carbonyl, 14638-72-3; ethyl 4-chloro-3-hydroxybutyrate, 10488-69-4; methyl 3,4-epoxybutyrate, 4509-09-5; methyl 4-hydroxycrotonate, 4508-99-0; 2,5-bis(carbomethoxymethyl)-1,4-dioxane, 14310-02-2; 3,4-epoxybutyronitrile, 624-58-8; 2-methylcyclopentanone, 1120-72-5.

Acknowledgment.—The author wishes to thank Dr. R. F. Fischer for some helpful discussions.

Linear Free-Energy Relationships in Heterogeneous Catalysis. VI.[1] Catalytic Elimination Reaction of Hydrogen Chloride from Chloroethanes on Solid Acids and Bases

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The elimination reaction of hydrogen chloride from chloroethanes on solid acids and bases was studied at 300° with the pulse technique in order to obtain the information about an acid–base nature of the various oxides. The relative reactivities of several reactants on the solid bases were different from those on solid acids. The reactivities on solid bases such as strontium oxide were found in the following order: (f) $CHCl{=}CCl_2$ from $CHCl_2CHCl_2$ > (d) $CCl_2{=}CH_2$ from $CHCl_2CH_2Cl$ > (c) $CCl_2{=}CH_2$ from CCl_3CH_3 > (e) $CHCl{=}CHCl$ from $CHCl_2CH_2Cl$ > (b) $CHCl{=}CH_2$ from CH_2ClCH_2Cl > (a) $CHCl{=}CH_2$ from $CHCl_2CH_3$, whereas they were in the order c > a > e > f > b > d on solid acids such as silica–alumina and alumina–boria. Alumina had a quite different reactivity order of c > f > a > e > b > d. The reactivity orders on strontium oxide and calcium oxide can be correlated with a reactivity index of the delocalizability, $D_r^{\mathrm{N}}(\mathrm{H})$, and on alumina with $D_r^{\mathrm{R}}(\mathrm{Cl}) + D_r^{\mathrm{R}}(\mathrm{H})$. The product distributions, $CH_2{=}CCl_2$, *trans*- and *cis*-$CHCl{=}CHCl$, from $CHCl_2CH_2Cl$ were 1,1 > *trans* > *cis* on solid bases, *cis* > *trans* > 1,1 on solid acids, and *cis* > 1,1 > *trans* on alumina. The selectivity variation can be understood if the reaction mechanism is a concerted E2 on the strong acids and varies gradually into a stepwise E2, where the proton-abstraction step is rate determining, as the basicity of the catalyst increases.

It is worthy of attention that the catalytic behaviors of some solid acids like silica–alumina and alumina–boria are not necessarily similar, but even contradictory, to those of alumina. The present authors found that alumina had an exceedingly high reactivity with methylene chloride to produce methyl chloride,[1] whereas it has a low catalytic activity in comparison with silica–alumina in typical solid acid-catalyzed reactions like dealkylation of alkylbenzenes.[2] This fact may indicate that surface hydroxyl groups on alumina have different chemical properties from those on silica–alumina. The surface hydroxyl protons on silica–alumina usually behave as the Brønsted acid sites and produce carbonium ions. However, the surface hydroxyl group on alumina was concluded to behave as a radical reactant for its reaction with methylene chloride.[1]

In the present work, the elimination of hydrogen chloride from chloroethanes to give chloroethylenes on various oxides was studied with the aid of the LFER (linear free-energy relationships) regarding the reactant effect;[2] the main intention is to obtain information about the differences in the catalytic properties of the oxides which may be caused by their acid–base characters.

Both the order of the reactivities in this elimination reaction among five chloroethanes and the stereoselectivity from 1,1,2-trichloroethane were also observed on solid acids and bases. They will be discussed with the aid of the reactivity indices derived from the molecular orbital theory.

Experimental Section

Reagents.—Chloroethanes used are listed in Table I. They were all of GR or EP grade (Tokyo Kasei Co.) and were not purified further, since no impurities were detected by gas chromatography.

