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THE REACTION OF METHYL CHLORIDE WITH CARBON MONOXIDE

BY JIRO OSUGI AND TETUO MIZUKAMI*

The reaction of methyl chloride with carbon monoxide in the presence of pumice-anhydrous sodium borate catalyst yields mainly hydrogen chloride, methane, acetyl chloride and phosgene, and deposits carbon. Moreover, hydrogen, methylene chloride, ethyl chloride and ethylene dichloride are obtained in a trace.

From the stand point of chemical kinetics the reaction is studied. From the initial rates of the products, the values of 18.1, 18.5, 28.2 and 27.0 kcal/mole are obtained as the apparent activation energies for the formation of acetyl chloride, phosgene, hydrogen chloride and methane respectively. Furthermore, the rates of formation of acetyl chloride and phosgene are discussed. From the apparent rate constants, the apparent activation energies are obtained. The values are 19.0 kcal/mole for acetyl chloride and 17.6 kcal/mole for phosgene.

The reaction mechanism is discussed.

Introduction

Since a few years ago, carbon monoxide has been considered as one of the important materials for organic chemical industry, so there are some utilizations, such as synthetic petroleum, Reppe's carboxylation reaction and oxo reaction etc. Particularly oxo reaction has been a unit process for chemical industry.

In these days, carbon monoxide is supplied abundantly from natural gas, by-product of petrochemicals and recovered gas of steel works etc. Then it is necessary and also interesting to study the reaction of carbon monoxide.

As for the reaction of carbon monoxide with alkyl halides, propionic chloride was obtained by the reaction between ethyl chloride and carbon monoxide[1] and chloroacetyl halides were prepared by the reaction of carbon monoxide with polyhalogenated methane[2].

Concerning the reaction of methyl chloride with carbon monoxide, there has been presented some patents, since it has been reported by I. G. that these materials produced acetyl chloride[3]. However there are no reports in which this reaction has been discussed in detail.

This paper reports the results obtained from the reaction of methyl chloride with carbon monoxide in the presence of pumice-anhydrous sodium borate catalyst.

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Experimentals and Results

Materials

Methyl chloride: Methyl chloride commercially offered is used. Purity over 99.8%.

Carbon monoxide: Carbon monoxide is produced by the decomposition of formic acid with conc. sulfuric acid and before use washed with 50% potassium hydroxide solution and dried thoroughly. Purity over 99.5%.

Catalyst: $1\,mm^2 \sim 2\,mm^2$ pumice is immersed in the aqueous solution of sodium borate, removed water, dried at 180°C for 3 hrs. and finally treated at 500°C for 6 hrs. The mixture of pumice and anhydrous sodium borate, the weight ratio 2:1, is used as catalyst.

Apparatus

The schematic layout of the apparatus is shown in Fig. 1. In order to dry carbon monoxide thoroughly, the storage B of carbon monoxide is filled up with dried silica gel and the mixing vessel C of reactants is 18-8 stainless steel autoclave 50 mm in inner diameter, 70 mm in outer diameter, and 1 m in length.

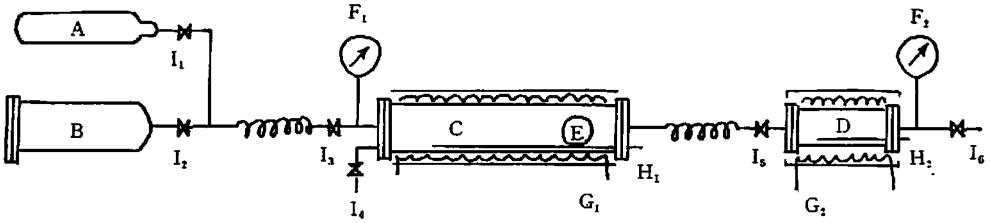

Fig. 1 Schematic layout of apparatus

A: methyl chloride bomb
B: storage of carbon monoxide, also used dryer
C: mixing vessel of reactants
D: reaction vessel
E: ball of porcelain

F_1 F_2: pressure gauge
G_1 G_2: electric heater
H_1 H_2: thermocouple
$I_1 \sim I_6$: high pressure valves

Using the pipe of 1 mm in inner diameter. 6 mm in outer diameter, this mixing vessel is spirally piped at both ends to the reaction vessel D and the reactant storages A, B, and placed a porcelain ball E in the vessel in order to stir and mix thoroughly the reactants.

The reaction vessel D is 18-8 stainless steel autoclave, 40 mm in inner diameter, 76 mm in outer diameter, 140 mm in length.

Operation

The mixing vessel C being evacuated, methyl chloride and carbon monoxide are introduced into the vessel from the methyl chloride bomb A and the carbon monoxide storage B. The mixed reactants are heated at 200°C~250°C over the critical temperature of methyl chloride and determined its mole ratio.

The reaction vessel D is filled up with the catalyst, and heated electrically to a required temperature. Into the evacuated reaction vessel the mixed gas of reactants is introduced from the mixing vessel to a required pressure. The operation is done as rapidly as possible, so it requires less than 15 sec.

