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Elimination Reactions of Ethylene Halohydrins on Solid Catalysts

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Elimination reactions of ethylene chlorohydrin and ethylene bromohydrin were studied over solid acids, solid bases, and metals supported by silica gel at 300°C using a microcatalytic gas chromatographic technique in order to elucidate the relationship between the elimination selectivity and the nature of active sites. Acetaldehyde was exclusively formed on solid acids and MgO. However, ethylene oxide as well was formed on solid bases. The ratio seems to depend on the basic strength of the solid bases. On the metals, ethylene was formed in addition to acetaldehyde. The former was the principal product on Pd and Pt. From these results, it was concluded that acetaldehyde was formed on acidic sites by halide-ion abstraction; ethylene oxide, on basic sites by proton abstraction, and ethylene, on less polar sites of metals by halogen atom abstraction.

It has been reported in previous papers that the halogen anion and proton abstractions play important roles in the catalytic elimination of hydrogen halide from haloethanes on solid acids and bases respectively.[1] On the other hand, OH-group abstraction has been thought to be important in the dehydration of ethanol on solid acids.[2] The elimination reactions of halohydrins on solid acids and bases may be interesting because the roles of two functional groups, halogen and OH, can be investigated under the same conditions. In this elimination several kinds of reaction products can be expected. This selectivity should reflect the acid-base character of the catalysts.

On the other hand, olefins are formed from halohydrins by metals such as magnesium and zinc in an acidic medium.[3] This result means that the metal surface has another kind of active site for the reactant.[4]

In the present research, the eliminations of two halohydrins were observed on solid acids, solid bases, and metals supported by silica gel, using the microcatalytic gas-chromatographic technique, mainly at 300°C. The poisoning effect of *n*-butylamine was also examined. The mechanisms of the elimination and the function of the catalysts were deduced from the reactivities of the reagents and the activities and selectivities of the catalysts on the basis of linear-free-energy-relationships.[1]

Experimental

Reagents. The ethylene chlorohydrin and ethylene bromohydrin (G.R.) were obtained from the Tokyo Kasei Co. They were used without further purifucation.

Catalysts. The solid acids and bases used in this work were described in previous papers.[1,2] Their abbreviations are summarized in Table 1. The metal catalysts were obtained by impregnating silica gel (Wako) with 0.4 mg-atom/g of each metal salt (Cu, Ag, Co, Ni: nitrate, Au, Pd, Pt: chloride, Fe: hydroxide) and by then drying it at 120°C in the air. They were all reduced in the reactor at 300°C except for Fe, Co, and Ni (Fe, Co: 450°C, Ni: 400°C) by hydrogen gas before the reaction.

TABLE 1. CATALYSTS

No.	Symbol	Name	Remarks
1	A	alumina	calcined at 550°C
2	A–Na	sodium poisoned alumina	0.3 meq Na/g
3	MS	Molecular Sieve Y	proton type
4	AB	alumina boria	10% B_2O_3
5	SA	silica alumina	13% Al_2O_3
6	MgO	magnesium oxide	calcined at 600°C
7	CaO	calcium oxide	calcined at 900°C
8	SrO	strontium oxide	calcined at 850°C
9	Na–S	NaOH–SiO_2	0.3 meq Na/g
10	K–S	KOH–SiO_2	0.3 meq Na/g

Procedures. The reaction rates and selectivities were measured with the pulse technique with a hydrogen carrier in the temperature range from 200°C to 450°C. The hydrogenolysis of halohydrins on Pd, Pt, and Ni was observed, but it was small compared with the other eliminations. Polyethylene glycol (PEG 1000) was used in an analytical column (60°C, 2 m) to get the conversion data, and a 4-m portion of PEG 1000 was used at room temperature for the determination of the ethylene oxide/acetaldehyde ratio. The reaction rates (m*l*/g·min) were calculated by dividing the conversion with the contact time below its value of 20%. The details of the experiments were described in previous papers.[1,2]

