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Isomerization of *n*-Butene on Cobalt Oxide: The Effect and Role of Hydrogen

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Isomerization of *n*-butene over a dehydrated surface of cobalt oxide has been studied for the effect of hydrogen. The prechemisorbed hydrogen remarkably enhances the isomerization in the initial period of the run, while the rate is rapidly decreased to a steady value with the reaction time. In conformity with this, the prechemisorbed deuterium appears in the product. The isomerization is also enhanced by the presence of gas-phase hydrogen. The rate is linear to the partial pressure of hydrogen. The C_2H_4–C_2D_4 exchange reaction is similarly accelerated by hydrogen.

The reaction of butene with D_2 produces minor amounts of butene-d_1, butane-d_1, and HD in addition to larger amounts of butane-d_2, whereas the H_2–D_2 exchange reaction is remarkably suppressed by the presence of butene. The formations of d_1-species are explained in terms of alkyl intermediate, suggesting that there are two different pathways of hydrogenation, one forming butane-d_2 and the other butane-d_1 in the deuterogenation of butene.

INTRODUCTION

A number of metal oxides are known to catalyze the double-bond shift isomerization of olefins. They are classified into three groups according to the nature of intermediate: (1) carbonium ion intermediate over acidic oxides such as Al_2O_3 (*1*) and silica-alumina (*2*); (2) carbanion intermediate over basic oxides such as CaO and MgO (*3*); and (3) π-allyl intermediate as found over ZnO (*4*). Another intermediate of the isomerization, metal alkyl, is known with those metals that catalyze hydrogenation of olefin (*5*).

On the other hand, Co_3O_4 (*6, 7*) as well as Cr_2O_3 (*8*), NiO (*9*) and ZnO (*10*) is known to catalyze the hydrogenation of olefin, although they give mainly $C_2H_4D_2$ (*7, 8, 10*) on deuterogenation of ethylene in contrast to the case on metals where hydrogen randomization usually takes place. This paired addition of hydrogen has been explained in terms of irreversible formation of intermediate metal alkyl (*8*). In conformity with this, the isomerization of *n*-butene over ZnO is not enhanced by the presence of hydrogen as observed by Tamaru *et al.* (*11*). If the formation of alkyl intermediate is reversible, the presence of hydrogen should enhance the isomerization reaction. Indeed, it has been found that the isomerization of *n*-butene over Co_3O_4 is, in the presence of hydrogen, much faster than the hydrogenation (*6*), although the main product of deuterogenation is still d_2-species. It is thus suggested that some modifications have to be made on the mechanism of isomerization over Co_3O_4. The present paper discloses characteristic features of the isomerization over Co_3O_4 as revealed by using deuterium tracer.

EXPERIMENTAL

The cobalt oxide was obtained by thermal decomposition of a reagent grade cobaltous nitrate at about 600°C and pressed into tablets and calcined at 600°C for 6 hrs in air (25 g, total area 59.7 m^2). This oxide sample was evacuated at 400°C and subjected to an irreversible adsorption of hydrogen or deuterium at room temperature to stabilize the catalytic activity.

The apparatus employed was a closed circulating system similar to that previously described (*6*). All the runs were made at 25°C.

Deuterium and heavy ethylene were prepared by the same method as before (*7*).

The samples for mass spectrometric analyses of hydrogen, ethylene, butene isomers, and butane were separated by gas chromatography and collected in a liquid nitrogen trap. For the isotopic analysis, ionization voltage of 10 or 80 eV was used.

Gas composition was intermittently analyzed by gas chromatography, and the analysis of D_2 and HD during the hydrogenation of butene was carried out by gas chromatography with a molecular sieve 5-A column at liquid nitrogen temperature.

RESULTS

Activity Change in Successive Runs

The cobalt oxide sample was first heated to 400°C for 2 hr in circulating air with a liquid nitrogen trap, evacuated at the same temperature for 5 hr and then cooled in vacuum to room temperature at which 60 mm Hg of H_2 was introduced over the evacuated oxide and kept there for 1 or 2 days. The oxide sample thus chemisorbed with hydrogen has been called "stabilized catalyst" since the previous paper (*7*). It was evacuated at room temperature for 15 hr and subjected to the isomerization runs. The time courses of successive runs are shown in Fig. 1. It is to be noted that a very rapid isomerization from *cis*- to *trans*-butene takes place in the beginning of the first run, although this does not reappear on and after the second run, showing a stabilized activity. The second and later runs were made on the oxide catalyst evacuated at room temperature for 30 min after the previous run.