The reaction temperature is controlled electrically within ±1°C.

The reaction products are sampled from the reaction vessel as rapidly as possible, less than 25 sec.

Reaction products

The main products are hydrogen chloride, methane, acetyl chloride and phosgene, the other trace products are hydrogen, methylene chloride, ethyl chloride and ethylene dichloride, and carbon is deposited in considerable amount.

Analysis

Gas chromatography is used for analysis of methyl chloride, carbon monoxide, methane, phosgene. hydrogen, methylene chloride, ethyl chloride and ethylene dichloride. The gas-chromatographic columns used are silica gel, activated charcoal, dioctylphthalate, tricresylphosphate and molecular sieve 5A etc.

In the products, acetyl chloride and hydrogen chloride gas are absorbed in water and the mixed aqueous solution of hydrochloric acid and acetic acid is analysed quantitatively by the method of conductometric titration.

Methylene chloride, ethyl chloride, and ethylene dichloride are trapped by a dry ice-alcohol bath, and identified by gas chromatography using tricresylphosphate column. For example, under the conditions of reaction time 90 minutes, temperature 400°C and pressure 100 kg/cm^2, the yields of methylene chloride, ethyl chloride and ethylene dichloride are 0.01%, 0.016%, 0.002% per reactant methyl chloride respectively.

Table 1 Pressure effect

Experimental condition: reaction temperature 400°C, reaction time 60 min., CO/CH_3Cl mole ratio 2.40

Reaction pressure (kg/cm^2)	Reactants (mole)		Recovered reactants (mole)		Products yield (mole %)※1			
	CH_3Cl	CO	CH_3Cl	CO	CH_4	$COCl_2$	HCl	CH_3COCl
50	0.0292	0.0702	0.0173	0.0679	25.7	3.3	32.6	1.27
100	0.0584	0.1404	0.0322	0.1356	25.6	4.0	30.6	2.10
150	0.0876	0.2106	0.0493	0.2038	24.8	4.4	31.0	2.23
200	0.1168	0.2808	0.0677	0.2700	24.0	4.8	29.0	2.36
250	0.1460	0.3510	0.1100	0.3382	24.5	5.3	30.1	2.44

※1 mole % is represented by each product per reactant, methyl chloride.

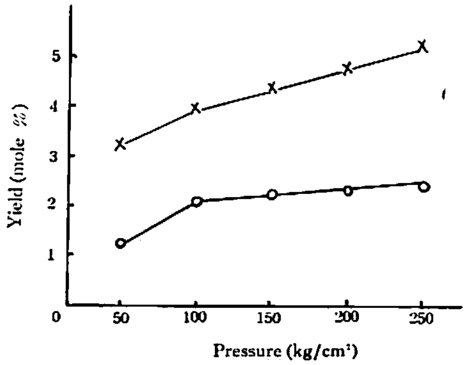

Fig. 2 Effect of pressure on the yields of acetyl chloride (○) and phosgene (×)

Pressure effect

The pressure effect is shown in Fig. 2 and Table 1. Rising pressure, the yields of acetyl chloride and phosgene are increased, but the increase of acetyl chloride is lowered over 100 kg/cm². On the other hand, it seems that the yields of methane and hydrogen chloride are somewhat decreased with rising pressure.

So, the following experiments are performed at the pressure of 100 kg/cm².

Effect of reaction time, temperature and CO/CH_3Cl mole ratio

The experiments are performed at the following conditions.

Experimental conditions

Reaction pressure:	100 kg/cm² constant
Reaction temperature:	340, 370, 400, 430°C
Reaction time:	5, 10, 20, 30, 60, 90 minutes
CO/CH_3Cl mole ratio:	5 plots in the range of 0.4~12.8

(At 400°C, the decomposition of pure methyl chloride is tried in the presence of the same catalyst.)

The tables for the yields of products at each experiment are omitted here, but the material balances of carbon monoxide, hydrogen and chlorine are always over 90% at each experiments, so it is considered that the deposit of carbon is found by the decomposition of methyl chloride.

On the other hand, the yield of hydrogen is constant at the same reaction temperature, namely the yields are 0.1% at 370°C, 0.2% at 400°C, 0.3% at 430°C.

Some typical examples of the effects of the reaction temperature and CO/CH_3Cl mole ratio are shown in Fig. 3.

(a) It is shown in Figs. 3-1 and 3-2 that the yield of acetyl chloride is remarkably enhanced at the

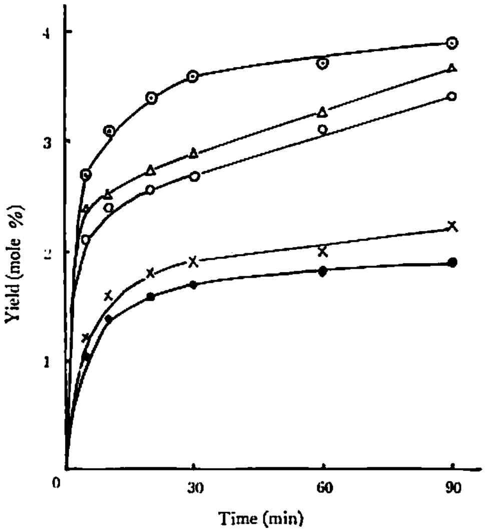

Fig. 3-1 Yield-time curves for acetyl chloride at constant temperature (430°C) and various CO/CH_3Cl mole ratio: 6 (◎), 3 (△), 2 (○), 0.9 (×), 0.4 (●).

