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Dehydrobromination of Bromoalkanes over Cabosil and Alkali-Ion-Exchanged Cabosils

I. A Stereochemical Study

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The stereochemistry of dehydrobromination of 2-bromobutane and 2,3-dibromobutane has been determined over cabosils, amorphous silicon dioxide prepared by a dry process, to which various amounts of Cs and Li were loaded by an ion-exchange method. Stereochemistry, product distribution, and Arrhenius parameters were essentially the same as those obtained for silica gels prepared by an ordinary wet process. This fact confirmed the idea that the steric course is controlled by the acid–base properties of catalysts: The steric course of dehydrobromination of 2-bromobutane is mainly anti mode over basic solid surfaces and syn mode over acidic surfaces. The reaction rates via anti mode increased in proportion to the number of Cs ions loaded on silica. Basic sites responsible for anti elimination are likely the oxide ions associated with electron-donating Cs ion. A possible mechanism of anti elimination, which does not necessitate any particular pore structure, was discussed on the basis of the experimental results.

INTRODUCTION

We have studied from a stereochemical viewpoint the mechanism of dehydrohalogenation of haloalkanes over various solid acids and bases and reached a general conclusion that the prime factor controlling the steric course (anti or syn mode) is acid–base properties (*1–4*). Dehydrobromination of 2-bromobutane proceeds mainly via syn mode over silica gel, but when the surface proton was exchanged with Cs or K ion anti elimination became predominant. In anti elimination, two groups, e.g., H and Br, must be removed, probably onto the surface sites from the opposite sides of a reactant molecule. However, it is not easy to conceive of a geometrical arrangement with two active sites fixed on the surface, which enables this steric course. Various models have been proposed for anti elimination in surface-catalyzed reactions, as described in the Discussion section.

In this study, we investigated dehydrobromination reactions over silicon dioxide which was prepared by a completely different method. Cabosil was chosen as the catalyst. This material is amorphous silicon dioxide prepared by a dry process, that is, the hydrolysis of silicon tetrachloride vapor in a hydrogen–oxygen flame at about 1800°C, and, therefore, this may have a different texture compared to the silica gel used in previous studies (*1*, *3*), which was prepared by an ordinary wet process. Primary particles of cabosil are very small (70–140 Å in diameter) and do not have micropores. It is expected that the results

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of the present study when compared with the previous ones will provide considerable insight into the role of the surface structure and the reaction mechanism.

The effects of the extent of cation exchange on the reaction rate, the steric course, and the composition of products were also investigated to elucidate the formation mechanism of sites active for anti elimination. The mechanism of anti elimination is discussed on the basis of these results and the infrared spectroscopic study which is described in detail in the succeeding paper (*9*).

EXPERIMENTAL

Apparatus and procedure. The apparatus and the procedure for rate measurement by a conventional pulse technique, product analysis, and determination of stereochemistry have been described previously (*1–4*). Dry helium carrier gas flowed over catalysts (100–400 mg) loaded in a microreactor at ca. 60 cm^3/min and at 1.4–1.9 kg/cm^2. After the catalysts were preheated for 1 hr, usually at 300°C, and cooled to reaction temperature, 1 μl of haloalkanes was injected into the helium stream with a microsyringe. Products were analyzed by gas chromatography and by mass spectrometry after gas chromatographic separation. Electron micrographs were taken by a replica method with carbon shadowing by use of a JEOL JEM-6AS. Scanning electron micrographs were taken after gold evaporation with the aid of a JEOL JSM-U3.

Catalysts and reagents. As the source of silica, CAB-O-SIL M-5 (Cabot Corp.) was used after washing with aqueous hydrochloric acid of pH 3. This acid-washed cabosil is denoted as H-cabosil. Alkali-exchanged cabosils were prepared from the H-cabosil as described previously (*3*), by soaking in N/20 aqueous solutions of alkali chloride and carbonate mixture (ca. 2:1). The pH was adjusted by the addition of a small amount of hydrochloric acid. For example, the cabosil exchanged in the solution of Cs salts at pH 10 is denoted as Cs(10)-cabosil. The contents of alkali and chlorine, as well as the surface area measured by N_2 adsorption, are given in Table 1. The silica gel prepared by hydrolysis of tetraethoxysilane in water, which was used previously (*1*, *3*, *4*), will be deonoted as SiO_2(W). The composition of two 2-bromobutane-3-d_1 samples (A and B) which were prepared by deuterobromination of 2-butene were determined in the previous work as follows (*3*):

	erythro (%)	threo (%)	d_0 (%)	
d_1 (A)	77	17	6	(erythro-rich)
d_1 (B)	28	66	6	(threo-rich)

