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Elimination Reactions of Propylene Chlorohydrins over Solid Acids

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In a previous paper, the elimination reactions of ethylene chlorohydrins over solid acids, solid bases, and metals supported by silica gel were investigated and the reaction mechanism was discussed.[1] In the present paper, the elimination reactions of propylene chlorohydrins over solid acids are studied in order to elucidate the effect of the methyl group on the reactivities and in order to examine the validity of the mechanism proposed for the reaction of ethylene chlorohydrin.

Experimental

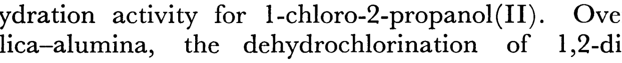
Silica-alumina and alumina were described in a previous paper.[2] 2-Chloro-1-propanol(I) and 1-chloro-2-propanol (II) were separated from commercial 1-chloro-2-propanol (Tokyo Kasei Co., E. P. grade; *ca.* 20% 2-chloro-1-propanol) by gas chromatography with a PEG column. The reaction rates were measured by the microcatalytic gas-chromatographic technique at 300°.[1-3] Hydrogen gas was used as the carrier. TCP (4 m, 60°) and Tween 80 (2 m, 80°) were used in a column in the reaction of 1-chloro-2-propanol and 2-chloro-1-propanol respectively. The conversions were reproduced from a pulse to a pulse, indicating that the elimination reactions of propylene chlorohydrins over the solid acid were catalytic.

Results and Discussion

The Reactivities of Propylene Chlorohydrins. The elimination reactions of propylene chlorohydrins on silica–alumina and alumina are summarized as follows:

Reactant	Catalyst	Product	Eliminated group
$CH_3CHClCH_2OH$ I	SiO_2-Al_2O_3	→ CH_3CH_2CHO → $CH_2{=}CHCH_2OH$	HCl
	Al_2O_3	→ CH_3CH_2CHO → $CH_2{=}CHCH_2OH$	HCl
$CH_3CHOHCH_2Cl$ II	SiO_2-Al_2O_3	→ CH_3COCH_3	HCl
		→ *trans*- and *cis*- $CH_3CH{=}CHCl$ → $CH_2{=}CHCH_2Cl$	H_2O
	Al_2O_3	→ CH_3COCH_3	HCl

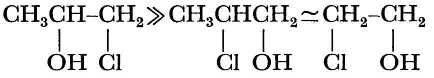
where allyl alcohol was not detected. The reaction rates are shown in Table 1, together with the elimination rates of some related reactants for the sake of comparison.[1,3] The dehydrochlorination reactivities of these reagents on both catalysts are summarized as follows:



$$CH_3\underset{Cl}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}} \gg CH_3\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}} \simeq \underset{OH}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}} \gg CH_3\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$$

(primary-chlorine elimination)

The dehydration reactivities on silica–alumina were:



$$CH_3\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}} \gg CH_3\underset{Cl}{\underset{|}{CH}}\underset{OH}{\underset{|}{CH_2}} \simeq \underset{Cl}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$

It should be noted that alumina did not show any dehydration activity for 1-chloro-2-propanol(II). Over silica–alumina, the dehydrochlorination of 1,2-dichloropropane gave the same reaction products as the dehydration of 1-chloro-2-propanol(II). The product distributions of the two reactants are compared in Table 2, where the same tendency is observed on silica–alumina.

The Reaction Mechanism. 1) *Silica–Alumina*: The authors have proposed a carbonium-ion mechanism for the dehydrochlorination of ethylene chlorohydrin on silica–alumina in a previous paper:[1]

$$CH_2OHCH_2Cl \overset{-Cl^-}{\nrightarrow} CH_2OHCH_2{}^+ \xrightarrow{-H^+} CHOH{=}CH_2 \longrightarrow CH_3CHO$$

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[1] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, This Bulletin, **45**, 1635 (1972).

[2] I. Mochida, Y. Anju, H. Yamamoto, A. Kato, and T. Seiyama *ibid.*, **44**, 3305 (1971).

[3] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, *ibid.*, **43**, 2245 (1970).

Table 1. The rate of elimination reaction at 300°C (ml/g min)

Reaction	Catalyst: Silica–alumina -HCl	Silica–alumina $-H_2O$	Alumina -HCl	Alumina $-H_2O$
Reactant				
$CH_3CHClCH_2OH$ (I)	11300	0	15000	0
$CH_3CHOHCH_2Cl$ (II)	870	1390	5000	0
CH_2ClCH_2OH[a]	1100	0	3300	0
$CH_3CHClCH_2Cl$[b]				
$\rightarrow \left\{ \begin{array}{l} CH_3CH{=}CHCl \\ CH_2{=}CHCH_2Cl \end{array} \right.$	950	—	220	—
$\rightarrow CH_3CCl{=}CH_2$	0	—	30	—
$CH_3CHOHCH_2OH$	—	0	—	1
CH_2ClCH_2Cl[a]	3.2	—	14.2	—

a) Ref. 1. b) Ref. 3.