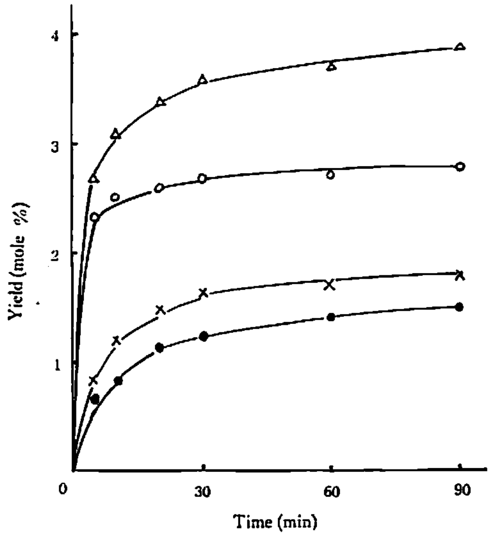

Fig. 3-2 Yield-time curves for acetyl chloride at constant CO/CH_3Cl mole ratio (6) and various temperature 430°C (△), 400°C (○), 370°C (×), 340°C (●).

initial period of the reaction and increased with rising reaction temperature and CO/CH_3Cl mole ratio.

(b) As shown in Figs. 3–3 and 3–4, the yield of phosgene is also increased with rising temperature and CO/CH_3Cl mole ratio.

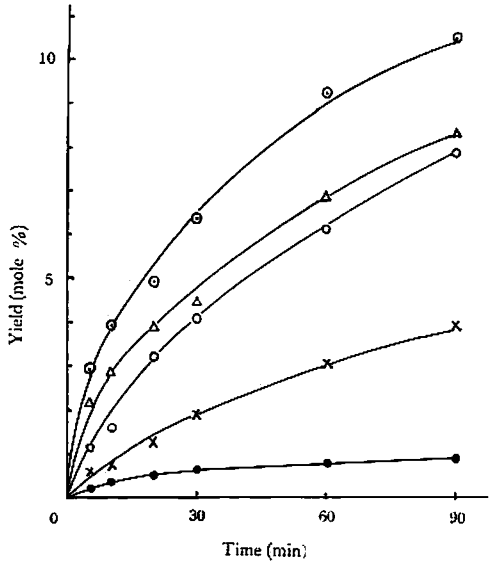

Fig. 3–3 Yield-time curves for phosgene at constant temperature (430°C) and various CO/CH_3Cl mole ratio 6 (⊙), 3 (△), 2 (○), 0.9 (×) 0.4 (●).

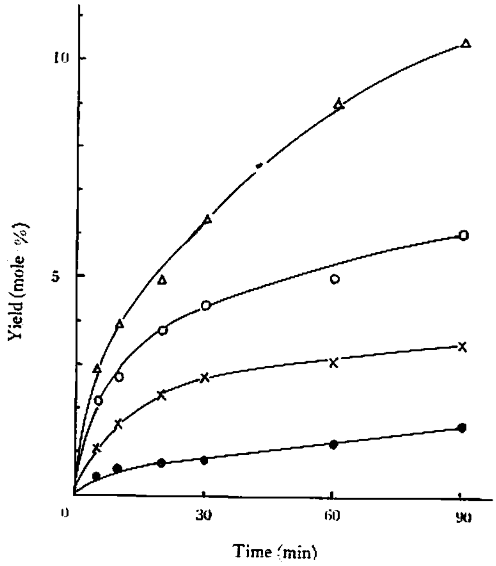

Fig. 3–4 Yield-time curves for phosgene at constant CO/CH_3Cl mole ratio (6) and various temperature 430°C (△), 400°C (○), 370°C (×), 340°C (●).

(c) As shown in Fig. 3–5, the effect of CO/CH_3Cl mole ratio for hydrogen chloride yield is negligible, so hydrogen chloride is produced constantly at the same reaction temperature and there is no relation between the yield of hydrogen chloride and carbon monoxide concentrations.

(d) On the contrary, the yield of methane is affected by the CO/CH_3Cl mole ratio as shown in Fig. 3–6. This suggests that methane is produced in the process of phosgene production and of methyl chloride decomposition. So it is shown in Fig. 3–7 that the temperature effect for methane yield at fixed CO/CH_3Cl mole ratio of 0.4.

(e) The material balance of this reaction is shown in Fig. 3–8 at the reaction condition: temperature 430°C, pressure 100 kg/cm^3, CO/CH_3Cl mole ratio 6. It is shown that the balances of carbon monoxide, hydrogen and chlorine are maintained.

