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INTERMEDIATE OF THE HYDROGENATION OF BUTADIENE ON A MoS_2 CATALYST

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Adsorbed iso-butenyl (σ-allyl) is formed on MoS_2 catalyst during the hydrogenation of butadiene, and is the intermeidate of hydrogen exchange reaction of butadiene as well as of the hydrogenation of butadiene. The σ-allyl species formed on the active sites do not isomerize to π-allyl form so that the reaction of butadiene with a mixture of H_2 and D_2 gives d_0-1-butene and d_2-1-butene with few d_1-1-butene, indicating high conservation of hydrogen molecular identity in the products.

The intermediate of the hydrogen exchange reaction of butadiene as well as of the hydrogenation of butadiene on a MoS_2 catalyst has been elucidated by using microwave spectroscopy. The molybdenum sulfide used in this experiment takes a hexagonal layer structure by X-ray diffraction, and has the surface area of 15 m^2/g by the BET method of nitrogen adsorption. The impurities of the catalyst analyzed by atomic absorption analysis were ; Fe 0.02, Mg 0.0015, Ca 0.0077, Na 0.012, Mn 0.0003, Cr < 0.0001, and K < 0.1 %. By evacuating the MoS_2 powder at about 450°C for several hours, it becomes active for the hydrogenation of butadiene at room temperature.

It is an interesting feature of MoS_2 catalyst that the hydrogen molecular identity is highly maintained in the hydrogenated products of olefins and butadiene.[2)] A typical result of the reaction of butadiene with D_2 is shown in Figure 1, and the d_2-1-butene was identified by microwave spectroscopy as 3,4-d_2-1-butene as shown in Table 1. The hydrogenation of butadiene with a mixture of H_2 and D_2 on the MoS_2 gives d_0-1-butene and d_2-1-butene with few d_1-1-butene at the initial stage of the reaction, however, HD content is gradually increased by the simultaneous H_2-D_2 equilibration reaction, which results in the formation of d_1-1-butene in proportion

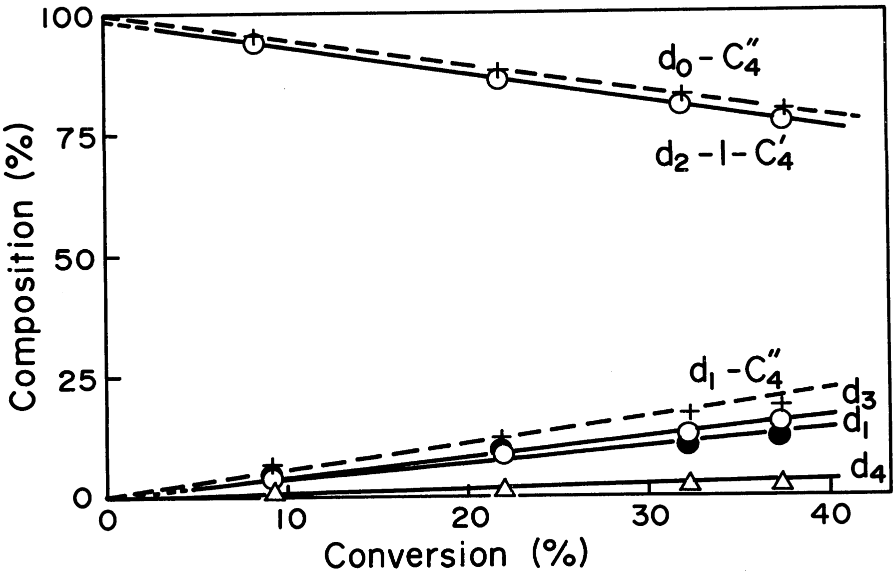
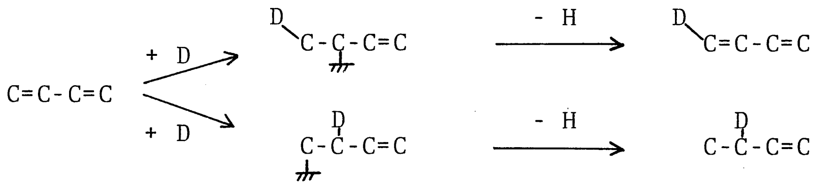


Figure 1. The reaction of butadiene with D_2 at room temperature. The initial composition was $C_4H_6/D_2 = 1/2$. ----- Butadiene (C_4''), ——— 1-Butene ($1\text{-}C_4'$)

to the HD content.

