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

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Elimination reactions of 2-bromobutane and 2,3-dibromobutane over silica gels in which silanol protons on the surface were exchanged with bivalent ions such as Ba(II), Ca(II), Mg(II), and Ni(II) have been investigated. Dehydrobromination of 2-bromobutane was found to proceed mainly with *syn* elimination. Debromination by *anti* mode and non-stereospecific dehydrobromination were observed for 2,3-dibromobutane. The catalytic activities of these silica gels exhibit reversed volcano-type patterns when they are plotted against the electronegativity of metal ion together with those of alkali-ion exchanged silica gels. Reaction intermediates consistent with the stereochemistry observed are a *s*-butyl cation and a bromonium ion, respectively for 2-bromobutane and 2,3-dibromobutane.

In the previous paper, we reported a remarkable effect of alkali ion exchange of silica gel on the acid-base properties and the stereochemistry of the title reactions.[1] The reactions proceeded with *anti* elimination over Cs- and K-exchanged silica gels in which basic sites play a primarily important role. However, the reaction of 2-bromobutane proceeded with *syn* mode over silica gel and Na- or Li-exchanged silica gel, all of which are weakly acidic. It was demonstrated that the acid-base properties are the prime factor determining the stereochemistry.[2] The observed dependence of the steric course of reaction on the acid-base properties was explained by the variation of the reaction mechanism from a concerted elimination over basic surfaces to a carbonium-ion like mechanism over acidic surfaces.

In the present work, we have extended the study to silica gels exchanged with bivalent metal ions which are expected to be more strongly acidic, with the aim of clarifying how the reaction rate, stereochemistry, and orientation of olefin formation vary with the acid strength of the catalyst surface. Acidic properties and catalytic activities have already been investigated for the metal ion-exchanged silica or porous glass.[3,4] The metal ion loaded on oxide surface may be regarded as a model of Lewis acid sites having a series of various acid strengths.

Experimental

Apparatus and Procedure. The procedure for the reaction study (pulse technique) and the analyses of products are the same as reported.[1] 10—50 mg of catalyst was used for the reaction of 2-bromobutane and 100—200 mg for that of 2,3-dibromobutane. Effect of pyridine adsorption on the catalytic activity was studied as follows. After ordinary pretreatment of the catalysts at 300 °C in a stream of helium, 10 μl of pyridine injected into the helium stream was passed through the catalyst bed at 150 or 160 °C. The temperature was then raised at a rate of 5 °C/min to the predetermined temprature. The reaction of 2-bromobutane was examined after the temperature had been lowered to 150 or 160 °C.

Catalysts and Reagents. The same silica gels as reported[1] were used as starting material. Ion-exchange was performed by impregnating the silica gel in aqueous solutions of metal chlorides followed by washing with water and drying at 110 °C overnight. The pH (5—7) of the solution was not intentionally controlled, a small amount of metal carbonate being added in some cases. The amount of loaded metal ion was as low as *ca.* 5 μg-ion/g. The surface area was *ca.* 500 m^2/g. The reagents used for the reactions were the same as reported.[1]

Results

Dehydrobromination of 2-Bromobutane. All the silica gels exchanged with bivalent metal ions (Mg(II), Ca(II), Ba(II), and Ni(II)) exhibited much higher activity for the dehydrobromination of 2-bromobutane than the alkali-ion exchanged silica gels.[1] Decrease in activity and change in butene composition were small during the repeated pulses. Although butene injected separately did not isomerize over these catalysts under the reaction conditions, 1-pentene pulsed together with 2-bromobutane isomerized in some cases to a small extent (*ca.* 5—10%). Hydrogen bromide formed from 2-bromobutane seemed to act as a temporary catalyst for the isomerization. The butene composition observed was probably affected by the secondary isomerization, but this influence should be small, since pentenes which are more reactive than butenes[2] did not isomerize to a great extent.

Butene compositions formed from 2-bromobutane-d_0 and the contents of d_1 species in each butene isomer formed from 2-bromobutane-3-d_1 (*erythro*:*threo*:d_0=77:17:6)[1] are given in Table 1. The ratios, $(trans/cis)_0/(trans/cis)_1$,[5] were 0.86—0.91, indicating that *syn* elimination was the major process over these four silica gels. The d_1 content of 1-butene which should agree with that of the starting 2-bromobutane-3-d_1 (94%) was low in some cases. This seems due partly to the secondary isomerization which may cause H–D exchange and partly to experimental error because of the small amount of 1-butene formed.