TABLE I

REAGENTS AND THEIR REACTIONS

Reagent	Reaction	Reaction products
1,1-Dichloroethane (I)	a	$CHCl{=}CH_2$
1,2-Dichloroethane (II)	b	$CHCl{=}CH_2$
1,1,1-Trichloroethane (III)	c	$CCl_2{=}CH_2$
1,1,2-Trichloroethane (IV)	d	$CCl_2{=}CH_2$
	e	*trans*-$CHCl{=}CHCl$ and *cis*-$CHCl{=}CHCl$
1,1,2,2-Tetrachloroethane (V)	f	$CCl_2{=}CHCl$

Catalysts.—Catalysts used are listed in Table II, together with some of their properties. They were all calcined for 8 hr in the atmosphere.

Apparatus and Procedures.—The pulse technique was adopted.[2-4] The hydrogen carrier gas was purified by removing water and oxygen with a Dry Ice–ethanol trap and activated copper on kieselguhr, respectively. Tricresyl phosphate (Japan Chromato Co.) was used for the analytical column (4 m, 70°).[5] The reaction temperature was 300 ± 2°. After the catalyst was pretreated for 1 to 3 hr in the hydrogen flow at 450°, 2 μl of the reactant was injected into the gas flow at the top of the reactor through a silicone serum cap with a microsyringe. Chloroethylenes and chloroethanes, the elimination products and the reactants, respectively, were analyzed with a gas chromatograph directly connected to the reactor. The elimination reaction was nearly first order under experimental conditions for all reactants, and the conversion was verified to be a linear function of the reciprocal space velocity under low conversions; thus the slope is the apparent rate constant, k (ml/g min).[4] This unit of the rate constant is converted into the usual one, mole/min atm g of catalyst, by the multiplication of a factor, 4.16×10^{-5}. Reactivities of the catalysts decreased remarkably by each pulse; therefore, the rate constant was calculated from the conversion

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[1] Part V: I. Mochida and Y. Yoneda, *J. Catalysis*, in press.

[2] I. Mochida and Y. Yoneda, *ibid.*, **7**, 386, 393 (1967).

[3] R. J. Kokes, H. Tobin, and P. H. Emmett, *J. Am. Chem. Soc.*, **77**, 5860 (1955).

[4] D. W. Bassett and H. W. Habgood, *J. Phys. Chem.*, **64**, 769 (1960).

[5] W. Funasaka and K. Ikegami, "Gas Chromatography," Hirokawa Shoten Co., Tokyo, 1965, p 583.

Table II

Catalysts

Catalyst			Surface area, m^2/g	Compn	Remarks
No.	Symbol	Name			
1	SA-1	Silica–alumina	540	13% Al_2O_3	a, b
	SA-1-Na-1	Silica–alumina–NaOH	450	0.048 mequiv of Na/g	a, c
	SA-1-Na-2	Silica–alumina–NaOH	480	0.087 mequiv of Na/g	a, c
2	SA-1-Na-3	Silica–alumina–NaOH	480	0.168 mequiv of Na/g	a, c
3	A-B-1	Alumina–boria	290	10% B_2O_3	Copptd[a]
4	SM-1	Silica–magnesia	560	16% MgO	a, d
5	Al-S	Aluminum sulfate–SiO_2	500	0.4 mmole of $Al_2(SO_4)_3$/g	a, e
6	Mg-S	Magnesium sulfate–SiO_2	500	0.4 mmole of $MgSO_4$/g	a, e
7	S-1	Silica	600	SiO_2	a, f
8	A-3-550	Alumina	170	γ-Al_2O_3	a, g
9	A-3-Na-550	Alumina–NaOH	150	0.02 mequiv of Na/g	a, h
10	A-3-F	Alumina–NH_4F	80	*ca.* 0.2 mmole of F/g	a, i
11	Na-S	NaOH–SiO_2		1.0 mequiv of Na/g	a, j
12	K-S	KOH–SiO_2		1.0 mequiv of K/g	a, j
13	MgO			MgO	k
14	CaO			CaO	l
15	SrO		1	SrO	m
16	K_2CO_3			K_2CO_3	n
17	$BaCO_3$			$BaCO_3$	n