Consideration

The initial rates

The reaction of methyl chloride with carbon monoxide in the presence of pumice-anhydrous sodium borate catalyst produces acetyl chloride and phosgene, and concurrently hydrogen chloride and methane

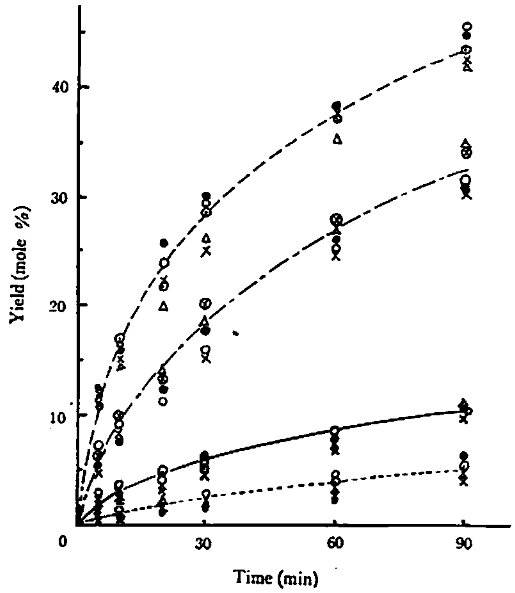

Fig. 3–5 Yield-time curves for hydrogen chloride at various temperature 430°C (- - -), 400°C (- - -), 370°C (——), 340°C (······), and various CO/CH_3Cl mole ratio 6 (◎), 3 (△), 2 (○), 0.9 (×), 0.4 (●), 0 (⊗).

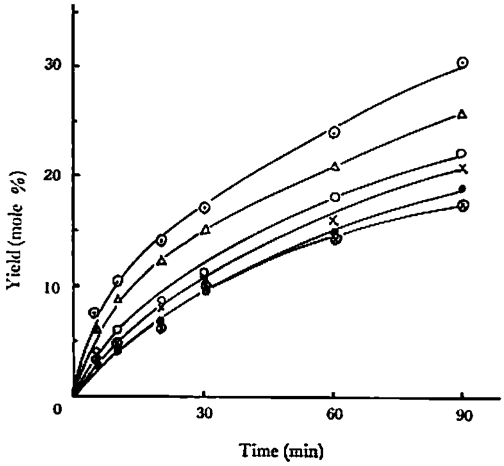

Fig. 3–6 Yield-time curves for methane at constant temperature (400°C) and various CO/CH_3Cl mole ratio 12.8 (◎), 6 (△), 2.5 (○), 1 (×), 0.5 (●), 0 (⊗).

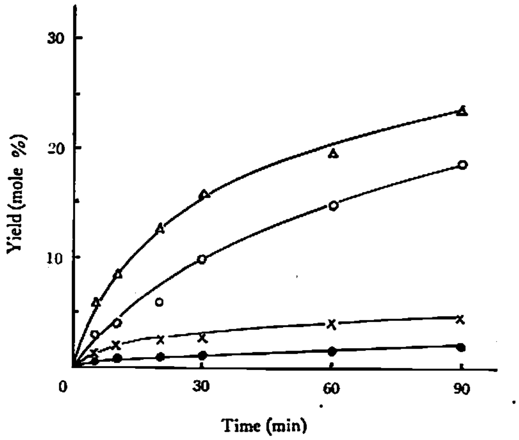

Fig. 3–7 Yield-time curves for methane at constant CO/CH_3Cl mole ratio (0.4) and various temperature 430°C (△), 400°C (○), 370°C (×), 340°C (●).

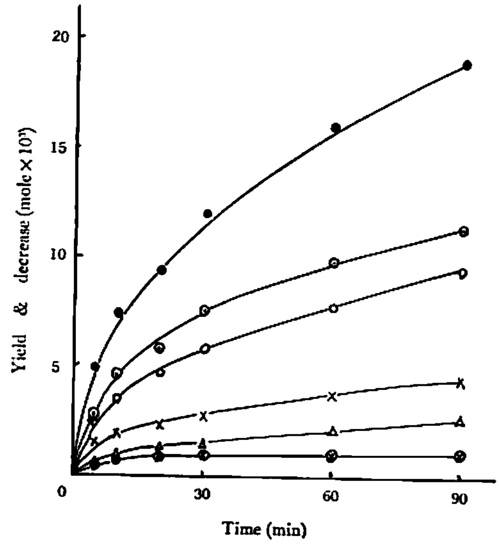

Fig. 3–8 Yield-time curves for hydrogen chloride (◎), methane (○) and acetyl chloride, and decrease-time curves for carbon monoxide (×) and methyl chloride (●) at constant temperature (430°C) and CO/CH_3Cl mole ratio (6).

are produced by the decomposition of methyl chloride. The initial rates of the main products are determined.

