(12) The procedure for the alkaline rearrangement of **1** (R = 2-pyridyl) differed only in that neutralization was effected after ~10 min and gave a 73% yield of **3** (R = 2-pyridyl).

(13) E. B. Knott, *J. Chem. Soc.*, 1644 (1956).

(14) Compound **8** was too insoluble for nmr characterization.

A Mechanistic Study on Elimination Reactions over Solid Acid and Base Catalysts

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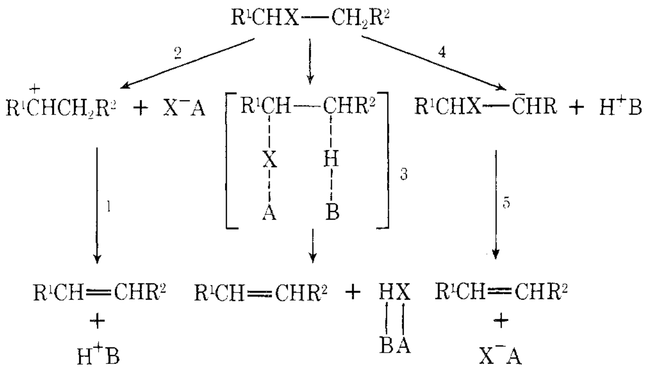
Scheme I



(A catalyst consists of acidic (A) and basic (B) sites.)

Type of Elimination Mechanism

Rate-determining step	Intermediate	Abbreviation of mechanisms
1	Carbonium ion	E1
2	Carbonium ion	$E2_{Ca}$
3	Simultaneous cleavage of C–H and C–X bonds	E2 concerted
4	Carbanion	$E2_{Cb}$
5	Carbanion	$E1_{Cb}$

Possible mechanisms[2,3] of ionic HX elimination from haloalkanes over solid catalysts are summarized in Scheme I. By taking account of the rate-determining step, five kinds of mechanisms are conceivable. The abbreviations are defined based on the following concept. Suffixes Ca and Cb in the abbreviation of the mechanism mean that carbonium ions and carbanions, respectively, are involved in the elimination process as intermediates. The rate-determining step distinguishes E1 and E2. That is, the step of intermediate formation is rate determining in E2 (except for E2 concerted, which is a one-step reaction), whereas the following step is in E1. E1, E2 concerted, and $E1_{Cb}$ need no comment, although conjugated acid or base of the catalyst might play some roles in $E1_{Cb}$ or E1 over the solid catalyst. $E2_{Ca}$ and $E2_{Cb}$ seem to be possible mechanisms over solid catalysts at elevated temperatures. The differences in these mechanisms can be considered to be present in the degree of C–H or C–X bond fission of the intermediate,[4] so that these mechanisms should change continuously according to the strength of interaction between a substrate and a catalyst. For elimination reactions of a certain reactant over a series of solid catalysts, the reaction may proceed *via* an $E2_{Ca}$ mechanism on a catalyst of moderate acidity, whereas with a basic catalyst it may occur *via* an $E2_{Cb}$ process. The E2 concerted mechanism may be possible on a catalyst which is neutral or consists of binary sites of acidity and basicity like alumina.[5] On a catalyst of which acidity or basicity is strong enough, the E1 or $E1_{Cb}$ mechanism may be realized. As for reactants, the same situation should occur. That is, a highly acidic reactant prefers a carbanion-type intermediate and a reactant in which halide is easily eliminated favors a carbonium ion-type intermediate. Continuous changes in acidity or basicity of catalysts and/or substrate structure[2c] may bring about continuous transitions of elimination mechanisms, as schematically described in Figure 1.

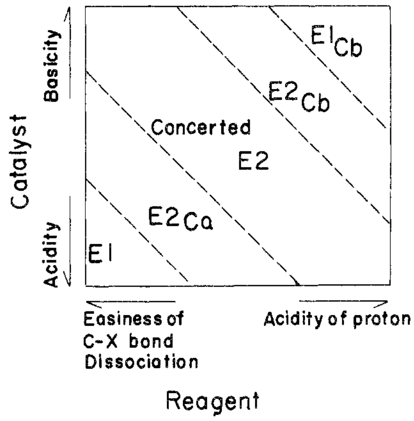


Figure 1. Schematic diagram of mechanism transitions according to the acid–base properties of catalysts and substrates. Abbreviations of mechanisms refer to the text.