[a] Calcined at 550°. [b] "Nippon Cat," a cracking catalyst (The Shokubai Kasei Co.). [c] SA-1 was impregnated with a fixed amount of aqueous NaOH and then calcined at 550°. [d] "TY-13," a cracking catalyst (The Nikki Kagaku Co.). [e] By impregnation on S-1 with aqueous $Al_2(SO_4)_3$ or $MgSO_4$. [f] "Q-12," an active silica gel for chromatography (The Wako Chemicals Co.). [g] "F-110," an active alumina (The Alcoa Co.). [h] A-3 impregnated with aqueous NaOH. [i] By treatment of A-3 with aqueous NH_4F. [j] By impregnation of S-1 with aqueous NaOH or KOH. [k] A GR grade reagent (The Kanto Kagaku Co.) calcined at 600°. [l] A GR grade reagent calcined at 900°. [m] A GR grade reagent calcined at 850°. [n] A GR grade reagent calcined at 350°.

of the first pulse over a fresh catalyst. This decline in the catalytic activities may be due to the reaction of the catalysts with the hydrogen chloride formed.

The calculation of the LCAO-MO was made on an OKITAC 5090 at the Data Processing Center of this university.

Results and Discussion

The Reaction Products.—The main products were chloroethylenes formed by the hydrogen chloride elimination as shown in Table I, where the alphabet designates the reactions. A small amount of other products, *i.e.*, carbon dioxide, alkynes, or some polymerized substances were detected, but their amounts were so minor that they were negligible under the experimental conditions. Three products from IV could be analyzed at one time. It was confirmed that these products were not isomerized mutually under the experimental conditions.

The Reactivity Order.—The reactivities of the reactants on SA-1, A-B-1, SrO, and A-3-550 are shown in Figure 1. The rate constants on SA-1 are taken as the abscissa and those on A-B-1, SrO, and A-3-550 as the ordinate. The reactivity orders on SA-1 and A-B-1 were well correlated with each other. On the contrary, relations of the reactivity orders between SA-1 and both SrO and A-3-550 were quite irregular. It has already been ascertained that SA-1 and A-B-1 have a common character as the solid acids,[2] whereas SrO is a solid base. Recently the same tendency of the reactivity order was reported in the liquid-phase reaction.[6] It is worthy of mention that A-3-550 has a different behavior from those of both SA-1 and A-B-1 in the reaction with halomethanes.[1]

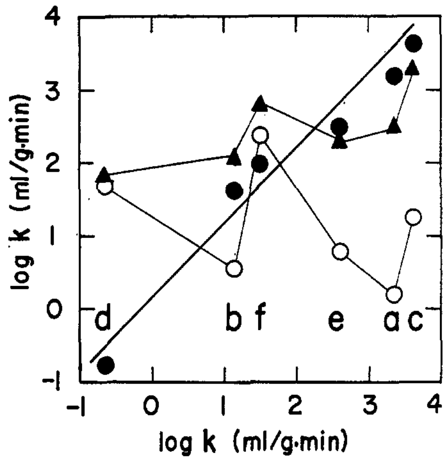

Figure 1.—Correlations among the rate constants of HCl elimination from chloroethanes on SA-1, SrO, A-3-550 and A-B-1. The abscissa is the logarithms of the rate constants on SA-1: ● = A-B-1, ○ = SrO, ▲ = A-3-550. The alphabet designates the reaction in Table I.

Correlation with the Quantum Chemical Reactivity Indices.—The elimination reaction over the solid bases like SrO may be assumed to take place through a stepwise E2 mechanism, where the proton abstraction is rate determining.[7] All the reactants were postulated to react through the α,β-hydrogen chloride elimination. Regarding the reactant IV, 1,1-dichloroethylene may be formed by the abstraction of an α-hydrogen atom and 1,2-dichloroethylene by that of a β-hydrogen atom. The delocalizability, a reactivity index defined by Fukui, *et al.*,[8] of the hydrogen atom for the nucleophilic abstraction, D_r^N(H), was calculated by the simple LCAO–MO method for σ electrons, as given in Table III. The Coulomb and resonance integrals employed in this

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(6) A. Suzuki, H. Iwata, and J. Nakamura, *Kogyo Kagaky Zasshi*, **69**, 1903 (1966).

