# Reaction of Chlorohydrocarbons. VI.
# Co-pyrolysis of Chloroethanes and Methanol on Activated Alumina

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Co-pyrolysis of chloroethanes and methanol on activated alumina was carried out in order to elucidate the reaction mechanism. The reaction rate was of first order in chloroethanes in the presence of excess methanol. A linear free energy relationship was found to exist between the reactivities of chloroethanes (at 230 °C) and Taft's $\sigma^*$ constants. $\rho^*$ values for reactions of $RCH_3$, $RCH_2Cl$ and $RCHCl_2$ series were 0.24, 0.45 and 0.70, respectively. It could be assumed that a $\beta$-hydrogen of chloroethanes was abstracted by the nucleophilic attack of methanol, chlorine being removed at the same time. *E*2 reaction seems to dominate in co-pyrolysis of chloroethanes and methanol on activated alumina.

Chloroethylenes and methyl chloride are formed by co-pyrolysis of 1,1,2-trichloroethane and methanol on activated alumina.[1] Andrussow and Edler[2] reported that in the co-pyrolysis of 1,1,2,2-tetrachloroethane and methanol on activated alumina the reaction proceeds according to the following equation.

$$CHCl_2CHCl_2 + CH_3OH \rightarrow CHCl{:}CCl_2 + CH_3Cl + H_2O$$

Dehydrochlorination of 1,1,2-trichloroethane at high temperature is unfavorable for the formation of 1,1-dichloroethylene.[3] Elimination of hydrogen chloride from 1,1,2-trichloroethane on solid acids such as activated alumina, has a poor selectivity for 1,1-dichloroethylene.[4,5] In contrast, the 1,1/1,2 ratio in co-pyrolysis of 1,1,2-trichloroethane and methanol amounted to several times as high as that of ordinary pyrolysis.[1] Another merit of the reaction is that the dehydrochlorination of chloroethanes can proceed at a lower temperature.

The present investigation was undertaken to study co-pyrolysis of several different chloroethanes and methanol on activated alumina with a conventional flow type reactor. The relation between the molecular structure and the rate of the dehydrochlorination is discussed.

## Experimental

*Reagents.* 1,1-Dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane (Wako Pure Chemicals Co.) were of reagent grade and were used without further purification. 1,1,1-Trichloroethane was washed several times with water, and then dried with calcium chloride and fractionated. Pentachloroethane and 1,1,1,2-tetrachloroethane were prepared by the chlorination of trichloroethylene and 1,1,1-trichloroethane in the presence of ferric chloride as a catalyst, washed with aqueous sodium carbonate solution and then with water, and fractionally distilled; bp 161.5 °C for pentachloroethane and 129—130 °C for 1,1,1,2-tetrachloroethane.

*Catalyst.* 0.4 cm pellets of activated alumina (KH-A24, Sumitomo Chemical Co.) with surface area 200 $m^2/g$ and 0.2% $Na_2O$ content were used.

*Apparatus.* A flow type reaction system was used. A Pyrex reaction vessel, tube of length *ca.* 30 cm and diameter 2.6 cm was heated in a vertical electric furnace. The evaporator, a glass tube, was placed in an electrically wound vertical furnace. The reaction temperature was measured with a Chromel-Alumel thermocouple in a thermowell placed in the catalyst bed.

*Procedure.* 20 g of catalyst was placed in the middle of the reactor, the bed being supported by necking the reactor tube. The catalyst was heated in the air at 350 °C for 3 to 5 hr. While the reaction temperature was regulated, nitrogen gas was passed over the catalyst. A mixture of chloroethanes and methanol was then fed into the evaporator with a microfeeder and preheated to 200°C, the vapor being passed to the reactor. The time factor ($W/F$: g·hr/g-mol) was varied by adjusting the feed rate of each chlorinated ethane ($F$: g-mol/hr), the weight of the catalyst ($W$ : g) being kept constant. The product gas stream entered a cooler and condensed in a water-ice trap. Organic products were separated from the water with a separating funnel.

Gas-chromatographic analyses were performed with a GC-5 type apparatus from Shimadzu Seisakusho. The column was Silicone DC 550 on Celite.

