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Isomerization of Butene Catalyzed by Solid Acids: Hydrogen Migration and "Rollover" of *s*-Butyl Cation Intermediate

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A method for detailed analysis of deuterium tracer studies of butene isomerization which proceeds via a *s*-butyl cation is described. This method takes into account the conformation of the *s*-butyl cation as well as the stereochemistry and isotope effects of proton addition and elimination. By applying this method to the data obtained for silica–alumina by Hightower and Hall [*J. Amer. Chem. Soc.* 89, 778 (1967)] and to those from experiments with metal sulfates, hydrogen migration and "rollover" of the *s*-butyl cation have been demonstrated.

INTRODUCTION

It is well established from tracer studies that, over acidic solids like silica–alumina and metal sulfates, butene isomerizes via a *s*-butyl cation: a proton is added to the butene in the first step and one of the hydrogen atoms of the protonated intermediate is removed in the next step to form one of the butene isomers. Ozaki and Kimura (*1*) found that butene isomerizes over protonic acid sites, in which the protons come from other olefin molecules when the catalyst was pre-evacuated at high temperatures. When the catalyst was pre-evacuated at low temperatures, protons from the catalyst are added to the butene.

Hightower and Hall (*2*) have introduced a useful method for investigating proton exchange accompanying the isomerization. A mixture of *cis*-2-butene-d_0 and -d_8 was co-isomerized over silica–alumina and alumina which had been evacuated at 530°C. The isomerization proceeded over protonic acid sites induced on silica–alumina from the carbon residue which was formed rapidly from butene. They concluded, on the basis of an analysis of the intermolecular hydrogen–deuterium exchange, that one hydrogen (or deuterium) atom was incorporated into a butene molecule each time either a double-bond shift or *cis–trans* isomerization occurred. Their results obtained for silica–alumina were successfully interpreted on the basis of a common *s*-butyl cation intermediate (*2*, *3*). The apparent isotope effects obtained were, respectively, 1.5 and 1.2 for 1-butene and *trans*-2-butene formations from *cis*-2-butene. Sakamoto and Hattori (*4*) recently extended the analysis of Hightower and Hall and applied it to the isomerization of butene over aluminum phosphate. In their analysis, the relative reactivities of butene-d_0 and -d_8 and for surface-H and -D are considered separately. The effect of C–C bond rotation of the intermediate (*s*-butyl cation) on the deuterium isotope distribution of butenes was also taken into account to some extent.

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a more detailed analysis of tracer studies of isomerization via an alkyl cation (*5*), in which isotope effects for proton addition to butene and for proton elimination were considered separately. Furthermore, the probability that the proton added to butene remains in the product was explicitly discussed as an important parameter which reflects the "rollover" of, and hydrogen migration in, the *s*-butyl cation. If the cation is very stable on the surface, hydrogen atoms may migrate among all or a part of the carbon atoms of the cation before the isomerization is completed. In a concerted mechanism, or if the cation has only a short life, the proton attached may not move to other positions before it is desorbed from the surface.

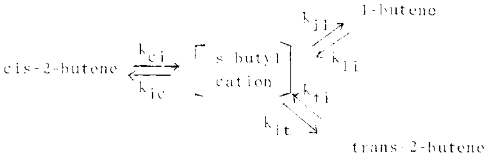
Sakurai and co-workers (*6*) have found that hydrogen migration does not take place in the case of 2-butene isomerization over deuterated *p*-toluene sulfonic acid supported on silica gel. Seyffarth *et al.* (*7*) have assumed a special structure for the protonated intermediate to explain the equal distribution of deuterium atoms between terminal and internal carbon atoms of 2-butene formed from 1-butene over a $MgSO_4$–DCl catalyst. Recently, it was observed that hydrogen migration takes place readily during the dehydrobromination of alkyl bromides over various solid acids. For example, 2-bromopentane was formed to a considerable extent in the reaction of 3-bromopentane at low temperatures. This reaction very likely proceeds via 3- and 2-pentyl cations (*8*).

Therefore, the hydrogen migration in the alkyl cation intermediate must be taken into account in the carbocation chemistry of heterogeneous catalysis, particularly in relation to the determination of the reaction mechanism in the acid-catalyzed reactions by tracer studies. In homogeneous liquid media, the migration of a proton in a carbocation is often very rapid (*9*).

