Stereochemical Studies of Elimination Reactions of 2-Bromobutane and 2,3-Dibromobutane over Alkali-Ion Exchanged Silica Gels

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The stereochemistry (*anti* or *syn* mode) of elimination reactions of 2-bromobutane and 2,3-dibromobutane over alkali-ion exchanged silica gels (Li, Na, K, and Cs) was determined at 100—300 °C from the products of the diastereomeric isomers of each alkyl bromide. They were *erythro*- and *threo*-2-bromobutanes-3-d_1 and *meso*- and *dl*-2,3-dibromobutanes. The steric course of dehydrobromination of 2-bromobutane changed nearly reversibly between *syn* and *anti* mode by the partial exchange of a surface proton with K^+ or Cs^+ ion, although the surface structure seemed to remain unchanged by the exchange procedure. On the other hand, the exchange with Na^+ or Li^+ ion did not change the steric course. Dehydrobromination of 2,3-dibromobutane proceeded by *anti* mode over Na–, K–, and Cs–SiO_2, while SiO_2 and Li–SiO_2 were not active. The poisoning effect of acidic and basic reagents as well as the indicator test revealed that basic sites played important roles over K– and Cs–SiO_2 where *anti* elimination prevailed, and that weakly acidic sites were responsible for *syn* elimination.

Study of the stereochemistry of reactions over solid catalysts is a useful tool for the elucidation of reaction mechanisms and for the characterization of surface active sites. The knowledge of the stereochemistry of liquid-phase elimination reactions seems well accumulated.[1,2] However, relatively few studies have been reported for heterogeneous systems. Although various factors such as the steric effect, the timing of bond breakings, and the shape of the transition state have been suggested,[3–7] the problem of what is the essential factor controlling the steric course of a reaction still remains unsettled.

We reported previously that the steric course of dehydrohalogenation of 2-bromobutane over silica gels varied markedly by the alkali-treatment, and proposed a postulate that the prime factor determining the stereochemistry is not the surface geometry but the acid-base properties of both catalyst and reactant in these systems; *syn* elimination prevalied over an acidic surface and *anti* over a basic one, regardless of the wide variation of surface area. This postulate was applicable to other basic solids such as alkaline-earth metal oxides, which are known to be strongly basic and to have substantially different surface structures.[8] We further suggested that the elimination reaction proceeded by a concerted mechanism over a basic surface and *via* a carbonium-ion like intermediate over an acidic surface.

In the present work, we studied the stereochemistry of dehydrobromination over silica gels containing different cations, since the previous results indicated that the cation species played important roles. For example, similar *anti*-selectivity was observed for KOH–SiO_2 and for K_2CO_3–SiO_2.[6] If the surface structure remains unchanged, it is expected that only the role of the acid-base properties of the surface would be important, as we reported preliminarily.[9] The silica gels studied were prepared carefully by means of ion-exchange, so as to keep the surface structure as constant as possible.

The acid-base properties of these silica gels were clarified from the indicator test and the poisoning effect of acidic and basic reagents. The correlations of these properties with the stereochemistry and the reaction mechanism are discussed.

Experimental

Apparatus and Procedure. A conventional pulse technique described previously was utilized.[6] The carrier gas was hydrogen or helium, which was deoxygenated and dried by a "DEOXO" column and a molecular-sieve trap kept at liquid N_2 temperature. Catalysts (100—500 mg) were ordinarily preheated at 300 °C for 1 h in the stream of carrier gas. After they were cooled to the reaction temperature, 1 or 2 μl of alkyl halide was injected into the gas stream with aid of a microsyringe. All the reactants submitted for elimination reactions in this study gave different stereoisomeric products depending on the steric course of reaction (*anti* or *syn*, *cf.* Scheme I). The stereochemistry of each reaction was determined from the product distribution. No isomerization of butenes of 2-bromo-2-butenes took place under the present reaction conditions.

The analysis of products followed the same procedure as before.[6] The deuterium content of each butene isomer was determined by use of a mass spectrometer (Hitachi, RMU-S) after gas chromatographic separation.

Catalysts. Silica gel was prepared from the hydrolysis of tetraethoxysilane, as before.[6] Ordinarily it was used after being calcined at 500 °C for 6 h and washed with dilute HCl aqueous solution and then with water. Alkali-exchanged silica gels, M–SiO_2 (M=Li, Na, K, or Cs), were prepared by soaking SiO_2 three times in an aqueous solution (N/20) of alkali chloride and carbonate (*ca.* 2: 1) with vigorous shaking for several hours each time at room temperature. The initial pH of the solutions was adjusted every time to 8.0 or 10.0 (low or high alkali content, respectively) by the addition of a small amount of hydrochloric acid. They were then washed and dried at 110 °C. Decationized M–SiO_2 was prepared by repeated washing with aqueous HCl solution (pH=4). The alkali ion contents were determined by flame photometry.