## Results

Co-pyrolysis of chloroethanes and methanol on activated alumina proceeded as follows.

$$C_2H_{6-n}Cl_n + CH_3OH \rightarrow C_2H_{5-n}Cl_{n-1} + CH_3Cl + H_2O$$

The side reaction products were dimethyl ether and a dechlorinated product. Dimethyl ether was formed by the dehydration of methanol on the surface of activated alumina. The dechlorinated product was formed by the pyrolysis of higher chlorinated derivatives such as 1,1,1,2-tetrachloroethane and pentachloroethane. Hydrogen chloride was formed in a trace amount. Dimethyl ether and methyl chloride were not determined. In all runs, two chloroethanes were competitively pyrolyzed in order to check the balance of the volatile products such as vinyl chloride.

1,1-Dichloroethane and 1,1,1,2-tetrachloroethane were mixed with methanol at the mole ratio 0.107 : 0.142 : 1.00. $W/F$ values were 305 and 403 for 1,1-dichloroethane and 1,1,1,2-tetrachloroethane, respectively. All other experiments were carried out with the chloroethanes to methanol mole ratio 0.5 : 0.5 : 3.0.

The design equation[6] for a catalytic flow reactor can be written as

$$W/F = \int_0^x dx/r \tag{1}$$

The reaction rate r is of first order in each chloroethane. r is a function of conversion since the concentration of chlorinated ethane varies with conversion.

The final equation[7] is

$$\frac{W}{F} = \frac{2.303}{k} \times \log \frac{n_0}{n_0 - x} \tag{2}$$

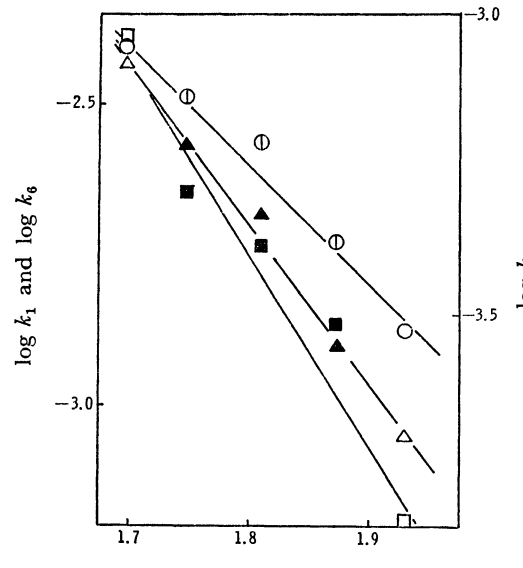


Fig. 1. Arrhenius plots for competitive pyrolysis of $CH_3CHCl_2$ and $CH_2ClCCl_3$.
*W*/*F*: 294, 305, 403 g·hr/g-mol

○, ⦶, —: $CH_3CHCl_2 \xrightarrow{k_1} CH_2:CHCl$
△, —, ▲: $CH_2ClCCl_3 \xrightarrow{k_6} CHCl:CCl_2$
□, —, ■: $CH_2ClCCl_3 \xrightarrow{k_7} CH_2:CCl_2$

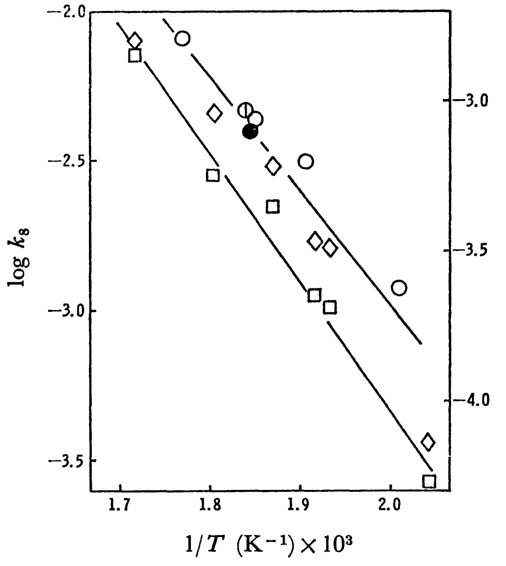


Fig. 2. Arrhenius plots for competitive pyrolysis of $CH_2ClCH_2Cl$ and $CHCl_2CHCl_2$.
*W*/*F*: 147, 294, 588 g·hr/g-mol

—, □, —: $CH_2ClCH_2Cl \xrightarrow{k_2} CH_2:CHCl$
(⦶), ◇(○), (●): $CHCl_2CHCl_2 \xrightarrow{k_8} CHCl:CCl_2$

The symbols in ( ) represent the values which were obtained from co-pyrolysis of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane.