In this paper, first, the method of analysis proposed previously (*5*) is discussed. This method can provide detailed information about the proton migration and the rotation of the carbocation intermediate on a solid surface. Second, the results of Hightower and Hall (*2*) obtained for isomerization over silica–alumina and the present results for metal sulfates are analyzed using this method.

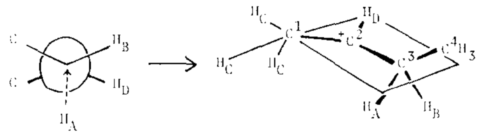
GENERAL CONSIDERATIONS AND METHOD OF ANALYSIS

If the isomerization of butene proceeds entirely via the *s*-butyl cation as a common intermediate, the reaction can be written as in Scheme 1 [cf. Refs. (*2*) and (*10*)].



Scheme 1. Isomerization of butene via *s*-butyl cation as a common intermediate.

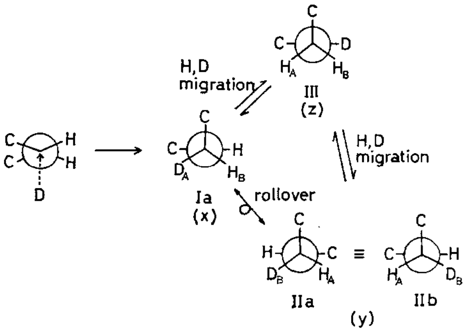
For example, the intermediate which is formed by the addition of a proton (H_A) to *cis*-2-butene is **I**:



I

Here, the suffixes, A, B, etc. indicate the *position* of the hydrogen in the cation. It must be noted that according to Scheme 1 the starting *cis*-2-butene isomer is also formed from the intermediate (path: k_{ic}), in addition to the 1- and *trans*-2-butenes (paths: k_{i1} and k_{it}). The elimination of H_B from the cation (I) leads to *trans*-2-butene and the elimination of H_A to *cis*-2-butene, regardless of the rotation of C^4, H_A, and H_B about the C^2–C^3 axis, if the side of H elimination is the same as that of H addition, as discussed previously (*3*). In this case, a hydrogen atom which has come from a catalyst always remains in the isomerized butene when *trans*-2-butene is formed, but the hydrogen atom is removed when *cis*-2-butene is formed. If rotation of C^1H_3 and H_D about C^2–C^3 (or "rollover" of the cation) or hydrogen migration occurs, the situation changes.

Consider the *s*-butyl cation (**Ia**) formed by the addition of a deuterium atom to *cis*-2-butene, as an example (H_A = D). "Rollover" of **Ia** forms **IIa** (Scheme 2).



SCHEME 2. Hydrogen (deuterium) migration and "rollover" in the *s*-butyl cation. *x*, *y*, and *z* are the fractions of **I**, **II**, and **III**, respectively.

Instead of **IIa**, we can consider **IIb**, which is the enantiomer of **IIa** and is equivalent to **IIa** for the present analysis. If we assume that the side of H or D elimination from the cation is the same as that of D addition (e.g., addition and elimination on the side facing catalyst surface), the elimination of H_A from **IIa** or **IIb** forms *cis*-2-butene-d_1 and that of D_B from **IIa** or **IIb** forms *trans*-2-butene-d_0. Before "rollover," D elimination forms *cis*-2-butene and H elimination forms *trans*-2-butene from **Ia**. Therefore, rapid "rollover" makes the positions A and B apparently indistinguishable. An equivalent effect is also brought about when D or H elimination can occur on the side opposite to D addition. But, so far the evidence for the latter is absent, so that we consider only "rollover" as representative.

Hydrogen migration forms **III**, from which removal of either of two hydrogen atoms at C^3 leads to *cis*- or *trans*-2-butene-d_1. Hydrogen migration to terminal methyls is not considered, because a primary cation is much less stable and was actually not observed with aluminum sulfate as described below.

