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Stereoselectivity of the Elimination Reactions of Alkyl Halides Over Silica Gel and Alkali-Treated Silica Gel

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The stereochemistry (*anti* or *syn* mode) of dehydrohalogenation of 2-bromobutane, 2,3-dichlorobutane and 2,3-dibromobutane over various solid acids and bases, such as silica gel and alkali salt-impregnated silica gels, at 95–300°C was determined from the products of the diastereomeric isomers of each compound. The steric course of dehydrobromination of 2-bromobutane at low temperatures was mainly *anti* mode over KOH–SiO_2, K_2CO_3–SiO_2 and *syn* mode over SiO_2. At high temperatures, *syn* elimination was the favored mode over most catalysts studied. The reactions of 2,3-dihalobutanes proceeded by *anti* elimination over those solid surfaces.

From the variation in the stereochemical reactions of the catalysts and reactants, the ease of β-proton elimination, which increases with the acidity of β-proton and basicity of solid, was found to be the prime factor determining the steric course of reaction.

The reaction mechanism is discussed on the basis of the stereochemistry, isotope effects and the relative reactivity of various alkyl halides.

INTRODUCTION

The stereochemistry of a reaction is closely associated with the nature of transition state and has been a useful tool for the elucidation of the reaction mechanisms, particularly in the field of organic reactions in the liquid phase. It is expected, therefore, that investigations of the steric course of reactions over solid surfaces and of the factors controlling the stereochemistry would provide important information about the catalyst surfaces and surface reactions, i.e., the nature of active sites and of the transition state.

The stereochemistry of elimination reactions (*anti* or *syn*) over solid catalysts has been studied by several investigators, who were mostly concerned with dehydration of alcohols. It has been reported that dehydration of cyclic (*1*) and acyclic alcohols (*2*) proceeds mostly via *anti* mode over alumina, but the latter reaction takes place via *syn* mode over thoria (*3*) and hydroxyapatite (*4*). Pines and co-workers (*1*) suggested that a certain surface structure such as a crevice or pore enables dehydration to proceed by *anti* elimination (*1*). According to Kibby, Lande and Hall (*4*), alcohol is adsorbed on alumina with its OH covering an exposed aluminum ion, so that the β-hydrogen directed away from the surface can transfer to a neighboring oxide ion of alumina from the top of the molecule, resulting in *anti* elimination. Over hydroxyapatite, on the other hand, a cyclic intermediate involving a surface proton effects *syn* elimination. A similar explanation for reactions over alumina is found in the paper of Knötzinger, Bühl and Kochlofel (*5*). Thomke and Noller (*6*) suggested that a steric effect, which is not specified, is responsible for *syn* dehydration over phosphates. Stereospecific *anti* elimination of 2,3-dichlorobutanes loses its specificity gradually as the catalyst is varied from basic to acidic (*7*). This result is explained by the change from a concerted mechanism to a stepwise carbonium-ion mechanism. A stable carbonium ion would lose its original conformation by rotation about the C^{α}–C^{β} bond. We reported that the steric course of dehydrobromination of 2,3-dibromobutane (*8a*) and 2-bromobutane (*8b*) varied depending on the nature of catalyst and the reaction temperature, and pointed out the importance of the acid–base interaction between reactant and catalyst (*8c*). The reaction mechanisms of dehydrohalogenation over solid acids and bases have also been discussed previously (*7*, *15*).

Thus, although several studies have been reported on this subject, together with different explanations, e.g., steric effect, geometry of intermediate and the timing of bond ruptures, more studies are needed to elucidate the factors controlling the steric course of a surface reaction. This study is primarily intended to determine the stereochemistry of dehydrohalogenation of simple monohalogenated acyclic hydrocarbons over solid surfaces, since no such study has been reported except for our preliminary report (*8b*). We also attemnted to find out the controlling factors in the steric course of reaction, using catalysts with various acid–base properties and several alkyl halides having similar molecular dimensions and different reactivities. The use of catalysts having various acid strengths proved to be useful, with aid of linear free energy relationships (*9a*), in the study of *n*-butene isomerization (*9b*). Further, we expected the reaction mechanism to be made clearer from a study of the stereochemistry and kinetic isotope effects.