In an attempt to study the transitions of elimination mechanisms, the kinetic isotope effects in dehydrohalogenation of 1,2-dibromoethane and 1,1,2,2,-tetrachloroethane and product distributions from 1,1,2-trichloroethane and 1,2-dihalopropanes over some solid catalysts have been investigated. The product distributions from 1,1,2-trichloroethane and reactivity orders of some chloroalkanes over solid catalysts have been explained in terms of $E2_{Ca}$ on solid acids, $E2_{Cb}$ on solid bases, and E2 concerted on alumina in previous papers.[6] Product distributions were found to change continuously according to the acidity of the catalysts.[6] An object of the present study is to understand such a continuous change from a mechanistic aspect.

Experimental Section

Reagents. Haloethanes used were obtained from Tokyo Kasei Co. Deuterated 1,2-dibromoethane ($C_2D_4Br_2$) and 1,1,2,2-tetrachloroethane ($C_2D_4Cl_4$) (Merck) were used without further purification.

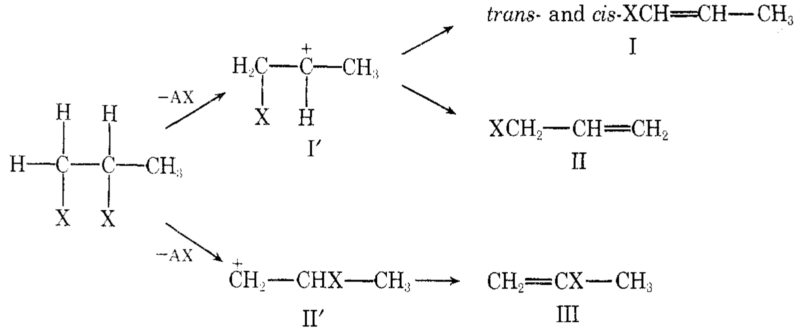
Catalysts. Silica–alumina (13% Al_2O_3), alumina, and KOH–SiO_2 were described in previous papers.

Apparatus and Procedures. Elimination reactions were observed by means of microcatalytic gas chromatography with a column of TCP (4m) at 60°. All reactions were carried out at 300° under a helium gas flow of atmospheric pressure. No occurrence of elimination was observable over the glass-wool packing, implying small contribution of simple pyrolysis. The elimination reaction was of 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 conversion/RSV gives the apparent rate constant, k (ml/g min). Experimental details have been described in previous papers.[8]

Results and Discussion

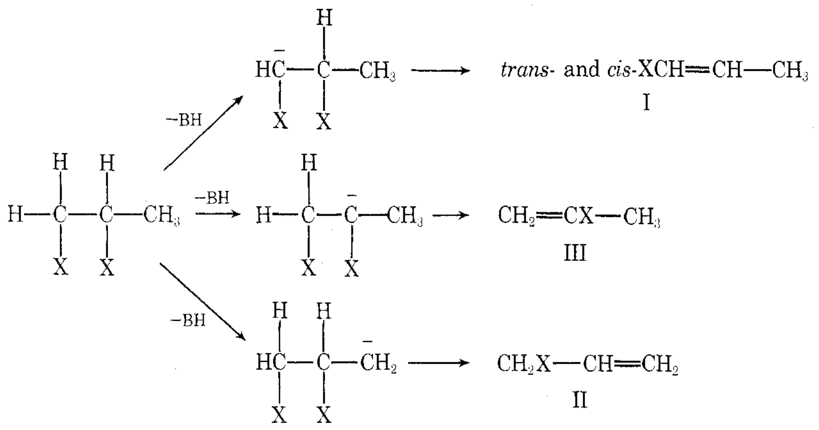
Product Distributions in Eliminations of Haloalkanes over Solid Catalysts. 1,2-Dihalopropane may give *trans*- and *cis*-1-halopropene (I), allyl halide (II), and 2-halopropene (III) through HX elimination over solid acids and bases. The reaction paths depicted in Schemes II–IV may explain formation of these products by various mecha-