(7) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., (1959), p 479.

(8) K. Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Japan*, **34**, 1111 (1961).

TABLE III

DELOCALIZABILITY OF THE REACTANTS

		Abstraction								
		Hydrogen					Chlorine			
	Reactant	Position	Sym. no.	D_r^N(H)	Reaction	D_r^R(H)	Position	Sym. no.	D_r^R(Cl)	D_r^E(Cl)
	α β									
I	$CHCl_2$–CH_3	α	1	1.739		1.345	α	2 (6)[a]	1.837	1.553
		β	3	1.035	a	1.032				
II	CH_2Cl–CH_2Cl	$\alpha = \beta$	4	1.208	b	1.102	$\alpha = \beta$	2 (4)[a]	1.512	1.577
III	CCl_3–CH_3	β	3	1.542	c	1.282	α	3 (9)[a]	5.412	1.514
IV	$CHCl_2$–CH_2Cl	α	1	1.882	d	1.413	α	2 (4)[a]	1.923	1.549
		β	2	1.323	e	1.156	β	1 (1)[a]	1.582	1.573
V	$CHCl_2$–$CHCl_2$	$\alpha = \beta$	2	2.380	f	1.657	$\alpha = \beta$	4 (4)[a]	2.225	1.543

[a] The number in parentheses is the α,β combination number of H and Cl.

calculation were also from Fukui, *et al.*[9] A good relationship was proved between the rate constant of the reactant divided by the symmetry number (w), the number of its equivalent hydrogen atoms, and D_r^N(H), as shown in Figure 2. No correlation was found between the rate constant and D_r^N(Cl), D_r^E(Cl), D_r^R(Cl), nor D_r^R(H)[10] given in Table III. These facts will support the reaction mechanism mentioned above. The order of the acidity of the reactants, V > IV > III > II > I,[11] also coincides qualitatively with the reactivity order.

The kinetic data of the elimination reaction of hydrogen fluoride from 1,1,1-trifluoro-2,2-dihaloethanes by a basic catalyst in the liquid phase measured by Hine, *et al.*,[12] were plotted against D_r^N(H), as shown in Figure 3, where the values of D_r^N(H) are given in Table IV.

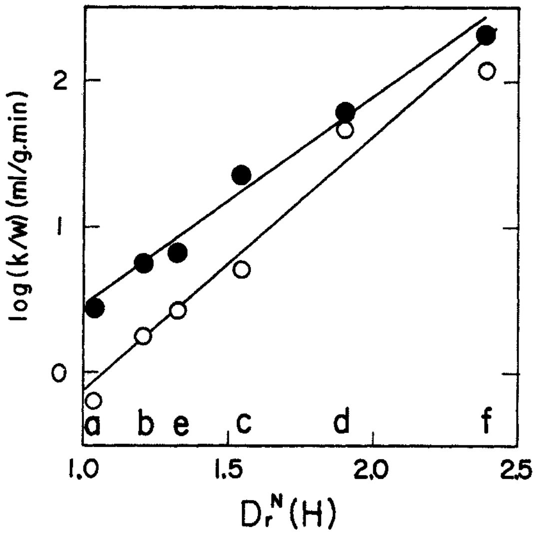

Figure 2.—Rate constants of the elimination on SrO and CaO are given as a function of the delocalizabilities of the reactants: ○ = SrO, ● = CaO. The alphabet designates the reaction in Table I.

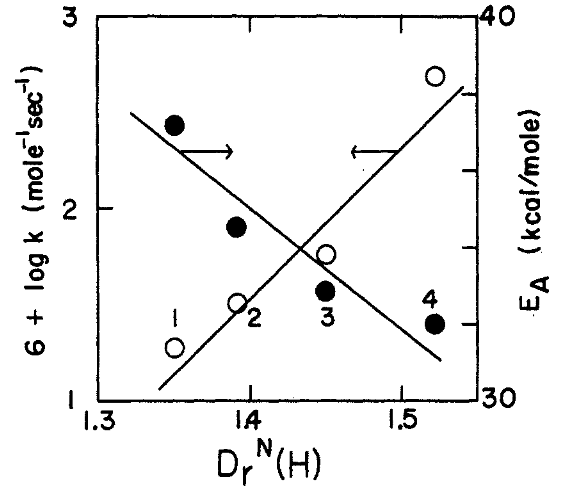

Figure 3.—The rate constants and activation energies of HF elimination reactions are given as a function of the delocalizabilities. Reactants are 1,1,1-trifluoro-2,2-dihaloethanes and methanolic sodium methoxide. Numbers refer to Table IV. Kinetic data are taken from Hine, *et al.*[12]

