

The Copyrolysis of 1,2,3-Trichloropropene and Methanol on Activated Alumina

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Synopsis. The copyrolysis of 1,2,3-trichloropropene and methanol gave 1,2-dichloro-3-methoxypropane as well as dichloropropenes and their derivatives. The formation of 1,2-dichloro-3-methoxypropane is also described.

Significant amounts of methoxy compounds are obtained by the copyrolyses of such allylic compounds as 3,4-dichloro-1-butene and 1,4-dichloro-2-butenes with methanol on activated alumina.^{1,2)} Allylic halides have been reported to undergo bimolecular nucleophilic replacement reactions in solutions.^{3–5)} On the other hand, the reaction of 1,2,3-trichloropropene (TCP) with methanolic sodium hydroxide affords only 2,3-dichloropropene (2,3-DCP), and scarcely no formation of 1,2-dichloro-3-methoxypropane (DCM) is observed.⁶⁾ The formation of DCM, which is formed by substituting a methoxyl group for a α -chlorine of TCP, characterizes the copyrolysis of TCP and methanol on activated alumina. It is a great difference in comparison with the previous works that TCP is substituted by a methoxyl group at the α -position. The copyrolysis of TCP and methanol on activated alumina was carried out under various conditions in order to understand the formation of DCM.

Results and Discussion

Time Factor (W/F). The time factor was varied by adjusting the feed rate of TCP (F : g-mol/h), the weight of catalyst (W : g) being kept at 20 g. The TCP was mixed with methanol at the mole ratio of 1.00 : 12.7. The product distributions in the copyrolysis with various time factors at 250 °C are shown in Table 1. 2,3-Dichloropropene and 1,3-dichloropropene are abbreviated as 2,3-DCP and 1,3-DCP respectively. As the time factor increased, the conversion of TCP and the formation of such methoxy compounds as DCM were conclusively increased.

Mole Ratio (MeOH/TCP). A 20 g portion of the catalyst was placed in the middle of the reactor, the reaction temperature being kept at 300 °C. Mixtures of TCP and methanol were prepared at various mole ratios, while the time factor was kept constant at 416.3 (g of catalyst/g-mol of TCP/h). Figure 1 shows the effect of the mole ratio on the product composition.

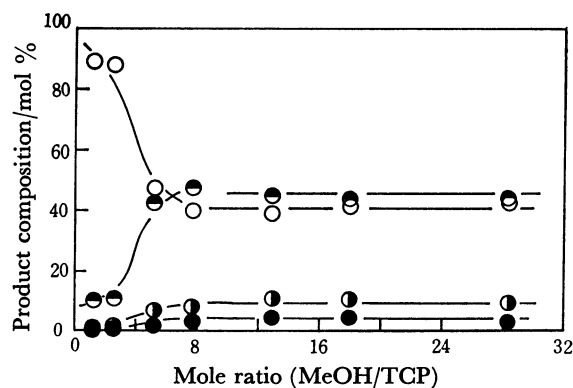


Fig. 1. The effect of the mole ratio on the product composition.

Reaction temperature: 300 °C, $W/F=416.3$ (g·h/g-mol). ○: TCP, ●: $\text{CH}_2=\text{CClCH}_2\text{Cl} + \text{CH}_2=\text{CClCH}_2\text{OMe}$, ◐: $\text{CHCl}=\text{CHCH}_2\text{Cl} + \text{CHCl}=\text{CHCH}_2\text{OMe}$, ●: DCM.

With a mole ratio of more than 7.0, the conversion of TCP remained constant, regardless of the mole ratio.

Reaction Temperature. TCP was mixed with methanol at the mole ratio of 1.0 : 12.7. The mixture was fed in over 20 g of activated alumina at a constant temperature with various feed rates. As the reaction temperature increased, the conversion of TCP increased. The effect of the reaction temperature on the conversion of TCP into DCM is shown in Fig. 2. Because of the decomposition of DCM on the alumina surface at higher temperatures, the yield of DCM showed a maximum value at 270 °C. DCM might catalytically dehydrochlorinate to the chloro(methoxy)propenes.