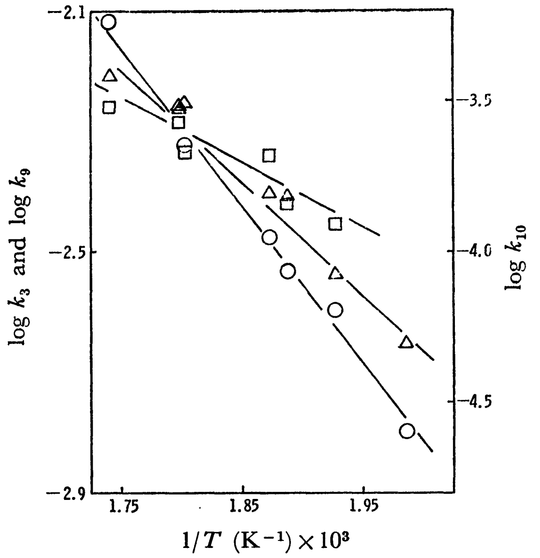


Fig. 3. Arrhenius plots for competitive pyrolysis of $CH_3CCl_3$ and $CHCl_2CCl_3$.
*W*/*F*: 294 g·hr/g-mol

○: $CH_3CCl_3 \xrightarrow{k_3} CH_2:CCl_2$
△: $CHCl_2CCl_3 \xrightarrow{k_9} CCl_2:CCl_2$
□: $CHCl_2CCl_3 \xrightarrow{k_{10}} CHCl:CCl_2$

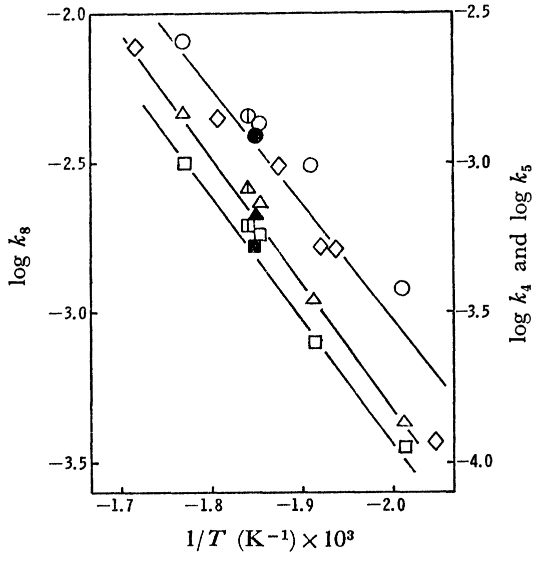


Fig. 4. Arrhenius plots for competitive pyrolysis of $CH_2ClCHCl_2$ and $CHCl_2CHCl_2$.
*W*/*F*: 147, 294, 588 g·hr/g-mol

⟁, △, ▲: $CH_2ClCHCl_2 \xrightarrow{k_4} CH_2:CCl_2$
◫, □, ■: $CH_2ClCHCl_2 \xrightarrow{k_5} CHCl:CHCl$
⦶, ○(◇), ●: $CHCl_2CHCl_2 \xrightarrow{k_8} CHCl:CCl_2$

The symbols in ( ) represont the values which were obtained from co-pyrolysis of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane.

where $n_0$ is the initial concentration of chlorinated ethane and $x$ is the amount of chlorinated ethylene formed.