Apparent activation energy The apparent activation energy is obtained from the slope of the

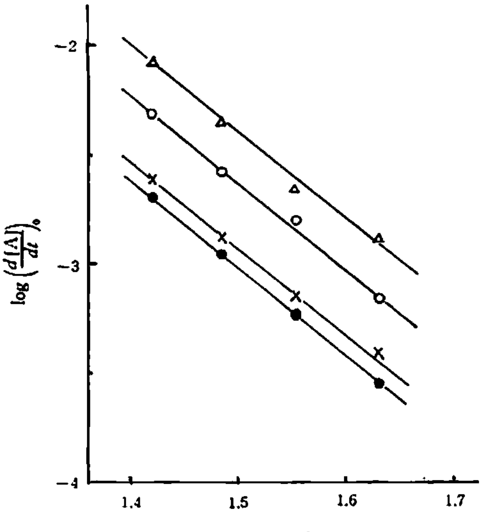

Fig. 4-1 Effect of temperature on the initial rate of acetyl chloride formed at various CO/CH_3Cl mole ratio 6 (△), 3 (○), 0.9 (×), 0.4 (●).

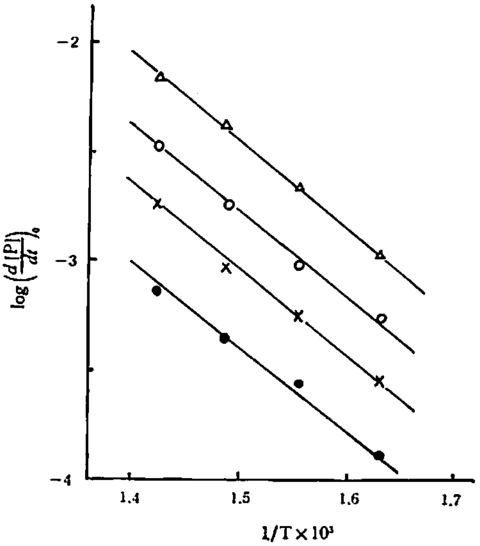

Fig. 4-2 Effect of temperature on the initial rate of phosgene formed at various CO/CH_3Cl mole ratio 6 (△), 3 (○), 0.9 (×), 0.4 (●).

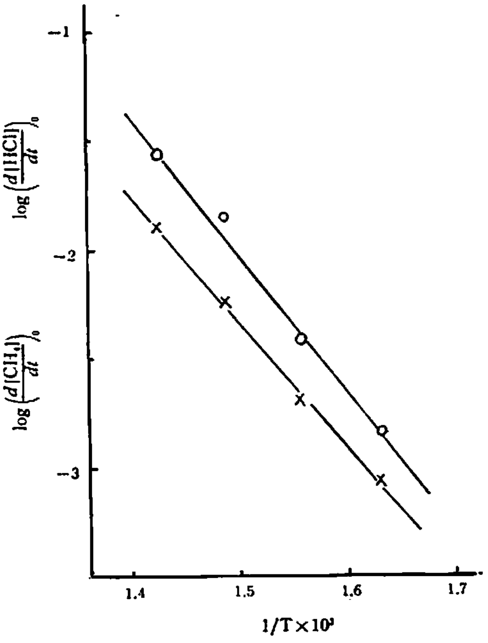

Fig. 4-3 Effect of temperature on the initial rates of methane (×), and hydrogen chloride (○) formed.

plots of the logarithm of the initial rate against the reciprocal of absolute temperature as shown in Figs. 4–1, 4–2 and 4–3. The obtained values are 18.1 kcal/mole for acetyl chloride, 18.5 kcal/mole for phosgene, 28.2 kcal/mole for hydrogen chloride and 27.0 kcal/mole for methane.

Effect of CO/CH$_3$Cl mole ratio Plotting the logarithm of the initial rates of acetyl chloride and phosgene against the logarithm of CO/CH$_3$Cl mole ratio, the linear relations are obtained respectively as shown in Figs. 5–1 and 5–2. From these slopes, the initial rate of acetyl chloride formed is proportional to the CO/CH$_3$Cl mole ratio to the power of 0.6, and phosgene to the mole ratio to the power of 0.77.

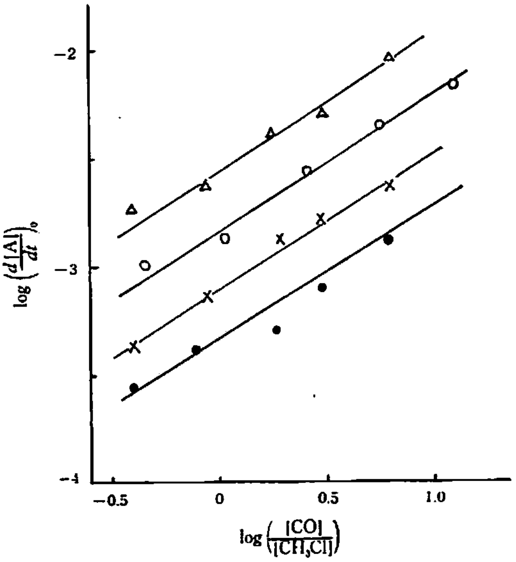

Fig. 5–1 Effect of CO/CH$_3$Cl mole ratio on the initial rate of acetyl chloride formed at various temperature 430°C (△), 400°C (○), 370°C (×), 340°C (●).