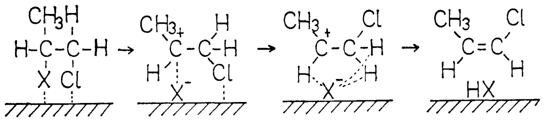
Table 2. The product distribution of the reaction:

$$CH_3CHXCH_2Cl \left\langle \begin{array}{l} \nearrow CH_3CH{=}CHCl + HX \quad (X{=}Cl \text{ or } OH) \\ \searrow CH_2{=}CHCH_2Cl + HX \quad (X{=}Cl \text{ or } OH) \end{array} \right.$$

Catalyst	Ratio: Allyl chloride / 1-Chloropropylene (X=OH)	Allyl chloride / 1-Chloropropylene (X=OH)	*trans*-1-Chloropropylene / *cis*-1-Chloropropylene (X=OH)	*trans*-1-Chloropropylene / *cis*-1-Chloropropylene (X=Cl)
Silica–alumina	1.10	0.61	0.25	0.14
Alumina	—	0.18	—	0.024

where the carbonium-ion formation may be the rate-determining step. The reactivity order above shown can be understood in terms of the stability order of carbonium-ion intermadiates: $CH_3\overset{+}{C}HCH_2OH \gg \overset{+}{C}H_2CHOHCH_3 \simeq \overset{+}{C}H_2CH_2OH > \overset{+}{C}H_2CHClCH_3$ and $CH_3\overset{+}{C}HCH_2Cl \gg CH_3CH_2Cl\overset{+}{C}H_2 \simeq CH_2Cl\overset{+}{C}H_2$. The lack of any dehydration reaction of 2-chloro-1-propanol(I) on silica–alumina may also be understood by this mechanism. To understand the two series of reactivity orders, $CH_3CHClCH_2OH > CH_3CHClCH_2Cl$ (the secondary chlorine elimination) and $CH_3CHOHCH_2Cl \gg CH_3CHClCH_2Cl$ (the primary chlorine elimination) which are due to the effects of the β-substituent, the strong adsorption ability of the hydroxyl group onto the solid acid may have to be taken into account in addition to the stability of the carbonium ion as has been described in the previous paper.[1]

The product distributions can also be understood by the carbonium-ion mechanism as follows. It may be natural that the product distributions in the dehydration of 1-chloro-2-propanol(II) and the dehydrochlorination of 1,2-dichloropropane are similar for the same carbonium ion ($CH_3\overset{+}{C}HCH_2Cl$) can be assumed as the intermediate for both reactions. Taking into account the steric hindrace as indicated by Tominaga *et al.*,[4] and the nonstereospecificity of the carbonium-ion mechanism in the dehydrohalogenation on solid acids,[5] the highly preferential formation of *cis*-1-chloropropylene may be explained by the interaction between the eliminating anion and proton to be abstracted;



(1) (2) (3) (4)
(X=OH,Cl)

The chlorine atom and the hydroxyl group may interact with surface acid sites at the initial stage (1), and then the carbonium ion may be formed by the abstraction of the hydroxyl group (2) because dehydration is now considered. The abstracted anion may interact with the hydrogen to be eliminated, resulting in methyl and Cl groups in a *cis*-position to each other (3). The subsequent cleavage of β-hydrogen results in the *cis*-olefin.

Alumina: The facts that no dehydration of 1-chloro-2-propanol occurred on alumina in spite of the secondary position of the hydroxyl group and that alumina had a greater activity for the dehydrochlorinations of halohydrins than silica–alumina indicate the characteristics of alumina as a catalyst. The former fact can not be explained by the carbonium-ion mechanism. We assume that the elimination reaction on alumina proceeds through a concerted mechanism.[2,6] It has been reported that the chlorine atom is more easily removed than the hydroxyl group in the S_N2 reaction.[7] The higher reactivity of chlorine may be true if the C–X bond still exists in the intermediate. This mechanism corresponds to the concerted one in the elimination reaction. The higher dehydrochlorination activity of alumina may be partly due to this mechanism.

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5) P. Andreu, S. S. Zerain, and H. Noller, *An. Quim.*, **55**, 141 (1969).

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7) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Henry Holt and Company, (1959), p. 261.