EXPERIMENTAL METHODS

Apparatus and procedure. A conventional pulse (microcatalytic) technique was utilized (*8*). Hydrogen carrier gas, which was deoxygenated and dried by passage through a "Deoxo" column and a trap cooled at −195°C, was flowed over catalysts (40–600 mg) sealed in microreactors at 60 ml/min and at 1.4–1.8 kg/cm². The amount of catalysts was varied depending on the catalytic activity so as to keep the conversion below 20%, usually at about 10%. After the catalysts were preheated at 300°C for 1 hr and cooled to reaction temperature (95–300°C), 1 μl of alkyl halides was injected in the hydrogen stream with aid of a microsyringe. It was ascertained that the conversion increased proportionally with the amount of catalyst. The products, collected by a −195°C trap when necessary, were analyzed by use of two parallel columns, directly connected to the reactor; dimethylsulfolane on Celite, 7 m, for butene analysis and Apiezon grease on Celite, 2 m, for the analysis of the rest. For the determination of the deuterium content of butenes, the products of 3–5 pulses were collected and submitted for mass spectrometric analysis after the gas chromatographic separation using a column of propylene carbonate on Chromosorb, 10 m.

Catalysts. Two silica gels [SiO_2(I) and (II)] were used as catalysts and supports. SiO_2(I) was prepared by the hydrolysis with distilled water of tetraethoxysilane which was distilled three times. SiO_2(II) was a commercial silica gel for chromatographic use (Wako gel, Q-12) obtained from Wako Pure Chemical Ind., Ltd., Osaka. Both were calcined in air at 550°C for 5 hr after dried at 120°C overnight. Other catalysts (KOH–SiO_2, etc.) were prepared by impregnation of SiO_2(II) with aqueous solutions of each salt (KOH, etc.). All reagents used for impregnation were of guaranteed grade obtained from Yoneyama Chemical Ind., Ltd., Osaka, and Tokyo Ohka Ind., Ltd., Kawasaki. Two other KOH–SiO_2 and K^+-exchanged silica gel catalysts were prepared to determine the effect of the method of preparation and silica gel support. The method of preparation and surface area of each catalyst are listed in Table 1. From the color changes of indicators [phenolphthalein, methyl red and benzeneazodiphenylamine (*9*)] and the intrinsic acidity of the supported salt (*10*), the basicity is likely to increase as $SiO_2\text{(II)} < SiO_2\text{(I)} < Na_2SO_4\text{–}SiO_2 < Na_2CO_3\text{–}SiO_2 < NaOH\text{–}SiO_2$, KOH–$SiO_2$.

Reagents. *Meso-* and *dl*-2,3-dichlorobutane(C_4Cl_2) were obtained by gas chromatographic separation of the commercially

TABLE 1
SOLID ACIDS AND BASES[a]

Material	Method of preparation	BET surface area (m^2/g)
SiO_2(I)	Hydrolysis of $Si(OC_2H_5)_4$	610
SiO_2(II)	Wako gel, Q-12	830
KOH–SiO_2	5 wt% of KOH impregnated on SiO_2(II)	190
KOH–SiO_2(Ia)	5 wt% of KOH impregnated on SiO_2(I)	90
KOH–SiO_2(Ib)	SiO_2(I) treated with KOH aq soln	100
K–SiO_2	SiO_2(I) was K^+-exchanged with K_2CO_3–KCl–HCl aq soln at pH 8 and dried after washing with water (K content, 0.5 wt%)	380
NaOH–SiO_2	5 wt% of NaOH impregnated on SiO_2(I)	65

[a] Na_2SO_4–, K_2CO_3– and Na_2CO_3–SiO_2 were prepared by impregnation of each salt on SiO_2(II) (5 wt%). Their surface areas were 200–500 m^2/g.

