Kinetics of Liquid-Phase Noncatalytic Methanol Hydrochlorination in Hydrochloric Acid

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Abstract—The kinetics of the liquid-phase noncatalytic hydrochlorination of methanol in hydrochloric acid is reported. The methyl chloride formation rate depends on the methanol concentration in hydrochloric acid and on the partial pressure of hydrogen chloride over hydrochloric acid. The activation energy of the reaction is 113 kJ/mol. The rate of the side process of dimethyl ether evolution is directly proportional to the methanol concentration energy of the reaction acid. The activation energy of the side process of dimethyl ether evolution is directly proportional to the methanol concentration and is inversely proportional to the partial pressure of hydrogen chloride over hydrochloric acid. The activation energy of the side reaction is about 33 kJ/mol. The results of the industrial implementation of methyl chloride synthesis from methanol and hydrochloric acid are in satisfactory agreement with the laboratory data.

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Although noncatalytic methyl chloride synthesis from methanol and hydrochloric acid is used in industry, literature data on the kinetics of liquid-phase noncatalytic methanol hydrochlorination are lacking.

The hydrochlorination of anhydrous methanol without a catalyst was reported in [1, 2]. The activation energy of this reaction is 26 kcal/mol [1]. The process is slowed down by the resulting water. It was inferred from the dependence of the reaction rate on the reactant concentrations that the apparent reaction order is <2 because of the inconstancy of the activity coefficient. The reaction mechanism was described by the following scheme [1]:

 $CH_3OH + HCl \rightleftharpoons [CH_3OH_2]^+Cl \rightleftharpoons CH_3Cl + H_2O.$

The rate of this reaction may depend on the rate of dehydration of methoxonium chloride species.

The relative equilibrium conversion of methanol changed insignificantly (from 96.5 to 96.1%) as the initial concentration of hydrogen chloride was varied between 0.115 and 1.623 mol/l [2].

We found no published data on the kinetics of the liquid-phase noncatalytic hydrochlorination of methanol. At the same time, several Russian enterprises are now interested in this process because of its simplicity [3-6], and two enterprises have already implemented it. Variants of the noncatalytic hydrochlorination of methanol in hydrochloric acid were also proposed abroad (see, e.g., [7]).

EXPERIMENTAL

The quantitative regularities of the liquid-phase noncatalytic hydrochlorination of methanol in hydrochloric acid were studied in a batch reactor fitted with a temperature-controlled heat-carrier jacket, a stirrer, and a reflux condenser. The design of the reactor made it possible to introduce methanol directly into the reaction zone and allowed the reaction mixture to be sampled for analysis during the run. The resulting methyl chloride was collected in a gasometer. During the run, the resulting methyl chloride was analyzed at intervals (5, 30, and 90 min after the beginning of the run) for the dimethyl ether content and the hydrogen chloride and methanol concentrations were determined in the reaction mixture. The methyl chloride evolution rate was determined with a soap-bubble flow meter during sampling.

Gaseous and liquid samples were analyzed on a chromatograph with a flame-ionization detector. A 6-m-long column was packed with Chromaton N containing 25 wt % diethylhexyl sebacinate. Gaseous samples were analyzed at 25°C; liquid samples, at 100°C. After measuring their volume, liquid samples were titrated with a sodium hydroxide solution to determine the hydrochloric acid concentration. The neutralized samples were analyzed to determine the methanol concentration in hydrochloric acid.

RESULTS AND DISCUSSION

The effects of temperature and hydrogen chloride and methanol concentrations of on the rates of formation of methyl chloride and dimethyl ether were studied. The results are presented in Table 1.

The data obtained at 80°C, a hydrogen chloride concentration of 7.55 mol/l, and various concentrations of methanol (entries 3.2, 5.3, and 6.1) indicate