Reagents. 2-Bromobutane (C_4Br), 2-bromobutane-3-d_1 and *meso*- and *dl*-2,3-dibromobutanes (C_4Br_2) were prepared and purified as described previously.[6] The purity of 2-bromobutane-3-d_1 was determined more strictly in the present work, as described in the following section.

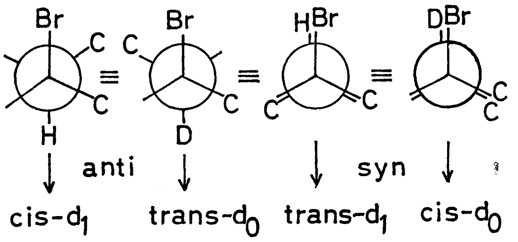
Results

Determination of Diastereoisomeric Purity of 2-Bromobutane-3-d_1. Two kinds of 2-bromobutane-3-d_1 which differed in the compositions of *erythro*-d_1, *threo*-d_1, and d_0 species were prepared from *trans*- and *cis*-2-butene as described above. The compositions were determined by the following method from the butene compositions and the contents of d_1-species in each butene isomer formed from the stereospecific dehydrobromination in liquid phase. The rates of *trans*- and *cis*-2-butene formation from 2-bromobutane-d_0 can be represented as (*cf.* Refs. 4 and 6)

$$v_{\mathrm{t}}^{\mathrm{o}} = k_{\mathrm{t}}^{\mathrm{a}} + k_{\mathrm{t}}^{\mathrm{s}} \tag{1}$$

$$v_{\mathrm{c}}^{\mathrm{o}} = k_{\mathrm{c}}^{\mathrm{a}} + k_{\mathrm{c}}^{\mathrm{s}} \tag{2}$$

normalizing the rate of 1-butene formation to unity. Then, since 1-butene formation is little affected by the deuterium atom at C-3 position, the rates of butene formation from 2-bromobutane-3-d_1 (*erythro*: *threo*: d_0= x:y: $1-x-y$) are, referring to Scheme I,



Scheme 1. Stereochemistry and butenes produced in the dehydrobromination of *erythro*-2-bromobutane-3-d_1.

$$v_{\mathrm{t}}(d_0) = xR_{\mathrm{t}}^{\mathrm{a}}k_{\mathrm{t}}^{\mathrm{a}} + yR_{\mathrm{t}}^{\mathrm{s}}k_{\mathrm{t}}^{\mathrm{s}} + (1-x-y)(k_{\mathrm{t}}^{\mathrm{a}}+k_{\mathrm{t}}^{\mathrm{s}}) \tag{3}$$

$$v_{\mathrm{t}}(d_1) = xr_{\mathrm{t}}k_{\mathrm{t}}^{\mathrm{s}} + yr_{\mathrm{t}}k_{\mathrm{t}}^{\mathrm{a}} \tag{4}$$

$$v_{\mathrm{c}}(d_0) = xR_{\mathrm{c}}^{\mathrm{s}}k_{\mathrm{c}}^{\mathrm{s}} + yR_{\mathrm{c}}^{\mathrm{a}}k_{\mathrm{c}}^{\mathrm{a}} + (1-x-y)(k_{\mathrm{c}}^{\mathrm{a}}+k_{\mathrm{c}}^{\mathrm{s}}) \tag{5}$$

$$v_{\mathrm{c}}(d_1) = xr_{\mathrm{c}}k_{\mathrm{c}}^{\mathrm{a}} + yr_{\mathrm{c}}k_{\mathrm{c}}^{\mathrm{s}} \tag{6}$$