Scheme II



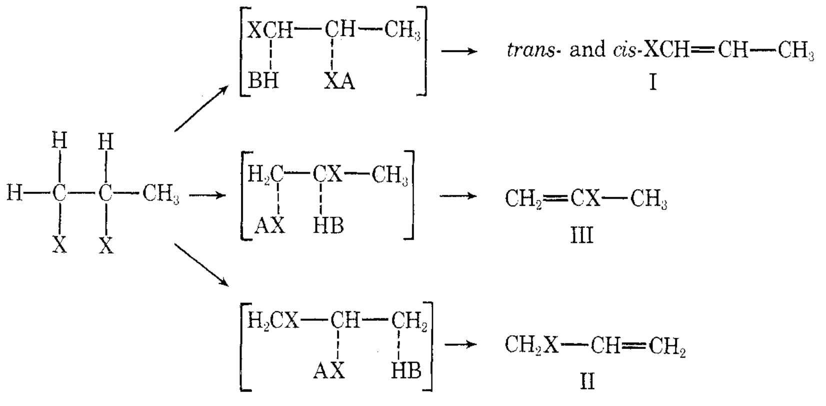
over a solid acid

Scheme III



over a solid base

Scheme IV



over alumina

nisms. Over the solid acid (Scheme II), secondary carbonium ion (I′) is more stable than a primary one (II′), leading to preferential formation of I and II relative to III. Schemes III and IV represent mechanisms for eliminations over solid base and alumina. Limited formation of II for the reaction with the solid base might be anticipated because of the lesser acidity of methyl proton compared with that of other protons. A positive charge on the secondary carbon of the intermediate assumed in the scheme may result in the preferential formation of I to that of III over alumina, although the ratio may not be so little as that over the solid acid because of the participation of protons in the reaction.

The relative proportions of unsaturated products derived from reactions of 1,2-dichloropropane, 1,2-dibromopropane, and 1,1,2-trichloroethane with silica–alumina, alumina, and KOH–SiO_2 are summarized in Table I. The selectivities calculated from Table I are shown in Table II. In Table II, one notices appreciable changes in the selectivity due to change of substituent groups. Such changes can be explained in terms of a transition of the reaction mechanism which corresponds to the change along with abscissa in Figure 1.

A marked change is observed in the III/(I + II) selectivities over silica–alumina by substitution of chlorine with bromine. The order of preferential production is I > II > III from 1,2-dichloropropane whereas it is II > I > III from 1,2-dibromopropane. Such changes can be attributable to less acidity of the proton and a weaker C–X bond in 1,2-dibromopropane which may facilitate easy formation of carbonium ion, provoking a shift from a typical $E2_{Ca}$ to an E1. For an E1 elimination from 1,2-dibromopropane, bridging structures (IV, V) would be expected to the intermediate and increase the III/(I + II) ratio because stability difference between IV and V would be decreased by bridging.

Table I
Relative Proportions of Unsaturated Products[a] from Reactions of 1,2-Dichloropropane, 1,2-Dibromopropane, and 1,1,2-Trichloroethane (%)

	Catalyst											
	Silica–alumina				Alumina				KOH–SiO$_2$			
	Product											
Reactant	*trans*-I	*cis*-I	II	III	*trans*-I	*cis*-I	II	III	*trans*-I	*cis*-I	II	III
1,2-Dichloropropane	7	54	38	0.1	2	74	14	10	46	28	Very small	26
1,2-Dibromopropane	5.5	14.4	75.0	4.5	6.8	50.7	36.5	6.0	34.9	29.6	0.1	35.5
1,1,2-Trichloroethane	7	93		0.1	19	58	23		7	2		9.1

[a] Products I, II, III refer to the text.

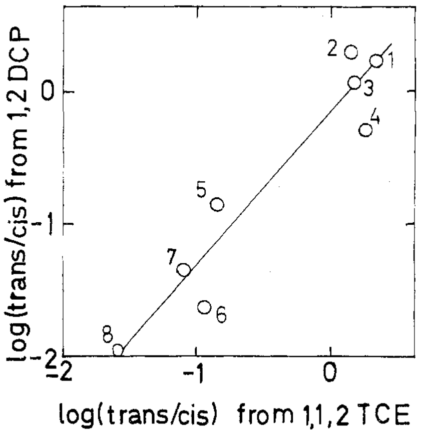
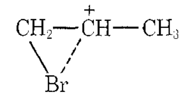
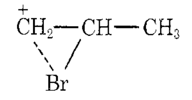


Figure 2. Continuous changes of trans/cis selectivities in elimination reactions of 1,2-dichloropropane and 1,1,2-trichloroethane: 1, KOH-SiO$_2$; 2, NaOH-SiO$_2$; 3, SrO; 4, MgO; 5, silica–alumina; 6, alumina; 7, NiSO$_4$-SiO$_2$; 8, NiSO$_4$.

The preferential formation of allyl bromide from IV (large II/I selectivity) is also explained by a facile elimination of methyl protons in the intermediate IV.



IV



V

Decreasing III/I selectivity of 1,1,2-trichloroethane in comparison with that of 1,2-dihalopropanes on alumina may be due to a shift from a typical concerted E2 to $E2_{Ca}$ induced by the decrease of proton acidity. In $E2_{Ca}$ the stability difference of primary and secondary carbonium ions may principally govern the value of III/I selectivity. Increased II/I selectivity of 1,2-dibromopropane may also be due to the increased $E2_{Ca}$ nature because of the weaker C–Br bond, being consistent with the decreased III/I value.