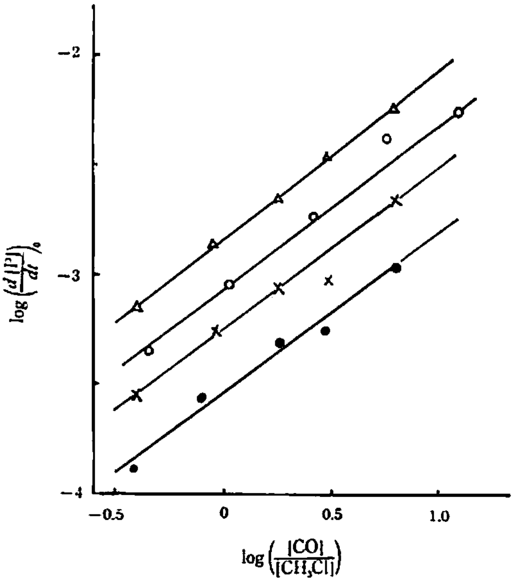

Fig. 5–2 Effect of CO/CH$_3$Cl mole ratio on the initial rate of phosgene formed at various temperature 430°C (△), 400°C (○), 370°C (×), 340°C (●).

Rate equation

As shown in Table 2, the reaction of methyl chloride with carbon monoxide in the presence of pumice yields phosgene but not acetyl chloride. It is considered that the two reactions of the producing acetyl chloride and phosgene are treated separately in the rate equation.

Table 2 Effect of pumice※2

Experimental condition: reaction temperature 400°C, reaction pressure 100 Kg/cm^2, reaction time 60 min., CO/CH$_3$Cl mole ratio 2.40

Reactants (mole)		Recovered reactants (mole)		Yield of products (mole %)			
CH$_3$Cl	CO	CH$_3$Cl	CO	CH$_4$	COCl$_2$	HCl	CH$_3$COCl
0.0395	0.0950	0.0327	0.0947	11.0	3.6	13.8	—

※2 See Table 1 for the effect of pumice-anhydrous sodium borate.

Rate equation for acetyl chloride formation The rate of the acetyl chloride formed is assumed to be the following equation where (A), (CO) and (Me) are concentrations of acetyl chloride, carbon monoxide and methyl chloride respectively. In equation (1), acetyl chloride concentration is affected by carbon monoxide and methyl chloride absorbed on the catalyst, where θ_{Me} represents the fraction of methyl chloride absorbed on the catalyst, and is assumed to be constant in the course of reaction. On the other hand, θ_{CO} represents the fraction of carbon monoxide absorbed on the active point of the catalyst for the reaction with methyl chloride. Therefore, if either carbon monoxide or acetyl chloride formed absorbs on the active point of the catalyst, θ_{CO} is expressed by equation (2), where β, β' and β'' are absorption coefficients of carbon monoxide, acetyl chloride and methyl chloride respectively. Hence, equation (1) can be rewritten as equation (3), when equation (3) is integrated, taking the intial concentration of carbon monoxide to be a, x_A concentration of acetyl chloride formed and t reaction time, equation (3) becomes equation (4). Assuming equations (6) and (7), k_{aA} is linear against v_A as shown in equation (5). As shown in Fig. 6–1, the linear relations always hold fairly good. The relation of equation (5) is satisfied. The above consideration and assumption are valid.

$$\frac{d(\mathrm{A})}{dt}=k_A\theta_{Me}\theta_{CO} \qquad (1)$$

$$k_A\theta_{Me}=k_A'$$

$$\theta_{CO}=\frac{\beta(\mathrm{CO})}{\beta(\mathrm{CO})+\beta'(\mathrm{A})+\beta''(\mathrm{Me})}=\frac{\beta(\mathrm{CO})}{\beta(\mathrm{CO})+\beta'(\mathrm{A})+\mathrm{C}} \qquad (2)$$

$$\beta''(\mathrm{Me})=\mathrm{C}$$

$$\frac{d(\mathrm{A})}{dt}=\frac{k_A'\beta(\mathrm{CO})}{\beta(\mathrm{CO})+\beta'(\mathrm{A})+\mathrm{C}} \qquad (3)$$

$$\frac{a\beta'+\mathrm{C}}{\beta'-\beta}\cdot\frac{1}{t}\ln\frac{a}{a-x_A}=\frac{\beta k_A'}{\beta'-\beta}+\frac{x_A}{t} \qquad (4)$$

$$k_{aA}=n_Av_A+m_A \qquad (5)$$

$$\begin{cases} k_{aA}=\dfrac{1}{t}\ln\dfrac{a}{a-x_A} & (6)\\[2ex] v_A=\dfrac{x_A}{t} & (7)\end{cases}$$

$$\begin{cases} m_A=\dfrac{k_A'\beta}{a\beta'+\mathrm{C}} & (8)\\[2ex] n_A=\dfrac{\beta'-\beta}{a\beta'+\mathrm{C}} & (9)\end{cases}$$