where $v_{\mathrm{i}}(d_m)$ is the relative rate of formation of butene i (*trans* or *cis*) with d_m (m=0, 1), $R_{\mathrm{i}}^{\mathrm{j}}$ and $k_{\mathrm{i}}^{\mathrm{j}}$ are the reciprocals of the primary deuterium isotope effect and the relative rate of formation of butene i by j mode (*anti* or *syn*), and r_{i} is the reciprocal of the secondary isotope effect for butene i formation. Since the reaction utilized for analysis is known to be 100% *anti* elimination ($k_{\mathrm{t}}^{\mathrm{s}}$, $k_{\mathrm{c}}^{\mathrm{s}}$=0),[11] the composition (x and y) of 2-bromobutane-3-d_1 can be determined from these equations. The compositions of butenes and their deuterium contents obtained from the reaction in EtOK–EtOH and KOH–ethylene glycol systems at 70 °C are given in Table 1. The content of d_1 species ($x+y$) was 94%, as seen from the d_1 content of 1-butene and confirmed by NMR. The position of deuterium atom was exclusively at 3-position, as evidenced by the microwave spectroscopic analysis of the 1-butene-d_1 formed.[10] Values of x and y are determined for each system by the method of least squares* using Eqs. (1) to (6) as given in the same table. The butene compositions in the case of the EtOK–EtOH system almost agreed with those in the literature, so that 100% *anti* elimination was reasonably assumed in the calculation ($k_{\mathrm{t}}^{\mathrm{s}}$=$k_{\mathrm{c}}^{\mathrm{s}}$=0). The compositions of two bromobutane-3-d_1 (**A** and **B**) are as follows, by taking the average of the values from the two systems.

Table 1. Butenes from the dehydrobromination of 2-bromobutanes in alcoholic KOH solutions and the isomeric compositions of 2-bromobutane-3-d_1 (**A** and **B**)

2-Bromo-butane	Solvent	Butene composition (d_1% in parentheses)			Composition (%)	
		1-	*trans*	*cis*	*erythro*	*threo*
d_0	Ethanol	1.0	2.65	0.88		
	Ethylene glycol	1.0	2.74	1.06		
3-d_1[b)] (**A**)	Ethanol	1.0 (96)	1.17 (36)	0.74 (91)	78	16
	Ethylene glycol	1.0 (93)	1.37 (36)	0.92 (85)	76	18
3-d_1[b)] (**B**)	Ethanol	1.0 (95)	2.01 (85)	0.47 (59)	29	65
	Ethylene glycol	1.0 (93)	2.35 (83)	0.65 (58)	26	68

a) Contents of d_0 species in 2-bromobutane-3-d_1 (**A**) and (**B**) are 6%. b) 2-Bromobutane-3-d_1 (**A**) and (**B**) were prepared by DBr addition of *trans*- and *cis*-2-butene, respectively.

	erythro	*threo*	d_0	
A	77%	17%	6%	(*erythro* rich)
B	28	66	6	(*threo* rich)

The primary isotope effects ($1/R$) for *trans*- and *cis*-2-butene formations were respectively 3.7 and 4.0 (EtOK–EtOH), and 3.0 and 3.5 (KOH-ethylene glycol).

Dehydrobromination of 2-Bromobutane over Silica Gels. Dehydrobromination of 2-bromobutane over Na– and Li–SiO_2 as well as SiO_2 seemed to proceed catalytically, as indicated by the small change in the rate from the repeated pulses. On the other hand, Cs– and K–SiO_2 showed rapid deactivation, and the reaction seemed stoichiometric at the initial stage, as in KOH–SiO_2.[6] However, catalytic elimination by *anti* mode at a stationary rate was possible also over Cs–SiO_2 in the later stage (Fig. 1). The butene compositions changed little in most cases from pulse to pulse. They were

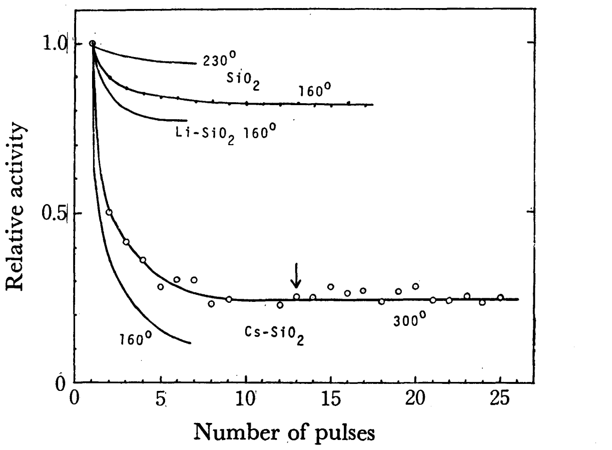


Fig. 1. Variation of activity for the dehydrobromination of 2-bromobutane by repeated pulses.
Arrow indicates that the amount of 2-bromobutane which reacted in repeated pulses was equivalent to that of Cs ion.

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* A library program (C7/TC/POW1) of the Computer Center of the University of Tokyo written by Y. Oyanagi, by use of the Powell's method.