RESULTS

Dehydrobromination of 2-Bromobutane over Cabosils

Results obtained with cabosils were similar in several respects to those reported previously for SiO_2(W) (*1*, *3*), in spite of the different method of preparation. Deactivation from pulse to pulse was as large with the Cs-cabosils as it was with Cs-SiO_2(W). The deactivation process was similar among all the Cs-cabosils, the percentage of deactivation per pulse being nearly independent of the amount of Cs loaded. This deactivation was small with cabosil itself, H-cabosil, SiO_2(W), Li-cabosil, and Li-SiO_2(W). The effect of pyridine added prior to the reaction was very small for the Cs-exchanged silicas, while it was significant for the silicas without the alkali exchange and for the Li-exchanged silicas. The butene compositions produced from 2-bromobutane over cabosils were close to those produced over SiO_2(W) catalysts, particularly in the case of the Cs-exchanged ones (Table 1).

In Table 1, the relative rate calculated from the conversion of the first pulse is

TABLE 1

Properties of Alkali-Ion-Exchanged Cabosils and Dehydrobromination of 2-Bromobutane over the Cabosils at 160°C

Cabosil[a]	Alkali content (mg-atom/g)	Chlorine content (mg-atom/g)	Surface area (m^2/g)	Relative rate[b]	Butene composition[c] (percentage of butene-d_1 in parentheses)[d]			$(trans/cis)_0$[e] / $(trans/cis)_1$	Percentage anti
					1-	*trans*	*cis*-		
Cabosil	—	—	188	4.8	1	3.16	3.06	0.84	syn
H(3)	—	—	181	3.4	1 (89)	3.01 (77)	3.01 (49)	0.86	23
Li(7)	0.01	—	—	1.2	1	2.32	2.73	0.78	syn
Li(8)	0.01	—	—	0.9	1	2.37	2.65	0.83	syn
Li(10)	0.16	0.002	134	1.1	1	2.14	2.47	0.93	syn
Cs(7)	0.01	—	—	2.7	1	2.77	1.87	1.49	(85)[f]
Cs(8)	0.03	—	132	5.4	1 (90)	2.76 (42)	1.89 (82)	1.54	88
Cs(9)	0.08	—	125	9.3	1 (94)	2.67 (36)	1.72 (80)	1.57	90
Cs(10)	0.10	0.001	115	12.5	1 (94)	2.76 (37)	1.73 (86)	1.54	91
Cs(10)	0.10	0.001	115	12.5	1 (95)	2.70 (37)	1.70 (82)	1.57	92
Cs(10)[g]	0.10	0.001	115	12.5	1 (95)	2.76 (74)	1.73 (52)	—	92
Cs(8)(W)[h]	0.08	—	250	3	1	2.7–2.9	1.7–1.8	1.50	anti
Cs(10)(W)[h]	ca. 0.5	—	180	37	1	2.8	1.7	1.54	anti

[a] Cs(10), for example, is Cs(10)-cabosil which was prepared by the ion exchange in aqueous solution of Cs salts of pH 10.

[b] Percentage conversion of first pulse normalized to that over 100 mg of catalyst.

[c] Butene composition from 2-bromobutane-d_0.

[d] Percentage of d_1 species in each butene isomer produced from 2-bromobutane-3-d_1 (A) (erythro:threo: d_0 = 77:17:6).

[e] See text.

[f] Estimated from the ratio in footnote *e*.

[g] From 2-bromobutane-3-d_1 (B) (28:66:6).

[h] Cs-exchanged SiO_2(W). Data taken from Ref. (*3*).

given for each catalyst. Although Cs-cabosils showed rapid deactivation, the results from the first pulses may well represent the activity of fresh catalysts, as the conversion from the first pulse was proportional to the amount of Cs-cabosil loaded in the reactor. The butene composition changed slightly from pulse to pulse; maximum change was observed with the *cis*/1 ratio from Cs-cabosils which increased by 10–20% after seven pulses. The butene compositions given in Table 1 are the compositions of butene isomers obtained from the first four successive pulses, since in the experiments with 2-bromobutane-3-d_1, butene formed from the first four or five pulses was collected for mass spectrometric analysis to determine the stereochemistry.