The plots of log $k$ against $1/T$ gave straight lines (Fig. 1). From the slopes of the straight lines, the activation energies for the dehydrochlorination of 1,1-dichloroethane and 1,1,1,2-tetrachloroethane were calculated to be 9100 and 12000 cal, respectively. In the case of 1,1,1,2-tetrachloroethane dechlorination, exchange of chlorine with hydrogen, took place besides the

TABLE 1. REACTION RATE CONSTANTS

| Reaction type | Reaction rate constant (g-mol/g·hr) | Entropy of activation (cal/deg.) |
|---|---|---|
| $CH_3CHCl_2 \rightarrow CH_2 : CHCl$ | $k_1=9.47 \exp(-9060/RT)$ | −55.13 |
| $CH_2ClCH_2Cl \rightarrow 1/2\, CH_2 : CHCl$ | $k_2=7.36\times10^3 \exp(-17900/RT)$ | −41.89 |
| $CH_3CCl_3 \rightarrow CH_2 : CCl_2$ | $k_3=3.38\times10^2 \exp(-12200/RT)$ | −48.02 |
| $CH_2ClCHCl_2 \rightarrow CH_2 : CCl_2$ | $k_4=1.00\times10^5 \exp(-20200/RT)$ | −36.71 |
| $CH_2ClCHCl_2 \rightarrow CHCl : CHCl$ | $k_5=1.67\times10^4 \exp(-18600/RT)$ | −40.28 |
| $CH_2ClCCl_3 \rightarrow CHCl : CCl_2$ | $k_6=1.08\times10^2 \exp(-12000/RT)$ | −50.30 |
| $CH_2ClCCl_3 \rightarrow CH_2 : CCl_2$ | $k_7=1.33\times10^2 \exp(-14000/RT)$ | −49.88 |
| $CHCl_2CHCl_2 \rightarrow 1/2\, CHCl : CCl_2$ | $k_8=4.69\times10^4 \exp(-17600/RT)$ | −38.23 |
| $CHCl_2CCl_3 \rightarrow CCl_2 : CCl_2$ | $k_9=2.30\times10 \exp(-9230/RT)$ | −53.37 |
| $CHCl_2CCl_3 \rightarrow CHCl : CCl_2$ | $k_{10}=1.58 \exp(-9700/RT)$ | −58.69 |

elimination of hydrogen chloride. The rate of dechlorination was found to be smaller than that of dehydrochlorination.

The effect of the temperature on co-pyrolysis of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane is shown in Fig. 2. The values indicated by symbol ○ were obtained from co-pyrolysis of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane to confirm the reproducibility of the experiment. We see that the dehydrochlorination rate of 1,1,2,2-tetrachloroethane is greater than that of 1,2-dichloroethane. However, the activation energies showed no difference under the experimental conditions within the limits of error.

Figure 3 shows the Arrhenius plots of co-pyrolysis of 1,1,1-trichloroethane and pentachloroethane. Dechlorination of pentachloroethane took place concurrently with dehydrochlorination to some extent. The activation energies for the dehydrochlorination of 1,1,1-trichloroethane and pentachloroethane were 12200 and 9200 cal, respectively.

The Arrhenius plots for the competitive pyrolysis of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane are shown in Fig. 4. The dehydrochlorinated products of 1,1,2-trichloroethane are 1,1-dichloroethylene, *cis*- and *trans*-1,2-dichloroethylene. The rate constant $k_5$ was a sum of the rates of the formation of *cis*- and *trans*-dichloroethylene. The ratio of 1,1-dichloroethylene to 1,2-dichloroethylene amounted to several times as high as that in ordinary pyrolysis.[1] However, the rate constants of the dehydrochlorination of 1,1,2-trichloroethane were considerably smaller than that of 1,1,2,2-tetrachloroethane. Activation energies for the formation of 1,1-dichloroethylene and 1,2-dichloroethylene were calculated from the slopes to be 20200 and 18600 cal, respectively.