TABLE 2. VARIATION OF STEREOCHEMISTRY OF DEHYDROBROMINATION OF 2-BROMOBUTANE OVER SILICA GEL BY K EXCHANGE

Catalyst	K content (mg-ion/g)	Surface area (m^2/g)	Relative activity[a]	d_1 content of 2-butene (%)[b] *trans*	*cis*	$(trans/cis)_0$[c] / $(trans/cis)_1$	Stereo-chemistry
SiO_2[d]	0.0	425	3.3	76	42	0.82	81% *syn*
K–SiO_2[e]	0.12	400	11.0	47	70	1.42	71% *anti*
H–SiO_2[f]	0.01	390	2.3	68	46	0.79	70% *syn*
SiO_2[g]	0.0	472	6.9	—	—	0.86	*syn*
K–SiO_2[h]	—	380	5.9	—	—	1.33	*anti*
H–SiO_2[i]	—	380	1.8	—	—	0.86	*syn*

a) Normalized to % conversion over 100 mg of catalyst at 160°C. b) From 2-bromobutane-3-d_1 (**A**; *erythro* rich). c) See text. d) Calcined at 800°C. e) SiO_2[d] was treated with KCl–K_2CO_3 aq solution (N/20, pH=8). See text. f) K–SiO_2[e] was decationized by washing with aq HCl solution (pH=4). g) Calcined at 500°C. h) and i) SiO_2[g] was treated as e) and f), respectively.

TABLE 3. STEREOCHEMISTRY OF DEHYDROBROMINATION OF 2-BROMOBUTANE OVER ALKALI-ION EXCHANGED SILICA GELS AT 160°C

Alkali (pH)[a]	Alkali content (mg-ion/g)	Surface area (m^2/g)	Relative[b] activity	Butene compositions[c] (d_1% in parentheses) 1-	*trans*	*cis*	$(trans/cis)_0$[d] / $(trans/cis)_1$	Stereo-chemistry
Li(8)	0.04	285	5.1	1.0(92)	2.5(67)	2.5(53)	0.92	62% *syn*
Li(10)	*ca.* 0.4	280	10.8	1.0(95)	2.1(78)	2.4(49)	0.87	77% *syn*
Na(8)	0.07	—	2.6	1.0(92)	1.9(75)	1.8(48)	0.88	74% *syn*
Na(10)	—	—	3.1	1.0	1.3	1.2	0.95	*syn*
K(8)	*ca.* 0.1	260	2.4	1.0	2.3	1.8	1.23	*anti*
Cs(8)	0.08	250	3.4	1.0(–)	2.9(38)	1.8(74)	1.49	80% *anti*
Cs(8)[e]	0.08	250	2.8	1.0	2.7	1.7	1.50	*anti*
Cs(10)[f]	0.41	92	12.6	1.0(96)	3.7(25)	2.8(87)	1.82	100% *anti*
Cs(10)	*ca.* 0.5	180	37	1.0	2.8	1.7	1.54	*anti*
SiO_2	0	470	3—8[g]	1.0	2.6—3.2[g]	2.5—3.2[g]	0.81—0.84[g]	*syn*

a) pH of ion exchange. b) See Table 2. c) Butene compositions from 2-bromobutane-d_0 and contents of d_1 species in butenes from 2-bromobutane-3-d_1 (**A**). d) See text. e) Preheated at 400 °C for 1.5 h. f) Reaction temperature was 100 °C. g) Rate and butene composition varied depending on pH of HCl solution used for SiO_2 washing.

determined from the first four pulses. It was ascertained that the conversion increased proportionally to the amount of catalyst, while the butene composition remained constant.

The absence of butene isomerization** and of d_2 species in butenes from 2-bromobutane-3-d_1, together with the agreement of the d_1 content of 1-butene to that of the starting 2-bromobutane-3-d_1, makes possible a reasonable application of Eqs. (1) to (6) for the determination of the stereochemistry. In practice, it was mostly determined only from the reaction of 2-bromobutane-3-d_1 (**A**), with the approximation that *anti*-selectivity is the same for *trans*- and *cis*-2-butene formations, as well as $r=1$ and $R_t=R_c$. These approximations may be rationalized by the results obtained in the cases of SiO_2 and KOH–SiO_2.[6]

The ratio $(trans/cis)_0/(trans/cis)_1$, which is the ratio of the *trans*-/*cis*-2-butene from 2-bromobutane-d_0 to that from 2-bromobutane-3-d_1 (**A**, *erythro* rich), is also a measure of the stereochemistry. This ratio becomes larger than unity for *anti* mode and smaller than unity for *syn* mode, since one of the 2-butene formations decreases substantially by the introduction of deuterium atom at 3-position, owing to the primary isotope effect.[6]