The methoxide anion generated on the basic sites of alumina⁷⁾ might play an important role, much as in the copyrolyses of allylic chlorides and chloroethanes with methanol.^{1,2,8)} However, it has been suggested that a β -chlorine of TCP was abstracted on the acidic sites of alumina, while a carbonium ion was formed and converted into 1,3-DCP (E1). E2 and S_N2 reactions were predominant in the copyrolysis of TCP and methanol on activated alumina, as is shown in Fig. 1. 2,3-DCP and 1,3-DCP were substituted for a chlorine in the allyl position with methanol to form chloro-

TABLE 1. PRODUCT DISTRIBUTION (mol %) IN THE COPYROLYSIS OF TCP AND METHANOL ON ACTIVATED ALUMINA AT 250 °C

Products	W/F (g·h/g-mol)					
	208.1	312.5	416.2	614.3	832.4	1248.6
$\text{CH}_2=\text{CClCH}_2\text{OCH}_3$	0.87	1.22	2.19	2.79	5.41	8.92
<i>cis</i> - $\text{CHCl}=\text{CHCH}_2\text{OCH}_3$	1.07	1.46	1.49	2.37	3.19	4.95
2,3-DCP	2.71	4.72	3.06	2.51	5.14	5.05
<i>cis</i> -1,3-DCP	0.17	0.15	0.12	0.10	0.17	0.14
<i>trans</i> -1,3-DCP	0.05	0.04	0.22	0.21	0.04	0.03
DCM	3.35	3.11	3.91	4.92	5.63	6.02
TCP	91.78	89.30	89.01	87.10	80.42	74.89

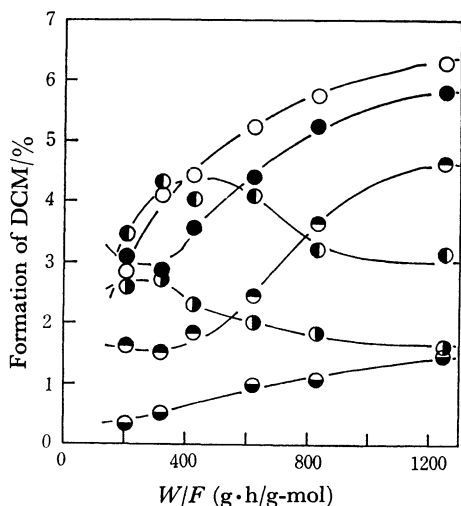
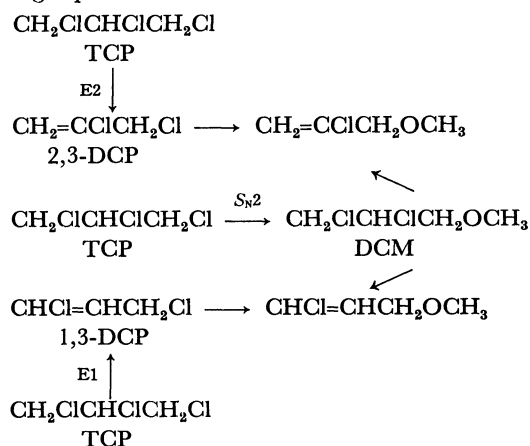


Fig. 2. The effect of the reaction temperature on the formation of DCM.

Mole ratio (MeOH/TCP): 12.7, reaction temperature (°C): ○: 200, ◐: 230, ●: 250, ○: 270, ●: 300, ●: 330.

(methoxy)propenes, according to the reaction mechanisms described in a previous paper.²⁾

Therefore, the reaction scheme can be given by the following equations:



Experimental

Catalyst. The activated alumina (KHO-24) was obtained from the Sumitomo Chemical Co.; the particle diameter was in the range of 2–4 mm.

Reagents. The methanol was purchased from the Nakarai Chemicals as guaranteed-reagent-grade. TCP of a guaranteed-reagent-grade was obtained from the Tokyo Kasei Co. 2,3-DCP, *cis*- and *trans*-1,3-DCP were purchased from the Tokyo Kasei Co. as extra-pure-grade. These reagents were used without further purification.

Equipment and Procedure. The experiments were conducted a continuous-flow type reactor, the details of which were reported in a previous paper.⁸⁾

Analytical Methods. The IR, NMR, and mass spectra were recorded on a Hitachi 125 spectrophotometer, a JMN-MH 100 spectrometer using TMS as the internal standard, and a Hitachi RMU-6MG spectrometer respectively. Gas-chromatographic analyses were performed on a Shimadzu GC-5A apparatus using a 2 m × 3 mm column with 10% PEG 6000 operating at 100 °C with a helium flow.