TABLE IV

DELOCALIZABILITY OF THE REACTANTS

No.	Reactant	D_r^N(H)
1	CF_3CHCl_2	1.348
2	$CF_3CHBrCl$	1.397
3	CF_3CHBr_2	1.450
4	CF_3CHI_2	1.517

The activation energy and rate constant were continually correlated to D_r^N(H), although they claimed that the proton-abstraction step was in the preliminary equilibrium. A qualitative correlation between the frontier (the lowest vacant orbital) electron density of a hydrogen atom and the elimination reaction of chlorobutane and 2-*exo*-chloronorbornane by the basic catalyst was reported by Fukui and Fujimoto.[13]

The reactivity on A-3-550 could be correlated not to D_r^N(H) but to D_r^R(Cl) + D_r^R(H), as shown in Figure 4. The rate constant as the ordinate was divided by the combination number of H and Cl on the postulation that the reaction on A-3-550 proceeded through an α,β elimination. This correlation may coincide with the previous conclusion that halomethanes react preferably with A-3-550 in a radical mechanism.[1] Noller, *et al.*,[14] reported that the hydrogen chloride elimination reaction of 2,3-dichlorobutane proceeded as an E2 on alumina. The reactivity index as the sum of the two terms is consistent with the concerted E2 mechanism.

It was attempted to correlate the reactivity on solid acids with D_r^E(Cl), D_r^N(H), or D_r^R(Cl) + D_r^R(H), but these trials were unsuccessful. The reactivity order of the reactants on solid acids, on which the elimination

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[9] K. Fukui, H. Saito, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Japan*, **35**, 1814 (1962).

[10] D_r^E and D_r^R are the delocalizabilities for an electrophilic and a radical abstraction, respectively. See ref 8.

[11] T. Yoshimoto, *Nippon Kagaku Zasshi*, **83**, 961 (1962).

[12] J. Hine, K. Wiesboek, and D. B. Ramsay, *J. Am. Chem. Soc.*, **83**, 1222 (1961).

[13] K. Fukui and H. Fujimoto, *Tetrahedron Letters*, 4303 (1965).

[14] H. Noller, K. Hantsche, and P. Andreu, *J. Catalysis*, **4**, 354 (1965).

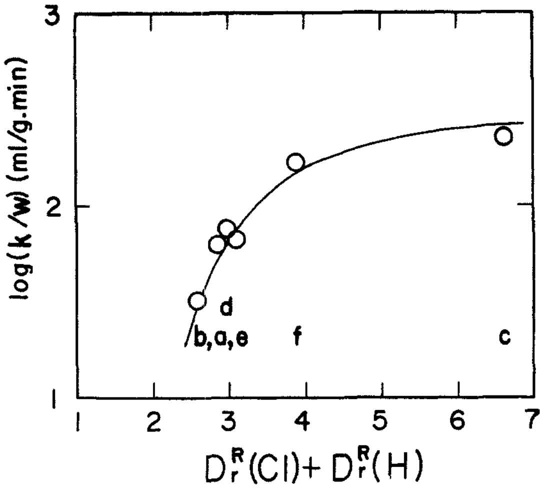

Figure 4.—The rate constants of the elimination reaction on A-3-550 are given as a function of the delocalizabilities. The alphabet designates the reaction in Table I.