The effect of K exchange is given in Table 2. *Syn* elimination was favored over SiO_2, as reported previously.[6] The favored steric course of the reaction changed to *anti* mode by the partial exchange of surface protons with K^+ ion. When K^+ ion was reexchanged with H^+ by washing with dilute acid, the steric course returned to *syn* mode almost reversibly. During this exchange procedure the surface area changed little (particularly in the $K^+ \rightarrow H^+$ treatment). The same change in the stereochemistry was observed with Cs exchange, as well as the K exchange of SiO_2 calcined at 1000 °C, which had surface area of 100 m^2/g.***

The effect of alkali-ion species is demonstrated by the results given in Table 3. *Syn* elimination was favored over Li– and Na–SiO_2 and *anti* over K– and Cs–SiO_2,

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** Besides the absence of reaction of butenes before and after the pulse of 2-bromobutane, it was also confirmed that pentenes pulsed together with 2-bromobutane did not isomerize.

*** SiO_2 calcined at 1000 °C showed appreciable activity after being washed with dilute HCl solution.

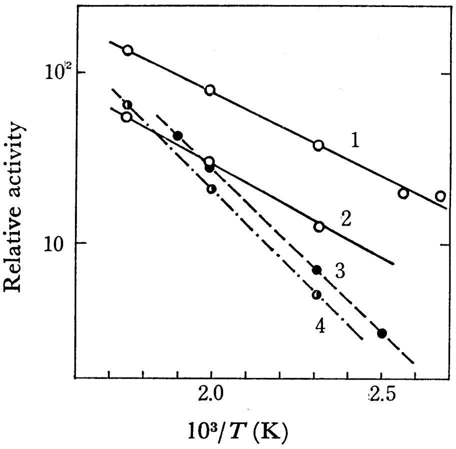


Fig. 2. Arrhenius plots of dehydrobromination of 2-bromobutane over several silica gels.
1. Cs–SiO_2 (*ca.* 0.5 mg-ion/g): $E_A=4.4$ kcal/mol,
2. Cs–SiO_2 (0.41 mg-ion/g): $E_A=4.8$ kcal/mol,
3. SiO_2: $E_A=8.6$ kcal/mol,
4. Li–SiO_2 (0.04 mg-ion/g): $E_A=8.7$ kcal/mol.

with *anti*-selectivity in the order of Cs>K>Na~Li. It is worthwhile to note that nearly 100% *anti* elimination was observed over the solid surface. The 2-/1-butene ratio was in the order of Cs>K>Na<Li and the *trans*/*cis* ratio of 2-butene formed increased as Li⩽Na<K<Cs.

The dependences of the reaction rates on the reaction temperature are shown in Fig. 2. The predominant steric course did not change for each silica gel at the temperature range studied, as far as judged from the $(trans/cis)_0/(trans/cis)_1$ ratio. The apparent activation energy for Cs–SiO_2 (*anti*) was smaller by about 4 kcal/mol than those for SiO_2 and Li–SiO_2 (*syn*), but the frequency factor for *anti* elimination was about 50 times less favorable.

Dehydrobromination of 2,3-Dibromobutanes over Silica Gels. 2-Bromo-2-butenes formed from dehydrobromination at 2,3-position were the only products over K– and Cs–SiO_2. This reaction proceeded very stereospecifically by *anti* mode; *e.g.*, *meso* isomer produced almost exclusively *cis*-2-bromo-2-butene (Table 4). Over Na–SiO_2, debromination took place besides the dehydrobromination. This debromination proceeded also by *anti* mode. Li–SiO_2 and SiO_2 were almost inactive for the dehydrobromination at this temperature.

TABLE 4. PRODUCTS FROM THE REACTIONS OF 2,3-DIBROMOBUTANES OVER ALKALI-ION EXCHANGED SILICA GELS AT 160 °C

Alkali (pH)[a)]	Relative activity[b)]	Pulse no.	Dibromobutane	Products (yield, %) 2-Bromo-2-butene *trans*	*cis*	2-Butene *trans*	*cis*
Cs(8)	11.2	(1)	*meso*	1.0	23.0	0	0
		(2)	*dl*	7.3	0	0	0
K(8)	5.9	(1)	*meso*	1.8	17.1	0	0
		(2)	*dl*	6.7	0	0	0
Na(8)	1.5	(1)	*meso*	tr	2.4	1.2	0
		(2)	*dl*	0.5	0	0	1.7

a) pH of ion exchange. b) See Table 2. Amounts of catalysts were 213, 316, and 255 mg for Cs–, K–, and Na–SiO_2, respectively.