Syntheses of Authentic Samples. **DCM:** Allyl methyl ether, generated by the action of allyl chloride with sodium hydroxide in methanol, was chlorinated in carbon tetrachloride. The DCM thus obtained was distilled at atmospheric pressure; bp 169.5 °C.

Chloro(methoxy)propenes: Chloro(methoxy)propenes were prepared from 2,3-DCP and 1,3-DCP by modifying the method of Henne and Haeckl.⁶⁾

Identification of Products. The crude solution obtained by the copyrolysis was poured into water. The organic layer was taken up and washed with water, dried (CaCl₂), and distilled. Each component of the products was separated by means of VPC. The identification was carried out by a comparison of their IR, NMR, and MS spectra with those of authentic samples. The spectroscopic data are as follows:

2-Chloro-3-methoxypropene. IR (cm⁻¹): 720 (C–Cl), 900

(C=C $\begin{smallmatrix} \text{H} \\ \diagup \\ \text{H} \end{smallmatrix}$), 1110 (C–O–C), 2830 (–OMe), 2940 (–CH₂–),

NMR (CCl₄) δ (ppm): 3.17 (3H, s) [–OCH₃], 3.75 (2H, s, t)

[–CH₂OMe], 5.09 (H, s, m) [H $\begin{smallmatrix} \text{H} \\ \diagup \\ \text{C}=\text{C} \end{smallmatrix}$ Cl], 5.17 (H, s, m)

[H $\begin{smallmatrix} \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{OMe} \end{smallmatrix}$], MS (*m/e*) (%): P+2=108 (2.5), P+1=107 (5.0), P=106 (6.0), P–1=105 (5.4), 71 (100), 45 (81), 41 (100).

***cis*-1-Chloro-3-methoxypropene.** IR (cm⁻¹): 750 (C–Cl),

1110 (C–O–C), 1630 (H $\begin{smallmatrix} \text{H} \\ \diagup \\ \text{C}=\text{C} \end{smallmatrix}$ H), 2820 (–OMe), 2920 (–CH₂–) NMR (CCl₄) δ (ppm): 3.16 (3H, s) [–OCH₃], 3.91

(2H, d, d) [–CH₂OMe], 5.63 (H, d, t) [C $\begin{smallmatrix} \text{CH}_2\text{OMe} \\ \diagup \\ \text{H} \end{smallmatrix}$], 5.83

(H, d, t) [C $\begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{H} \end{smallmatrix}$], MS (*m/e*) (%): P+2=108 (3.2), P+1=

107 (12.4), P=106 (3.6), P–1=105 (20.6), 75 (100), 71 (100), 45 (100), 41 (100).

***trans*-1-Chloro-3-methoxypropene.** IR (cm⁻¹): 800 (C–Cl),

930 (H $\begin{smallmatrix} \text{H} \\ \diagup \\ \text{C}=\text{C} \end{smallmatrix}$ H), 1110 (C–O–C), 2820 (–OMe), 2920 (–CH₂–), NMR (CCl₄) δ (ppm): 3.15 (3H, s) [–OCH₃], 3.70

(2H, d, d) [–CH₂OMe], 5.70 (H, d, t) [C $\begin{smallmatrix} \text{CH}_2\text{OMe} \\ \diagup \\ \text{H} \end{smallmatrix}$], 5.84

(H, d, t) [C $\begin{smallmatrix} \text{H} \\ \diagup \\ \text{Cl} \end{smallmatrix}$], MS (*m/e*) (%): P+2=108 (0.3), P+1=

107 (3.4), P=106 (2.4), P–1=105 (6.4), 71 (100), 41 (59).

DCM. IR (cm⁻¹): 740 (C–Cl), 1130 (C–O–C), 2830 (–OMe), 2940 (–CH₂–), NMR (CCl₄) δ (ppm): 3.40 (3H, s) [–OCH₃], 3.62 (2H, q) [–CH₂OMe], 3.72 (2H, q) [–CH₂Cl], 4.00 (H, m) [–CHCl–], MS (*m/e*) (%): P+4=146 (1.4), P+2=144 (5.6), P=142 (7.6), 45 (100).

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