The reaction rate increased with the Cs exchange of cabosil and SiO_2(W). The Li exchange of cabosil decreased the activity a little. In the case of SiO_2(W) containing small amounts of Li or Na, the rate changed little with the Li exchange and decreased with the Na exchange.

TABLE 2

Dehydrobromination of 2-Bromobutane over Cs(10)-Cabosil at 160°C

(A) Products from 2-Bromobutane-d_0 and -3-d_1[(A) and (B)]

Reactant	Butene composition (percentage of d_1 in parentheses)		
	1-	*trans-*	*cis-*
d_0	1.0	2.76	1.73
d_1(A)	1.0 (93.5)	1.60 (37.4)	1.55 (85.6)
d_1(B)	1.0 (94.6)	2.16 (73.9)	1.08 (51.5)

(B) Analysis of the Results in (A)

	Formation of 2-butene	
	trans-	*cis-*
Rate constant[a]		
k^a	2.47	1.62
k^s	0.29	0.11
Stereochemistry[b]		
Percentage anti	90	93
Isotope effects[b]		
$1/R^a$	2.35	2.55
$1/r$	1.05	0.95

[a] Relative rate constants (rate of 1-butene formation = 1). k^a and k^s are the rate constants by anti and syn mode respectively.

[b] For explanation of percentage anti, $1/R^a$, and $1/r$, see text.

Stereochemistry of Dehydrobromination and Effects of the Extent of the Cs-Exchange

By use of 2-bromobutane-3-d_1 (erythro and threo), the stereochemistry of dehydrobromination was determined. The absence of isomerization or hydrogen–deuterium exchange of butenes during the elimination reaction was confirmed as before (*1–3*). First, the ratio, $(trans/cis)_0/(trans/cis)_1$, which is the ratio of *trans*/*cis*-2-butene from 2-bromobutane-d_0 to that from 2-bromobutane-3-d_1 (A), was utilized to estimate the predominant steric course. Owing to deuterium isotope effects, this ratio becomes larger than unity when anti elimination is predominant and is less than unity for syn elimination (*3*). It is seen from the results in Table 1 that anti elimination is the favored mode over all Cs-cabosils and, syn elimination is the favored mode over cabosil itself, H-cabosil, and Li-cabosils, the trend being in accordance with that found for SiO_2(W) catalysts (*3*, *4*).

In Table 2, part A, the data obtained from the reaction of 2-bromobutane over Cs(10)-cabosil are collected. Analysis of the data by the method described earlier (*3*) gives the rate parameters given in Table 2, part B, where k^a and k^s are the rates of the formation of 2-butene isomers by anti and syn mode, respectively, and $1/R^a$ and $1/r$ are the primary isotope effect for anti elimination and the average secondary isotope effect, respectively. High anti preference and the primary isotope effects of 2.3–2.5 were obtained for both *trans*- and *cis*-2-butene formation. Both the stereochemistry and the isotope effects are close enough between two 2-butene formations to permit the reliable estimation of the stereochemistry by using only the data of 2-bromobutane-3-d_1(A) [cf. Ref. (*3*)]. The stereochemistry of dehydrobromination (percentage anti) thus determined is listed in Table 1.

Changes in the reaction rate, percentage anti, and the butene composition (given in Table 1) with the extent of the Cs exchange are illustrated in Fig. 1. In this figure, the rates by anti and syn mode, which were calculated by use of percentage anti in Table 1, are also plotted. The percentage anti and the butene composition were almost independent of the Cs content. The rate via anti mode increased linearly with the amount of Cs introduced on the surface of cabosil, while the rate via syn mode decreased rapidly upon the Cs exchange. Dehydrobromination of 2,3-dibromobutane was much more reactive than 2-bromobutane as it was over other basic solids (*1–3*), and the rate also increased with the extent of the Cs exchange (Fig. 2).