Under the same assumptions that the isotope effect and % *anti* (the fraction of reaction which proceeded by *anti* mode) are the same for *trans*- and *cis*-2-butene formation,[1] % *anti* was calculated to be *ca.* 20—30% (% *syn*: 70—80%) for these silica gels (Table 1). The elimination reaction may actually be more stereospecific than the values thus determined. Hydrogen shift in an alkyl cation intermediate was found to take place during the course of reactions of alkyl halides over solid acids.[6] This hydrogen shift as well as the H–D exchange by secondary isomerization should diminish the difference in d_1 content between

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Table 1. Dehydrobromination of 2-bromobutane over bivalent ion-exchanged silica gels

Metal ion	Relative[a)] activity	Butene composition[b)] (% d_1 in parentheses) 1-	*trans*-	*cis*-	Stereochemistry % *anti*
Mg(II)	42	1.0(88)	3.4(73)	3.2(56)	33
Ca(II)	47	1.0(91)	3.4(77)	3.3(51)	25
Ba(II)	38	1.0(93)	3.5(80)	3.5(42)	14
Ni(II)	148	1.0(88)	4.8(76)	4.3(51)	25
SiO_2[c)]	3—8	1.0	2.6—3.2	2.5—3.2	*syn*

a) Conversion (%) at 160°C normalized to that over 100 mg catalyst. b) Butene composition from 2-bromobutane-d_0 and content (%) of d_1 species in each butene from 2-bromobutane-d_1 (*erythro*: *threo*: d_0 = 77 : 17 : 6). c) Ref. 1.

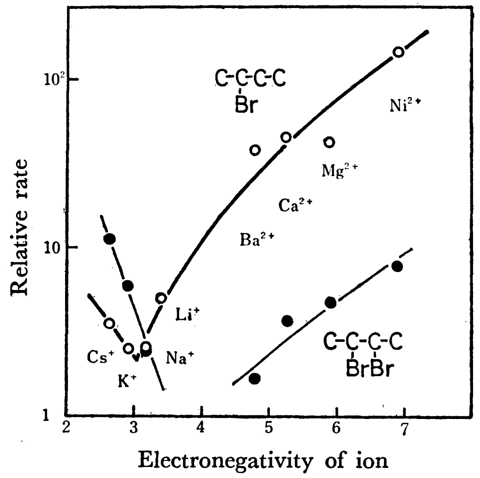


Fig. 1. Rates of elimination reactions of 2-bromobutane (○) and 2,3-dibromobutane (●) over metal-ion exchanged silica gels at 160 °C.

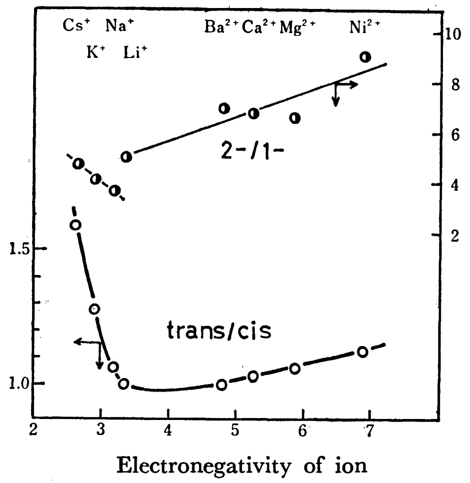


Fig. 2. Compositions of butenes formed from dehydrobromination of 2-bromobutane over metal-ion exchanged silica gels at 160 °C.

trans- and *cis*-2-butene. Thus the apparent % *anti* becomes closer to 50%.

Figure 1 shows how the catalytic activity changes with the electronegativity of metal ion[7)] loaded. The results of alkali ion[1)] are also given. Although the amount of metal ion loaded differs between mono- and bivalent ions, it is obvious that the activity increases from Na(I) to Ni(II) with increasing electronegativity. Since the activity increases with decreasing electronegatively from K(I) to Cs(I), a reversed volcano-type pattern exists in the activity-electronegativity correlation.

Positional and geometrical orientation of butene formation over these silica gels is shown in Fig. 2. The higher 2-/1-butene ratio (Saytzeff orientation) and the *trans*/*cis* ratio close to unity, together with the predominant *syn* elimination, are characteristic of bivalent-ion exchanged silica gels. This is in line with the view that these silica gels behave as acids like Li–SiO_2 but have much stronger acid strength. Figure 3 shows the effect of pyridine on the catalytic activity. Active sites of silica gel poisoned by pyridine were mostly regenerated at 150 °C 20 min after the addition, while only about a half was recovered in the case of Ni–SiO_2 even at 300—350 °C in a helium stream. It is seen that the strength of pyridine adsorption to active sites, which should reflect the acid strength, increases in the order Ca(II)<Mg(II)<Ni(II) in accordance with electronegativity. The apparent energy of activation obtained at the state of stationary activity was 11.2 kcal/mol for Ca–SiO_2. The value is closer to that of Li–SiO_2 (9 kcal/mol) than to that Cs–SiO_2 (4—5 kcal/mol).[1)] The activation energy for *trans*- and *cis*-2-butene formation was respectively 2.1 and 2.4 kcal/mol lower than that for 1-butene formation.

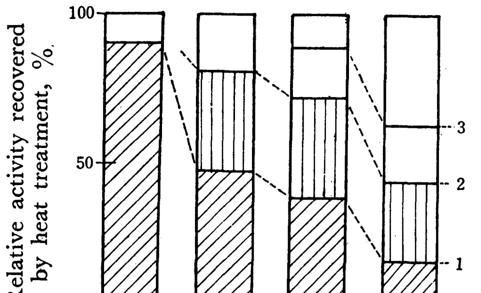
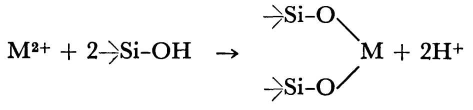


Fig. 3. Relative activity of silica gels poisoned by pyridine for dehydrobromination of 2-bromobutane. Reaction temp. : 150 °C (160 °C for Ca-SiO_2)
1: After heat treatment at the reaction temperature.
2: After heat treatment at 300 °C.
3: After heat treatment at 350 °C.

Reactions of 2,3-Dibromobutane. 2,3-Dibromobutane was less reactive than 2-bromobutane over bivalent-ion exchanged silica gels. Butadiene formation by the elimation of two molecules of hydrogen bromide and debromination to form 2-butene (*anti* elimination) were the major reactions. Minor reaction of dehydrobromination to form 2-bromo-2-butene was not stereospecific. No apparent difference in selectivity for these elimination reactions was observed among the bivalent ions, the fraction of debromination being 50—60% of total reactions. These elimination reactions also show a reversed volcano-type pattern when plotted against electronegativity (Fig. 1). It is to be noted that 2,3-dibromobutane is more reactive than 2-bromobutane (both with *anti* elimination) on the left branch, while the relative reactivity is the reverse on the right branch.

Discussion

Bivalent metal ions undergo exchange with two silanol groups over the surface of silica gel when the extent of exchange is low.[3]

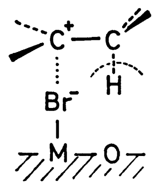


$$\mathrm{M^{2+}} + 2\not>\mathrm{Si\text{-}OH} \rightarrow \begin{array}{l}\not>\mathrm{Si\text{-}O}\diagdown \\ \qquad\qquad \mathrm{M} + 2\mathrm{H^{+}} \\ \not>\mathrm{Si\text{-}O}\diagup\end{array}$$

The acidic sites increase in number with the amount of metal ion loaded at least at low extent of exchange, and Lewis acid sites which were proposed to be active for dehydrochlorination of isopropyl chloride are predominant after evacuation above 300 °C.[3]

The relative catalytic activity, $(\mathrm{Ni(II)}>\mathrm{Ca(II)}\approx\mathrm{Mg(II)}\approx\mathrm{Ba(II)}\gg\mathrm{Li(I)}\approx\mathrm{Na(I)})$(Fig. 1), parallels the acid strength of catalysts which can be estimated from the electronegativity of metal ion and the effect of pyridine adsorption on activity (Fig. 3). We proposed that the reaction intermediate or the transition state resembles a carbonium ion more over Li–SiO$_2$ than over Cs–SiO$_2$, since the stronger acidity of the former makes the C–Br bond breaking easier. This explanation can be applied to the present results. As the acid strength increases further by the exchange with bivalent ion, the C–Br bond breaks more readily and the rate of reaction *via* a carbonium ion will increase. Thus, the activity for elimination over metal-ion exchanged silica gels shows a reversed volcano-type pattern (Fig. 1), when the results of Cs– and K–SiO$_2$ are included, where the activity increases with base strength.[1]