Thus, if H_A is isotopically labeled as in Scheme 2, it is possible to determine the possibility of "rollover" or hydrogen migration in the intermediate, by examining the deuterium contents of all three butene isomers during the course of the isomerization reaction. For example, Scheme 2 predicts that, when the composition **I**:**II**:**III** is $x{:}y{:}z$,

$$\frac{d(trans\text{-2-butene-}d_1)}{d(trans\text{-2-butene-}d_0)} = \frac{k_{it}^{\mathrm{H}}(x+z)}{k_{it}^{\mathrm{D}}y}, \quad (1)$$

$$\frac{d(cis\text{-2-butene-}d_1)}{d(cis\text{-2-butene-}d_0)} = \frac{k_{ic}^{\mathrm{H}}(y+z)}{k_{ic}^{\mathrm{D}}x}, \quad (2)$$

and

$$\frac{d(trans\text{-2-butene-}d_1)}{d(cis\text{-2-butene-}d_1)} = \frac{k_{it}^{\mathrm{H}}(x+z)}{k_{ic}^{\mathrm{H}}(y+z)}, \quad (3)$$

where k_{ic}^{H}, k_{ic}^{D}, etc., are the rate constants for the processes, ion → *cis*-2-butene, in which H and D are transferred, respectively, and k_{it}^{H} and k_{it}^{D} are the equivalents for *trans*-2-butene formation. Similar equations are derived for the other processes. Here, we introduce for convenience of calculation the new parameters, e_{kj}, a_k, b_j, and γ, which are defined below and which can be easily converted to the above variables, i.e., x, y, z, k^{H}, k^{D}, etc. With these parameters, the relative rates of the following processes are obtained as given by

$$\begin{array}{llll} & & \text{Relative rate} & \\ C_4H_8 + H^+ \longrightarrow & C_4H_8 + H^+ & 1 \quad \left.\right\} d_0 & (4) \\ + D^+ \longrightarrow & C_4H_8 + D^+ & a_k\gamma b_j/(1+e_{kj}) & (5) \\ & C_4H_7D + H^+ & a_k\gamma e_{kj}/(1+e_{kj}) \; d_1. & (6) \end{array}$$

Similarly, for the co-isomerization of a C_4H_8 and C_4D_8 mixture where $C_4D_8:C_4H_8 = f:1$, the following three expressions may also be derived,

$$\begin{array}{lll l l}
 & & & \text{Relative rate} & \\
C_4D_8 + H^+ & \xrightarrow{\quad} & C_4D_7H + D^+ & f\cdot b_j\cdot e_{kj}/(1+e_{kj})d_7 & (7) \\
 & \xrightarrow{\quad} & C_4D_8 + H^+ & \left.\begin{array}{l} f/(1+e_{kj}) \\ \\ f\cdot a_k\cdot b_j \end{array}\right\} d_8 & (8) \\
+ D^+ & \xrightarrow{\quad} & C_4D_8 + D^+ & & (9)
\end{array}$$

where e_{kj}, a_k, b_j, and γ are defined as follows.

e_{kj} is a parameter related to the probability that a proton attached to butene k remains in the isomerized butene j in the absence of isotope effect. Of the cations formed, the $e_{kj}/(1 + e_{kj})$ fraction retains the proton attached during the transformation to butene j, and the $1/(1 + e_{kj})$ fraction looses the proton. This is determined by the extent of hydrogen migration and "rollover," and is readily related to the relative compositions of **I**, **II**, and **III** in Scheme 2. For example, e_{kj} becomes $(x + z)/y$ when k and j are *cis*-2-butene and *trans*-2-butene, respectively [see Eq. (1)]. $1/a_k$ is the isotope effect for proton addition to butene k. $1/b_j$ is the isotope effect for proton elimination from the cation forming butene j $(= k_{ij}^{H}/k_{ij}^{D})$. γ is the ratio of the number of D sites to the number of H sites.

The value, e_{kj}, becomes infinite, if one hydrogen atom is exchanged every time butene isomerizes. The value is zero for *cis*-2-butene formation from **Ia** in the absence of hydrogen migration and "rollover" in Scheme 2.

ANALYSIS OF THE RESULTS OF HIGHTOWER AND HALL

The results of Hightower and Hall (*2*) are good examples for application of the present analysis. In their experiments, a mixture of *cis*-2-butene-d_0 and -d_8 was co-isomerized on the surface of silica-alumina pre-evacuated at high temperature, and the isotope mixing during isomerization was followed for each butene isomer by means of mass spectrometric analysis. The results indicate that every hydrogen-deuterium exchange process is accompanied by the isomerization of butene via the *s*-butyl cation, as they explained. A simple exchange process which does not proceed via the cation appears to be absent, as is seen from the low deuterium content of the starting *cis*-2-butene. When the deuterium content of each butene isomer is plotted against the extent of isomerization [Table IV in Ref. (*2*)], nearly constant values are obtained for low extents of conversion. Therefore, if we confine the analysis to the initial reaction stage, the effect of secondary isomerization or a variation in the H/D ratio (γ) of protonic sites during the course of the reaction may be neglected. Table 1 collects the values of the deuterium contents extrapolated to zero conversion.