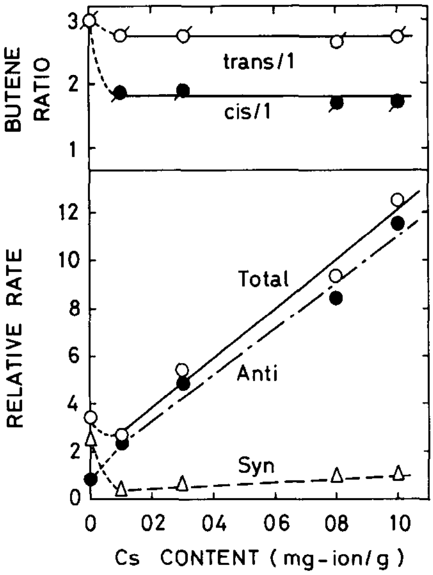


FIG. 1. Rate and product composition of dehydrobromination of 2-bromobutane over Cs-cabosil as a function of Cs content. Rates are given by percentage conversion over 100 mg of cabosil at 160°C.

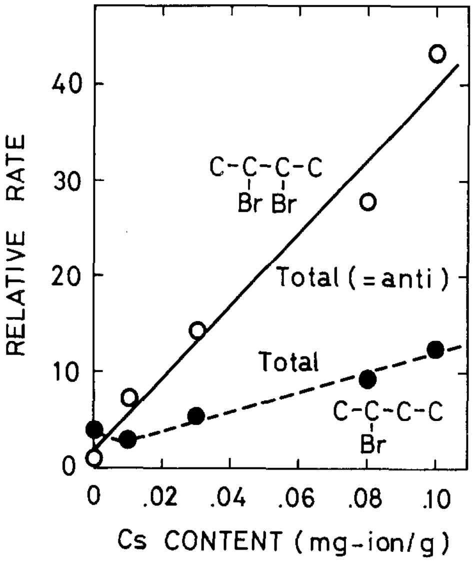


FIG. 2. Rates of dehydrobromination of 2,3-dibromobutane and 2-bromobutane over Cs-cabosil as a function of Cs content. Rates are given as in Fig. 1.

The steric course of this reaction was entirely anti elimination over the Cs-cabosils.

Effects of Reaction Temperature on the Reaction of 2-Bromobutane

The percentage anti of dehydrobromination of 2-bromobutane over the Cs-cabosils decreased with the increasing reaction temperature: 91–92% at 160°C, 89% at 230°C, and 70% at 301°C for Cs(10)-cabosil. These results may be compared with those for KOH-SiO_2 (*1*). In the case of KOH-SiO_2, the percentage anti also decreased with the temperature but was lower than that for Cs-treated silica, and the preferred steric mode tended to be opposite, above 250°C. Arrhenius parameters for the dehydrobromination and the activation energies for the formation of each butene isomer were obtained from the plots of the relative rates and the butene compositions against the reciprocal of the absolute temperature, by assuming that the rate equation did not change significantly in the temperature range studied. The results are listed in Table 3.

TABLE 3

Arrhenius Parameters of Dehydrobromination of 2-Bromobutane

Catalysts	Overall rate		Activation energies for formation of butene isomer (kcal/mol)		
	Activation energy (kcal/mol)	Pre-exponential factor (relative)	1-	*trans*-	*cis*-
Cabosil	9.1	56	11.3	8.9	8.9
SiO_2(W)	8.6	69	11.3	7.7	7.8
Li-SiO_2(W)	8.7	43	9.8	8.4	8.7
Cs-SiO_2(W)[a]	4.8	1.3	6.2	4.0	5.1
Cs-SiO_2(W)[a]	4.4	1.1	5.3	3.6	4.4
Cs(10)-cabosil	4.5	1.0	5.3	3.4	4.2

[a] Different lots.

The activation energies and the pre-exponential factors are larger for silica itself and Li-silicas (predominantly syn elimination) than for Cs-exchanged silicas (anti elimination), regardless of the origin of silica. Apparent activation energies for the formation of each butene isomer seem to reflect the composition of butene formed from 2-bromobutane. The values are relatively low for the formation of predominant butene isomer. However, these values for Cs-cabosils were not very accurate owing to the change in the butene composition from pulse to pulse at high temperatures.

Scanning Electron Microscopy (SEM) and Electron Microscopy (EM)

It was noted from SEM (×10,000) and EM (×40,000) that the particles of cabosil aggregated further during the acid-washing, but the primary particles seemed to remain unchanged, and that there was no significant difference in appearance between Cs-cabosils and Li-cabosils. On the other hand, the appearances of SiO_2(W) and alkali-treated SiO_2(W) were quite different from those of cabosils. It must be remarked, however, that the textures observed by SEM and EM are of much larger scale compared with the size of a reactant molecule.