obtained 2,3-dichlorobutane (Tokyo Kasei, Ltd.). The diastereomeric purity was over 98 and 94% for *meso*- and *dl*-isomers, respectively. *Meso*- and *dl*-2,3-dibromobutane (C_4Br_2) were prepared by the bromination of *trans*- and *cis*-2-butene in methylene chloride at 0°C, respectively (*11*). The purity was higher than 99% for both isomers. 2-Bromobutane-d_0(C_4Br) was obtained commercially (Tokyo Kasei Ltd.). *Erythro*- and *threo*-2-bromobutane-3-d_1 were prepared at −70°C under uv irradiation from deuterobromination of *cis*- and *trans*-2-butene, respectively (*12*). The analysis of the deuterium content of the butene isomer obtained by the stereospecific dehydro- or dedeuterobromination in alcoholic KOH at 68°C (*12*) showed that *erythro*-2-bromobutane-3-d_1 contained 4% of d_0-species and 9% *threo*-2-bromobutane-3-d_1, and *threo*-2-bromobutane-3-d_1 contained 10% of d_0-species and 18% of *erythro* isomer. The diastereomeric purity was calculated following Kibby, Lande and Hall (*4*). The position of deuterium substitution was exclusively at 3-carbon as confirmed independently by use of microwave spectroscopy.*

RESULTS

All the reactants submitted for elimination reaction in this study give different products depending on the stereochemistry of reaction (*anti* or *syn*) as shown in Table 2. The stereoselectivity of each reaction was determined from the product distribution. No isomerization of butenes or halobutenes was detected under the present reaction conditions. Dehydrohalogenation over SiO_2 and Na_2SO_4–SiO_2 seemed to proceed catalytically, since little deactivation of the catalyst was observed on repeated pulse injections. On the other hand, the reaction seemed to be nearly stoichiometric over basic solids such as KOH–SiO_2 and K_2CO_3–SiO_2, since rapid deactivation took place, probably due to the irreversible reaction between hydrogen halide and the solid surface. Even though the reaction varied from catalytic to stoichiometric among catalysts, knowledge of the stereochemistry of the surface reaction provided useful information.

Elimination reactions of 2,3-dihalobutane. Typical results are given in Table 3. Dehydrohalogenation of 2,3-dihalobutanes (C_4X_2) proceeded very stereospecifically by *anti* elimination over basic solids such as NaOH–, KOH– and Na_2CO_3–SiO_2 and nearly stereospecifically over Na_2SO_4–SiO_2. Debromination which predominated in the case of SiO_2 and Na_2SO_4–SiO_2 also proceeded by *anti* elimination. Butadiene which formed over less basic solids was most likely produced through an allyl intermediate by the dehydrohalogenation of 3-halo-1-butene, the 1,2-elimination product of

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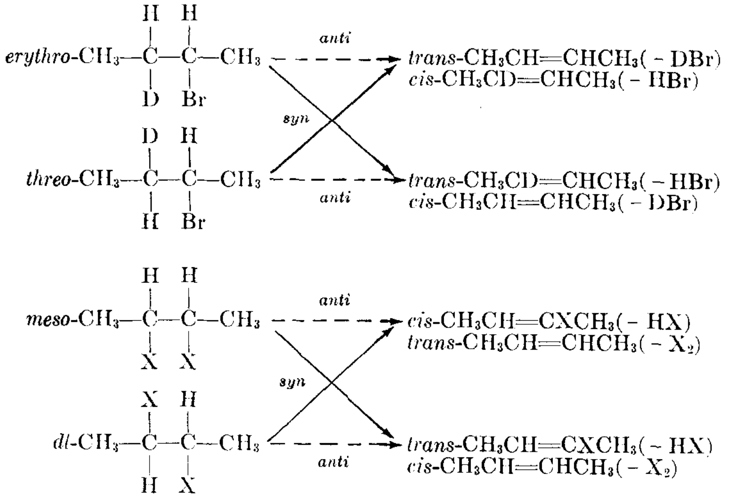
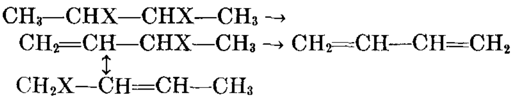
* Deuterium position of 1-butene-d_1 formed from 2-bromobutane-3-d_1 was determined following the literature (*13*).