TABLE 5. EFFECT OF PREADSORBED PYRIDINE ON THE ACTIVITY OF ALKALI-ION EXCHANGED SILICA GELS FOR DEHYDROBROMINATION OF 2-BROMOBUTANE

Catalyst	Alkali content (mg-ion/g)	Amount of pyridine added (mmol/g)	Relative activity[a)]
Cs–SiO_2	0.41	0	12.6
		0.13	13.0
Cs–SiO_2	*ca.* 0.5	0	37
		0.23	42
		0.98	39
Li–SiO_2	0.04	0	5.1
		0.04	2.6
Li–SiO_2	*ca.* 0.4	0	10.8
		0.25	5.6

a) See Table 2.

Acid-Base Properties of Alkali-Ion Exchanged Silica Gels. The effect of preadsorbed pyridine (a basic reagent which will poison the acidic sites) on the activity was investigated. As the typical results given in Table 5 show, the rate remained unchanged or increased slightly with Cs–SiO_2, while it decreased significantly with Li–SiO_2 and SiO_2. The deactivation by the repeated pulses, which is probably due to HBr (an acidic reagent) formed by the reaction, and, therefore, reflects the basicity of the active sites, was large with Cs– and K–SiO_2, but small with the others. Although these silicas were not as strongly basic as the alkaline-earth oxides nor as strongly acidic as silica alumina, observation of the color changes of indicators (methyl red, bromothymol blue, and cresol red) shows that the acidity increases (or basicity decreases) in agreement with the order of the electronegativity, as Cs<Na<Li (Table 6). The acid strength of silica was comparable with or a little less than Li–SiO_2. Methyl red turned to pink over SiO_2. All of these results demonstrate that the basic sites play important roles over *anti*-prevailing Cs– and K–SiO_2, and the acidic sites over *syn*-prevailing ones.

TABLE 6. INDICATOR TEST OF ALKALI-ION EXCHANGED SILICA GELS[a)]

Indicator	Li–SiO_2	Na–SiO_2	Cs–SiO_2
Methyl red	red	yellow	yellow
Bromothymol blue	(bluish) yellow	yellowish blue	blue
Cresol red	yellow (-red)	red	red

a) Ion-exchanged at pH 10. Pretreated at 300 °C for 2 h.

The results of thermogravimetric analysis (TGA) of SiO_2, Li– and Cs–SiO_2 are given in Fig. 3. Prior to TGA analysis, samples were equilibrated with water vapor for 3 days in a desiccator which contained 50% sulfuric acid. The rate of temperature increase was 10 °C/min.

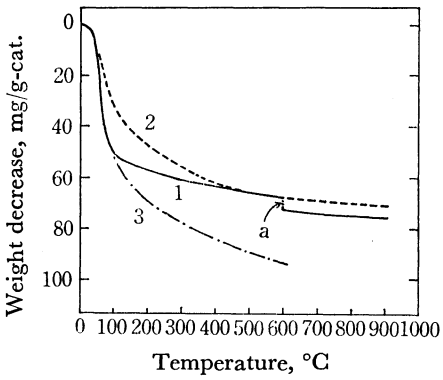


Fig. 3. Thermogravimetric analysis of silica gels.
1. SiO_2 (472 m^2/g),
2. Cs–SiO_2 (*ca.* 0.5 mg-ion/g, 180 m^2/g),
3. Li–SiO_2 (*ca.* 0.4 mg-ion/g, 280 m^2/g).
a. Temperature was kept at 600 °C for 1 h.

Discussion

Stereochemistry of Dehydrobromination and Acid-Base Properties. The present results obviously show that a close correspondence exists between the prevailing steric course of dehydrobromination and the acid-base properties of the catalyst surface. In the case of 2-bromobutane, *anti* mode prevailed over basic surface (Cs– and K–SiO_2) and *syn* mode over acidic surface (SiO_2, Na– and Li–SiO_2).