First, the incorporation of deuterium atoms into the starting *cis*-2-butene is compared with those into the isomerized 1- and *trans*-2-butenes. In Fig. 1, the relative number of butene molecules that have exchanged one or more H or D atoms (d_1, d_2, and d_3 species plus d_5, d_6, and d_7 species; corrected for d_7 (and d_6) species in the starting material) is plotted against the extent of isomerization. It is noted that the numbers of butene molecules which exchange H or D are nearly equal for *cis*- and *trans*-2-butenes. The probability of retaining the attached proton in the product (or the probability of H or D exchange) is calculated for 1- and *trans*-2-

TABLE 1

Isotopic Compositions of Butenes Formed by the Co-isomerization of *cis*-2-Butene-d_0 and -d_8 Extrapolated to Zero Conversion[a]

	Isotopic composition of butenes (%)					
	d_0	d_1	d_2	d_6	d_7	d_8
1-Butene	37.5	25.0	1.0	2.5	22.0	14.7
	(38.4)	(25.3)	(0)	(0)	(21.6)	(14.7)
trans-2-Butene	34.5	17.0	0.5	1.5	20.5	26.5
	(35.8)	(17.4)	(0)	(0)	(19.7)	(27.1)
cis-2-Butene (reactant)	45.5	0.3	0	0.2	3.0	51.0
	(47.1)	(0)	(0)	(0)	(0)	(52.9)

[a] The data are from Ref. (*2*).

Values estimated for the case when the starting *cis*-2-butene contains only d_0 and d_8 are given in parentheses.

butenes by simply dividing the numbers in Fig. 1 by the amounts of each isomer present at each stage of the reaction. The probability for *cis*-2-butene was similarly calculated, by tentatively assuming that the number of *cis*-2-butene molecules formed from the intermediate is equal to that for *trans*-2-butene, since the *cis*-/*trans*-2-butene ratio from 1-butene ($=k_{ic}/k_{it}$) is nearly unity in most cases (*2, 3, 11*). In Fig. 2, these probabilities are plotted. It is confirmed that *cis*-2-butene picks up a hydrogen or deuterium atom at about the same rate as do the other two isomers.

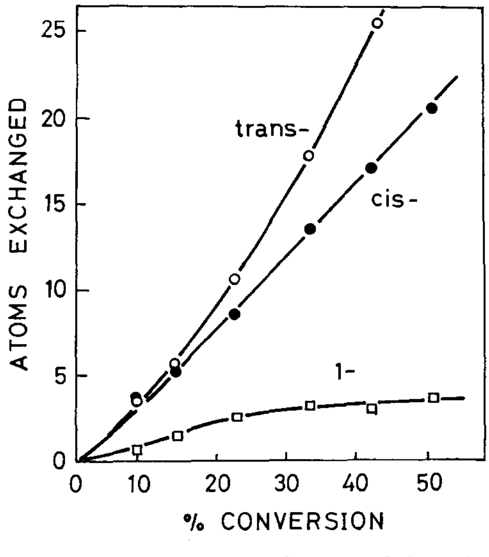


FIG. 1. The number of hydrogen and deuterium atoms incorporated into butenes during the co-isomerization of *cis*-2-butene-d_0 and -d_8.

$$\text{Atoms exchanged} = \left[\sum_{i=0}^{4} iN_i + \sum_{i=5}^{8} (8-i)N_i\right] \times (\%\ \text{butene}).$$

N_i is the fraction of butene-d_i. The values of atoms exchanged were corrected for the small amount of d_6 and d_7 species present in the starting material as was done in Ref. (*2*). The data are from Table IV of Ref. (*2*).