TABLE 2

STEREOCHEMISTRY AND PRODUCTS OF ELIMINATION REACTIONS



C_4X_2. It was observed that butadiene formation from 3-halo-1-butene as well as its allyl isomerization took place very readily under the same reaction conditions.



$$\begin{array}{l} CH_3{-}CHX{-}CHX{-}CH_3 \rightarrow \\ \quad CH_2{=}CH{-}CHX{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 \\ \quad \quad \updownarrow \\ \quad CH_2X{-}CH{=}CH{-}CH_3 \end{array}$$

Dehydrobromination of 2-bromobutane. Table 4 shows the butene compositions obtained from dehydrobromination of 2-bromobutanes over KOH–SiO_2 and SiO_2, together with the content of butene-d_1 in each butene isomer. Each butene contained only d_0 and d_1 species. Note that the butene composition varied with the deuterium substitution at carbon-3 due to kinetic isotope effects. 2-Butene formation by the elimination of DBr (primary isotope effect) was retarded more effectively than that of HBr (secondary isotope effect) and 1-butene formation was little affected, so that the difference in butene composition between deuterated and undeuterated bromobutane reflected the stereochemistry.

The fact that the ratio of *cis*-2-butene to 1-butene over SiO_2 at 150°C decreases from 2.7 to 2.0 and that of *trans*-2-butene decreases from 2.6 only to 2.4 for *erythro* isomer (Table 4) indicates that *syn* elimi-

TABLE 3

ELIMINATION REACTIONS OF *dl*- AND *meso*-DIHALOBUTANES OVER SOLID ACIDS AND BASES

Solid acids and bases	Reaction temp (°C)	Wt (mg)	Dihalobutane	% Conversion to 2-Halo-2-butene *trans*	 *cis*	 Butadiene	 Butene *trans*	 *cis*
NaOH-SiO_2	170	100	*dl*-C_4Br_2	6.4	0	0	0	0.6
	170	100	*meso*-C_4Br_2	0	5.3	0	0.8	0
Na_2CO_3-SiO_2	170	100	*dl*-C_4Br_2	8.0	<0.3	0	0	0.8
KOH-SiO_2	250	60	*meso*-C_4Cl_2	Tr	9.5	0	0	0
SiO_2(II)	170	40	*meso*-C_4Br_2	Tr		0.8	2.2	Tr
Na_2SO_4-SiO_2	170	350	*meso*-C_4Br_2	Tr		3	6	Tr
	250	350	*meso*-C_4Cl_2	0.8	3.6	2.5	Tr	

TABLE 4
DEHYDROBROMINATION OF 2-BROMOBUTANE-d_0(I), *erythro*-2-BROMOBUTANE-3-d_1(II) AND *threo*-2-BROMOBUTANE-3-d_1(III)

Catalyst	Reaction temp (°C)	Reactant	Butene composition[a] (d_1% in parentheses)			Stereo-selectivity % *anti*[b]	Primary isotope effect[c]
			1	*trans*	*cis*		
$KOH-SiO_2$	95[d]	I	1.0	3.4	2.7		
		II	1.0 (98)	2.0 (34)	2.4 (85)	87 (+74)	1.9
	160	I	1.0	1.65	1.55		
		II	1.0 (96)	1.05 (43)	1.4 (84)	77 (+54)	2.0
		III	1.0 (98)	1.4 (78)	1.0 (45)		
	300	I	1.0	1.2	1.4		
		II	1.0 (96)	1.1 (72)	1.1 (44)	34 (−32)	1.4
SiO_2(I)	150	I	1.0	2.6	2.7		
		II	1.0 (97)	2.4 (86)	2.0 (29)	11 (−78)	1.7
		III	1.0 (93)	1.9 (28)	2.5 (84)		
	300	I	1.0	1.6	1.7		
		II	1.0	1.5	1.3		

[a] Butene compositions are normalized to 1-butene. d_1% are corrected for butene-d_0 coming from 2-bromobutane-d_0 contained in the starting 2-bromobutane-d_1.

[bc] Average values for *trans*- and *cis*-2-butene formation (see text). In parentheses are given percentage selectivities of *anti* elimination (% *anti* − % *syn*).