The steric effect or the geometry of the surface must influence the steric course, in the general case. In *anti* elimination, the two leaving groups or atoms must be released from the opposite sides of a reactant molecule. Therefore, the number of active sites and/or the shape of transition state for *anti* mode may be more restricted by geometrical reasons than those for *syn* elimination. The apparent frequency factor of Cs–SiO_2 was actually much smaller than that over SiO_2 or Li–SiO_2, while activation energy was favorable for *anti* elimination. Thus, it may be expected that *anti* elimination is more sensitive to the surface structure. However, as far as the present systems are concerned, the surface structure is not important from the following reasons in addition to those described before.[6,8]

(i) By the exchange of a small portion of surface silanols by K^+ or Cs^+ ion and then by H^+ (SiOH→SiOM→SiOH), the stereochemistry changed reversibly between *syn* and *anti* mode. During this exchange procedure (particularly in the $K^+ \rightarrow H^+$ treatment), the surface seemed to remain unchanged except for the cation species, as indicated by the small change in the surface area.

(ii) A marked effect of the alkali-ion species on the stereochemistry was observed, although it is unlikely that the surface structures were much different among the four alkali-ion exchanged silicas.

It is difficult to clarify the reason why the stereochemistry seems insensitive to the surface structure and how H and Br can be moved onto the surface from the opposite sides of a reactant molecule. Probably the surface of the silica gel is rough and irregular enough in the dimension of a reactant molecule so as to satisfy the geometrical requirements both for *anti* and *syn* elimination. Therefore, either mode can occur depending on the acid-base properties of surface and reactant. Possible explanations are also found in the proposals by Kibby, Lande, and Hall[4] and Knözinger, Bühl, and Kochloefl.[12]

Acidic and Basic Centers Created by Alkali-ion Exchange of Surface Silanols. The results of many investigations by various methods agree in general as regards the density of silanol groups on the silica surface.[13,14] Adsorbed water on silica gel is desorbed by the evacuation at room temperature. Water adsorbed by hydrogen bonding to silanols is also desorbed by the evacuation at as low as 150 °C. The surface density of silanols after evacuation at 150—300 °C is *ca.* 5/100 Å^2. Heating at higher temperature causes surface dehydroxylation, and "free" silanols of 1/100—2/100 Å^2 remain after evacuation at 600—800 °C. TGA of SiO_2 (Fig. 3) agreed in general with those reported.[14f]

The introduction of alkali ions increased the amount of adsorbed water, which was retained on the surface more tightly, as indicated by the TGA curves in the range of 100—300 °C. However, there was little difference between Cs and Li, if one takes into account the difference in surface area. It has been reported that Na-doped silica retained no water after evacuation at 170 °C, as evidenced by the absence of the combination mode of stretching and bending of water in the IR spectrum.[14e] Therefore, heating at 300 °C probably eliminated almost all of the adsorbed water on the alkali-ion exchanged silica gels. Then it may be irrational to assume the existence of a liquid water phase only on the surface of Cs–SiO_2 for the explanation of the *anti* elimination. In conformity with this, Cs–SiO_2 preheated at 400 °C and 300 °C showed no significant difference in *anti*-selectivity and butene composition (Table 3).

Surface silanol exchanges its proton with alkali ion as

$$\geqslant\mathrm{SiOH} + M^+ \rightleftarrows \geqslant\mathrm{SiOM} + H^+ \qquad (7)^{15)}$$

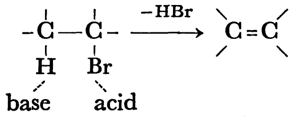
According to Boehm,[13] the extent of the exchange with Na^+ ion increases with pH and almost 100% exchange is attained at pH 9—10. However, surface siloxane bonds open and silica starts to dissolve at high pH. In fact, the surface area considerably decreased by the exchange at pH 10, but the decrease was small at pH 8 and negligible at pH 4 (Table 2). In support of Eq. (7), the pH changes during exchange at lower pH were in good agreement with those expected from Eq. (7) and the alkali content determined by flame photometry. If one takes 5/100 Å^2 as the density of surface silanols, the extents of exchange in the present work are, for example, 4% for Cs–SiO_2 (Cs: 0.08 mg-ion/g) and *ca.* 50% for Cs–SiO_2 (Cs: 0.41 mg-ion/g).

Usually alkali-ion exchange acts as a poison to the surface acidity and catalytic activity in the case of strongly acidic silica alumina or zeolite. Cs exchange decreased the activity for dehydrobromination of 2-bromobutane at low Cs content, but further exchange increased the activity. Since the stereochemistry was opposite to SiO_2, even for Cs– and K–SiO_2 with low activity, it is obvious that the exchange with these alkali ions created new active sites, besides acting as a poison. An increase in the activity with the extent of exchange was observed also in the case of Li–SiO_2. However, the change was small in this case and was negligible for Na–SiO_2. Therefore, it is not certain whether or not the exchange created new sites in these cases, besides acting as a poison. From the indicator test and the catalytic activity, the weak acidity or basicity of the sites of the original silica surface and those created by the exchange seems sufficient for the reaction to occur.