Next, a_k, b_j, etc., are calculated exactly from the deuterium distribution in Table 1, using expressions (4)–(9). The calculated values are collected in Table 2. The changes in isotopic composition with time are fairly reproduced by numerically solving the differential equations for the rates of production of deuterated isomers at the early stage of the reaction. The values of e_{kj} obtained for 1-butene formation from *cis*-2-butene is infinite as expected, reconfirming the Hightower and Hall conclusion that each isomerization step picks up a proton from the catalyst or other butene molecules. The value for *trans*-2-butene formation, which is approximately equal to that for *cis*-2-butene formation (see Figs. 1 and 2), does not agree with their conclusion in some respects. One fourth of the *trans*-2-butene produced lost the proton which had been transferred from the protonic sites.

From Eqs. (1)–(3) and expressions (5) and (6), the compositions of the s-butyl cation (x, y, z in Scheme 2) are calculated from b_j and e_{kj} in Table 2. For *trans*-2-butene formation,

$$\frac{x+z}{b_j y} = \frac{e_{kj}}{b_j} = \frac{3.16}{b_j}, \tag{10}$$

and

$$\frac{x+z}{y+z} = \frac{k_{ic}^{\mathrm{H}}}{k_{it}^{\mathrm{H}}} \frac{d(trans\text{-2-butene-}d_1)}{d(cis\text{-2-butene-}d_1)} \equiv c. \tag{11}$$

First, $x \doteqdot y$, since $d(trans\text{-2-butene-}d_1)/d(cis\text{-2-butene-}d_1) \doteqdot 1$ and $d(trans\text{-2-butene-}d_1)/d(trans\text{-2-butene-}d_0) \doteqdot 1$, as is seen in Fig. 1, indicating that rapid "rollover" or hydrogen migration rendered the A and B positions nearly equivalent. If $k_{ic}^{\mathrm{H}}/k_{it}^{\mathrm{H}} = 1$, c becomes unity and the composition can be calculated from these equations to be $x:y:z = 0.24:0.24:0.52$. However, a value of z higher than x is physically unreasonable. This discrepancy may be due to the inadequate estimation of the c values in expression (6) (too small). If one takes into account the *cis*/*trans* ratio which varies from 0.9 to 1.3 over silica–alumina and the experimental error in the determination of the deuterium content of *cis*-2-butene (±1% in absolute value), the c value may be chosen to be as high as 2. If hydrogen migration is absent ($z = 0$), $(x/y) = c = 3.16$ from Eqs. (10) and (11); c becomes too high. Therefore, hydrogen migration must exist to some extent. Very rapid hydrogen migration between only the A and D positions ($x = z$) leads to $c = 1.22$, $y = 0.24$, and thus, $x = z = 0.38$. This case may determine the lower limit of the c value. If we take as probable c values, 1.5 or 1.7, the compositions ($x:y:z$) become 0.55:0.24:0.21 or 0.49:0.24:0.27, which appear acceptable. In spite of the ambiguity in the quantitative values, it may be stated that both "rollover" and hydrogen migration occur to a considerable extent over silica–alumina.

TABLE 2

Calculated Parameters, a_k,[a] b_j, γ, and e_{kj}

	b_j^{-1}	$a_k.\gamma$	e_{kj}
1-Butene formation	1.98	0.67	~200
trans-2-Butene formation	1.39	0.72	3.16

[a] k = *cis*-2-butene.

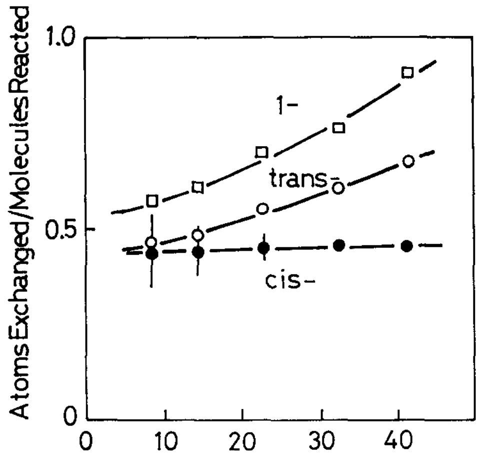


FIG. 2. The probability of butene isomers exchanging hydrogen and deuterium atoms during proton elimination from the s-butyl cation. The data are from Table IV of Ref. (2).

Thus, although most of the conclusions of Hightower and Hall are essentially valid, a detailed analysis of their results provides further insight into the nature of alkyl cation intermediates in heterogeneous catalysis.

ISOMERIZATION AND HYDROGEN-DEUTERIUM EXCHANGE OVER METAL SULFATES

i. Experimental procedure. The reactions were carried out in a closed circulation

TABLE 3

The Distribution of Propene-d_1 Isomers Formed by the Exchange of Propene-d_0 over Deuterated Aluminum Sulfate at 40°C

	%		%
Propene-d_0	32	(E)-Propene-1-d_1	20.9
Propene-d_1	40	(Z)-Propene-1-d_1	20.7
Propene-d_2	28	Propene-3-d_1	58.4

system (150 or 400 cm^3), from which gas samples were collected intermittently through stopcocks. Aluminum and magnesium sulfates (Al–S and Mg–S) supported on silica gel were prepared as described elsewhere (10, 12). Surface areas were 500 and 700 m^2/g for Al–S and Mg–S, respectively. Catalysts were deuterated by repeating three times the evacuation–D_2O exposition cycle at 150°C. Pre-evacuation and reaction temperatures were usually 60 and 40°C for Al–S and 80 and 60°C for Mg–S. The butene pressure was usually 100–150 mmHg. Numbers of surface deuterium atoms incorporated into butene molecules after a prolonged reaction time were 0.7 (80°C-evacuated Mg–S) and 1.7 mg-atom/g (60°C-evacuated Al–S). Water molecules desorbed by 400°C-evacuation was 1.3–1.4 mmole/g for 60°C-evacuated Al–S and Mg–S. To obtain data at the initial stage of the reaction, a conventional pulse technique was utilized in some experiments. In this case, the deuteration was performed by flowing carrier gas saturated with D_2O vapor for 1 hr at 150°C. The deuterium distribution of each butene isomer was determined at various stages of isomerization by mass spectrometry after gas chromatographic separation of the butene isomers. The positions of deuterium atom in propene-d_1 and 1-butene-d_1 were determined by microwave spectroscopic analysis (13).

ii. Hydrogen–deuterium exchange of propene over deuterated metal sulfates. Propene (32 mmHg) reacted over 1 g of deuterated Al–S at 40°C for 90 min and the distribution and position of the deuterium atom in the recovered propene were measured to be as given in Table 3. The ratio of 1-d_1:3-d_1 was close to 2:3, demonstrating that the exchange reaction proceeds via an isopropyl (cation) intermediate, in which two methyl groups become equivalent (14, 15). For Mg–S, it was speculated that a concerted mechanism may be responsible for the double-bond shift of butene (12), but a later study indicated that the *s*-butyl cation mechanism is more probable (10). Recently, the isopropyl intermediate was demonstrated for the propylene–D_2O reaction over Mg–S (15). Butene has a proton affinity not less than propene, so that *s*-butyl cation may reasonably be assumed for butene isomerization over these metal sulfates.

iii. Isomerization of cis-2-butene over deuterated metal sulfates. The results are shown in Figs. 3 and 4. Deuterium atoms of the catalysts were significantly incorporated into the products, in agreement with the observations of Ozaki and Kimura (1) with deuterated nickel sulfate evacuated at low temperatures. In the experiments with the pulse technique, the isomerized

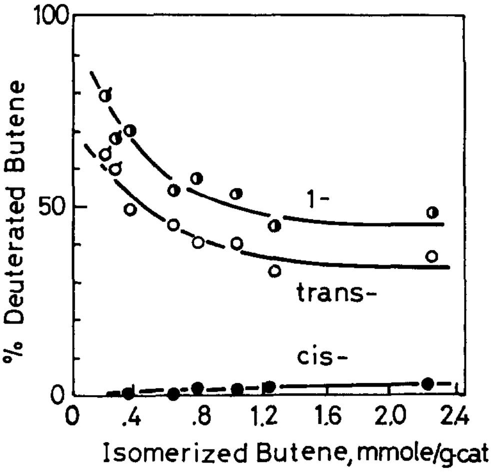


FIG. 3. The fraction of deuterated butene isomers formed during the isomerization of *cis*-2-butene over deuterated Al–S at 40°C. The flags indicate the data from the pulse method.