The extraordinary high activity in the beginning suggests that the prechemisorbed hydrogen is acting as an active species, although it is rapidly displaced with butene, resulting in the striking decrease in the rate of isomerization.

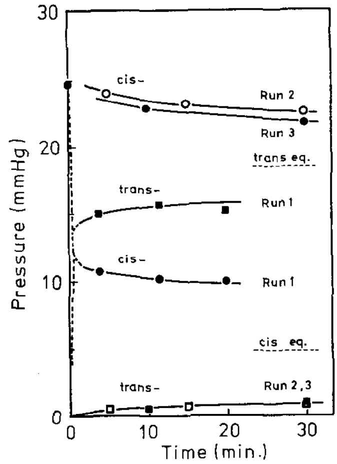


FIG. 1. Time courses of successive isomerization runs over cobalt oxide with prechemisorbed hydrogen.

In order to prove this presumption, the isomerization was made on the catalyst chemisorbed with D_2 instead of H_2. The amount of chemisorbed D_2 was 2.2×10^{14} molecules/cm², and the amount of reactant *cis*-butene was about two-thirds of that in run 1. Within the first minute, the extent of isomerization of *cis*-butene reached 93% to the equilibrium and butene-d_1 was found both in reactant and products. The amount of D atoms thus incorporated into butenes was 2.6×10^{12} atoms/cm², which is close to the number of active site for the ethylene hydrogenation as estimated from fatal amount of carbon monoxide (*7*). The formation of butene-d_1 strongly supports the finding that the chemisorbed hydrogen acts as the active species for the isomerization.

In view of the above results, the previous finding that the prechemisorbed hydrogen does not exchange with gas phase deuterium (*7*) seems to deserve reexamination. The H_2-chemisorbed catalyst was treated with 30 mm Hg butene for 2 min to remove the active hydrogen as revealed by the above-mentioned experiments. After evacuation for 30 min at room temperature, 98.6% D_2 was introduced. The gas phase compositions (%) were as follows.

Time (hr)	H_2	HD	D_2
0.5	0	7.3	92.7
2.5	1.8	20.0	78.2

This result shows that the chemisorbed hydrogen does exchange with gas-phase deuterium in a longer period.

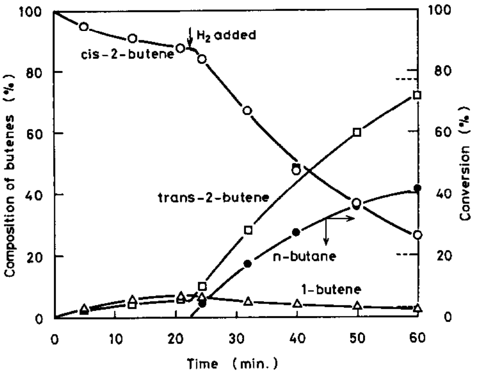


FIG. 2. The effect of hydrogen addition on the isomerization of butene.

Isomerization in the Presence of Hydrogen

Hydrogen (2.7 mm Hg) was introduced in the course of the isomerization of *cis*-butene (30 mm Hg) over the stabilized catalyst. The result is shown in Fig. 2, where it is disclosed that the isomerization is enhanced by the presence of hydrogen and that the isomerization is faster than the hydrogenation.

The isomerization runs were made in the presence of varied amounts of hydrogen. The time courses observed were in agreement with the first order kinetics as shown in Fig. 3, where x_0, x_e, and x are the mole fractions of reactant *cis*-butene at time zero, equilibrium and time t, respectively. Since the rate of hydrogenation of butene over this oxide catalyst is zero-order in butene as reported in the previous paper (*6*), the active sites are nearly occupied by butene during the hydrogenation. The first-order kinetics in butene isomer indicates that the surface concentration of butene isomer can be approximated to that in the gas phase.