Results

Elimination of Halohydrins on Solid Acids and Bases. Ethylene halohydrins may give vinyl halide upon dehydration; vinyl alcohol and its isomers, by dehydrohalogenation, and ethylene, by the use of dehypohaloic acid. Only acetaldehyde was formed from halohydrins on solid acids. Ethylene oxide and acetaldehyde were formed on all the solid bases except MgO. The formation of ethylene oxide has also been reported in elimination in an alkaline solution.[5]

1) The Reactivities of Ethylene Chlorohydrin and Ethylene Bromohydrin: The catalytic activities of solid acids and bases are shown in Fig. 1. The activities were cal-

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[1] a) I. Mochida, J. Take, Y. Saito, and Y. Yoneda, *J. Org. Chem.*, **32**, 2894 (1967); *ibid.*, **33**, 2161, 2163 (1968); I. Mochida, A. Kato, and T. Seiyama, *J. Catal.*, **18**, 33 (1970). b) I. Mochida, Y. Anju, H. Yamamoto, A. Kato, and T. Seiyama, This Bulletin, **44**, 3305 (1971).

[2] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, This Bulletin, **43**, 2245 (1970).

[3] H. O. House and R. S. Ro, *J. Amer. Chem. Soc.*, **80**, 182 (1958).

[4] I. Mochida, Y. Anju, H. Yamamoto, A. Kato, and T. Seiyama, This Bulletin, in press.

[5] A. A. Frost and R. G. Person, "Kinetics and Mechanism" 2nd Edition, John Wiley and Sons, New York 1961, p. 288.

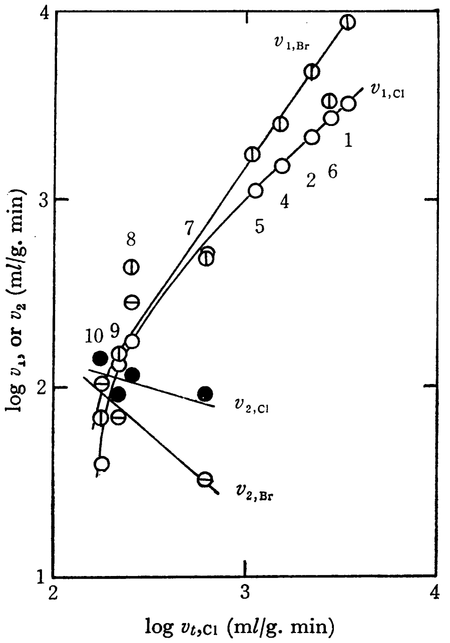

Fig. 1. Catalytic activities of solid acids and bases. (300°C) The abscissa corresponds to the total elimination reactivities of ethylene chlorohydrin (v_t,Cl).

○; rates of acetaldehyde formation from ethylene chlorohydrin (v_1,Cl),

●; rates of ethylene oxide formation from ethylene chlorohydrin(v_2,Cl),

⦶; rates of acetaldehyde formation from ethylene bromohydrin, (v_1,Br),

⊖; rates of ethylene oxide formation from ethylene bromohydrin. (v_2,Br).

Numbers refer to Table 1.

culated from the first pulse. The total elimination reactivities of ethylene chlorohydrin were taken in the abscissa, and the rates of acetaldehyde and ethylene-oxide formation from ethylene chlorohydrin and ethylene bromohydrin were taken in the ordinate. The rates of acetaldehyde formation from ethylene bromohydrin were larger than those from ethylene chlorohydrin throughout the solid acids and bases. In contrast, as to the rates of ethylene oxide formation, ethylene chlorohydrin was more reactive than ethylene bromohydrin except in the case of SrO.

The rate of acetaldehyde formation was larger on solid acids than on solid bases, except for the case of MgO. Among the so-called basic oxides, their activities for acetaldehyde formation increased with the decrease in the basicity ($K_2O>Na_2O$, and $SrO>CaO>MgO$), whereas the activity for ethylene-oxide formation was the reverse. The catalytic behavior of MgO was close to that of typical solid acids, as has also been observed in the dehydrohalogenation of 1,2-dibromoethane and isopropyl halides.[1b)]

2) Poisoning Effect: The decrease in catalytic activities with regard to ethylene-oxide formation was very striking from pulse to pulse on solid bases, but not so with regard to acetaldehyde formation on either acidic or basic solids. In the former case, the activities were almost lost by the first pulse. This poisoning effect may be due to the adsorption of hydrogen halide, one of the elimination products, onto the basic site. The poisoning of catalysts with *n*-butylamine suppressed acetaldehyde formation very much on solid acids and bases, but it did not affect ethylene oxide formation at all. These poisoning effects, in accordance with the variation in activities shown in Fig. 1, indicate that acidic sites and basic sites play an important role in the acetaldehyde and ethylene-oxide formations respectively.

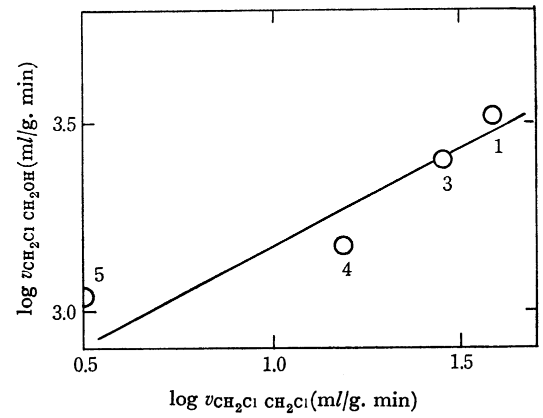

Fig. 2. Correlation between the rates of dehydrochlorination of 1,2-dichloroethane ($v_{CH_2Cl\ CH_2Cl}$) and ethylene chlorohydrin ($CH_2Cl\ CH_2OH$). The former are taken in the abscissa and the latter in the ordinate.

Numbers refer to Table 1.

3) A Comparison between the Dehydrochlorination Reactivities of 1,2-Dichloroethane and Ethylene Chlorohydrin: Between the reactivities of chlorohydrin and 1,2-dichloroethane on some solid acids, a certain correlation can be observed, as is shown in Fig. 2; this suggests a similarity in mechanism for the two dehydrochlorinations. The reactivity of ethylene chlorohydrin was larger than that of 1,2-dichloroethane by two orders of magnitude. Ethylene chlorohydrin was more reactive than 1,2-dichloroethane on solid bases, too. However, no correlation between the two reactivities could be found on solid bases.

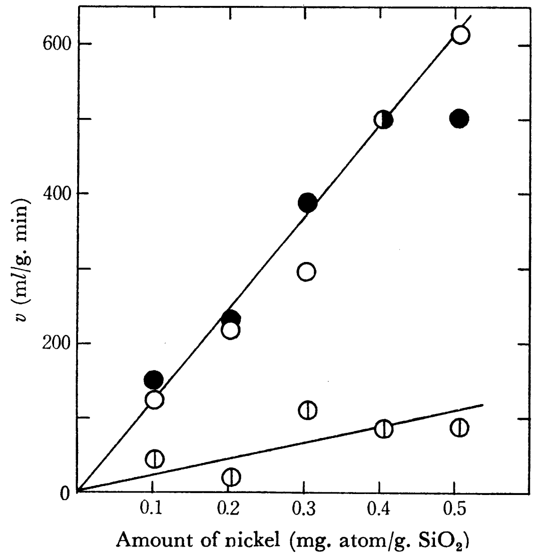

Fig. 3. The effect of the amount of nickel on catalytic activities for ethylene chlorohydrin at 300°C.

○; the rates of ethylene formation.

●; the rates of acetaldehyde formation.

⦶; the rates of ethanol formation.

Elimination of Halohydrins on Metals Supported by Silica Gel. *1) Catalytic Activities and Selectivities of Metals*: Acetaldehyde and ethylene were formed from halohydrins on metals supported by silica gel. The catalytic activity was increased, but the selectivity did not change, with the amount of metal mounted, as is shown in Fig. 3. Furthermore, the selectivities of non-supported metals (Cu, Ni, Pd) were equal to those of metals supported by silica gel, although the activity per unit weight of the supported metals was much larger than that of unsupported metals. These facts indicate that silica gel does not affect the catalytic selectivity. The catalytic activities of supported metals are shown in Fig. 4. Ethylene bromohydrin was more reactive for both product formations than ethylene chlorohydrin, as was observed for the acetaldehyde formation on solid acids. The selectivities (rate of ethylene formation/total rate of elimination) are shown as a function of the standard heats of the formation of metal chloride per chlorine atom (ΔH°_f)[6] in Fig. 5. There are volcano correlations, with the highest selectivity at Pt. Such a volcano relation has also been observed in the dechlorination of 1,2-dichloropropane.[4] Generally speaking, the more reactive bromohydrin was less selective for ethylene formation than was chlorohydrin.

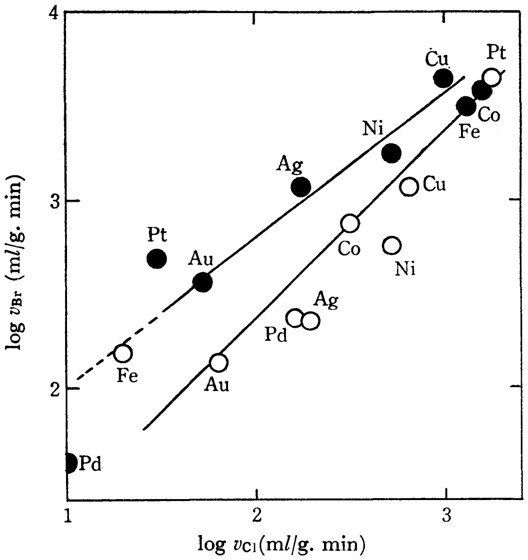

Fig. 4. Catalytic activities of metals at 300°C.
○; the rates of ethylene formation.
●; the rates of acetaldehyde formation.
log v_{Cl} (abscissa) is regarding ethylene chlorohydrin and log v_{Br} (ordinate) regarding ethylene bromohydrin.

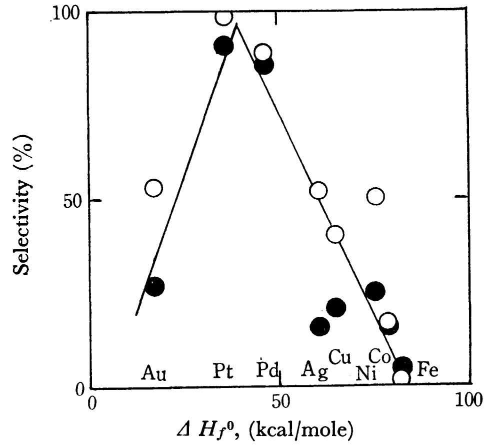

Fig. 5. The selectivities for ethylene formation of metals (rate of ethylene formation/total rate of elimination) at 300°C as a function of standard heats of formation of metal chloride per chlorine atom (ΔH_f°).
○; for ethylene chlorohydrin.
●; for ethylene bromohydrin.

The apparent activation energies for the acetaldehyde formation are larger than those for the ethylene formation, as is shown in Table 2.

TABLE 2. APPARENT ACTIVATION ENERGIES OF HCl OR HClO ELIMINATION FROM ETHYLENE CHLOROHYDRIN ON METALS

Catalysts	Acetaldehyde (–HCl)	Ethylene (–HClO)
Cu–SiO$_2$	15 kcal/mol	4 kcal/mol
Ag–SiO$_2$	12	9
Au–SiO$_2$	21	15
Fe–SiO$_2$	14	[a]
Co–SiO$_2$	12	9
Ni–SiO$_2$	14	14
Pd–SiO$_2$	[a]	10.5
Pt–SiO$_2$	[a]	10

a) Activity was too small to be measured.

2) The Poisoning Effect: The poisoning effect with *n*-butylamine was severe for the acetaldehyde formation, but was negligible for the ethylene formation, among all the metal catalysts examined.

The catalytic activities of all the metals except Pd and Pt for acetaldehyde and ethylene formations decreased to a half of the original activity upon a pulse injection. Pd and Pt showed no activity change from pulse to pulse.

3) A Comparison between the Dechlorination of 1,2-dichloroethane and Dehypochloric Acid of Ethylene Chloro-

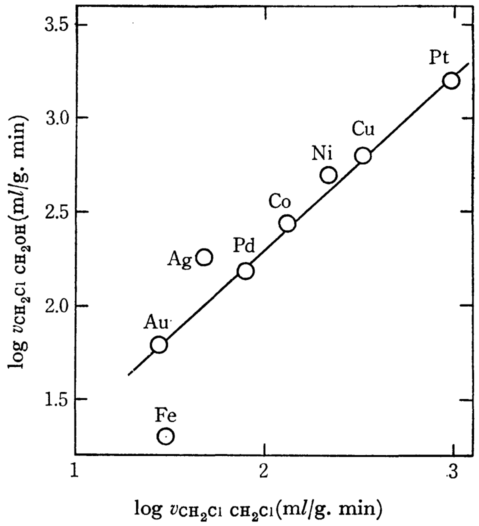

Fig. 6. Correlation between the rates of dechlorination of 1,2-dichloroethane ($v_{CH_2Cl\ CH_2Cl}$) and those of dehypochloric acid of ethylene chlorohydrin ($v_{CH_2Cl\ CH_2OH}$) at 300°C.
The former are taken in the abscissa and the latter in the ordinate.

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[6] "Kagaku Binran", Maruzen 1966, p. 817.

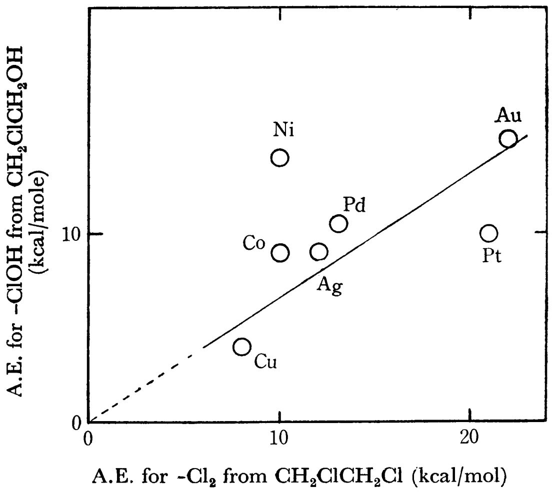


Fig. 7. Correlation of apparent activation energies between dechlorination of 1,2-dichloroethane and dehypochloric acid of ethylene chlorohydrin.

hydrin on Metals: A good correlation was recognized between the dechlorination-reactivities of 1,2-dichloroethane[4] and the dehypochloric-acid-reactivities of ethylene chlorohydrin, as is shown in Fig. 6. Furthermore, the activation energies of the two elimination reactions on the same metal were also correlated with each other, as is shown in Fig. 7. Both correlations were observed between the corresponding reactions of 1,2-dibromoethane and ethylene bromohydrin. Such correlations indicate that the ethylene formation from halohydrins proceeds through a mechanism similar to that of the dehalogenation of haloethanes.

Discussion

Acetaldehyde Formation. Acetaldehyde is formed on acidic sites, as has been described above. The following facts suggest that the halogen-abstraction step is important. 1) There is a good correlation between the reactivities of 1,2-dichloroethane and ethylene chlorohydrin on solid acids, as is shown in Fig. 2. 2) Bromohydrin, the C–Br bond of which is weaker than the C–Cl bond of ethylene chlorohydrin, was more reactive than chlorohydrin. From these findings, it seems that acetaldehyde formation may proceed through a mechanism by which the halogen is eliminated as an anion in the first stage, and then the β proton may leave through an $\alpha\beta$ elimination mechanism to give vinyl alcohol, which isomerizes immediately to acetaldehyde:

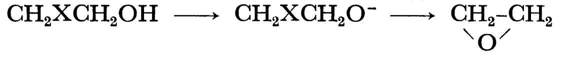
$$CH_2OHCH_2X \xrightarrow{-X^-} CH_2OHCH_2^+ \xrightarrow{-H^+} CHOH{=}CH_2 \longrightarrow CH_3CHO$$

As alumina had a higher catalytic activity than silica-alumina, it is difficult to assume only protonic acid as the active site for the acetaldehyde formation. Such a situation was also observed in the dehydration of ethanol.[2] The higher reactivity of halohydrin in comparison with that of 1,2-dichloroethane may be due to the interaction between the hydroxyl group of halohydrin with acid sites in the same manner as in the dehydration of ethanol, in addition to the difference in enthalpy changes between the two reactions.[7]

The linear correlation observed through solid acids and bases (Fig. 1) and the similar poisoning effect may indicate an analogous mechanism for the acetaldehyde formation on solid bases.

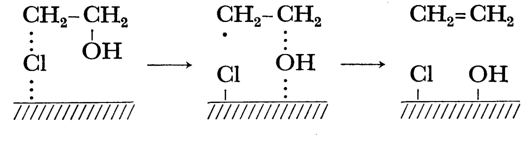
Similar poisoning effects of *n*-butylamine and the higher reactivity of ethylene bromohydrin than ethylene chlorohydrin were also observed for the reactions on metal catalysts as well as on solid acids, indicating a similar mechanism for acetaldehyde formation on metals. The acidic nature of the metal atom may be due to its vacant *d*- or *f*-orbitals.

Ethylene Oxide Formation. Ethylene oxide was formed on the catalysts which were located on the left side of Fig. 1, that is, the solid bases. The poisoning effect of HX was remarkable for the ethylene-oxide formation. Therefore, the active site for the ethylene-oxide formation may be basic. Basic sites may eliminate the proton from the hydroxyl group at first:


$$CH_2XCH_2OH \xrightarrow{-H^+} CH_2XCH_2O^- \xrightarrow{-X^-} \underset{\diagdown O \diagup}{CH_2\text{–}CH_2}$$

This scheme is the same one as that suggested for the reaction in basic media.[8] According to this scheme, the reactivity may depend on the acidity of the hydrogen atom to be eliminated. Thus, the reactivity difference between chloro- and bromohydrins can be understood. The higher acidity of the hydrogen in the OH group than in the CH group may also explain the higher reactivity of halohydrin in comparison with haloethanes on solid bases.

Ethylene Formation on Metals. The larger reactivity of bromohydrin than that of chlorohydrin suggested the importance of the halogen-abstraction step for the ethylene formation. The correlations of the activities and activation energies of metals for the ethylene formation with those for the dechlorination of 1,2-dichloroethane in Figs. 6 and 7 indicate the similarity of the rate-determining steps in these two reactions. The poisoning with *n*-butylamine does not affect the ethylene formation, in contrast to the acetaldehyde formation, which is considered to proceed through the ionic mechanism on metals described above. Therefore, the following mechanism is considered to hold for the ethylene formation on metals:



It is interesting that the less electronegative and higher back-donating metals, such as Pt and Pd, show a high selectivity for ethylene formation.

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[7] $\Delta Hf°_{(298)} = -39.86$, -70.3, 8.4, and -31.0 (kcal/mol) for acetaldehyde, ethylene chlorohydrin, vinyl chloride, and 1,2-dichloroethane respectively. (D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York 1968, p. 641.

[8] S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **61**, 1576 (1939); D. Porret, *Helv. Chim. Acta*, **30**, 701 (1947).