The electronegativity or the acid strength of alkali ions increases in the order of $Cs<K<Na<Li$.[16] The active sites responsible mainly for *syn* elimination, which is acidic, may be the alkali ion and/or the protonic sites of silica. The *anti*-selectively increased in the reverse order. The basic strength of the oxide ion will increase by the coordination of the alkali ion in the decreasing order of the electronegativity ($OCs>OK>ONa>OLi$), so that this oxide ion may play essential roles in *anti* elimination. As a result, the activity order including both steric modes becomes $Cs>K\sim Na<Li$, as observed. The active basic sites on Cs–SiO_2 which was deactivated quickly in the initial stage was roughly 20—40% of the total Cs ions. It has been suggested by Imanaka, Hayashi, and Teranishi that K or Cs exchange of porous glass creates basic sites.[17] Yashima *et al.*[18] reported that K- or Cs-exchanged zeolites exhibit a basic character, although Li-zeolite is acidic. Malinowski and coworkers[19] have measured acidic and basic sites on NaOH-treated SiO_2 and correlated its catalytic activity with them.

The marked change in the catalytic action from one alkali ion to another seems to be one of the remarkable characteristics of the solid surface. In aqueous solutions, there is little difference expected among alkali ions owing to the levelling effect of water. Even in aprotic solvent, although the rate changed, the selectivity remained essentially the same in the isomerization of an olefin.[20]

Reaction Mechanisms, Stereoselectivity, and Stereochemistry. In the dehydrobromination, the surface acts as an acid-base bifunctional catalyst; the acid site abstracts a bromide ion and the basic center a β-proton. The reaction mechanism, therefore, may be classified by the timing of the C–H and C–Br bond breaking,



$$-\underset{H}{\overset{|}{C}}-\underset{Br}{\overset{|}{C}}- \xrightarrow{-HBr} >C=C<$$

although it is very difficult to determine strictly whether the two bonds break simultaneously or not.[21]

A carbanion mechanism in which the C–H bond breaks (or becomes loose) in the first step seems unlikely because of the observed relative reactivity (*sec*-butyl$>$isopropyl$>$ethyl) and the butene composition from C_4Br (2-$>$1-butene). The primary isotope effect and the stereospecificity observed suggest a concerted mechanism where two bonds break in a single concerted step. A carbonium-ion mechanism may also be applied in some cases, if the turnover of the ion on the surface is restricted.

The present results are reasonably explained as in the previous papers by the application of the extended Bunnett's hypothesis of the variable transition state,[2] which was originally proposed for concerted elimination reactions in the liquid phase. The reaction mechanism of elimination varies from an ideally concerted to a carbonium-ion like mechanism, as a reagent attacking the C–H bond becomes less basic or that attacking the C–Br bond becomes more acidic. A variation of the mechanism of the elimination reaction consistent with this idea has been reported also in solid catalysis.[5,22]

When the surface basicity decreases as in Li– and Na–SiO_2, it will become difficult for the surface to abstract a β-proton. But it may be removed to a bromide ion which is already or nearly released, so that *syn* elimination results.[6] The opposite stereochemistry observed with Na–SiO_2 between C_4Br and C_4Br_2 is attributed to a similar variation of mechanism caused by the much higher tendency of β-proton of dihalide to dissociate as a proton, which enables *anti* elimination even over a weak base like Na–SiO_2. The higher reactivity of dibromide than of monobromide ($C_4Br_2>C_4Br$), as well as the elimination of HBr exclusively from 2,3-position (not from 1,2-position), is explained similarly by the strong acidity of β-proton of dihalide. These trends are well recognized in the liquid-phase elimination.[2,23,24] The C–Br bond breaking, on the contrary, is retarded by β-halogen. These effects explain the reversed reactivity of alkyl bromide over Li–SiO_2 ($C_4Br>C_4Br_2$) and the activity order for C_4Br_2 of $Cs>K>Na>Li$.

The fact that the relative reactivity of C_4Br to isopropyl bromide was about 4 over Cs–SiO_2 but about 10 over Li–SiO_2 also supports the idea that the transition state exhibits a more carbonium-ion character in the latter surface. Changes in the rate and butene composition with acid-base properties are also consistent with the mechanisms described here. For example, increases in 2-/1- and *trans/cis* ratios from Li to Cs are expected, when the mechanism becomes more concerted[2,25] and the stability of the transition state reflects more that of the products.

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