The initial rates of isomerization are obtained from the slopes of first-order plots as shown in Fig. 3 and plotted against the initial hydrogen pressure (Fig. 4). It is clear that the rate of isomerization increases linearly with the hydrogen pressure. In view of this result, it is to be mentioned that the first-order plots as shown in Fig. 3 are realized because of the faster rate of isomerization than hydrogenation. The first-order plot of isomerization reasonably deviates from straight line for a longer period of reaction, because of decrease in the hydrogen pressure.

C_2H_4–C_2D_4 Exchange in the Presence of Hydrogen

Since the isomerization of butene is enhanced by the presence of hydrogen, the similar enhancement is expected for C_2H_4–C_2D_4 exchange reaction in view of the alkyl intermediate mechanism. This was confirmed as shown in Fig. 4, where the rate of exchange R was obtained from the equation

$$R = \frac{N}{t}\log(m_t - m_e)/(m_o - m_e)$$

m_o, m_t, and m_e denote the mole fractions of ethylene d_o at time zero, t and equilibrium, and N the amount of ethylene in the reactor.

Deuterogenation of Butene

The enhancement of isomerization by hydrogen suggests that the isomerization pro-

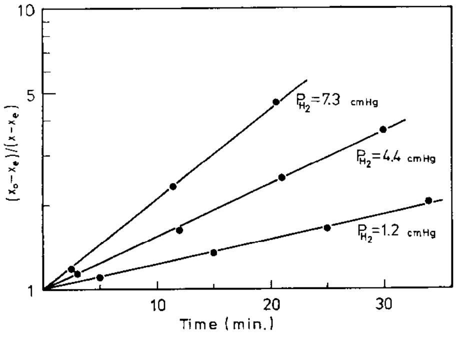


FIG. 3. First order plots for the isomerization runs in the presence of hydrogen.

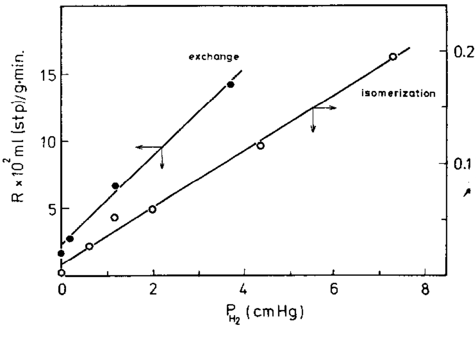


FIG. 4. The rates of isomerization of butene and isotopic exchange of C_2H_4–C_2D_4 as functions of hydrogen pressure.

TABLE 1

DEUTEROGENATION OF BUTENE. INITIAL PRESSURES P_{D_2} = 21 MM HG, P_{butene} = 31 MM HG. COMPOSITION OF D_2 d_2 = 98.6%, d_1 = 1.4%

Run	Cat.	Reactant butene/D_2 ml/ml (stp)	Conversion (%)		Product composition										
					deuterium		1-butene		t-butene		c-butene		n-butane		
			Isom.	Hydro.	d_1	d_2	d_0	d_1	d_0	d_1	d_0	d_1	d_1	d_2	d_3
1	H	8.87/6.76	40.1	3.9	4.2	95.8	88.7	11.3	97.5	2.5	99.0	1.0	16.0	83.1	0.9
2	H	9.15/6.32	24.2	3.0	3.4	96.6	99.5	0.5	94.6	5.4	95.9	4.1	18.4	80.9	0.7
3	H	9.26/6.29	39.2	6.8	4.6	95.4	99.2	0.8	94.1	5.9	94.6	5.4	18.7	80.4	0.9
4	H	9.11/6.29	50.3	8.8	6.2	93.8	98.6	1.4	93.8	6.2	93.5	6.5	19.2	79.6	1.2
5	D	9.27/6.45	21.6	2.6	2.7	97.3	99.2	0.8	94.2	5.8	95.0	5.0	14.1	85.3	0.6
6	D	9.14/6.65	33.7	4.8	4.0	96.0	98.8	1.2	94.1	5.9	94.2	5.8	15.5	83.9	0.6
7	D	9.20/6.68	45.9	7.2	5.7	94.3	98.4	1.6	93.4	6.6	93.1	6.9	16.5	82.0	1.4

ceeds via a butyl-intermediate formed by reaction with dissociatively adsorbed hydrogen. This mechanism is, however, inconsistent with the paired addition of hydrogen as observed in the deuterogenation of ethylene. Thus, the deuterogenation of butene was carried out over the cobalt oxide catalyst stabilized by chemisorption of H_2 or D_2 followed by treatment with butene. The results are shown in Table 1, where percent conversion for the isomerization is the extent of approach to equilibrium defined by $100(1 - x)/(1 - x_e)$ with mole fractions of reactant butene at time t and equilibrium x and x_e, respectively. The reactant butene was *cis*-butene for run 1 and 1-butene for runs 2–7.

