount of Sb(V) was determined as a difference between the overall amount of antimony and the amount of Sb(III) in a sample.

The complete analysis of the liquid phase in the reactor, including antimony chlorofluorides and synthetic products, was rather complex, and the accuracy of measurements was low because of the absence of reliable techniques for the sampling and analysis of the above mixture. Therefore, the composition of the liquid phase was determined by calculating the phase equilibrium between gaseous products, whose concentrations were determined in the experiment, and the liquid phase.

We used hydrogen fluoride (GOST 14022-88) and dichloromethane (GOST 9968-86) of the highest quality, and antimony pentachloride prepared in our laboratory. Antimony pentachloride contained 99.9 wt % of the main substance.

RESULTS AND DISCUSSION

As seen from the literature data [2, 3], the first stage of the liquid-phase fluorination of halogen-substituted hydrocarbons in the presence of antimony chlorofluorides is the interaction of antimony pentachloride with hydrogen fluoride:

$$SbCl_5 + mHF \longrightarrow SbCl_{5-m}F_m + mHCl.$$
 (I)

Kolditz and Daunicht [4] showed that reaction (I) is fast in excess hydrogen fluoride. The analyses of catalyst samples withdrawn during the reaction, as well as the calculations of the material balance of hydrogen fluoride fed to the reaction zone and hydrogen chloride formed in the reaction, showed that m = 3 in the reaction of dichloromethane with hydrogen fluoride. Moreover, we found that the catalyst contains Sb(III) (see below for details). This led us to propose the following scheme of reactions [2].

$$CH_2Cl_2 + CatF \xrightarrow{\kappa_1} CH_2ClF + CatCl,$$
 (II)

$$CH_2ClF + CatF \xrightarrow{k_2} CH_2F_2 + CatCl,$$
 (III)

where CatF and CatCl are fluorinated and chlorinated forms of the catalyst and k_1 and k_2 are the rate constants of steps (II) and (III).

We carried out a series of experiments where we varied the concentrations of the catalyst and organic reactants.

The gaseous reaction products were used to stir the reaction mixture. The specific volume of gases consumed for a unit of time characterized the intensity of stirring [5]. This was calculated by the formula:

$$\varphi = \frac{W \frac{T_r}{T_e} (R'+1)}{S \frac{P_r}{P_e}},$$
(1)

where φ is the specific flow of gases per unit time (mm s⁻¹); W is the flow of reaction products (m^{3}/s) leaving the reflux condenser of the distillation column (this was calculated from the flowmeter readings and the results of the analyses of the neutralization system content) (m^{3}/s) ; T is temperature (K); S is the cross-section of the reactor (m^2) ; P is pressure (Pa); R' is the reflux ratio of the distillation column; the subscripts r and e refer to the parameters in the reactor (r) and at the outlet of reflux condenser (e). The values W, T_r, T_e, P_r and $P_{\rm e}$ were measured in each run. The value of R' was calculated by solving the equations describing phase equilibria and the material balance of the products at the inlet and outlet of the reflux condenser [6]. In all of the runs, the values of φ ranged from 0.003 to 0.010 m s⁻¹, which correspond to the medium to high stirring intensities [5].

At a constant rate of reactant supply, the stationary regime is set up in the flow reactor [7]. This regime is characterized by the constant flows at the inlet to and outlet from the reactor, the constant level of the reaction mixture, and constant temperatures and reactant concentrations over the whole volume of the reaction mixture. The flow of initial components (dichloromethane and hydrogen fluoride) was chosen so that it was the highest possible while maintaining the constant level of the reaction mixture in the reactor. The reaction rate was determined by measuring the molar flow of the *i*th component at the inlet to and outlet from the setup. The results of measurements were divided by the volume of the reaction mixture. In the general form, the reaction rate is expressed as follows:

$$r_{i} = k_{0,i} \exp\left(-\frac{E_{i}}{RT}\right) C_{s,i}^{n_{s,i}} C_{c,i}^{n_{c,i}}, \qquad (2)$$

where r is the reaction rate (kmol m⁻³ min⁻¹); k_0 is the preexponential factor ((m³/kmol)^{1-(n₁+n_c)} min⁻¹); E is the activation energy (J/kmol); T is the temperature of a run (K); C is the reactant concentration (kmol/m³); R = 8314 J kmol⁻¹ K⁻¹ is the gas constant; n is the reaction order with respect to the corresponding reactant; subscript *i* refers to a substance or a reaction that describes its transformation; subscript c refers to the catalyst; and subscript s refers to the reactant.