reaction may proceed through an ion mechanism consisting of abstractions of a chloride anion and a proton, can be qualitatively understood by the following criterion concerning the stability of the hypothetical concerted E2 intermediate and the reaction rate. When the charge of the carbon atom is intensified, the intermediate ion becomes less stable and consequently the reaction rate may decrease. The chlorine atom usually behaves as an electron-withdrawing substituent through the inductive effect. However, only when the chlorine atom is substituted to the positively charged carbon, it may donate an electron to the carbon atom through the resonance effect, so that it stabilizes the cation.[15] Recently Taft, *et al.*,[16] measured the heats of formation of the chlorine-substituted methyl cations by mass spectroscopy. Their result is that the methyl cation substituted by more chlorine atoms is formed more easily, which coincides with the above assumption. The stability order of the hypothetical intermediate in the hydrogen chloride elimination reaction from chloroethanes is thus deduced as the following: $\underset{+}{\mathrm{CCl_2}}\text{–}\underset{-}{\mathrm{CH_2}} > \underset{+}{\mathrm{CHCl}}\text{–}\underset{-}{\mathrm{CH_2}} > \underset{+}{\mathrm{CHCl}}\text{–}\underset{-}{\mathrm{CHCl}} > \underset{+}{\mathrm{CHCl}}\text{–}\underset{-}{\mathrm{CCl_2}} > \underset{+}{\mathrm{CH_2}}\text{–}\underset{-}{\mathrm{CHCl}} > \underset{+}{\mathrm{CH_2}}\text{–}\underset{-}{\mathrm{CCl_2}}$. The reactivities on solid acids such as SA-1 and A-B-1 are of exactly the same order as is seen in Figure 1.

Stereoselectivity of the Elimination Reaction of Hydrogen Chloride from 1,1,2-Trichloroethane.—One can explain the selectivity among the reaction products from 1,1,2-trichloroethane by classifying the catalysts into three groups, that is, solid bases, solid acids, and alumina. The 1,1/1,2 and *trans/cis* ratios in this reaction are shown in Figure 5 for the catalysts given in Table II. Generally speaking, the ratios of 1,1/1,2 >1 and *trans/cis* > 1 were obtained for solid bases, whereas the ratios of 1,1/1,2 $\ll 1$ and *trans/cis* < 1 for solid acids. A common line can be drawn throughout solid bases and acids for the selectivity correlation in Figure 5. In comparison among the selectivities on MgO, CaO, and SrO, 1,1/1,2 and *trans/cis* selectivities become larger in the order of their base strength, as shown in Figure 5. As for alumina, the selectivity gives another line as a function of the calcination temperatures. The orders of three products were 1,1 > *trans* > *cis* on bases, *cis* > *trans* > 1,1 on acids, and *cis* > 1,1 > *trans* on alumina calcined at lower temperatures. Thermodynamic data[17,18] of three dichloroethylene isomers are listed in Table V. It is clear from Table V that the selectivity of this reaction was not necessarily determined by the thermodynamic stability.

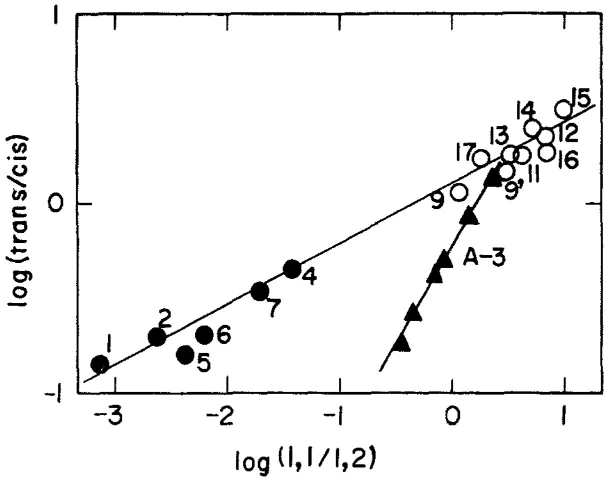

Figure 5.—Correlations between *trans/cis* and 1,1/1,2 selectivities in the HCl elimination reaction from 1,1,2-trichloroethane on solid catalysts: ○ = solid bases, ● = solid acids, ▲ = alumina. The numbers refer to Table II.