It is again demonstrated that the hydrogenation is much slower than the isomerization. It is to be noted that nearly 20% of the product butane is d_1-species and that the isomerization products contain higher concentrations of d_1-species than the reactant butene. Although the paired addition of D_2 is predominant, there must be another scheme of hydrogenation, because the concentration of HD that appeared in D_2 is too small to explain the formation of d_1-butane by paired addition of HD. The observed amount of HD should have been, at least partly, formed by an exchange reaction with butene, since there is no other source of H in the reaction system with chemisorbed D_2. It can be seen that the more amount of HD is formed on the surface with chemisorbed H_2 than on the D_2 surface. This result again indicates that the chemisorbed hydrogen takes part in the reaction.

H_2–D_2 Exchange During Hydrogenation of Butene

If the isomerization proceeds via the alkyl intermediate, there should be an active chemisorbed hydrogen during the hydrogenation of butene, although the kinetics of hydrogenation is zero order in butene, suggesting that the active sites are fully occupied by butene. Indeed, it was previously reported that H_2–D_2 exchange reaction takes place during the hydrogenation of ethylene, although the rate of exchange is extremely slowed down by the presence of ethylene (*7*). Since the adsorption strength of butene is much weaker than that of ethylene on the cobalt oxide as previously shown (*6*), the H_2–D_2 exchange during hydrogenation of butene would be easier.

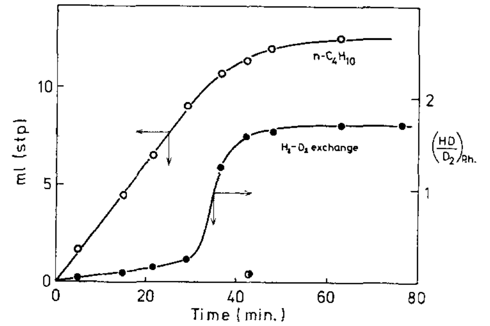


FIG. 5. Time course of hydrogenation of butene with H_2–D_2 equimolar mixture.

This prediction was confirmed by hydrogenation of *cis*-butene with 1 to 1 H_2–D_2 mixture. The result, as shown in Fig. 5, is qualitatively similar to that for ethylene. That is, the H_2–D_2 exchange reaction slowly takes place in the initial period and accelerates with a decrease in the amount of butene. However the mode of acceleration is quite different: more drastic in the case of ethylene in conformity with larger adsorption strength. Thus, it appears that the more weakly adsorbed butene leaves more sites for H_2–D_2 exchange reaction.

It should be examined whether the HD formed is the real product of H_2–D_2 exchange, because HD is also formed by C_4H_8–D_2 exchange as shown in Table 1. The half-filled circle in Fig. 5 indicates the corresponding amount of HD formed by the reaction of C_4H_8 with D_2 of the same initial pressure. It is clear that HD is formed in excess of the exchange with butene. Thus, it may be concluded that some amount of sites are available for the H_2–D_2 exchange during the hydrogenation and act as the active sites for the exchange even in the presence of butene.

DISCUSSION OF REACTION MECHANISM

Formation of Butene-d_1

There is evidence, as described above, that the isomerization proceeds via alkyl

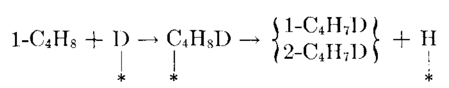
TABLE 2

AMOUNT OF BUTENE-d_1 AND HD FORMED × 10^2 ML STP

Run	Conv.	1-butene	t-butene	c-butene	ΔHD
2	24%	3.4	2.6	6.6	11.7
3	39	4.3	4.5	13.6	17.2
4	50	6.0	6.0	20.0	25.2
5	22	5.7	2.7	7.2	7.7
6	34	7.0	4.4	12.2	15.6
7	46	7.6	6.8	19.1	24.9

intermediate. If this is the case, the formation of butene-d_1 is quite reasonable in the presence of D_2. The amount of butene-d_1 formed during the isomerization of 1-butene is calculated from the data in Table 1 and shown in Table 2 as a function of conversion.