[d] Pretreated in the reactor in a stream of hydrogen at 150°C. Others were pretreated at 300°C.

nation is favored over SiO_2. Butene composition from *threo* isomer is also consistent with *syn* elimination (cf. Table 2). Over $KOH-SiO_2$, *anti* elimination prevails at 160°C and *syn* elimination at 300°C. Relative rates of formation of *trans*- and *cis*-2-butene from C_4Br-d_1 over $KOH-SiO_2$ compared to those from C_4Br-d_0 are plotted in Fig. 1 as a function of reaction temperature. This figure demonstrates that the inversion of stereochemistry from *anti* to *syn* occurs at about 250°C. *Anti*-preference similar to $KOH-SiO_2$ was observed over all silica catalysts containing potassium at 160°C. Small *anti*-preference over NaOH- and Na_2CO_3–SiO_2 and *syn*-preference over Na_2SO_4–SiO_2 were also observed.

The deuterium content of each butene isomer given in Table 4 confirms the stereoselectivity suggested above by the butene compositions; e.g., higher deuterium content in *cis*-2-butene for *anti* elimination of *erythro* isomer, and in *trans*-2-butene for *syn* elimination. These results are discussed more quantitatively in the later section.

That 1-butene formation was actually little affected by the deuterium atom at 3-carbon was ascertained by the fact that the relative rate of C_4Br-d_0 to that of C_4Br-3-d_1 almost agreed with that estimated from the change in butene composition. For example, the former was 1.25 and the latter was $1.2 = (1 + 2.6 + 2.7)/(1 + 2.4 + 2.0)$ at 150°C over SiO_2, and both were 1.30 over $KOH-SiO_2$.

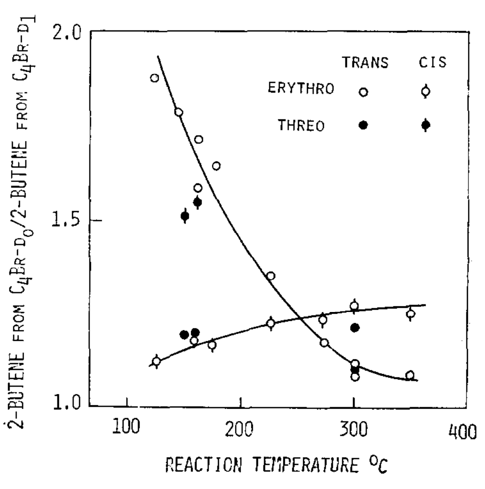


FIG. 1. Relative rate of 2-butene formation from 2-bromobutane-d_0 to that from 2-bromobutane-3-d_1.

Relative reactivity of alkyl halides. Relative reactivity of alkyl halides over solid acids and bases was as follows. Over all catalysts studied, the reactivity decreased as

$$CH_3CH_2CHXCH_3 > CH_3CHXCH_3 > CH_3CH_2X \quad (X = Br, Cl),$$

and

$$RBr > RCl \quad (R = sec\text{-butyl, isopropyl}).$$

It is remarked that C_4X was dehydrohalogenated much faster than C_4X_2 over SiO_2, while the reactivity was reversed over $KOH–SiO_2$.

DISCUSSION

Reaction mechanism. Let us consider whether the reaction mechanism consists of the dissociation of two bonds, C–H and C–X, taking place simultaneously (concerted mechanism, E2) or stepwise, and which step occurs first (carbonium ion, E1, or carbanion mechanism, E1cB) if the bond-breaking takes place stepwise. Terms such as E1, E2 and E1cB used in this discussion do not mean exactly the same mechanism as when used in liquid-phase reactions, but only the resemblance of a transition state.

Observed results of a kinetic deuterium effect and stereospecific reaction are consistent with a concerted mechanism. Even if the reaction proceeds stepwise, the breaking of a C–X bond is not rate-determining and the lifetime of the intermediate should not be long enough to allow rotation about the C^α–C^β bond. The relative reactivity of alkyl halides, i.e., *sec*-butyl > isopropyl > ethyl and alkyl bromide > alkyl chloride, may exclude the possibility that the C–H bond breaking occurs in the first step, since the stability of the carbanion would decrease with alkyl substitution and the β-proton of an alkyl chloride is believed to be more acidic and more easily to be abstracted than from an alkyl bromide (*14*).

