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The Catalytic Dehydrohalogenation of Haloethanes on Solid Acids and Bases

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The elimination reactions of haloethanes and halopropanes on solid acids and bases, including a series of metal sulfates supported by silica gel, were studied at 300°C by means of the pulse technique in order to clarify the mechanism of the catalytic dehydrohalogenation. The *trans*-1,2-dichloroethylene/*cis*-1,2-dichloroethylene (*trans*-1,2/*cis*-1,2) selectivities from 1,1,2-trichloroethanes as well as the activities of the metal sulfates supported by silica gel were well correlated with the electronegativities of the metal ions. Generally speaking, the rates of the dehydrochlorination from chloroalkanes were nearly equal to those of the dehydrobromination from bromoalkanes on the solid acids, but the latter were larger than the former on solid bases. The reactivities of the alkylhalides on solid acids and bases were examined from the electronic view-point, and we tried to correlate them with some reactivity indexes. A kinetic isotope effect with regard to hydrogen was observed on solid bases, but not on solid acids, in the dehydrobromination of 1,2-dibromoethane. From these facts, it was concluded that the dehydrohalogenation proceeds through a carbonium-ion mechanism on solid acids and *via* an E2 step-by-step mechanism on solid bases.

It has been reported in previous papers[1)] that the dehydrochlorination of 1,1,2-trichloroethane proceeds with different selectivities on solid bases, solid acids, ion-exchanged molecular sieves, chromia, and metal sulfates. The reaction mechanism was discussed on the basis of the linear-free-energy-relationships (LFER) approach, regarding five chloroethanes as well as the *trans*-1,2/*cis*-1,2 selectivities. The selectivity of *trans*-1,2/*cis*-1,2 on the metal sulfate was found not to be related with the electronegativity of the metal ion,[1b)] which has been thought to represent the acid strength of the metal sulfate,[2)] but to depend on the geometries of the catalysts. The effect of the geometries can be diminished among a series of metal sulfates by using the silica gel as the catalyst support.[3,4)]

In the present study, the correlation of the catalytic activities and selectivities with the activities of a series of metal sulfates mounted on silica gel was investigated. At the same time, the reactivities of several haloethanes and halopropanes were measured on typical solid acids, solid bases, and the intermediate in order to obtain more information about the effects of substituents and leaving halogens on the elimination reactivity. The kinetic isotope effect of HBr (DBr) elimination from 1,2-dibromoethane was also measured in order to determine whether or not the C–H bond cleavage was the rate-determining step. A more probable mechanism of the elimination of hydrogen halide may be deduced from these results.

Noller *et al.* have reported that, for dehydrohalogenations over metal salts, the ionic contribution (El-character) increased with the increasing acidity of the cation.[5)] They also examined the substituent effect on the reactivity over metal salts.[6)] However their studies seem to be lacing in the consideration of the acid-base interaction between catalysts and reagents.

Experimental

Reagents. All the reagents used in this work were obtained from Tokyo Kasei except for 1,2-dibromo-tetradeuteroethane, which was obtained from Merck. They were all of G. R. or E. P. grade and were not purified further.

Catalysts. The catalysts of metal sulfates supported by silica gel were obtained by impregnating silica gel (Wako) with 0.3 meq/g of each metal sulfate (G. R. from the Hayashi Co.), and then dried at 120°C in the atmosphere.[3)] The other catalysts were described in the previous papers.[1)]

Apparatus and Procedures. The reaction rates and selectivities were measured at 300°C by the pulse technique, as has been described in the previous papers.[1)] The catalysts were pretreated in a helium-gas flow for 3 hr at 300°C. The calcination temperature between 300 and 500°C had little effect on either the activity or the selectivity of nickel sulfates on silica gel in the HCl elimination from 1,1,2-trichloroethane, although distinct effects were observed in other reactions.[3,7)] The elimination reaction was of nearly first order under the experimental conditions, and the conversion was verified to be a linear function of the reciprocal space velocity (RSV) at low conversions. Thus, the slope of the conversion/RSV gives the apparent rate constant, k (ml/g·min). The details of the experiments were described in the previous papers.[1)]

Results

Dehydrochlorination of 1,1,2-Trichloroethane on Metal Sulfates Supported by Silica Gel. The dechlorination and exchange of chlorine with hydrogen took place in addition to the dehydrochlorination on the metal sulfates supported by silica gel in manners similar to those observed on the unsupported metal sulfate.[1b)] The dehydrochlorination was of principal concern in the present study because all the other reactions were minor except for the dechlorinations

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[1)] a) I. Mochida, J. Take, Y. Saito, and Y. Yoneda, *J. Org. Chem.*, **32**, 3894 (1967); **33**, 2161, 2163 (1968). b) I. Mochida, A. Kato, and T. Seiyama, *J. Catal.*, **18**, 33 (1970).

[2)] K. Tanaka and A. Ozaki, *ibid.*, **8**, 1 (1967); K. Tanaka, in "Catalytic Engineering. X. Catalyst Handbook," Chijin Shokan, Tokyo (1967), p. 739.

[3)] I. Mochida, A. Kato, and T. Seiyama, *J. Catal.*, **17**, 317 (1970).

[4)] M. Misono, Y. Saito, and Y. Yoneda, *ibid.*, **9**, 135 (1967).

[5)] P. Andreu, J. Bellorin, G. Cunto, and H. Noller, *Z. Phys. Chem.* (Neue Folge), **64**, 71 (1969).

[6)] P. Andreu, R. Ballesteros, S. Villaba, J. F. Garcia, and H. Noller, *An. Quim.*, **65**, 931 (1969).

[7)] K. Tanabe and T. Takeshita, *Advan. Catal.*, **17**, 317 (1967).

on cupric and ferric sulfates.

1) The Catalytic Activity: The products of the dehydrochlorination from 1,1,2-trichloroethane were *trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene, and 1,1-dichloroethylene. The catalytic activity varied very much among metal sulfates. The catalytic activities of various supported metal sulfates are shown in Fig. 1 as the function of the electronegativities of the metal ions, the values of which were taken from the literature.[2] Here, the catalytic activity was expressed by the total reaction rate of dehydrochlorination. The logarithms of the reaction rates have a reverse-volcano relationship with the electronegativities of the metal ions except for the thallium ion, although only a few observations were made on the basic side of the catalysts. The minimum activity was found at the silver ion, whose electronegativity was 5.6.

2) The Stereoselectivity: The *trans*-1,2/*cis*-1,2 ratios on the catalysts, the stereoselectivities of this dehydrochlorination, are shown in Fig. 2 as the function of the electronegativities of the metal ions. The logarithms of the ratios are linearly correlated with electronegativities over one and a half orders of magnitude in the ratios. The ratio of 1,1-dichloroethylene/1,2-dichloroethylene (1,1/1,2) was another selectivity of this elimination, although 1,1-dichloroethylene could not be detected on the metal sulfates of high electronegativity. This selectivity was linearly correlated with the *trans*-1,2/*cis*-1,2 selectivity on the same catalyst, as is shown in Fig. 3, where the solid line was that obtained using typical solid acids and bases such as silica-alumina and strontium oxide in a previous paper.[1a)] A linear relation was observed in this case, too.

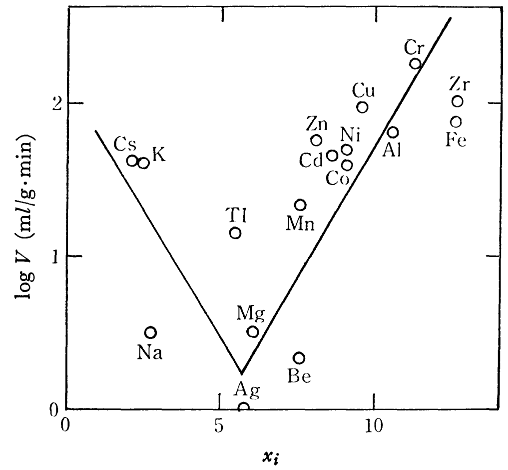

Fig. 1. Catalytic activities of metal sulfates supported by silica gel for the dehydrochlorination of 1,1,2-trichloroethane were plotted against the electronegativities of the corresponding metal ions.
The values of electronegativities, x_i, are taken from Ref. 2.

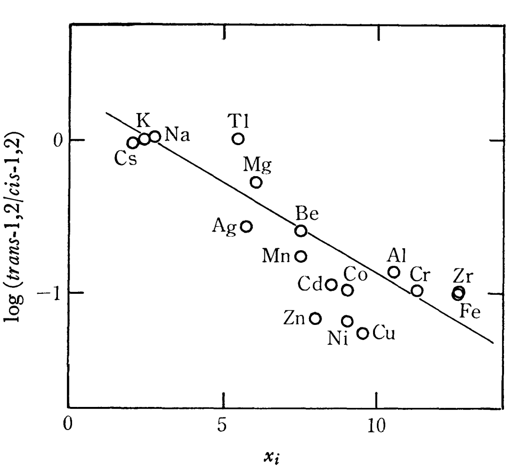

Fig. 2. The *trans*-1,2/*cis*-1,2 selectivities of metal sulfates supported by silica gel were correlated with the electronegativities of the corresponding metal ions.
The values of electronegativities, x_i, are taken from Ref. 2.

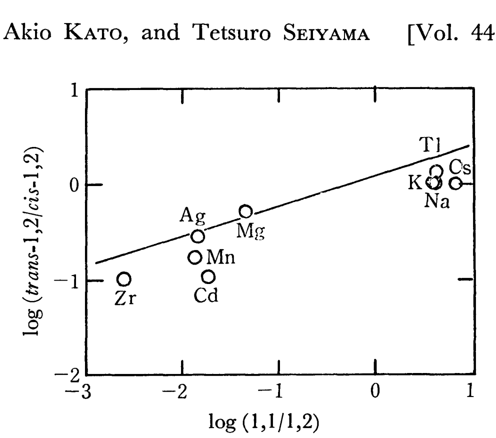

Fig. 3. A correlation between *trans*-1,2/*cis*-1,2 and 1,1/1,2 selectivities from 1,1,2-trichloroethane on metal sulfates supported by silica gel.

3) Reactivity Orders of the Five Chloroethanes: The reactivity orders of the five chloroethanes were 1,1,1-trichloroethane (1,1,1) > 1,1-dichloroethane (1,1) > 1,1,2-trichloroethane into 1,2-dichloroethylene (1,1,2 into 1,2) > 1,1,2,2-tetrachloroethane (1,1,2,2) > 1,2-dichloroethane (1,2) > 1,1,2-trichloroethane into 1,1-dichloroethylene (1,1,2 into 1,1) on nickel, cupric cadmium, and ferric sulfates supported by silica gel, whereas they were 1,1,1>1,1,2,2>1,1,2 into 1,1>

TABLE 1. REACTIVITY ORDER OF FIVE CHLOROETHANES IN DEHYDROCHLORINATION

a) On sulfates of a high electronegativity.

Reactant / Catalyst	1,1,1	1,1	1,1,2 into 1,2	1,1,2,2	1,2	1,1,2 into 1,1
$NiSO_4$-SiO_2	1910	214	48	2	1.3	0
$CuSO_4$-SiO_2	2575	198	90	6.4	0.5	0
$Fe_2(SO_4)_3$-SiO_2	2490	237	73	6.9	2.7	0
$CdSO_4$-SiO_2	2870	432	45	3.5	1.2	0

b) On sulfates of a low electronegativity.

Reactant / Catalyst	1,1,1	1,1,2,2	1,1,2 into 1,1	1,1	1,1,2 into 1,2	1,2
Tl_2SO_4-SiO_2	219	57	11	5.6	2.6	1.2
K_2SO_4-SiO_2	139	100	31	9.3	7.9	7.5

1) Figures in Table show the reaction rate (ml/min. g).
2) Abbreviations of the reactants and products refer to the text.

1,1>1,1,2 into 1,2>1,2 on potassium and thallium sulfates, as is shown in Table 1. The former reactivity order and the large difference among the reactivities of chloroethanes observed on a metal sulfate of a high electronegativity were like those on a solid acid such as silica-alumina.[1a] On the other hand, the latter reactivity order on a metal sulfate of a low electronegativity was similar to that observed on a basic catalyst such as strontium oxide,[1a] except for the high reactivities of 1,1,1 and 1,1 on such metal sulfates. The reactivity difference between the most and the least reactive chloroethanes on potassium sulfate was only one and a half orders of magnitude. Such a small difference has been observed on the molecular sieve 13X, which was considered to be neutral in the Hammett indicator test.[1a]

Dehydrohalogenation of Haloethanes and Halopropanes on Solid Acids and Bases. *1) Comparison between Dehydrochlorination and Dehydrobromination*: The reactivities of the dehydrohalogenation of several dihaloethanes and monohalopropanes on solid acids and bases are shown in Figs. 4 and 5, where the rates of dehydrochlorination are shown in the abscissa, and those of dehydrobromination, by the ordinate. The dotted lines in both figures show the equal reactivities of the two reactants. The structures of the halides had a considerable effect on the rates over the solid acids. In contrast, only a small effect was observed on the solid bases. The difference was more than five hundred on solid acids, whereas it was less than one hundred on solid bases.

On solid acids, the rates of dehydrochlorination and those of dehydrobromination were nearly equal, as is shown in Fig. 4. The dehydrobromination was two times faster than the dehydrochlorination on solid bases, as is shown in Fig. 5. In any case, it seems from these linear correlations that both dehydrohalogenations, —HCl and —HBr, can be discussed on the common basis of the reaction mechanism, although a discrimination between acidic and basic catalysts is essential.

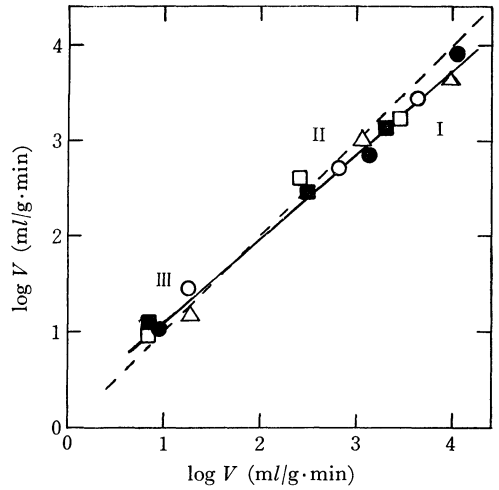

Fig. 4. The reactivities of dehydrochlorination and dehydrobromination on solid acids, ● for silica-alumina, △ for alumina-boria, ■ for nickel sulfate, □ for $NiSO_4$-SiO_2 and ○ for alumina. Group I corresponds to the reactivity regarding iso-PrX, II to n-PrX and III to $BrCH_2CH_2X$, where X is chlorine in the case of dehydrochlorination and that is bromine in the case of dehydrobromination.

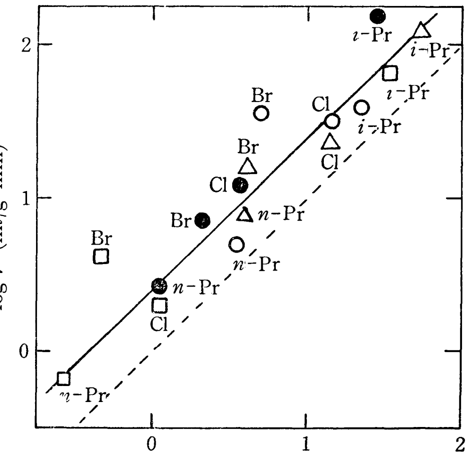

Fig. 5. The reactivities of dehydrochlorination and dehydrobromination on solid bases, ○ for KOH-SiO_2, △ for NaOH-SiO_2, ● for K_2SO_4-SiO_2, □ for SrO. The symbols of Br, Cl, n-Pr, and iso-Pr, represent the reactivities of dehydrohalogenation of $BrCH_2CH_2X$, $ClCH_2CH_2X$, n-PrX, and iso-PrX, respectively. (X is Cl or Br)

2) Substituent Effects: The reactivities of *iso*-PrBr, *n*-PrBr, EtBr, 1,2-dibromoethane, and 1-bromochloroethane for dehydrobromination on solid acids are plotted against the Taft's σ^* of the R group in RBr in Fig. 6. The σ^* is thought to represent the electronic effect of the substituent in the saturated compounds.[8] The reactivity decreased monotonously with the increasing σ^*. The correlation seems to consist of two straight lines. The slope of the line through *iso*-, and *n*-propyl bromides and ethyl bromide might indicate the carbonium-ion

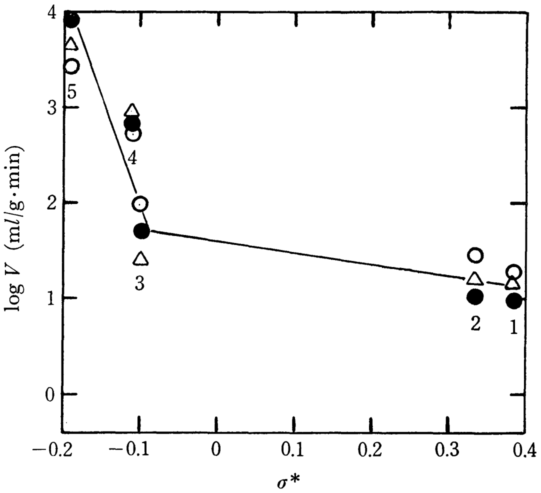

Fig. 6. The reactivities of dehydrobromination on solid acids as a function of σ^*, ● for silica-alumina, △ for alumina-boria and ○ for alumina. The values of σ^* were taken from literature (8). Numbers refer to the reagents, 1; 1-bromo-2-chloroethane, 2; 1,2-dibromoethane, 3; ethyl bromide, 4; n-PrBr and 5; iso-PrBr.

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[8] R. W. Taft, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, Wiley, New York (1956), p. 206.

mechanism, because many reactions which are thought to proceed through the carbonium ion give slopes of such a degree.[9] The reactivities of dihaloethanes are too large if the reaction proceeds through the same carbonium-ion mechanism. In reaction of 1-bromo-2-chloroethane, a considerable amount of 1,2-dibromoethane and 1,2-dichloroethane, the products of the halogen exchange reaction, were detected on solid acids. These rather complicated results should be taken into account in the discussion of the reaction mechanism of the elimination.

The NMR chemical shifts were thought to represent the static electron density of the hydrogen. The reactivities on solid bases are compared with the chemical shift of hydrogen to be eliminated in Fig. 7. Except for isopropyl halide, a certain relation can be considered to exist between the reactivity and the chemical shift of the proton, although more adequate reactivity indices should be considered. It may be a dynamic one.[11]

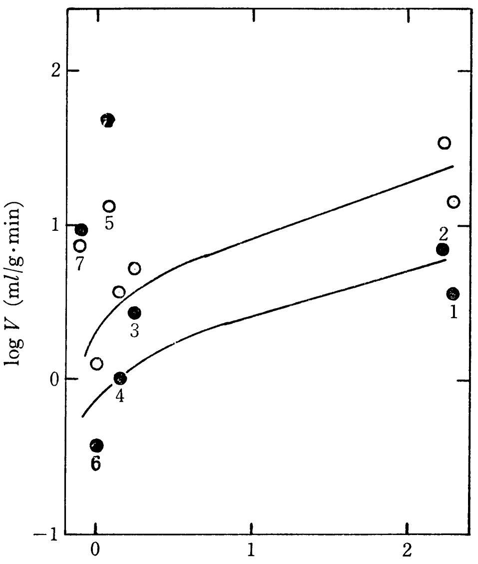

Fig. 7. The reactivities of dehydrohalogenation divided by the symmetry number, the number of its equivalent hydrogen atom, as a function of the NMR chemical shift of hydrogen to be eliminated, ○ for KOH-SiO$_2$ and ● for K$_2$SO$_4$-SiO$_2$. The relative values of the abscissa were taken from literature (10). Numbers refer to the reagents, 1; 1,2-dichloroethane, 2; 1,2-dibromoethane, 3; *n*-PrBr, 4; *n*-PrCl, 5; *iso*-PrBr, 6; EtBr, and 7; *iso*-PrCl.

Kinetic Isotope Effect. The kinetic isotope effect in dehydrobromination from 1,2-dibromoethane was measured on solid acids and bases. The rates of dehydrobromination (k_H), those of dedeuterobromination (k_D), and the values of k_H/k_D are shown in Table 2. The maximum theoretical value of k_H/k_D at 300°C is 2.7.[12] The k_H/k_D values on all solid bases except magnesium oxide were greater than 1.5, whereas those on solid acids were nearly unity. Sodium-poisoned alumina had a value of k_H/k_D intermediate between solid acids and bases. This fact may correspond to the amphoteric character of this catalyst.

Table 2. Kinetic isotope effect in dehydrobromination of 1,2-dibromoethane

Catalyst	k_H[1]	k_D[2]	k_H/k_D
SrO	8.6 ±0.2	4.0 ±0.1	2.15±0.11
CaO	0.56±0.04	0.34±0.08	1.65±0.66
MgO	4.8 ±0.6	4.7 ±0.7	1.02±0.24
KOH-SiO$_2$	70±0	44±1	1.59±0.04
NaOH-SiO$_2$	33±2	18±0	1.83±0.12
K$_2$SO$_4$-SiO$_2$	14±1	8.5 ±0.3	1.65±0.18
Alumina-NaOH	114±1	87±1	1.31±0.03
Alumina	56±0	57±1	1.00±0.02
NiSO$_4$	14±1	14±2	1.00±0.25
Alumina-boria	22±6	21±4	1.05±0.60
Silica-alumina	11±2	11±3	1.00±0.62
NiSO$_4$-SiO$_2$	9.7±0.1	7.9±2.8	1.23±0.69

1) The rate of dehydrobromination from 1,2-dibromoethane.
2) The rate of dedeuterobromination from 1,2-dibromotetradeuteroethane.

Discussion

Correlation of Catalytic Activity and Selectivity with the Acid-base Character of Catalysts and a Gradual Change in the Dehydrohalogenation Mechanism. The availability of the electronegativities of the metal ions has been established in many acid-catalyzed reactions.[2-4] The HCl-elimination from 1,1,2-trichloroethane may be included as one such example. The electronegativity of the metal ion was excepted to express the acid strength of the metal sulfate.[2] At higher *Xi* values, the ratio of *trans*-1,2/*cis*-1,2 from 1,1,2-trichloroethane was as small as 0.1, as is shown in Fig. 2, the reactivity order of chloroethanes was also similar to that on typical solid acids. At lower *Xi* values, on the other hand, the ratios are unity, and their plots in Fig. 3 are close to those on typical solid bases, furthermore, the reactivity order is similar to that on solid bases. These facts indicate that the gradual change in the reaction mechanism previously concluded[1] can be applied to this series of catalysts, also.

It is interesting that the catalytic activities *vs.* *Xi* plots are shaped in a reverse-volcano, with a minimum at the silver ion. 1,2-dichloroethylene was primarily formed on the metal sulfates with the high *Xi* values as is shown in Fig. 1. This product may be explained by the abstraction of 1-chlorine,[13] which

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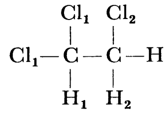
[9] J. E. Leffler and E. Gruneald, "Rates and Equilibria of Organic Reactions," Wiely, New York (1963), p. 171; I. Mochida and Y. Yoneda, *J. Catal.*, **7**, 386 (1967); I. Mochida, Y. Anju, A. Kato, and T. Seiyama, This Bulletin, **44**, 2326 (1971).

[10] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Spectroscopy," Vol. 2, 1120, Pergamon Press, Oxford (1966), p. 672.

[11] K. Fukui, H. Kato, and T. Yonezawa, This Bulletin, **34**, 1111 (1961).

[12] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

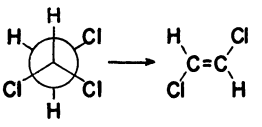
[13]

$$\begin{array}{ccccc} & & Cl_1 & & Cl_2 \\ & & | & & | \\ Cl_1 & - & C & - & C-H_2 \\ & & | & & | \\ & & H_1 & & H_2 \end{array}$$

seems to be easily eliminated as an anion by the acidic sites. On the other hand, 1,1-dichloroethylene, that would be produced by the abstraction of the 1-hydrogen[13] easily eliminated as a proton is formed from 1,1,2-trichloroethane on the sulfates with the low *Xi* values. Thus, the gradual change in the reaction mechanism may explain the change in the selectivity according to the acid-base character of the catalyst.

The Mechanism of Dehydrohalogenation on Solid Acids. The fact that no kinetic isotope effect in the dehydrobromination from 1,2-dibromoethane was observed on solid acids indicates that the cleavage of the C–H bond is not involved at or before the rate-determining step. The negative slopes of the lines in Fig. 6 indicate that the reaction intermediate is positively charged. These facts suggest that the active site on solid acids may abstract halogen as an anion. An E2 concerted mechanism has been previously proposed for the HCl elimination on solid acids based on the distribution of the products from 1,1,2-trichloroethane.[1a] The substitution effect shown in Fig. 6 can not be explained by the stabilities of a hypothetical intermediate in an E2 concerted mechanism ($CH_3\overset{-}{C}H\overset{+}{C}H_2$ from $CH_3CH_2CH_2Br$ < $\overset{-}{C}HBr\overset{+}{C}H_2$ from CH_2BrCH_2Br, for example). This fact as well as the absence of any isotope effect rules out the E2 concerted mechanism.

The reactivity order of five chloroethanes on metal sulfates with high *Xi* can be understood on the consideration that the carbonium ion is stabilized by the α-substituted chlorine atom but is unstabilized by the β-substituted chlorine atom.[1a] The equal reactivity between dehydrochlorination and dehydrobromination can also easily be explained by the small free energy differences in $RCl+H^+ \rightarrow R^+ + HCl$ and $RBr+H^+ \rightarrow R^+ + HBr$.[14]

Between two conformations of 1,1,2-trichloroethane, the *trans* form I is more stable than the *cis* one II in a vapor phase,[15] whereas II may be predominant due to strong interaction between electronegative halogen and the acidic surface of solid acids.[3] Whether the *cis* or *trans* elimination is assumed, the stereoselective formation of *cis*-1,2-dichloroethylene can be explained as follows:



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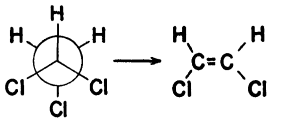

II

As a explanation of the preferential *cis*-1,2-dichloroethylene formations, which, in some catalysts, are far over the equilibrium value (*cis*-1,2/*trans*-1,2 = 30,[1b] equilib. one = 1.55[16]), this carbonium-ion mechanism containing an electrostatic interaction between acid sites and chlorine atoms may be more adequte than an E2 one.

Alumina has less catalytic activities as to *iso*-Pr and *n*-Pr, but more as to other reactants, than does silica-alumina. Alumina is generally thought to be less active for the carbonium-ion formation, but strikingly more active for some reactions, than is silica-alumina.[17] Therefore, regarding the less reactive reagents, another mechanism should be considered. A homolytic C–Cl cleavage may take to some extent. A considerable exchange of the halogens of 1-bromo-2-chloroethane and the markedly small slope in Fig. 6 may be understood in terms of this additional mechanism.

The Mechanism of Dehydrogenation on Solid Bases. The values of k_H/k_D over unity on solid bases in the elimination of HBr from 1,2-dibromoethane indicate that the C–H bonds were cleaved at or before the rate-determining step. There are three possible mechanisms: that is an E2 concerted, an E2 step-by-step (proton abstraction), or a carbanion mechanism. The dehydrohalogenation selectivity of the preferential elimination of hydrogen bromide from 1-bromo-2-chloroethane on solid bases can be explained in terms of neither the stability of the intermediate in a carbanion mechanism, which is expected from the stabilizing effect of bromine and chlorine on the carbanion ($Br\overset{-}{C}HCH_2Cl > Cl\overset{-}{C}H\text{-}CH_2Br$), nor the stability of a hypothetical intermediate in an E2 concerted mechanism ($Br\overset{-}{C}H\overset{+}{C}H_2 > Cl\overset{-}{C}H\overset{+}{C}H_2$). Taking account of the higher reactivity of chlorine in comparison with that of bromine, as deduced from the preferential HCl-elimination of 1-bromo-2-chloroethane on solid acids, the selective HBr-elimination on the basic catalyst cannot be explained by an E2 concerted mechanism, either. Thus, both mechanisms must be abandoned. If an E2 step-by-step mechanism with the determining step of the proton abstraction is assumed, the preferential dehydrobromination from 1-bromo-2-chloroethane can be explained in terms of the effect of halogen in the α- and β-positions.[1b] The preferential stereoselectivity of *trans*-1,2 formation from 1,1,2-trichloroethane and the reactivity order of the five chloroethanes on solid bases can also be well explained by the E2 step-by-step mechanism.[1a] The higher reactivity for dehydrobromination than dehydrochlorination on solid bases can be explained from the effect of the halogen of the β-position, and the greater reactivity for the dehydrohalogenation of dihaloethanes may be due to the inductive effect of the halogen of the α-position. All these results may support the idea that the dehydrohalogenation on

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[14] For example, in the case of R = *n*-Pr, the free energies of formation for compounds are as follows: *n*-PrCl, 8.54 kcal/mol; *n*-PrBr, 14.85; HCl, −23.41; HBr, −13.76 at 300°C. (D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York (1968), p. 518).

[15] K. Kuratani and S. Mizushima, *J. Chem. Phys.*, **22**, 1405 (1954).

[16] K. S. Pitzer and J. L. Hollenberg, *J. Amer. Chem. Soc.*, **67**, 1493 (1954).

[17] I. Mochida, J. Take, Y. Saito, and Y. Yoneda, This Bulletin, **41**, 65 (1968); I. Mochida, Y. Anju, A. Kato, and T. Seiyama, *ibid.*, **43**, 2245 (1970).

solid bases proceeds through an E2 step-by-step mechanism, although the reactivity of the haloethane can not yet be quantitatively explained.

The peculiarly high reactivities of *iso*-PrBr and *iso*-PrCl on solid bases cannot be explained by this mechanism. In the dehydrohalogenation of these secondary halides, a carbonium-ion character may increase, because the secondary carbonium ion is easily formed. Noller *et al.* have reported that the dehydrohalogenation of 2-chlorobutane proceeded through a two-step mechanism with a carbonium ion intermediate.[18] This mechanism may be valid in the case of isopropyl halides.

A quantitative explanation of the reactivity must be made next. The MO approach will be useful if its accuracy can be increased.

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18) H. Noller, W. Low, and P. Andreu, *Ber. Bunsenges., Phys. Chem.*, **68**, 663 (1964).