butene contained minor but considerable amounts of the d_2 species (10–20%) in addition to the d_0 and d_1 species. This is because the conversion became high (15–25%) due to the low butene-to-catalyst ratio. For the pulse experiments, $(d_0 + d_1)\%$ is tentatively plotted in Figs. 3 and 4, assuming that the d_2 species mainly came from butene-d_1 by picking up a deuterium atom from the catalyst with the same probability as for the d_0 species. In spite of the ambiguity due to this assumption and scarcity of data for Mg–S, it is useful to examine the deuterium contents at zero conversion. The content of 1-butene was extrapolated to 100% at zero conversion for both Al–S and Mg–S, since it is very likely that a deuterium atom is picked up each time 1-butene is formed, as for silica–alumina. Then, the deuterium contents at zero conversion for *trans*-2-butene are 70 to 75% for Al–S and 80 to 90% for Mg–S. These values, which were lower than those for 1-butene and higher than 50%, suggest that hydrogen migration, "rollover" and/or isotope effects are present.

In Fig. 5, the numbers of the d_1 species formed are compared for the *cis*- and *trans*-2-butenes. The ratio was about 2 for Mg–S and about 1 for Al–S, showing that deuterium atoms are picked up also into *cis*-2-butene at a comparable rate. The ratio of unity for Al–S indicates that the A and B positions are almost equivalent [see Scheme 2 and Eq. (11)]. In the case of Mg–S, the deuterium atoms transferred from the catalyst appear to be present more at the B position than at the A position of **I**. Probably, "rollover" or hydrogen migration occurs to a lesser extent on Mg–S.

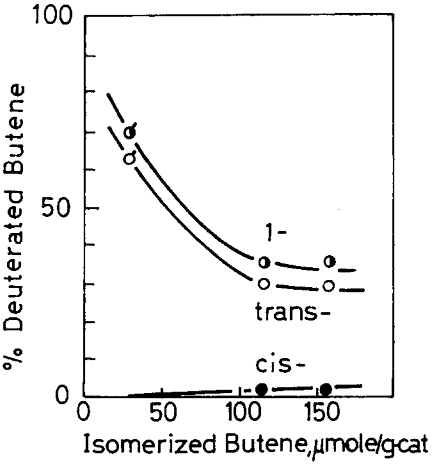


FIG. 4. The fraction of deuterated butene isomers formed during the isomerization of *cis*-2-butene over deuterated Mg–S at 60°C.

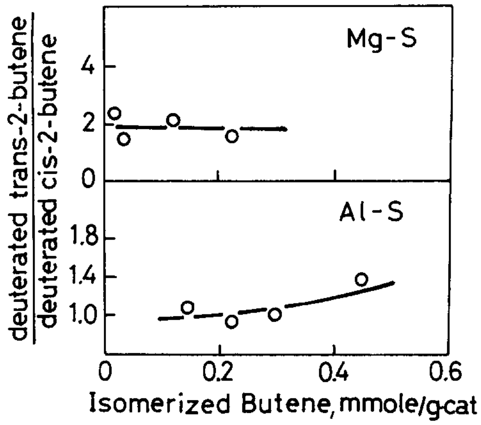


FIG. 5. The ratio of deuterated *trans*-2-butene to deuterated *cis*-2-butene formed in the isomerization of *cis*-2-butene over deuterated Al–S (at 40°C) and Mg–S (at 60°C).

In Fig. 6, the contents of the 2-d_1 species in 1-butene formed from the isomerization of *cis*-2-butene over deuterated Al–S and Mg–S are given. The remainder of the 1-butene-d_1 was the 3-d_1 species. A nearly constant 2-d_1 concentration for Al–S may eliminate the possibility that this 2-d_1 species was produced by secondary isomerization. Since, in the absence of hydrogen migration, the 3-d_1 species must comprise all the products, the presence of the 2-d_1 species demonstrates that hydrogen migration is actually present.

Reactions of 1-butene-3-d_1 over Mg–S have been reported previously (*16*). Additional data was obtained using 1-butene-

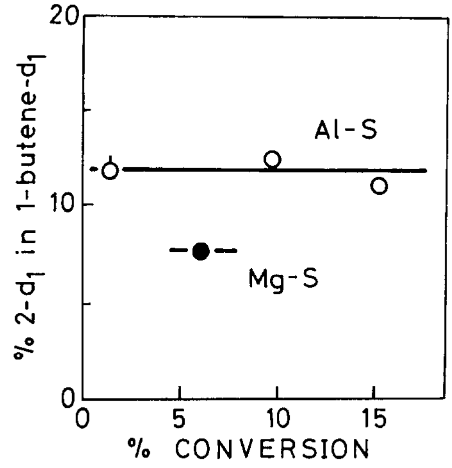


FIG. 6. 1-Butene-2-d_1 contents in 1-butene-d_1 formed from *cis*-2-butene (○, ●) and *trans*-2-butene (ȯ) over Al-S (at 40°C) and Mg-S (at 60°C).