DISCUSSION

Factors Controlling the Steric Course of Dehydrobromination

We proposed previously the idea that the prime factor controlling the steric course of dehydrobromination reactions is not factors such as pore structures, but the acid–base properties of solid surfaces and reactants. This idea was deduced on the basis of the following experimental facts. (i) Close correspondence was found between the acid–base properties and the stereochemistry of the reaction (bases favor anti mode and acids mostly syn mode) (*1–4*). (ii) A reversed volcano pattern exists in the correlation between the activity and the electronegativity of metal ion loaded on the surface of silica gel (*4*). (iii) The ion exchange at the surface effected a reversible change in the stereochemistry without significant structural changes (*3*). (iv) Basic solids like CaO and K_3PO_4 exhibited a high anti-preference, in spite of the absence of measurable micropores (*10*). (v) Opposite steric courses of reaction were observed over Na-SiO_2 (*3*) and Na_2SO_4–SiO_2 (*1*) between 2-bromobutane and 2,3-dibromobutane, which are of similar molecular size.

Present results provide additional evidence to support this idea. As described in

Results section, there were no essential differences between cabosils and SiO_2(W) in several aspects of the reactions, so that the differences in the method of preparation and the pore structure seem to play minor roles in the dehydrobromination over silicas. The effect of acidic or basic reagents confirms, as in previous work (*3*), that acidic sites are active over the H-cabosil and the Li-cabosils and that basic sites are important on the Cs-cabosils. Over an acidic surface, a carbonium-ion type mechanism [a carbonium ion (or ion-pair) mechanism over relatively strong acids and a concerted mechanism with a transition state having a cationic character over weak acids] is likely operative, resulting in syn elimination. Probably, β-hydrogen and bromine atom are removed from the opposite sides of bromoalkane in a concerted way over basic solids like Cs-cabosil. Variation of the mechanism of dehydrohalogenation with changes in the acid-base properties has been discussed elsewhere (*1–4*) and by other investigators (*5*, *6*).

Furthermore, the close similarity between the Cs-cabosils and the Cs-SiO_2(W) even in the butene composition and the activity indicates that the active sites of two silicas are very close both in geometrical shape and in chemical properties. Therefore, special pore structures or crevices, such as those suggested in earlier studies (*7*), seem to be unnecessary for anti elimination. The arrangement of surface sites involved in the transition state may be like that found in, or very close to, the ordinary structure of silicon dioxide crystal. Probably deviation from the ordinary bulk structure and "complete planarity" must be considered to some extent, since the silicas used are amorphous (*11*) and the sites are on the surface.

Mechanism of Anti Elimination on the Solid Surface

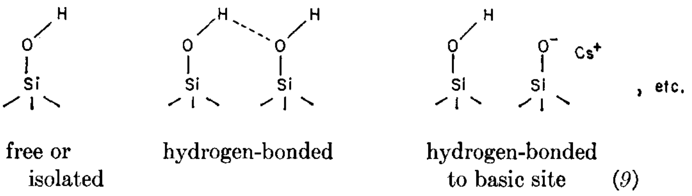
How anti elimination takes place on the surface of solid catalysts is a controversial matter. Anti elimination is widely observed in homogeneous liquid-phase reactions, but in reactions on the surface, geometric constraints would be expected to favor syn elimination. In several surface-catalyzed reactions, syn elimination has been actually observed (*1–4*, *8*, *12*, *13*). However, Pines and co-workers (*7*) found in their pioneering works that the dehydration of alkyl cyclohexanols proceeded over alumina nearly stereospecifically by the anti mode. To explain anti elimination, they suggested that the reaction took place in submicroscopic micropores, crevices, or channels of alumina.

Later, Kibby *et al.* (*8*), observed that anti elimination was the main steric course for dehydration of *cis*-2-methylcyclohexanol even over nonporous hydroxyapatite, on which 2-butanol was dehydrated by syn elimination, and questioned the hypothesis that anti elimination must occur in particular pores. According to their explanation, a β-proton in the position *trans* to the hydroxyl group of alcohols, which are adsorbed on exposed aluminum ions, can be released onto the top of an adjacent large oxide ion on the surface. Probably, the mechanism proposed by Knözinger *et al.* (*14*) does not need any particular pore structure either. They assumed that when an adsorbed alcohol molecule is "inclined" on the surface the β-proton in the *trans* position can be discharged to a basic site, e.g., at edges or corners of "rough" surface. Noller and Kladnig (*15*) also suggested that anti elimination is possible on a "plane" surface and does not require small pores or crevices. They supposed a transition state similar to that proposed by Knözinger *et al.* (*14*).