The favored steric course over basic surface was *anti* mode.[1] On the other hand, over acidic surface *syn* elimintion is favored in the case of 2-bromobutane. 2,3-Dibromobutane is likely to form a bromine-bridged intermediate after heterolytic C–Br bond breaking. The intermediate decomposes to butene (*anti* elimination), 2-bromo-2-butene (non-stereospecific) and butadiene (—2HBr *via* CH$_2$=CH-CHBr-CH$_3$).[2b,8] Although the ionic radii are similar for Ba(II) (1.50Å) and K(I)(1.52Å),[9] the preferred steric mode of the dehydrobromination of 2-bromobutane was opposite. This suggests that the ionic radius by itself is not the prime factor determining the stereochemistry of elimination. A trend of % *syn* elimination of 2-bromobutane as Ba(II) (86%)>Ca(II) (75%)>Mg(II) (67%) was found for alkali-earth metal ions. This may be a reflection of acid strength, but factors such as the difference in metal content and the secondary isomerization (or hydrogen shift during reaction) as well as experimental error should be considered before coming to such a conclusion. However, it seems remarkable that considerable stereospecificity (*syn*>75%) was observed in case that the carbonium-ion mechanism is most probable. In order to complete dehydrobromination by *syn* mode, a proton must be transferred from *s*-butyl cation toward the direction to which a bromide ion is released, possibly by a model as proposed previously,[2a] before the "roll-over" of or the hydrogen shift in the intermediate completely takes place.



Correlations of the catalytic activity, the orientation of olefin formation, and the stereochemistry with the acid-base properties of catalyst are summarized in Table 2. We see that the stereochemistry of reaction which reflects the reaction mechanism differs for acidic and basic catalysts, their activity and selectivity definitely exhibiting different dependency on the acid–base properties. Similar changes in activity or reaction mechanism with the acid-base properties have been discussed by Noller *et al.*[10] and Mochida *et al.*[11] Trends as shown in Figs. 1 and 2 were also found in the case of metal chlorides supported on silica gel.[12] Lewis acid sites were considered to be the active sites in these catalysts. For example, they were as active as metal sulfates for dehydrobromination, but were much less active for olefin isomerization. Although the acid strength of protonic sites can increase with electroneg-

TABLE 2. SUMMARY OF DEHYDROBROMINATION OF 2-BROMOBUTANE OVER METAL-ION EXCHANGED SILICA GELS

Metal ions	Cs(I), K(I)	Ca(II), Ni(II)
Electronegativity	Low	High
Surface	Basic	Acidic
Easiness of bond-breaking	C-Br≈C-H	C-Br>C-H
Activity increases with	Base strength	Acid strength
Butene composition		
2-/1-	4—5	6—9
trans/cis	>1	≈1
Stereochemistry	*anti*	*syn*
Mechanism[a]	Concerted	*s*-Butyl cation (ion pair)

a) Reaction mechanism for 2,3-dibromobutane seems to be a concerted elimination over a basic surface as for 2-bromobutane, but a bromine-bridged bromonium ion is the intermediate in the case of acidic surface.

ativity as in the case of butene isomerization catalyzed by metal sulfates,[13] it is most likely that metal ion itself acts as a Lewis acid in the present system.

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5) This is the ratio of *trans-/cis*-2-butene ratio from 2-bromobutane-d_0 to that from 2-bromobutane-3-d_1(*erythro* rich). The ratio is larger than unity for *anti* elimination and smaller than unity for *syn* elimination, owing to the deuterium isotope effect.[1]

6) 2-Bromobutane-2-d_1 was formed from the reaction of 2-bromobutane-3-d_1, and 2-bromopentane from 3-bromopentane over $CaCl_2$, $CuCl_2$, and Ba–SiO_2(M. Ishikawa, M. Misono, and Y. Yoneda, 34th Annual Meeting of the Chemical Society of Japan, lJ36, Hiratsuka, April, 1976).

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