At $C_{\rm c}$ = const, formula (2) takes the following form:

$$r_i = k_i \exp\left(-\frac{E_i}{RT}\right) C_{s,i}^{n_{s,i}},$$
(3)

where

$$k_i = k_{0,i} C_{c,i}^{n_{c,i}}.$$
 (4)

The values of k_i , E_i , and $n_{s,i}$ in (3) were found by regression analysis after carrying out a series of experiments with $C_c = \text{const}$ and different temperatures T and concentrations of reactants C_s . These can be varied by changing the temperature of the coolant supplied into the reflux condenser. The values of $k_{0,i}$ and $n_{c,i}$ were

KINETICS AND CATALYSIS Vol. 41 No. 3 2000

Substance	Composition of gas phase	Composition	Composition at the outlet	
	phase $(Y_{i\neq c}^{a})$, mol. fr.	<i>X_i</i> , mol. fr.	C_i , kmol/m ³	from the setup, mol. fr.
CH ₂ F ₂	0.185	0.018	0.26	0.301
CH ₂ ClF	0.102	0.055	0.81	0.025
CH_2Cl_2	0.210	0.427	6.27	0.002
HF	0.339	0.291	4.27	0.044
HCl	0.164	0.004	0.06	0.628
Catalyst		0.204	3.00	-

Table 1. Calculation of the reaction mixture in a run at $P_0 = 0.15$ MPa and $C_c = 3.00$ kmol/m³

found by the regression analysis of expression (4) in the series of experiments with various catalyst concentrations C.

To determine the concentrations of substances in the reactor, we calculated the phase equilibrium between the reaction mixture and gaseous products, whose composition were determined in the experiment [8, 9]. In this work, we used the following equations:

$$Y_i = F(X_i, P_0, T_r),$$
 (5)

$$C_{\rm c} = X_{\rm c} / \sum_{i} \frac{X_{i}}{\rho_{i}}, \tag{6}$$

$$Y_i = Y_{i \neq c}^{a} (1 - Y_c),$$
 (7)

$$\sum_{i} X_i = 1, \tag{8}$$

where Y and X are the compositions of gaseous products, which are in equilibrium with the gas phase of the reactor, and liquid products in the reactor (molar fraction); P_0 is the total pressure in the reactor (Pa); T_r is temperature (K); ρ is the molar density of substances at T (kmol/m³); C is the molar concentration of the liquid phase (kmol/m³); Y^a is the experimental composition of gaseous products which are in equilibrium with the liquid phase (the composition does not include catalyst vapor) (molar fraction). The function F describes the liquid-vapor phase equilibrium, calculated using the correlation equations [9] taking into account the association of hydrogen fluoride in the gas phase. This association is described by the model that accounts for the presence of monomers and hexamers of HF [10]. This model suggests the following equations:

$$Y_{i\neq \rm HF} = \frac{P_{i\neq \rm HF}^{\rm sat} \gamma_{i\neq \rm HF} X_{i\neq \rm HF}}{P_0 + 5P_6},$$
(9)

$$Y_{\rm HF} = \frac{P_1^{\rm sat} \gamma_{\rm HF} X_{\rm HF} + 6P_6}{P_0 + 5P_6},$$
 (10)

$$P_1^{\text{sat}}, P_6 = f(T_r),$$
 (11)

KINETICS AND CATALYSIS Vol. 41 No. 3 2000

where P is the partial pressure (Pa); P^{sat} is the pressure of saturated vapors of a substance at the temperature T_r (Pa); γ is the activity coefficient; and subscripts 1 and 6 refer to the monomers and hexamers of hydrogen fluoride, respectively. The function f describes the correlation between the above parameters and temperature [10].

The data on phase equilibria in the binary systems of difluoromethane synthesis products were borrowed from [6, 11, 12]. These were necessary for the calculation of activity coefficients. We assumed that the binary systems containing the catalyst in their compositions are ideal. The data on the pressures of saturated vapor and their molar densities were taken from [1, 9, 13-15]. The data on saturated catalyst vapor were taken equal to the partial pressure of the saturated antimony pentachloride vapor [16]. This assumption did not make the calculations inaccurate because the partial pressure of antimony pentachloride was much lower than the partial pressures of other reaction products. At the temperatures above critical values for hydrogen fluoride and difluoromethane, the pressure of saturated vapors and the molar density were found by extrapolating the corresponding values to a supercritical region [8, 9].

Upon substituting the experimental values of $Y_{i\neq c}^{a}$, C_{c} , and P_{0} into equations (5)–(8), we calculated the values of X_{i} , Y_{i} , and T_{r} . Then, equations analogous to (6) were used to calculate the concentrations C_{i} .

An example of the calculation of the product composition in one of the runs is presented in Table 1. The same table shows the gaseous products at the outlet from the setup for liquid-phase synthesis.

The temperature in the reactor calculated for the run described in Table 1 was 96.5°C. The calculated temperatures differ from the experimental values by 1.5-2.0°C. This confirms the correctness of the method and the assumptions made in the calculations. In further calculations, we used T_r in K, measured in the experiments.

Tables 2–6 show the results of experiments on dichloromethane fluorination in the presence of various catalyst amounts. Equation (3) in the numerical form

P ₀ , MPa	Temperature, °C	T _{ca} , ℃	$C_{\rm CH_2Cl_2}$, kmol/m ³	C _{CH2CIF} , kmol/m ³	$-r_{\rm CH_2Cl_2},$ kmol m ⁻³ min ⁻¹	r _{CH2F2} , kmol m ⁻³ min ⁻¹
0.10	78.7	0	9.67	0.91	0.0091	0.0071
	80.4	10	9.83	0.87	0.010	0.0078
	82.8	20	10.0	0.82	0.011	0.0082
0.15	87.7	0	9.51	1.01	0.014	0.014
	89.9	10	9.55	0.95	0.016	0.015
	92.4	20	9.61	1.04	0.018	0.017
0.20	94.7	0	9.59	1.00	0.020	0.020
	96.5	10	9.61	0.95	0.022	0.021
	98.2	20	9.81	0.92	0.026	0.022

Table 2. Dichloromethane fluorination at $C_c = 1.40 \text{ kmol/m}^3$

Table 3. Dichloromethane fluorination at $C_c = 2.20 \text{ kmol/m}^3$

<i>P</i> ₀ , MPa	Temperature, °C	T _{ca} , ℃	$C_{\rm CH_2Cl_2}$, kmol/m ³	C _{CH2CIF} , kmol/m ³	$-r_{CH_2CI_2}$, kmol m ⁻³ min ⁻¹	r _{CH2F2} , kmol m ⁻³ min ⁻¹
0.10	79.5	0	8.36	0.74	0.011	0.010
	82.4	10	8.41	0.69	0.013	0.010
	84.1	20	8.44	0.68	0.015	0.012
0.15	89.3	0	7.85	0.78	0.018	0.017
	91.4	10	7.94	0.75	0.020	0.019
	94.4	20	8.20	0.74	0.024	0.022
0.20	95.8	0	7.86	0.79	0.025	0.025
	98.6	10	8.20	0.77	0.029	0.028
	99.6	20	8.23	0.74	0.032	0.031

Table 4. Dichloromethane fluorination at $C_c = 3.00 \text{ kmol/m}^3$

<i>P</i> ₀ , MPa	Temperature, °C	T _{ca} , °C	$C_{\rm CH_2Cl_2}$, kmol/m ³	C _{CH2CIF} , kmol/m ³	$-r_{CH_2CI_2}$, kmol m ⁻³ min ⁻¹	r _{CH2CIF} , kmol m ⁻³ min ⁻¹
0.10	84.1	0	7.09	0.87	0.016	0.014
	85.8	10	7.12	0.78	0.018	0.014
	86.9	20	7.14	0.76	0.019	0.014
0.15	93.8	0	6.17	0.83	0.023	0.022
	94.9	10	6.27	0.81	0.025	0.023
	95.3	20	6.29	0.74	0.026	0.023
0.20	98.3	0	6.12	0.83	0.029	0.029
	100.8	10	6.30	0.82	0.033	0.034
	102.4	20	6.41	0.79	0.038	0.035

for each case are given below the tables. These equations describe the rates of dichloromethane consumption and difluoromethane formation. The values of $T_{\rm ca}$ presented in the tables are the temperatures of the coolant in the jacket of the reflux condenser.

$$-r_{\rm CH_2Cl_2} = 2.9 \times 10^5 \exp\left(-\frac{5.7 \times 10^7}{RT}\right) C_{\rm CH_2Cl_2}^{0.95}, \quad (12)$$

$$r_{\rm CH_2F_2} = 1.2 \times 10^7 \exp\left(-\frac{6.2 \times 10^7}{RT}\right) C_{\rm CH_2ClF}^{0.92},$$
 (13)

$$-r_{\rm CH_2Cl_2} = 4.3 \times 10^5 \exp\left(-\frac{5.7 \times 10^7}{RT}\right) C_{\rm CH_2Cl_2}^{0.93}, \quad (14)$$

$$r_{\rm CH_2F_2} = 1.6 \times 10^7 \exp\left(-\frac{6.2 \times 10^7}{RT}\right) C_{\rm CH_2CIF}^{0.72},$$
 (15)