Tempera- ture, °C	Entry no.	C _{CH3OH} , mol/l	C _{HCl} , mol/l	P _{HCl} , atm	$w_{CH_3Cl},$ mol l ⁻¹ h ⁻¹	$w_{(CH_3)_2O} \times 10^4$, mol l ⁻¹ h ⁻¹	$k_{\rm CH_3Cl},$ atm ⁻¹ h ⁻¹	$\frac{k_{\rm (CH_3)_2O} \times 10^5}{\rm atm/h}$
70	1.1	1.79	9.16	0.216	0.301	1.7	0.778	2.05
	1.2	1.66	8.99	0.169	0.207	2.2	0.670	2.24
	1.3	1.46	8.77	0.147	0.164	2.8	0.764	2.82
	2.1	1.85	9.48	0.272	0.335	1.0	0.666	1.47
	2.2	1.69	9.31	0.242	0.268	1.5	0.655	2.15
	2.3	1.47	8.89	0.169	0.160	1.7	0.644	1.95
		average				I	0.696	2.11
80	3.1	2.03	7.72	0.101	0.357	8.2	1.74	4.08
	3.2	1.85	7.55	0.086	0.350	7.8	2.20	3.62
	3.3	1.56	7.26	0.066	0.241	8.0	2.34	3.38
	4.1	0.99	8.10	0.136	0.295	1.2	2.19	1.65
	4.2	0.71	7.88	0.115	0.205	1.4	2.51	2.27
	4.3	0.53	7.54	0.085	0.082	1.7	1.82	2.73
	5.1	0.85	7.90	0.117	0.193	1.4	1.94	1.93
	5.2	0.71	7.77	0.105	0.151	1.6	2.03	2.37
	5.3	0.57	7.55	0.086	0.107	1.2	2.18	1.81
	6.1	0.95	7.55	0.086	0.170	2.4	2.08	2.17
	6.2	0.81	7.41	0.074	0.137	2.6	2.29	2.38
	6.3	0.71	7.31	0.068	0.109	2.7	2.26	2.59
		ļ.	ave	erage	I.	ļ	2.13	2.58
90	7.1	0.90	6.82	0.077	0.375	3.9	5.41	3.34
	7.2	0.70	6.63	0.065	0.271	5.3	5.96	4.92
	7.3	0.32	6.40	0.054	0.097	1.7	5.61	2.87
	8.1	0.82	7.60	0.090	0.587	2.3	7.95	2.52
	8.2	0.52	7.35	0.070	0.272	4.0	7.47	5.38
	8.3	0.30	7.15	0.060	0.136	2.2	7.56	4.40
		average					6.66	3.91
100	9.1	0.75	5.56	0.045	0.557	7.8	16.5	4.68
	9.2	0.52	5.37	0.037	0.308	9.4	16.0	6.69
	9.3	0.12	5.15	0.031	0.055	1.2	14.8	3.10
	average					15.8	4.82	

Table 1. Kinetics of methanol hydrochlorination with hydrochloric acid

that the hydrochlorination rate depends on the methanol concentration to the first power.

The results of experiments carried out at a fixed methanol concentration but various concentrations of hydrochloric acid (entries 4.2, 5.2, and 6.3) show that

the methyl chloride formation rate depends on the hydrochloric acid concentration to a power of \sim 7. The evaluation of other factors suggests that the partial pressure of hydrogen chloride over hydrochloric acid depends on the hydrochloric acid concentration

approximately in the same way as the reaction rate. Thus, the rate of methyl chloride formation also depends on the partial pressure of HCl over hydrochloric acid to the first power within $\pm 10\%$ accuracy.

To explain the unusual dependence of the reaction rate on the hydrochloric acid concentration, we used data on the partial pressures of hydrogen chloride over hydrochloric acid [8] and also on the activity of hydrogen chloride in its solutions [9]. Since measurement of partial pressures over solutions is one of the methods for finding the activity of solutes [9], the experimental results can satisfactorily be described in terms of both partial pressures and activities.

The data obtained agree well with one of the main concepts of catalysis science, according to which medium strength binding, not strong binding (such as strong adsorption on a heterogeneous catalyst), is optimal for a catalytic process. In our case, hydrogen chloride strongly bound to water does not contribute to the partial pressure of HCl over hydrochloric acid and, at the same time, does no react with methanol. Weakly bound HCl participates in both processes.

Table 1 lists the rate constants of liquid-phase noncatalytic methanol hydrochlorination calculated from the dependences of the methyl chloride formation rate on the methanol concentration and on the partial pressure of hydrogen chloride over hydrochloric acid:

$$w_{\mathrm{CH}_{3}\mathrm{Cl}} = k_{\mathrm{CH}_{3}\mathrm{Cl}}C_{\mathrm{CH}_{3}\mathrm{OH}}P_{\mathrm{HCl}}.$$

The average values of the rate constant $k_{\text{CH}_3\text{CI}}$ at 70, 80, 90, and 100°C are 0.696, 2.13, 6.66, and 15.8 h⁻¹ atm⁻¹, respectively. Data processing in the lnk-1/T coordinates leads to an activation energy of 27 kcal/mol (113 kJ/mol) for liquid-phase noncatalytic methanol hydrochlorination. This value is close to the earlier reported value [1]. The preexponential factor is 1.1 × 10¹⁷ atm⁻¹ h⁻¹.

Thus, the rate of liquid-phase noncatalytic methanol hydrochlorination in hydrochloric acid is described by the equation

$$w_{\rm CH_3Cl} = 1.1 \times 10^{17}$$

 $\times \exp\left(-\frac{113000}{RT}\right) C_{\rm CH_3OH} P_{\rm HCl} \text{ mol } 1^{-1} \text{ h}^{-1}.$

An analysis of the dependences of the apparent rate constant of dimethyl ether evolution $(w_{(CH_3)_2O})$ on the methanol and hydrogen chloride concentrations and on the partial pressures of HCl or the activity of solution is rather difficult to carry out. The matter is that three processes contribute to the value of $w_{(CH_3)_2O}$: dimethyl ether formation from methanol, the consumption of dimethyl ether through its hydrochlorination into methyl chloride, and dimethyl ether carryover from the reactor. The overall process is described by empirical relationships. The dimethyl ether formation rate decreases and, accordingly, the rate of methyl chloride formation increases with a decreasing methanol concentration and an increasing hydrogen chloride concentration.