Rate equation for phosgene formation It is suggested from the experimental fact in the formation of phosgene that the same rate equation as adopted to acetyl chloride is applicable to the rate of formation of phosgene. Using the same consideration for the formation of acetyl chloride in equation (3), equation (10) is used for phosgene, and equation (11) is obtained by the integration of equation (10).

$$\frac{d(\mathrm{P})}{dt}=\frac{k_P'l(\mathrm{CO})}{l(\mathrm{CO})+l'(\mathrm{P})+\mathrm{M}} \qquad (10)$$

$$\frac{al'+\mathrm{M}}{l'-l}\cdot\frac{1}{t}\ln\frac{a}{a-x_P}=\frac{lk'_P}{l'-l}+\frac{x_P}{t} \qquad (11)$$

$$k_{aP} = n_P v_P + m_P \tag{12}$$

$$\left\{\begin{aligned} k_{aP} &= \frac{1}{t}\ln\frac{a}{a - x_P} && (13)\\ v_P &= \frac{t}{x_P} && (14) \end{aligned}\right.$$

$$\left\{\begin{aligned} m_P &= \frac{lk_P'}{al' + M} && (15)\\ n_P &= \frac{l' - l}{al' + M} && (16) \end{aligned}\right.$$

where (P) and x_P represent the concentration and yield of phosgene and M is constant as C in equation (3), and a and t is the same as in equation (4). Substituting k_a and v_P defined by equation (13) and (14), and plotting k_{aP} against v_P, the linear relations are obtained as shown in Fig. 6-2. It is proved that equations (10) and (11) are valid.

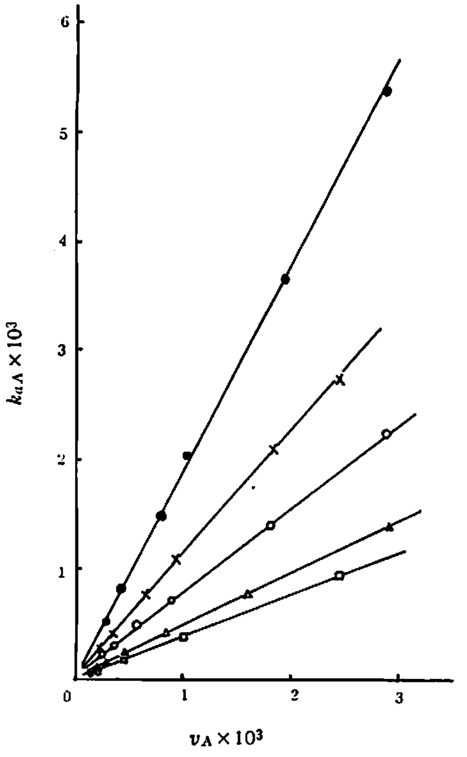

Fig. 6-1 Relations between k_{aA} and v_A at constant temperature (430°C) and various CO/CH_3Cl mole ratio. 6 (□), 3 (△), 2 (○), 0.9 (×), 0.4 (●).

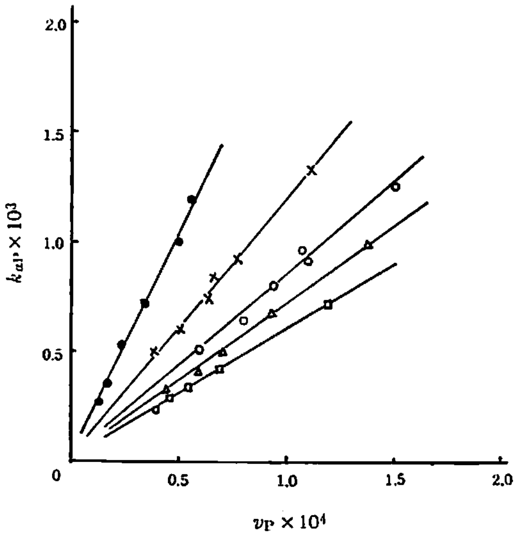

Fig. 6-2 Relations between k_{aP} and v_P at constant temperature (430°C) and various CO/CH_3Cl mole ratio. 6 (□), 3 (△), 2 (○), 0.9 (×), 0.4 (●).

Apparent activation energy Plotting k_a against v at the reaction temperatures 400°C, 370°C and 340°C for the formations of acetyl chloride and phosgene, m_A and m_P are estimated graphically. Then the apparent activation energy for acetyl chloride is obtained from the slope of logarithm of m_A against the reciprocal of the absolute temperature, as shown in Fig. 7. For phosgene, it is obtained in the same way from Fig. 7. The values of the apparent activation energies are 19.0 kcal/mole for acetyl chloride and 17.6 kcal/mole for phosgene. Those values are in good agreement with the values obtained from the initial rates, 18.1 kcal/mole for acetyl chloride and 18.5 kcal/mole for phosgene.