## Discussion

The reaction rate constants were obtained by means of the activation energies and intercepts of Arrhenius plots (Table 1). Since the reactivity seemed to be affected by the polar nature of the substituent, Taft's equation was applied to this heterogeneous cataylsis.

$$\log k/k_0 = \rho^*\sigma^* \qquad (3)$$

where $k/k_0$ is the relative rate constant with respect to standard reaction (1,2-dichloroethane in this case), and $\sigma^*$ represents the alkyl substituent parameter which is a measure of the inductive effect.[8] Rate constants at 230 °C were calculated from the equations in Table 1. The relative reactivities obtained in the competitive co-pyrolysis of chloroethanes and methanol on activated alumina are given in Table 2. A linear free energy relationship was found to exist between the reactivities of chloroethanes and Taft's $\sigma^*$ constants (Fig. 5). Values of $\rho^*$ were calculated by the method

TABLE 2. RELATIVE REACTIVITIES FOR CO-PYROLYSIS OF CHLOROETHANES AND METHANOL ON ACTIVATED ALUMINA AT 230 °C

| Reaction site | Substituent | Relative reactivity |
|---|---|---|
| $-CH_3$ | $-CCl_3$ | 13.71 |
| | $-CHCl_2$ | 9.34 |
| $-CH_2Cl$ | $-CCl_3$ | 5.49 |
| | $-CHCl_2$ | 1.14 |
| | $-CH_2Cl$ | 1.00 (Standard) |
| $-CHCl_2$ | $-CCl_3$ | 19.06 |
| | $-CHCl_2$ | 8.90 |
| | $-CH_2Cl$ | 1.46 |

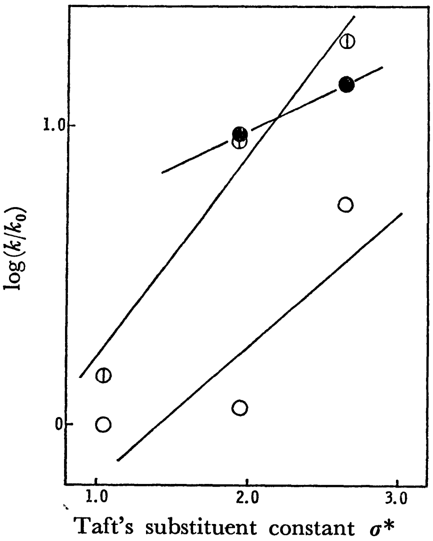


Fig. 5. Hammett plots for co-pyrolysis of chloroethanes and methanol.
●: $-CH_3$, ○: $-CH_2Cl$, ⦶: $-CHCl_2$

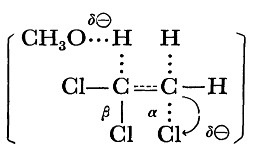
of least squares. $\rho^*$ values for reactions of $RCH_3$, $RCH_2Cl$ and $RCHCl_2$ series were 0.24, 0.45 and 0.70, respectively.

For the photochlorination and chlorine-sensitized photooxidation of chloroethanes, $\rho^*$ values were negative, indicating an electrophilic reaction mechanism.[9-11] On the other hand, positive $\rho^*$ values were observed for co-pyrolysis of chloroethanes and methanol on activated alumina.

For the formation of ethers from alcohols over alumina catalysts, Knözinger and Bühl observed a positive $\rho^*$ value.[12] Adsorption of alcohol molecules on basic sites of alumina by hydrogen bonding through the hydrogen of the hydroxyl group generates incipient alkoxide anions.[13] Thus, it was suggested that a $\beta$-hydrogen of chloroethanes was abstracted by the nucleophilic attack of methanol, chlorine being removed at the same time. For example, the reaction scheme in the case of 1,1,2-trichloroethane can be given by the following equations.

$$CH_3OH \xrightarrow{\text{basic sites of alumina}} CH_3O^{\ominus} + H^{\oplus}$$

$$CH_3O^{\ominus} + \underset{\beta}{C}HCl_2\underset{\alpha}{C}H_2Cl \rightarrow$$



$$CH_3OH + CCl_2 : CH_2 + Cl^{\ominus}$$

$$H^{\oplus} + Cl^{\ominus} \rightarrow HCl$$

$$CH_3OH + HCl \xrightarrow{\text{activated alumina}} CH_3Cl + H_2O$$

Dechlorination occurred considerably with the pyrolyses of 1,1,1,2-tetrachloroethane and pentachloroethane. The acid sites of alumina seemed to play an important role in the elimination reaction. The reaction could proceed according to *E*1 on the acid sites and *E*2 on the basic sites of the catalysts. It was found that *E*2 reaction dominated in the co-pyrolysis of chloroethanes and methanol on activated alumina.

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