Similar explanations are also applicable to reactions over the solid base. A decrease of III/I selectivity of 1,2-dihalopropanes in comparison with that of 1,1,2-trichloroethane is explained in terms of a shift in the mechanism from $E2_{Cb}$ to E2 concerted which is produced by decreased acidity of proton.

A linear relation between trans/cis selectivities of 1,2-dichloropropane and 1,1,2-trichloropropene over some solid catalysts is shown in Figure 2. Although factors influencing the trans/cis selectivity in the elimination reactions could not be discussed in the present study, the linear relation may suggest that the mechanisms shown as Schemes II–IV play important roles in the decision of this selectivity. Then, such a continuous change of the trans/cis selectivity may also be explained by the continuous change of the elimination mechanism as shown by the change along the ordinate axis in Figure 1.

Table II
Elimination Selectivities of 1,1,2-Trichloroethane, 1,2-Dichloropropane, and 1,2-Dibromopropane

	Catalyst					
	Silica–Alumina		Alumina		KOH–SiO$_2$	
	Selectivity					
Reactant	III/(I + II)[a]	II/I[a]	III/I[a]	II/I[a]	III/I[a]	II/I[a]
1,2-Dibromopropane	4.7×10^{-2}	3.86	0.10	0.64	0.53	10^{-3}
1,2-Dichloropropane	10^{-3}	0.61	0.14	0.18	0.35	Very small
1,1,2-Trichloroethane	10^{-3}[b]		0.30[b]		10[b]	

[a] Products I, II, III from dihalopropanes refer to the text. [b] The ratio of 1,1-dichloroethylene/*trans*- and *cis*-1,2-dichloroethylene. 1,1,2-Trichloroethane (VI) has a similar structure to those of the 1,2-dihalopropanes except for their methyl groups substituted by chlorine, so that product distributions were arranged by a similar way in this table.

Table III
Kinetic Isotope Effects in the Elimination Reaction of 1,2-Dibromoethane and 1,1,2,2-Tetrachloroethane

	k_H/k_D	
Catalyst	1,2-Dibromoethane[a]	1,1,2,2-Tetrachloroethane[a]
Silica–Alumina	1.0 ± 0.1	1.5 ± 0.1
Alumina	1.0 ± 0.1	1.2 ± 0.1
KOH–Silica	1.6 ± 0.2	1.2 ± 0.1

[a] Reagent.

Changes in Kinetic Isotope Effect (k_H/k_D). Kinetic isotope effects in dehydrohalogenation of 1,2-dibromoethane and 1,1,2,2-tetrachloroethane over the solid acid and the base are summarized in Table III. Primary and secondary effects are included in these values because all hydrogens were replaced by deuteriums. The limiting value of the primary isotope effect at 300° is estimated to be 2.7.[7] On silica–alumina, the value as for 1,2-dibromoethane is unity, whereas it clearly increased for 1,1,2,2-tetrachloroethane. A similar change was also observable on alumina although the values were near unity. In contrast, the situation is reversed on KOH–silica.

Although definite mechanisms cannot be deduced from these values of kinetic isotope effect near unity, their changes are reasonably explained in terms of continuous transitions of the elimination mechanism (Figure 1) due to the acid–base character of the reagents, taking account of the relation of the kinetic isotopic effect with the elimination mechanism extensively reviewed by Fry.[8]

The acid–base natures of 1,2-dibromoethane and 1,1,2,2-tetrachloroethane concerning the ionic elimination can be summed up as follows: (1) acidity of proton, 1,1,2,2 > 1,2 and (2) strength of C–X bond, 1,1,2,2 > 1,2 (all protons and C–X bonds of each reagent are equivalent). These factors may contribute to a shift of the mechanism from $E2_{Ca}$ of 1,2-dibromoethane to concerted E2 of 1,1,2,2-tetrachloroethane on the solid acid, increasing the value of the kinetic isotope effect. The same situation may occur on the alumina catalyst where the low acidity of the proton and a weak C–Br bond may facilitate an $E2_{Ca}$ mechanism for 1,2-dibromoethane in spite of binary sites on the catalyst. The value of the isotope effect may, thus, increase for 1,1,2,2-tetrachloroethane because the mechanism is nearer to the typical concerted E2 than that of 1,2-dibromoethane. In the case of solid base, more $E1_{Cb}$ nature of 1,1,2,2-tetrachloroethane compared with 1,2-dibromoethane gives a low value for the kinetic isotope effect for the former. Thus, changes in the selectivity and the kinetic isotopic effect in the elimination due to the change of reactants are consistently explained in terms of continuous transitions of the reaction mechanism according to the acid–base nature of reagents as described in Figure 1.