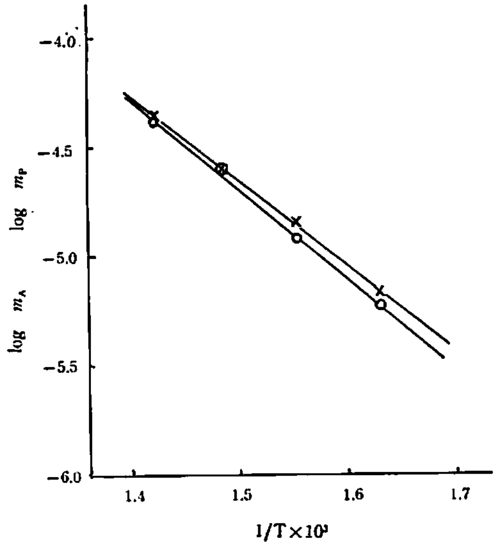

Fig. 7 Effect of temperature on the apparent rate constants of acetyl chloride (○), and phosgene (×), formed.

Reaction mechanism

The mechanism of the reaction of methyl chloride with carbon monoxide in the presence of pumice-anhydrous sodium borate catalyst is assumed as follows.

$$CH_3Cl \longrightarrow CH_3\cdot + Cl\cdot \qquad (\mathrm{I})$$

$$CO + Cl\cdot \longrightarrow COCl\cdot \qquad (\mathrm{II})$$

$$COCl\cdot + CH_3Cl \longrightarrow CH_3COCl + Cl\cdot \qquad (\mathrm{III})$$

$$\longrightarrow COCl_2 + CH_3\cdot \qquad (\mathrm{IV})$$

$$CH_3\cdot + CH_3Cl \longrightarrow CH_4 + CH_2Cl\cdot \qquad (\mathrm{V})$$

$$Cl\cdot + CH_3Cl \longrightarrow HCl + CH_2Cl\cdot \qquad (\mathrm{VI})$$

$$CH_3\cdot + HCl \longrightarrow CH_4 + Cl\cdot \qquad (\mathrm{VII})$$

$$CH_2Cl\cdot + CH_3Cl \longrightarrow CH_2Cl_2 + CH_3\cdot \qquad (\mathrm{VIII})$$

$$\longrightarrow C_2H_5Cl + Cl\cdot \qquad (\mathrm{IX})$$

$$2CH_2Cl\cdot \longrightarrow C_2H_4Cl_2 \qquad (\mathrm{X})$$

$$H\cdot + CH_3Cl \longrightarrow H_2 + CH_2Cl\cdot \qquad (\mathrm{XI})$$

This reaction is initiated by the methyl radical and chlorine atom formed by the decomposition of methyl chloride. Considering the fact that no trace of acetone is formed but phosgene is found in the products, the formation of acetyl radical can not be recognized. Therefore, it should be appropriate that the both acetyl chloride and phosgene are formed by the reaction of monochlorocarbonyl radical which is formed by reaction (II) with methyl chloride as shown in reactions (III) and (IV). In this connection, the activation energy of reaction (I) has been reported as 9.8 kcal/mele, and that of reaction (II) is the order of a few kcal per mole.

Detecting ethylene dichloride in the reaction products, it is suggested that monochloromethylene radical is formed by the reaction between methyl radical and methyl chloride and in this reaction methane is also prepared as shown in reaction (V). Chlorine atom reacts with methyl chloride as shown in reaction (VI), to yield monochloromethylene radical and hydrogen chloride.

However, comparing reactions (V) with (VI), it seems that reaction (VI) occurred more easily than reaction (V), from the view point of the activation energies. That is, the activation energy of reaction (V) is 9.4 kcal/mole and that of reaction (VI) is 3.4 kcal/mole. So, it is considered that the formation of methane is performed by reaction (VII). The activation energy of reaction (VII) is 2 kcal/mole.

Methylene chloride, ethyl chloride and ethylene dichloride are detected and they must be formed by the reaction of monochloromethylene radical as shown in reactions (VIII), (IX) and (X), but those yields are trace.

From the material balance, the formations of acetyl chloride and phosgene and the decomposition of methyl chloride are expressed stoichiometrically in the following reactions.

$$CH_3Cl + CO \longrightarrow CH_3COCl$$

$$2CH_3Cl \longrightarrow 2HCl + CH_4 + C$$

$$4CH_3Cl + 2CO \longrightarrow 2COCl_2 + 3CH_4 + C$$

Namely, the formation of hydrogen chloride is not affected by carbon monoxide, on the other hand, the formation of methane is affected by carbon monoxide as shown in Figs. 3–5 and 3–6. Therefore the yield of methane is the sum of one-half of hydrogen chloride yield and three-halves of phosgene yield. These relations are confirmed with the experimental data, for example, as shown in Fig. 3–8.

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Laboratory of Physical Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan