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Author(s)	ISHIMURA, Yoshimasa; FUKUSHIMA, Takakazu; OZAKI, Atsumu
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VERIFICATION OF ALKYL REVERSAL MECHANISM OF BUTENE ISOMERIZATION ON COBALT OXIDE

By

Yoshimasa ISHIMURA^{*)}, Takakazu FUKUSHIMA^{*)}
and Atsumu OZAKI^{*)}

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Abstract

The alkyl reversal mechanism of *cis-trans* isomerization of butene has been examined on cobalt oxide catalyst with preadsorbed hydrogen which acts as the active species. The active hydrogen is continuously deuterized by coexistent C_2D_4 so that the product *trans*-butene-2 is expected to be C_4H_7D . The prediction is borne out to be valid by the experimental result. An isotope effect in C-H bond splitting is given to be $k_D/k_H=0.28$.

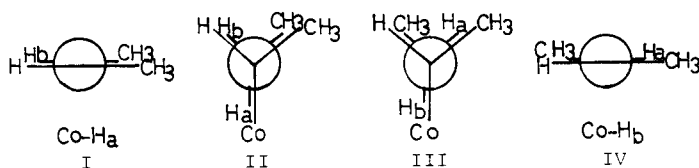
It has been reported that butene isomerization rapidly takes place at room temperature on hydrogen-preadsorbed cobalt oxide through an alkyl intermediate, while the catalytically active hydrogen is lost in a few minutes by a reaction with butene to form butane so that the rapid isomerization stops within a few minutes and a much slower isomerization follows.¹⁾ The necessity of adsorbed hydrogen as an active species is also demonstrated by enhancement of the isomerization on addition of gaseous hydrogen. The alkyl intermediate for the isomerization is supported by formation of butene- d_1 on deuterium-preadsorbed catalyst. An analogous intermediate for ethylene should result in formation of ethylene- d_1 on the deuterium preadsorbed catalyst. In fact an isotopic equilibration in C_2H_4 - C_2D_4 mixture readily takes place on the cobalt oxide.

Thus the isotopic equilibration of ethylene and the isomerization of butene take place simultaneously competing for the active site. Taking advantage of this situation, relative adsorption strength of ethylene and butene on the active site has been determined during the simultaneous reaction, disclosing that ethylene is 2.5 times more strongly adsorbed on the active site than butene, in conformity with π -coordination of olefin to exposed cobalt ion²⁾.

^{*)} Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama.

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The present paper also utilizes the above situation to study mechanism of the isomerization through alkyl intermediate. The *cis-trans* isomerization *via* alkyl intermediate can be depicted as follows:



Scheme

Where I and IV are respectively π -adsorbed *cis*- and *trans*-butene-2, and II and III are alkyl intermediates with different conformation. The real act of isomerization is made by the rotational transformation from II to III followed by β -hydrogen elimination to form IV.

If the above scheme is valid, the isomerization should be accompanied by change in hydrogen atom from H_a to H_b . Thus when H_a is marked by deuterium, the product *trans*-butene-2 should be C_4H_7D . In order to test this prediction the catalytically active hydrogen should be kept deuterized during the reaction. Otherwise the hydrogen coming from butene will be used consecutively for the isomerization giving butene- d_0 as the product. Since the turnover frequency of the rapid isomerization is estimated to be as large as 10 per sec,²⁾ preadsorbed deuterium is rapidly consumed, thus giving rise to predominant formation of butene- d_0 . It is very difficult to obtain a very initial product which may show up the scheme.

In order to overcome the above situation, a competitive reaction of C_2D_4 and *cis*- C_4H_8 was adopted. Since ethylene has been proved to be adsorbed more strongly than butene on the active site,²⁾ it was hoped to be able to keep the active hydrogen deuterated, with deuterium coming from C_2D_4 . The present paper reports the result of such experiment.

Experimental

The cobalt oxide catalyst was prepared by decompositions of cobalt nitrate in air at 600°C. The oxide powder was pressed into tablets. The amount of catalyst used was 15 g and the specific surface area was 2.8 m²/g. After evacuation at 400°C, a limited amount of hydrogen was preadsorbed to control the isomerization activity to give about 5% conversion in the initial rapid reaction period. It has been reported that the isomerization activity can be controlled by the amount of preadsorbed hydrogen.²⁾ The reduced activity was preferable to avoid an extensive isomerization, which

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gave rise to formation of butene- d_2 . Thus the required condition of catalyst was realized by hydrogen adsorption for 1 hr at 25°C.

cis-Butene-2 was obtained from Takachiho shoji Co. and ethylene- d_4 from Merck Sharp & Ohme Cana Ltd. *cis*-Butene was freed from permanent gases by solidification at liquid nitrogen temperature followed by evacuation. Analyses were made by gas-chromatography and mass-spectrometry.