The changes in Table III may correspond to the transitions of the mechanism according to the acid–base nature of the catalyst. As for 1,2-dibromoethane, increasing the basicity of the catalyst should shift the mechanism from $E2_{Ca}$ to $E2_{Cb}$ *via* E2 concerted, as indicated by the isotope effect. Alternatively, elimination from 1,1,2,2-tetrachloroethane proceeds by an E2 concerted mechanism with acidic catalysts but shifts to an $E1_{Cb}$ mechanism *via* an $E2_{Cb}$ mechanism with basic catalysts.

Registry No.—1,2-Dichloropropane, 78-87-5; 1,2-dibromopropane, 78-75-1; 1,1,2-trichloroethane, 79-00-3; 1,2-dibromoethane, 106-93-4; 1,1,2,2-tetrachloroethane, 79-34-5; silica, 7631-86-9; alumina, 1344-28-1; KOH, 1310-5S-3.

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Photolysis of 1-Methoxy-1,2,3-benzotriazole

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Recent experiments in our laboratory regarding the derivatives of 1-methoxy-1,2,3-benzotriazole (1) as potential pesticides prompted us to consider the photolytic decomposition of these molecules to see what harmful products would result upon the absorption of ultraviolet light. The photolysis of 1,2,3-benzotrizole (2) and several of its 1-substituted derivatives had been reported,[1–5] but the photochemistry of 1 had not been studied. Thus, we decided to photolyze 1 in several solvents in order to (a) obtain information regarding the photolytic reaction pathway and (b) determine whether a solvent effect was operative in the photolysis.

1 was prepared by treating 1-hydroxy-1,2,3-benzotriazole with sodium ethoxide and methyl iodide. Solvents ranging in polarity from cyclohexane and benzene to methanol and acetonitrile were used. All samples were 0.005 *M* in 1 degassed using a freeze–vacuum–thaw sequence and irradiated under a helium atmosphere at 300 nm for 6 hr, after which the solution had darkened to such an extent that further irradiation proved fruitless. The major products were isolated by chromatography on alumina and silica gel and identified by comparison of their spectral properties with those of known samples. The minor products were identified by comparison of their glpc retention times and tlc R_f values with those of known compounds. The results of the photolyses are listed in Table I.

Table I
The Photolysis of 1 at 3000 Å (Per Cent Yields)

Product	In benzene	In methanol	In cyclohexane	In acetonitrile
1-Methoxy-1,2,3-benzotriazole (1)	13	9	15	6
Aniline		4	4	8
Benzotriazole (2)		9	28	
Azobenzene (6)	63	61	11	81
2-Aminobiphenyl	8			
Biphenyl	6			
Bicyclohexyl			8	
N-Cyclohexylaniline			24	

From Table I it is readily apparent that the 1-methoxy group is lost during the photolyses in all the solvent systems studied. The formation of 2 in the methanol and cyclohexane photolyses can most easily be pictured as forming *via* a homolytic cleavage of the N–OCH_3 linkage followed by abstraction of a hydrogen atom from the solvent (Scheme I, path a). Supporting evidence for the occurrence of this pathway came from the isolation of bicyclohexyl from the cyclohexane photolysis. The dimer expected from the methanol photolysis, ethylene glycol, was also detected. Although no 1,2,3-benzotriazole was isolated from the benzene photolysis, its initial formation by the path mentioned above is strongly suggested by the isolation of 2-aminobiphenyl and biphenyl, both of which were found in the reported photolysis of 1,2,3-benzotriazole in benzene.[2]

An interesting feature of the photolyses was the isolation of azobenzene 6 as the major product in all the solvent systems studied with the exception of cyclohexane. The absence of any product containing the N–OCH_3 linkage together with the previously reported isolation of 6 from azidobenzene *via* phenylnitrene[6] 5 suggested path b (Scheme I) as a possible way of accounting for the formation of 6 from the photolysis of 1. 1 upon irradiation can lose a molecule of nitrogen to yield the diradical 3, which intramolecularly or intermolecularly abstracts a hydrogen to give the new diradical 4. 4 in turn undergoes a homolytic cleavage of the N–O bond to eliminate a molecule of formaldehyde and generate 5. Dimerization of 5 could then yield azobenzene. The isolation of formaldehyde *via* its 2,4-dinitrophenylhydrazone in acetonitrile lent credence to the proposed path b mechanism.

It was noted above that cyclohexane was the only solvent in which 6 was not found to be the major product. How-