KINETICS AND CATALYSIS Vol. 41 No. 3 2000

P ₀ , MPa	Temperature, °C	T _{ca} , ℃	$C_{\rm CH_2Cl_2}$, kmol/m ³	C _{CH2CIF} , kmol/m ³	$-r_{CH_2Cl_2}$, kmol m ⁻³ min ⁻¹	$r_{\rm CH_2F_2}$, kmol m ⁻³ min ⁻¹
0.10	86.2	0	5.15	0.40	0.014	0.013
	88.6	10	5.25	0.38	0.016	0.014
	90.2	20	5.38	0.38	0.018	0.016
0.15	96.0	0	5.36	0.39	0.023	0.022
	96.1	10	5.37	0.38	0.024	0.022
	98.2	20	5.52	0.37	0.027	0.023
0.20	100.2	0	5.15	0.41	0.028	0.028
	101.8	10	5.29	0.38	0.031	0.029
	103.1	20	5.38	0.38	0.036	0.032

Table 5. Dichloromethane fluorination at $C_c = 3.90 \text{ kmol/m}^3$

Table 6. Dichloromethane fluorination at $C_c = 5.10 \text{ kmol/m}^3$

P ₀ , MPa	Temperature, °C	T _{ca} , ℃	C _{CH2Cl2} , kmol/m ³	$C_{\rm CH_2ClF}$, kmol/m ³	$-r_{CH_2Cl_2}$, kmol m ⁻³ min ⁻¹	$r_{\rm CH_2F_2}$, kmol m ⁻³ min ⁻¹
0.10	90.5	0	2.66	0.17	0.011	0.0090
	92.3	10	2.81	0.17	0.012	0.010
	93.8	20	2.90	0.16	0.014	0.010
0.15	99.3	0	2.36	0.17	0.014	0.014
	99.6	10	2.50	0.17	0.016	0.014
	100.1	20	2.68	0.18	0.017	0.015
0.20	101.8	0	2.11	0.16	0.016	0.016
	103.6	10	2.28	0.15	0.019	0.016
	105.6	20	2.48	0.17	0.022	0.022

$$-r_{\rm CH_2Cl_2} = 5.8 \times 10^5 \exp\left(-\frac{5.9 \times 10^7}{RT}\right) C_{\rm CH_2Cl_2}^{1.2}, \quad (16)$$

$$r_{\rm CH_2F_2} = 1.8 \times 10^7 \exp\left(-\frac{6.2 \times 10^7}{RT}\right) C_{\rm CH_2CIF}^{0.83},$$
 (17)

$$-r_{\rm CH_2Cl_2} = 6.6 \times 10^5 \exp\left(-\frac{5.7 \times 10^7}{RT}\right) C_{\rm CH_2Cl_2}^{0.92}, \quad (18)$$

$$r_{\rm CH_2F_2} = 1.9 \times 10^7 \exp\left(-\frac{6.1 \times 10^7}{RT}\right) C_{\rm CH_2CIF}^{0.73},$$
 (19)

$$-r_{\rm CH_2Cl_2} = 9.8 \times 10^5 \exp\left(-\frac{5.8 \times 10^7}{RT}\right) C_{\rm CH_2Cl_2}^{0.81}, \quad (20)$$

$$r_{\rm CH_2F_2} = 4.9 \times 10^7 \exp\left(-\frac{6.4 \times 10^7}{RT}\right) C_{\rm CH_2CIF}^{0.81}.$$
 (21)

For the regression analysis of equation (4), we had to know the catalyst concentration C_c and the preexponential factor k_0 of the reaction of CH₂Cl₂ and CH₂F₂ formation. These values are given in the titles of Tables 2– 6 and corresponding equations (12)–(21).

KINETICS AND CATALYSIS Vol. 41 No. 3 2000

Using the above values, we arrive at the expressions

$$k_1 = 2.1 \times 10^5 C_{\rm c}^{0.91},\tag{22}$$

$$k_2 = 7.8 \times 10^6 C_{\rm c}^{0.89},\tag{23}$$

where subscripts 1 and 2 refer to CH_2Cl_2 and CH_2F_2 , respectively.