The reaction runs were made always at 25°C in a closed circulating system of 113 ml, in which butene and ethylene- d_4 were thoroughly mixed by-passing the reactor for more than half hour prior to each run. Since the active hydrogen was known to be consumed within 2 min, the run was terminated 2 min after start by trapping gases with liquid nitrogen and the gas mixture was separated with a gas-chromatograph to obtain samples for analysis.

Results and Discussion

A preliminary result of *cis*-butene-2 isomerization in the presence of C_2D_4 gave about 50% d_1 in the product *trans*-butene-2, suggesting that the probability of active hydrogen to be in the form of H is significantly large

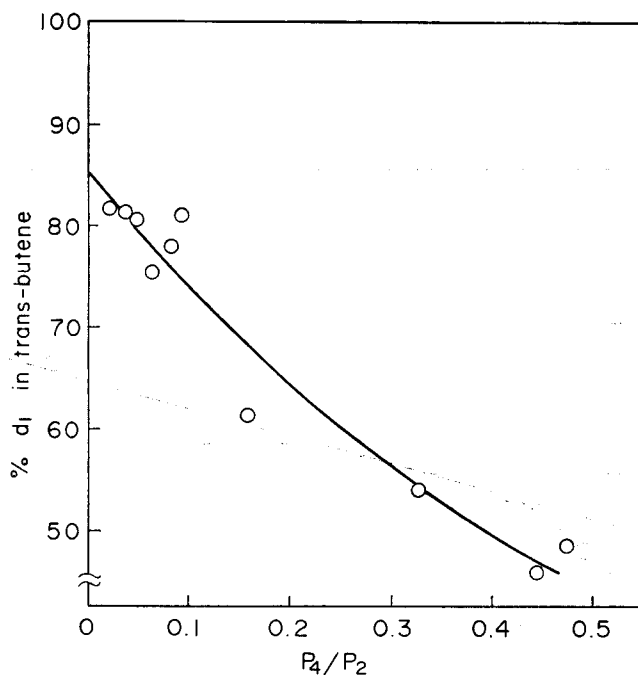


Fig. 1. Mole fraction of d_1 species in product *trans*-butene-2 as a function of mole ratio of reactants (P_4/P_2).

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even in the presence of C_2D_4 . The probability would increase, however, by decreasing the ratio C_4H_8/C_2D_4 . Thus the proportion of d_1 -species in the product *trans*-butene-2 was determined as a function of the ratio C_4H_8/C_2D_4 . The result is given in Fig. 1. The d_1 -*trans*-butene-2 increases with decrease in the C_4H_8/C_2D_4 ratio as expected, while unlikely reaches 100%.

One possible reason can be given for the failure to reach 100%. As already introduced, the initial rapid isomerization is followed by a slow isomerization for which likely intermediate is allylic because butadiene is detected in the product of slow reaction carried out on the fresh oxide which has no active hydrogen¹¹. Since the allyl type isomerization proceeds through intramolecular hydrogen transfer, it gives rise to butene- d_0 in the product. Thus the rate of slow isomerization was determined on the present catalyst after the normal treatment with hydrogen. The result is shown in Fig. 2. The rate of slow reaction in the later period is estimated to be about 1/10 of the initial rapid rate.

The extent of non-alkyl type isomerization may be estimated from analysis of the result shown in Fig. 1. When the *cis-trans* isomerization takes place *via* the scheme, Co-D is changed to Co-H. The rate of Co-H formation is given by $f_D R_4$, with f_D being D fraction of active hydrogen and R_4 the rate of isomerization of butene. The rate of Co-D formation is given by $\frac{2}{3} Z(1-f_D) R_2$, with R_2 being the rate of exchange of ethylene

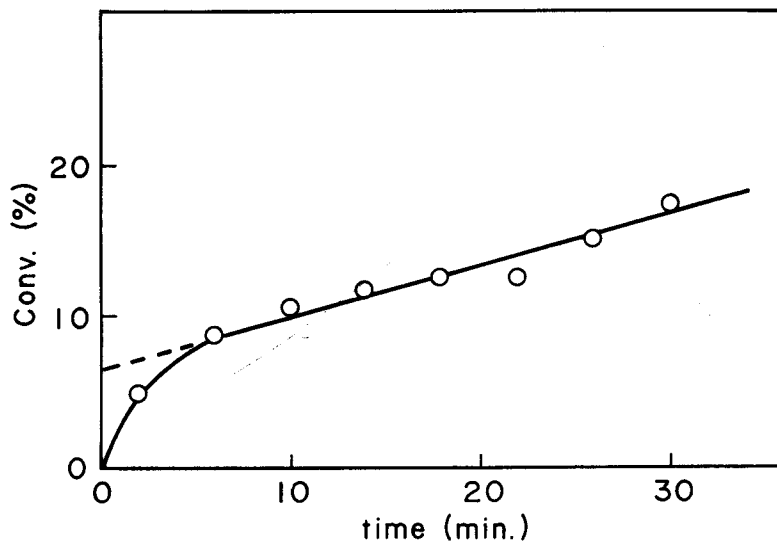


Fig. 2. Slow isomerization subsequent to the rapid reaction.

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and Z the isotope effect (k_D/k_H) of C-H splitting. Under the steady state, the above two rates are equalized to give f_D during reaction.

$$f_D = 1 / \left(1 + \frac{R_4}{R_2} \cdot \frac{3}{2Z} \right) \quad (1)$$

As described previously,²⁾

$$R_4/R_2 = k_4 K_4 P_4 / k_2 K_2 P_2 \quad (2)$$

where k , K and P are rate constant, adsorption constant and partial pressure, respectively, of butene (4) or ethylene (2). Thus $1/f_D$ is a linear function of P_4/P_2 .

$$1/f_D = 1 + \frac{k_4 K_4}{k_2 K_2} \cdot \frac{3}{2Z} \cdot \frac{P_4}{P_2} \quad (3)$$

Since the d_1 fraction of *trans*-butene-2, F_{D_1} , should be equal to f_D in this scheme, $1/F_{D_1}$ is plotted against P_4/P_2 in Fig. 3. The linearity of plot is almost satisfactory. The F_{D_1} value obtained from extrapolation to $P_4/P_2=0$

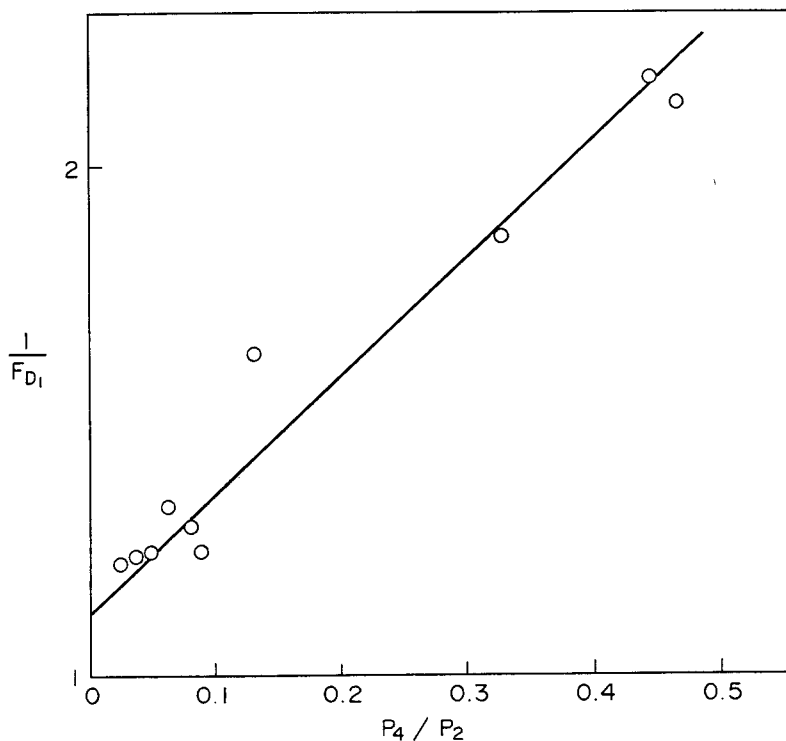


Fig. 3. Test of Eq. (3).

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is 0.89 which means that about 90% of isomerization proceeds through the alkyl-reversal mechanism in agreement with the estimation from the rate of slow reaction. Thus the alkyl reversal mechanism as depicted by scheme is proved to be valid.

From the slope of linear plot the value of $\frac{k_4 K_4}{k_2 K_2} \frac{3}{2Z}$ is given to be 2.33. By introducing known value of $\frac{k_4 K_4}{k_2 K_2} = 0.43$ reported previously,²⁾ the isotope effect Z is given to be 0.28, which is a reasonable value for the splitting of C-H bond at 25°C.

References

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