The amount of d_1-species increases with increase in conversion as expected. It is thus concluded that the butene-d_1 is formed by the reaction:

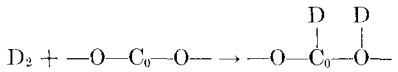


$$1\text{-}C_4H_8 + \underset{\underset{*}{|}}{D} \rightarrow \underset{\underset{*}{|}}{C_4H_8D} \rightarrow \left\{\begin{matrix}1\text{-}C_4H_7D\\ 2\text{-}C_4H_7D\end{matrix}\right\} + \underset{\underset{*}{|}}{H} \quad (1)$$

The relatively low concentration of butene-d_1 indicates that the isomerization repeatedly takes place before the active chemisorbed hydrogen is replaced by deuterium.

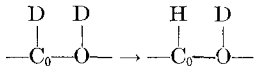
Formation of HD

Since the active form of cobalt oxide is obtained by dehydration from surface, and poisoned by carbon monoxide (*7*), the active site has been considered to be the exposed cobalt ion surrounded by oxide ion. The chemisorption of hydrogen on such a site admittedly results in a heterolytic splitting (*12*):



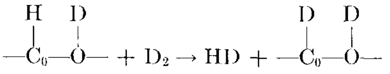
$$D_2 + \text{—O—Co—O—} \rightarrow \text{—O—}\overset{D}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} \quad (2)$$

If the half of this pair site acts as the active site for the isomerization as expressed by Eq. (1), it undergoes the change:

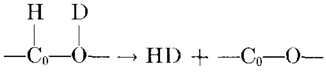


$$\text{—}\overset{D}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} \rightarrow \text{—}\overset{H}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} \quad (3)$$

Since there is no other source of H to be incorporated into HD, the HD formation observed during the isomerization must be caused by an exchange with butene. Indeed, as shown in Table 2, the amount of HD formed increases with increase in butene-d_1. Thus, it seems that the HD comes from H–D pair site. There are two ways of HD formation:



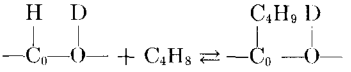
$$\text{—}\overset{H}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} + D_2 \rightarrow HD + \text{—}\overset{D}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} \quad (4)$$



$$\text{—}\overset{H}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} \rightarrow HD + \text{—Co—O—} \quad (5)$$

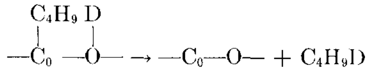
Formation of Butane-d_1

Butane-d_1 must be formed, to some extent, by paired addition of HD to C_4H_8. But this cannot be the only way of butane-d_1 formation as mentioned already. When the isomerization takes place on the pair site H–D, it follows:



$$\text{—}\overset{H}{\overset{|}{\text{Co}}}\text{—}\overset{D}{\overset{|}{\text{O}}}\text{—} + C_4H_8 \rightleftarrows \text{—}\overset{C_4H_9}{\overset{|}{\text{Co}}}\text{ —}\overset{D}{\overset{|}{\text{O}}}\text{—} \quad (6)$$

Here, it seems possible that the C_4H_9 intermediate reacts with the adjacent O–D to form C_4H_9D.



$$\text{—}\overset{C_4H_9}{\overset{|}{\text{Co}}}\text{ —}\overset{D}{\overset{|}{\text{O}}}\text{—} \rightarrow \text{—Co—O—} + C_4H_9D \quad (7)$$

The identical reaction has been postulated over Cr_2O_3 (*8*) and proved over ZnO (*13*). Since the isomerization is much faster than hydrogenation, the reaction (6) would take place more frequently than (7). The observed ratio of butene-d_1/butane-d_1 = 3 ~ 4 may be the relative rate of reaction (1) over (7).