TABLE V

THERMODYNAMIC DATA OF DICHLOROETHYLENES

	$\Delta H_f°_{298}$,[a] kcal/mole	$S_f°_{298}$,[a] cal/mole deg
1,1-Dichloroethylene	+8.0	68.8
cis-1,2-Dichloroethylene	−1.5	68.8
trans-1,2-Dichloroethylene	−1.1	71.1
$K(trans/cis)_{573.2} = 0.645$[b]		

[a] See ref 17. [b] See ref 18.

The elimination reaction may proceed through the stepwise E2 mechanism on the basic catalysts as mentioned before, so the intermediate still keeps the single bond nature in the C–C bond. Then, the intermediates from A1 and B1 would be preferred to those from A2 and B2 in the *trans* and *cis* eliminations, respectively, as is deduced from the thermodynamic stabilities of 1,1,2-trichloroethane rotamers (Scheme I).[19] Thus, *trans*-dichloroethylene may be formed predominantly on bases.

On the other hand, the reaction may proceed through the concerted E2 on solid acids and alumina; then both C–Cl and C–H bonds of the intermediate may be so loosened that the C–C bond would have the double bond nature to some extent. Therefore, the *trans–cis* equilibrium of the intermediate resembles that of dichloroethylenes. Hence, *cis*-1,2,dichloroethylene would preferentially be produced. This explanation is due to the product development selectivity.[20]

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(15) J. Hine and D. E. Lee, *J. Am. Chem. Soc.*, **73**, 22 (1951).

(16) R. H. Martin, F. W. Lampe, and R. W. Taft, Jr., *ibid.*, **88**, 1353 (1966).

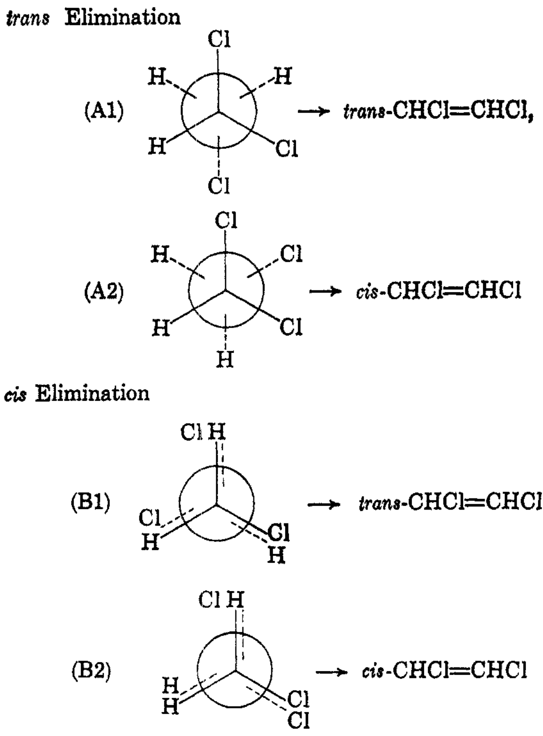
(17) P. Goldfinger and G. Martens, *Trans. Faraday Soc.*, **57**, 2220 (1961).

(18) K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **76**, 1493 (1954).

(19) The *trans* rotamer of 1,1,2-trichloroethane is 2.9 kcal/mole more stable than the *gauche* rotamer in the gas phase: K. Kuratani and S. Mizushima, *J. Chem. Phys.*, **22**, 1403 (1954).

(20) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

SCHEME I



The reaction mechanism may vary gradually from the concerted E2 on the solid acids to the stepwise E2 on the solid bases according to the acid–base character of the catalysts, and this gradual change gives the variable selectivity.

Calcination and Impregnation Effects on Stereoselectivity of A-3 and SA-1. A. Effects of the Calcination Temperature.—The 1,1/1,2 and *trans/cis* selectivities of alumina increased as the calcination temperature was raised, as shown in Figure 5, whereas the total reaction rate was found to decrease slightly. The relation between the 1,1/1,2 selectivity and the calcination temperature is shown in Figure 6. The A-3 catalyst, calcined at 1000° (A-3-1000), had the selectivity of a solid base; A-3-1000 was found to have an α-alumina structure by the X-ray diffraction. A high temperature calcination may destroy the active radical sources in the alumina surface. This trend of the selectivity dependency on the calcination temperature was found also for A-3-Na, as shown in Figure 6. In connection with these trends, reportedly the dehydrogenation selectivity of formic acid decomposition became large when alumina catalysts were calcined at higher temperatures,[21] and was accelerated by basic catalysts.[22]

In marked contrast to the case of A-3, the calcination temperature had no effect on the selectivity of SA-1, although the activity fell down to one-tenth when the calcination temperature was raised from 550 to 600°.