After rounding the reaction orders with respect to substances to unity, averaging the activation energies to $E_1 = 5.8 \times 10^7$ J/kmol and $E_2 = 6.2 \times 10^7$ J/kmol, and recalculating the preexponential factors $k_{0,i}$ in formula (3), we have the following formulas:

$$-r_{\rm CH_2Cl_2} = 2.2 \times 10^5 \exp\left(-\frac{5.8 \times 10^7}{RT}\right) C_{\rm CH_2Cl_2}C_{\rm c}, \quad (24)$$

$$r_{\rm CH_2F_2} = 8.3 \times 10^6 \exp\left(-\frac{6.2 \times 10^7}{RT}\right) C_{\rm CH_2CIF} C_{\rm c}.$$
 (25)

The analysis, which takes into account metrological characteristics of the instruments used in our study, showed that the absolute error of the above values is not higher than the last significant digit.



Fig. 1. Measured (points) and calculated (solid line) rates of dichloromethane fluorination in the setup for liquid-phase synthesis.

The values of activation energies point to the absence of diffusion control [17]. This confirms that the reactor is well stirred. Figure 1 compares the calculated and measured rates of dichloromethane transformation. The rates were calculated by equation (24) by substituting the values of T_r , $C_{CH_2Cl_2}$, and C_c presented in Tables 2–6. The data obtained on a pilot-scale setup for liquid-phase synthesis with a reactor volume of 40 I are marked with a circle. This setup worked for several years at the pilot plant "Applied Chemistry." The construction of the setup was analogous to the laboratory setup.

Figure 1 shows that equations (24) and (25) corresponding to reactions (II) and (III) describe well the process of dichloromethane reaction with hydrogen fluoride in the presence of the antimony catalyst.

The catalyst samples were analyzed to find the concentrations of Sb(III) and Sb(V), chlorine, and fluorine. The fluorine concentration was determined as a difference between the analytically measured general amount of fluorine and the amount of fluorine existing in the form of hydrogen fluoride, which was calculated from the material balance between supplied HF and HCl formed during the reaction. We also used the calculations of phase equilibria. As a result, we found that the freshly prepared, actively working catalyst for the liquid-phase synthesis of difluoromethane has the elemental composition $[SbF_3]_{0.3}[SbCl_2F_3]_{0.7}$. Antimony chlorofluorides formed by $SbCl_5$ fluorination by reaction (I) probably dissociate to form Sb^{3+} .

During fluorination, the catalyst activity steadily decreases. This is mainly associated with a decrease in the Sb⁵⁺ concentration (Fig. 2).

The catalyst activity can be retained by supplying chlorine into the reaction zone. However, Sb^{3+} would not be completely reduced to Sb^{5+} . The reaction $SbF_3 + Cl_2 \longrightarrow SbCl_2F_3$ was described in [3]. The formation of chlorine in the reaction zone observed in experiments



Fig. 2. The rate of dichloromethane transformation (triangles) and Sb⁵⁺ concentration (circles) vs. duration of the run at $P_0 = 0.15$ MPa, $T_r = 94.9^{\circ}$ C, and $T_{ca} = 10^{\circ}$ C.

suggests that the process is reversible and the catalyst activity decreases because of the reaction

$$SbCl_2F_3 \Longrightarrow SbF_3 + Cl_2.$$
 (IV)

SbF₃ is less active in the Swarts reaction than SbCl₂F₃ [2, 3]. Chlorine formed in the reaction is partially dissolved in the reaction mixture. Because of this, the catalyst activity is kept constant for several tens of hours. All the experiments described above were carried out with freshly prepared catalysts. The duration of each run was several hours while the catalyst activity was constant. The catalyst activity may be decreased because of corrosion products appearing in the reaction mixture. These are formed by the reaction of the mixture with the reactor material (stainless still). Also, the catalyst activity may be decreased because of moisture and sulfur dioxide, which exist as admixtures in the starting materials.

CONCLUSION

Thus, the reaction of dichloromethane with hydrogen fluoride in the presence of antimony chlorofluorides is consecutive. It occurs via the formation of chlorofluoromethane and has the first order with respect to the catalyst and the second overall order. The values of activation energy of dichloromethane consumption and difluoromethane formation are 58 and 62 kJ/mol, respectively. They show that the reaction is not controlled by diffusion. The catalyst for difluoromethane synthesis has the composition $[SbF_3]_{0.3}[SbCl_2F_3]_{0.7}$. The catalyst activity decreases because of an increase in the concentration of Sb(III).

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KINETICS AND CATALYSIS Vol. 41 No. 3 2000

Vol. 41

No. 3

2000

KINETICS AND CATALYSIS

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