A Possible Model of the Transition State for Anti Elimination on Cs-Cabosil

A model of transition state for anti elimination, which does not require any particular pore structure and in which a proton and a bromide ion are removed from the opposite sides of 2-bromobutane by a concerted mechanism [synchronous or two-stage reaction (*16*)], may be conceived of as follows.

Cs ions exchange with protons of surface silanol groups as discussed elsewhere (*3*). Figures 1 and 2 indicates that the number of basic sites increases in proportion to the number of Cs ions introduced on the surface of cabosil. So, it is most likely that the basic sites on Cs-cabosils are oxide ions coordinated with an electron-donating Cs ion. On the surface of Cs-cabosil, the following silanol groups seem to exist mainly on the basis of infrared spectroscopic studies.



2-Bromobutane interacts with acidic silanol groups at the position of bromine atom and with basic sites at β-proton. The hydrogen atom removed as a proton from 2-bromobutane is to form a new silanol group after the C–H bond breaks (*9*). The bromide ion produced probably combines with a Cs ion, as in the case of the reaction between 2-halopropane and metal-ion-exchanged zeolites (*17*), or combines with a proton. The coordination of a bromide ion with the Cs ion must be strong (consider an acid–base reaction between HBr and a basic site) so as to cause almost irreversible deactivation of the basic sites. This is supported by the disappearance of the hydroxyl band connected with basic sites (*9*) and by the rapid deactivation from pulse to pulse in the reaction of 2-bromobutane. A possible model of the transition state, therefore, may be illustrated as in Fig. 3. Rather high 2/1-butene ratios in the products (Saytzeff orientation) and higher reactivity of 2-bromobutane than 1-bromobutane may suggest that the C–Br bond is more loosened or polarized than the C–H bond at the transition state.

In any structure of silica, the packing of oxide ion is much less dense than that in a closest packing, resulting in a rather rough surface in atomic dimension. Dehydroxylation of the surface may also create some roughness of similar dimensions (*19*). These factors together with the disorders accompanying amorphous structures will make it easier for a reactant molecule to find two active sites (acidic and basic sites) having an appropriate configuration for anti elimination. The model in Fig. 3 resembles in some respects those proposed for dehydration of alcohols by Kibby *et al.* (*8*) and Knözinger *et al.* (*14*).

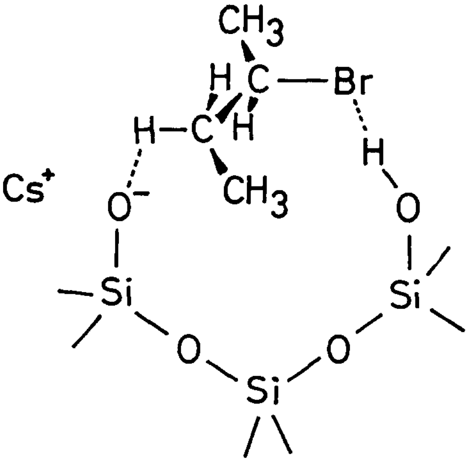


FIG. 3. A possible configuration of the transition state for anti elimination of 2-bromobutane over Cs-cabosil. Partially dehydroxylated (100) surface of "amorphous" crystobalite is considered as an example [cf. Ref. (*19*)].

In anti elimination of alcohols, *cis*-olefins are frequently favored over *trans*-olefins. This *cis* preference was explained by smaller steric hindrance in the transition state for the *cis*-olefin formation (*14*, *15*). However, *trans*-olefin was favored in the present system. Further, the correlation of the *trans*/*cis* ratio with the electronegativity of metal ion (*3*, *4*) indicates that *trans*-olefin is more favored over anti-preferring basic silicas. Although the reason for the *trans* preference in the present system is not clear, the steric interactions seem to be less important. Probably the interaction between the reactant molecule and the surface is loose and the distance between them is large enough at the transition state. In the absence of steric effects, more stable *trans*-olefins may be favored. In homogeneous liquid-phase reactions, the *trans*/*cis*-olefin ratio is often large in "concerted" E2 mechanisms (*18*).

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