B. Sodium and Fluoride Ion Impregnation Effects.—An addition of about 0.02 mequiv of Na/g to A-3

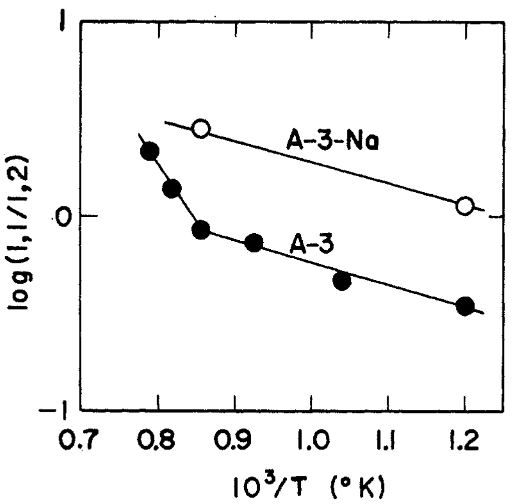


Figure 6.—The effects of the calcination temperature on the selectivities of alumina catalysts in the HCl elimination reaction from 1,1,2-trichloroethane: ● = A-3, ○ = A-3-Na.

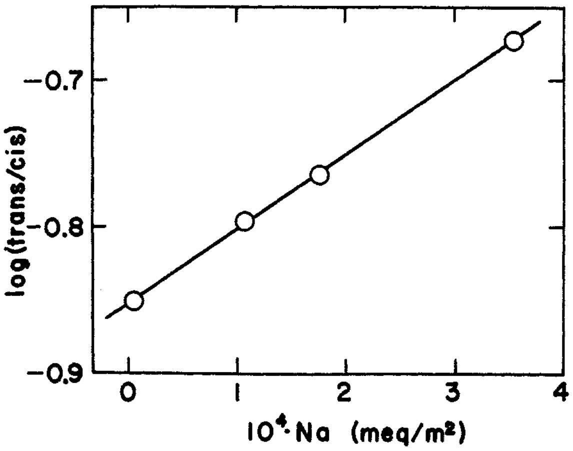


Figure 7.—The *trans/cis* selectivity as a function of the amount of Na poisoning on SA-1 in the HCl elimination reaction from 1,1,2-trichloroethane.

to give A-3-Na-550 changed the 1,1/1,2 and *trans/cis* selectivities from 0.32 to 1.20 and from 0.20 to 1.20, respectively. The changes of the selectivities of SA-1 were, however, much smaller than those of A-3.

A linear correlation between the *trans/cis* selectivity and the amount of sodium ions on SA-1 is shown in Figure 7. This correlation may be understandable to be due to the acid strengths of these silica–alumina catalysts as in the case of dealkylation reaction.[2]

The ammonium fluoride treatment of the alumina catalyst increased the dealkylation activity.[2] On the contrary, 1,1-dichloroethylene formation was vigorously suppressed in the hydrogen chloride elimination of 1,1,2-trichloroethane by the same treatment. A small amount of fluoride ion seems to make alumina behave like silica–alumina. The *trans/cis* selectivity also decreased from 0.20 to 0.13. The fluoride treatment may enhance the acidity of alumina.

Registry No.—I, 75-34-3; II, 107-06-2; III, 71-55-6; IV, 79-00-5; V, 79-34-5; hydrogen chloride, 7647-01-0.

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(21) G. M. Schwab and E. Schwab-Agallidis, *ibid.*, **71**, 1806 (1949).

(22) P. Mars in "The Mechanism of Heterogeneous Catalysis," J. H. de Boer, Ed., Elsevier Publishing Co., Amsterdam, 1960, p 49.