3-d_1 which contains 19% of 1-butene-d_0, as given in Table 4.

iv. Analysis. Considering that the *cis*/*trans* ratio formed from 1-butene ($k_{ic}{}^H/k_{it}{}^H$) is 1.3 for Mg-S and 1.0 for Al-S (*10*), one can estimate the extent of hydrogen migration and "rollover" during the isomerization using Eqs. (2) and (3). Here, the fractions of 3, z, are taken to be 0.12 and 0.08, respectively, for Al-S and Mg-S, from the results in Fig. 5. The contents of the d_1 species in *trans*-2-butene at zero conversion may be taken to be 70% for Al-S and 85% for Mg-S. Thus, the calculations give $x:y:z = 0.44:0.44:0.12$ (Al-S) and $0.7:0.22:0.08$ (Mg-S). The isotope effects for proton elimination ($1/b_j$) are 1.9 (Al-S) and 1.6 (Mg-S).

The results for 1-butene-3-d_1 (Table 4) are also utilized to estimate the isotope effects. This species forms equal amounts of **I** and **II** by proton addition ($x = y$). Taking into account that the reactant contained $(1 - w)$% of the d_0 species, one can derive, from Eqs. (1) and (2),

$$\frac{d[\textit{trans}(\text{or } \textit{cis})\text{-2-butene-}d_1]}{d[\textit{trans}(\text{or } \textit{cis})\text{-2-butene-}d_0]} = \frac{k^{\mathrm{H}}[z + x(\text{or } y)]w}{k^{\mathrm{D}}[y(\text{or } x)]w + k^{\mathrm{H}}[1 - w]}. \quad (12)$$

The isotope effects ($k^{\mathrm{H}}/k^{\mathrm{D}}$) thus estimated are also given in Table 4. The isotope effect appears to decrease with increasing isomerization, probably due to secondary isomerization, and is 2 ± 0.5 for the formation of both 2-butenes over Mg-S, in fair agreement with those calculated above. The isotope effect for Al-S is probably of similar magnitude.

The isotope effect for proton addition was previously reported to be about 1.7 for Mg-S (*17*). The isotope effect for silica-alumina was about 1.4, since $a_k \cdot \gamma$ is 0.7 (Table 2) and γ must be not far from 1.

TABLE 4

Isotopic Compositions of Butenes Formed from 1-Butene-3-d_1

Catalyst	Reactant[a]	Butene compositions and d_1% in parentheses			Isotope effect	
		1-	*trans*-	*cis*-	*trans*-	*cis*-
Mg-S	B	94.2 (81)	2.2 (57)	3.6 (53)	2.7	2.0
	B	89.7 (80)	4.2 (52)	5.9 (49)	1.7	1.4
	A[b]	85.5 (93)	5.9 (55)	8.6 (57)	1.3	1.4
	A[b]	83.3 (91)	6.4 (56)	10.3 (58)	1.3	1.4
Al-S	A	80.9 (92)	9.5 (51)	9.6 (49)	1.6	1.3
	B	73.0 (81)	13.2 (51)	13.8 (53)	1.0	1.1

[a] A contained 1-butene-3-d_1, 92%, and 1-butene-d_0, 8%. B contained 1-butene-3-d_1, 81%, and 1-butene-d_0, 19%.

[b] Taken from Ref. (*16*).

The calculated values in the present analysis are not fully reliable regarding quantitative values, owing to the experimental difficulties in obtaining accurate and reproducible data. However, it is obvious that hydrogen migration and "rollover" [1] are present, and the extents of the occurrence of these processes appear to reflect the catalyst properties (acid strength and stability of the *s*-butyl cation on the surface) as discussed previously (*10*). Therefore, the method of analysis presented in this paper is useful for understanding the detailed mechanism of the reaction which proceeds via an alkyl cation intermediate.

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[1] It must be reminded that "rollover" can be equivalently explained by the stereochemistry of proton addition and elimination as described in a previous section.