All of the results presented are best explained by a concerted mechanism with a variable transition state (*14*): the transition state over a basic solid such as $KOH–SiO_2$ resembles that of a "central E2" mechanism, C–H and C–X being loosened to a similar extent (*14*), and the transition state over a weak acid such as silica gel resembles that occurring in a "carbonium-ion-like E2" mechanism, the C–X bond being loosened more extensively (*14*). A change in reaction mechanism for elimination with acidity or basicity of reactant and catalyst has been suggested in heterogeneous reactions (*6*, *15*), as well as in homogeneous reactions (*14*). The observed inversion of reactivity of C_4X and C_4X_2 between solid acids and bases is consistent with the above mechanism, because β-halogen substitution will promote the reaction with "central E2" transition state and retards that with "carbonium-ion-like" transition state, by increasing β-proton acidity and suppressing C–X bond breaking (*14*, *15*). The possibility that the reactions proceed over some of the catalysts by a carbonium-ion-pair mechanism, in which starting configurations are retained as suggested in liquid-phase reactions (*16*), may not be eliminated. But the essential part of the following discussion on the stereochemistry may hold also for ion-pair mechanism.

The possibility that elimination reactions of C_4X_2 proceed via a halogen-bridged intermediate can be excluded, at least for dehydrobromination, by the fact that *cis*-2-butene and *trans*-2-bromo-2-butene were formed from *dl*-C_4Br_2, because the bridged intermediate from *dl*-C_4Br_2 would form only *cis*-olefins.

Stereochemistry and isotope effects in the dehydrobromination of 2-bromobutane. Since a concerted mechanism may be reasonably assumed for the elimination reaction in the present systems, the stereochemistry and deuterium kinetic isotope effects can be calculated from the data in Table 4, following the method of Kibby, Lande and Hall (*4*). Hydrogen–deuterium exchange which might contaminate the deuterium distribution of butenes did not occur to any extent, since the content of d_1-species of 1-butene in the product was close to 100% and no d_2-species were detected. The rate of formation of 1-butene should be very nearly the same for all three 2-bromobutanes as described above. Normalizing these rates to unity, the relative rates

TABLE 5

Dehydrobromination of 2-Bromobutane[a]

	SiO_2(I)		KOH–SiO_2	
	trans	*cis*	*trans*	*cis*
Reaction temp (°C)	150		160	
Relative rates				
k^a	0.24	0.37	1.27	1.25
k^s	2.36	2.33	0.38	0.30
Isotope effects (k_H/k_D)				
$1/r$	1.0	1.0	1.05	1.0
$1/R^a$	(1.2)	(1.9)	2.0	2.0
$1/R^s$	1.5	1.5	(1.5)	(1.7)

[a] Stereoselectivity and kinetic isotope effects. Values in parentheses are not reliable (see text).

of formation of the 2-butenes from 2-bromobutane-d_0 are

$$v_t^0 = k_t^a + k_t^s,$$
$$v_c^0 = k_c^a + k_c^s,$$

and those from *erythro*-2-bromobutane-3-d_1 are

$$v_t^e(d_0) = 0.9R_t^a k_t^a + 0.1R_t^s k_t^s,$$
$$v_t^e(d_1) = 0.9r_t k_t^s + 0.1r_t k_t^a,$$
$$v_c^e(d_0) = 0.9R_c^s k_c^s + 0.1R_c^a k_c^a,$$
$$v_c^e(d_1) = 0.9r_c k_c^a + 0.1r_c k_c^s,$$

where $v_i^n(d_m)$ is the relative rate of formation of butene i (*cis* or *trans*) containing d_m from 2-bromobutane n (*erythro* or *threo*), R_i^j and k_i^j are reciprocal of the primary isotope effect and relative rate of formation of butene i by the j mode (*anti* or *syn*) and r_i is the reciprocal of the secondary isotope effect for butene i formation. Similarly four equations are derived for the rates of 2-butene formation from *threo* isomer.