Overall Scheme

The overall scheme of the above reactions is shown in Fig. 6. If this is the case, the

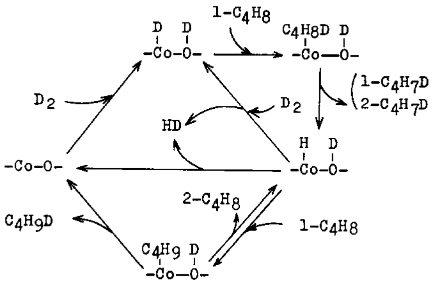


FIG. 6. Reaction scheme for the formation of d_1-species.

formation of butene-d_1 always results in the formation of adsorbed H–D pair, which will be converted into gaseous HD or C_4H_9D. Thus, there should be a correlation:*

$$NC_4H_7D = NHD + NC_4H_9D \quad (8)$$

where N's are amounts of d_1-species. Relative amounts of them are obtained from Table 1 as follows:

Run	NC_4H_7D	NHD	NC_4H_9D	NHD + NC_4H_9D
2	1	0.93	0.37	1.30
3	1	0.77	0.49	1.26
4	1	0.79	0.45	1.24
5	1	0.50	0.20	0.70
6	1	0.66	0.26	0.92
7	1	0.74	0.30	1.04

The results show that the deviation from Eq. (8), which is at most 30%, depends on the isotopic species prechemisorbed on the oxide, indicating that the deviation is mainly caused by the incorporation of prechemisorbed hydrogen. Thus, it appears that the results are in conformity with Eq. (8). In this way the formation of butane-d_1, which cannot be understood on the ground of paired addition of hydrogen, is reasonably explained and strongly suggests a concurrence of the reaction (7) in addition to the paired hydrogenation.

Reexamination of Mechanism for the Paired Addition

In the previous paper, where hydrogenation of ethylene over cobalt oxide was investigated, the paired addition as well as the isotopic mixing in ethylene was explained in terms of ethyl intermediate. If the alkyl intermediate is involved in both, the isotopic mixing reaction of ethylene corresponds to the isomerization of butene. Indeed, the isotopic mixing is also enhanced by hydrogen as in the isomerization as shown in Fig. 4.

The conclusion derived from the preceding discussion indicates that two different competing reactions are involved in the hydrogenation of butene. This situation would be similar in the hydrogenation of ethylene. Indeed, a small amount of ethane-d_1 was found in the product of deuterogenation of ethylene, and ascribed to a slow backward reaction of the ethyl intermediate to reproduce ethylene. Thus, it seems necessary to reexamine the mechanism of the paired addition.

Since the isomerization of butene or the isotopic mixing in ethylene is faster than the hydrogenation, the paired addition of hydrogen via alkyl intermediate is improbable, if the paired addition takes place on the same site where the isomerization takes place. There is, however, no sign of two different sites for the two reactions. Both reactions are simultaneously poisoned by CO or H_2O. It is thus suggested that the paired addition does not proceed by way of alkyl intermediate. At least, the intermediate of the paired addition should be different from that of the isomerization. A direct attack of molecular hydrogen onto the chemisorbed olefin seems more probable, although there has been no ample justification for the direct attack.

The final problem to be mentioned is what decides the reaction path between the direct attack and the alkyl intermediate. This seems simple. The chemisorbed ethylene and hydrogen atom are respectively required for the former and the latter. Since

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* Part of HD and C_4H_7D may have been consumed to form butane-d_2, but Eq. (8) is independent of this reaction, because HD and C_4H_7D are equally consumed. The amount of C_4H_7D consumed to form butane-d_3 is estimated to be about 1%. The amount of butane-d_1 formed from the HD initially involved in the D_2 sample is estimated by the following equation and subtracted from the observed value:

$$C_4H_9D \text{ from } (HD)_0 = \frac{0.014}{0.986} \times \text{butane-}d_2$$

chemisorbed hydrogen is scarce in the presence of olefin, the former path would be predominant, thus resulting in the predominant formation of d_2-alkane. Since hydrogen competes with olefin for a same site, and olefin is more strongly chemisorbed, the amount of chemisorbed hydrogen pair should be proportional to hydrogen pressure. In view of this situation, the linear dependence of the isomerization rate on hydrogen pressure is quite reasonable. The less extensive but detectable isomerization in the absence of hydrogen might require a different mechanism. This will be discussed in a subsequent paper.

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