We attempted to describe the experimental dimethyl ether evolution rate data as a function of the methanol concentration and of the partial pressure of hydrogen chloride over hydrochloric acid in terms of the different equations

$$w_{1} = k_{1}C_{CH_{3}OH}P_{HCI}^{-1},$$

$$w_{2} = k_{2}C_{CH_{3}OH}^{2}P_{HCI}^{-1},$$

$$w_{3} = k_{3}C_{CH_{3}OH}^{2}P_{HCI}^{-2},$$

$$w_{4} = k_{4}C_{CH_{3}OH}P_{HCI}^{-2}.$$

It turned out that these data are best described by the first equation (maximum deviations of $\pm 40\%$):

$$w_{(CH_3)_2O} = k_{(CH_3)_2O}C_{CH_3OH}P_{HCI}^{-1}$$

The activation energy of dimethyl ether formation is 8 kcal/mol (33 kJ/mol), and the preexponential factor is 2.3 atm/h. Thus, the equation for calculation of $w_{(CH_3)_2O}$ has the following form:

$$w_{(CH_3)_{2O}} = 2.3 \exp\left(-\frac{33000}{RT}\right) C_{CH_3OH} P_{HCl}^{-1} \text{ mol } 1^{-1} \text{h}^{-1}.$$

From the data obtained, we infer that an increase in the rate of methyl chloride synthesis is favored to the greatest extent by an increase in the hydrochloric acid concentration. An increase in pressure also accelerates the process by raising the acid concentration at a fixed temperature. The reaction temperature also exerts a significant effect on the reaction rate. Our experimental results make it possible to perform necessary calculations for designing an industrial synthesis unit.

INDUSTRIAL IMPLEMENTATION OF THE PROCESS

A scheme of the industrial setup for methyl chloride synthesis from methanol and hydrochloric acid with a production capacity of about 4000 t/yr is presented in the figure. Concentrated hydrochloric acid and methanol are fed to the first reactor stage I_1 , from which they flow via an overflow pipe to the second stage I_2 . The reacted mixture is directed to column 3, where unreacted methanol and HCl are stripped off and are then directed to condenser 2. The reaction gas from reactors I_1 and I_2 comes to condenser 2 as well. The hydrochloric acid condensed in condenser I_2 with dissolved methanol returns to reactor I_1 . For preparation of a commercial-grade product, methyl chloride is subjected to neutralization, drying, and purification. The hydrochloric acid azeotrope in apparatus 4 is

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Industrial plant for methyl chloride synthesis from methanol and hydrochloric acid: (I_1, I_2) first and second stages of the methanol hydrochlorination reactor; (2) condenser, (3) methanol stripping column, and (4) apparatus for hydrochloric acid strengthening.

strengthened with hydrogen chloride from the reaction gas of the methane chlorination process. To remove water resulting from methanol hydrochlorination, a portion of the acid in the form of an azeotrope or concentrated acid is taken out of the system as a commercial-grade product.

Methanol was hydrochlorinated in the existing reactors at a pressure of up to 70 kPa and a temperature of $105 \pm 3^{\circ}$ C at the top of the reactor.

A comparison between the actually achieved performance parameters of the methyl chloride synthesis unit and the desired performance characteristics of this unit is presented in Table 2.

According to our experimental data, even a slight change in the hydrochloric acid concentration exerts a considerable effect on the methanol hydrochlorination rate. For this reason, an increase in the concentration of the initial hydrochloric acid by 1.3% (the calculated concentration is 28%, and the actual value is 29.3%) increases the partial pressure of HCl and the process rate by 40%. As a result, the methanol conversion increases from 59.9–50.8% to 79.9–70.5%.

Parameter	Desired	Actual
Initial acid concentration, %	28	29.3
Acid concentration in the reactor, %		
1st stage	22.2	22.8
2nd stage	19.9	22.7
Methanol concentration in the reactor, %		
1st stage	0.97	1.15
2nd stage	0.5	0.33
Conversion of methanol, %		
1st stage	59.9	79.9
2nd stage	50.8	70.5
Conversion of methanol with its recycle taken into account, % 98.5		
Selectivity of formation of methyl chloride from reacted methanol, $\%$	99.86	99.91

Table 2. Comparison between the desired and actual performance parameters of the industrial unit for methanol hydrochlorination with hydrochloric acid

An increase in the hydrochloric acid concentration is accompanied by a decrease in the yield of dimethyl ether; i.e., the methyl chloride selectivity increases (from 99.86 to 99.91%).

Thus, we have investigated the kinetics of the liquid-phase noncatalytic hydrochlorination of methanol in hydrochloric acid. The kinetic parameters of the equations describing the rate of methyl chloride formation (main reaction) and the rate of dimethyl ether isolation (side process) were determined. The results of the laboratory studies were used to design an industrial unit for methyl chloride production by the liquidphase noncatalytic hydrochlorination of methanol with hydrochloric acid. The results obtained with the industrial unit agree satisfactorily with the laboratory data.

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