Using these equations and the data in Table 4, k_i^j, etc., are calculated as summarized in Table 5. Values in parentheses in Table 5 are less reliable, because they are those for minor steric processes and are not discussed. There is little difference in the stereochemistry [e.g., $k_t^a/(k_t^a + k_t^s)$] and isotope effects between *cis*- and *trans*-2-butene formation. Average percentages of *anti* elimination and primary isotope effect are given in Table 4. Where only data for two 2-bromobutanes exist, they are estimated neglecting the specificity for *cis*- and *trans*-2-butene formation. The isotope effects (1.4–2.0) are similar to those reported for the dehydration of 2-butanol over alumina and hydroxyapatite (*4*).

Factors determining the steric course of reaction. Steric effects, such as the geometry of acidic and basic sites, and the acid–base properties of the catalyst have been suggested as factors determining the stereochemistry (*1–8*). Both of them must be important, in general. However, as far as the present reactions and catalysts are concerned, the surface structure does not seem to play a decisive role in the determination of the steric course of reaction, for the following reasons: (i) The stereoselectivity differs markedly between C_4Br and C_4X_2, although their molecular dimensions are nearly the same. (ii) Inversion of stereochemistry takes place with reaction temperature over KOH–SiO_2. (iii) Although SiO_2 has a higher surface area and probably many smaller pores than KOH–SiO_2, and therefore, would favor *anti* elimination from the viewpoint of steric effects,† the results show the opposite. (iv) All four silica catalysts containing K^+, whose surface areas are quite different, show similar

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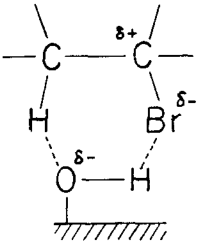
† Surface area and the distribution of pore size (measured only for pores wider than 75 Å in diameter) indicated that small pores of silica gel disappeared and large pores increased upon the treatment with KOH solution. Pores or crevices which accommodate *anti* elimination may be very small, probably 5–10 Å in diameter (*1*).

anti-preference for the reactions of C_4Br at 160°C. Further, the re-exchange of K^+ of $K\text{–}SiO_2$ by H^+ returned the steric course to a *syn* mode similar to that of SiO_2 from an *anti* mode without a change in the surface area (*17*). This indicates the importance of the cationic species in determining the stereochemistry.

These results can reasonably be interpreted in terms of the acid–base properties of alkyl halide and solid surfaces. The observed trend that *anti* elimination predominates when the solids are basic and when the β-proton is acidic as in C_4X_2 agrees with the trend of the transition becoming more concerted as discussed above. In other words, *anti* elimination is the favored mode over the surface studied, if a concerted mechanism with a "central E2" transition state operates. *Anti* elimination in the central E2 mechanism is widely observed in homogeneous liquid-phase reactions (*14*). It is hard, however, to speculate at the present moment how H and X can transfer onto the surface from the opposite sides of a reactant molecule. Possibly, the sites required for *syn* and *anti* elimination are potentially present on the surface of silica gel, so that either mode of reaction could prevail depending upon the acid–base interactions between the surface and alkyl halide. Possible explanations for concerted *anti* elimination may be found in proposals by Kibby, Lande and Hall (*4*), and Knötzinger, Bühl and Kochlofel (*5*).

When the difficulty of β-proton elimination by basic sites increases (e.g., C_4Br over a weak protonic acid such as silica), the transition state more closely resembles a carbonium ion by analogy to liquid-phase reactions (*14*). A β-proton may be transferred via a cyclic intermediate, as suggested by Kibby, Lande and Hall (*4*), to a hydroxyl group coordinated with a halogen atom (I) or an almost released halogen atom (II), since basic sites originally present on silica may not be strong enough to remove the proton. Variation of stereochemistry with the basicity of solvent has been reported for eliminations in the liquid phase (*16*). As the solvent becomes more acidic, the steric course becomes *syn* mode, a proton being removed by the released negative ion.



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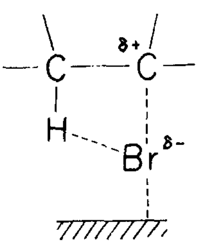

II

SUMMARY

The stereochemistry of dehydrohalogenation was determined and the importance of the acid–base properties of catalysts and reactants in determining the steric course of reaction is pointed out. We feel that a knowledge of the stereochemistry of the surface reaction and factors controlling it contributes to the understanding of the solid surface and its surface reaction.

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