In the case of the reaction of butadiene with D_2, the exchange reaction between D_2 and butadiene, being slower than the H_2-D_2 equilibration, gives HD and d_1-butadiene, and the formed HD reacts with butadiene to give d_1-1-butene as shown in Figure 1.

In this brief paper, the intermediate of this exchange reaction was determined and was compared with that of the hydrogenation reaction. In a separate experiment, it has been confirmed that the isotopic mixing between d_0-butadiene and d_6-butadiene is markedly enhanced by adding hydrogen. This fact suggests the associative mechanism for the hydrogen exchange reaction of butadiene, that is, the exchange reaction seems to proceed via the half-hydrogenated intermediates.
Accordingly, the D-atom position of the d_1-butadiene may give an important clue to the intermediate of the exchange reaction, either n-butenyl or iso-butenyl ·;



In order to determine the D-atom location in the d_1-butadiene, the reaction of butadiene with D_2 was stopped at a certain conversion (35 % in Table 1) and the butadiene containing d_1-butadiene was separated by gas chromatography, and was followed by its hydrogenation with H_2 over the MoS_2 catalyst. This procedure accompanies little hydrogen scrambling of the butadiene so that the d_1-butadiene is hydrogenated to d_1-1-butene in maintaining' its D-atom position. The d_1-1-butene obtained in this way was subjected to microwave spectroscopic analysis.
The results of microwave spectroscopic analysis are summarized in Table 1.
Table 1 (A) and (B) show the deuterium distributions of the hydrogenated products, d_1-1-butene and d_2-1-butene, respectively. The deuterium distribution of the d_1-1-butene from the d_1-butadiene shown in Table 1 (C) indicates few deuterium atom on the inner carbons. The fact that the D-atom in the d_1-1-butene from the d_1-butadiene locates nearly 100 % on the terminal carbons indicates undoubtedly the iso-butenyl intermediate for the hydrogen exchange reaction of butadiene.

Table 1. Deuterium distribution determined by microwave spectroscopy. Hydrogenation conversion was 35 %. Initial composition ; C_4H_6/D_2 = 1/2. $\overset{1}{H_2C} = \overset{2}{CH} - \overset{3}{CH_2} - \overset{4}{CH_3}$

Butadiene			Hydrogen			1-Butene				
d_o	d_1	d_2	H_2	HD	D_2	d_o	d_1	d_2	d_3	d_4
80.0%	14.0	6.0	2.0	10.0	88.0	0.6	6.7	80.8	10.0	1.8

(C) d_1-1-Butene

1-d_1	49 %
4-d_1	51
2-d_1	0
3-d_1	0

(A) d_1-1-Butene

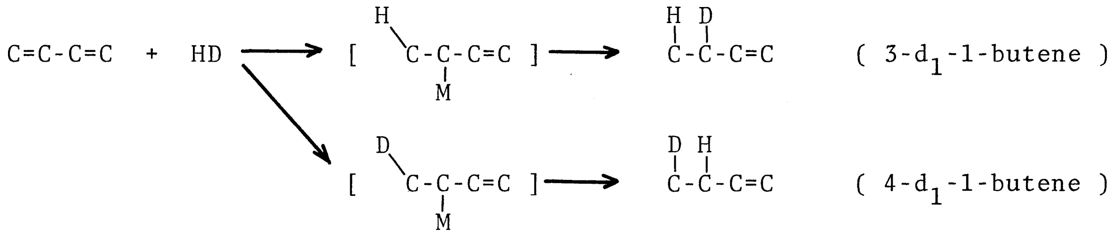
3-d_1	65 %
4-d_1	35
1-d_1	0
2-d_1	0

(B) d_2-1-Butene

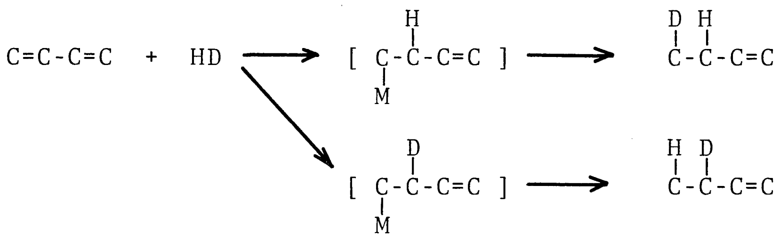
3,4-d_2	100 %
3,3-d_2	0
2,3-d_2	0

The estimation of the intermediate of the hydrogenation of olefins and/or of dienes so far have been done from the exchange reactions providing that the both hydrogenation and the exchange reaction take place via a common intermediate. However, the intermediate of the hydrogenation is not necessarily identical with that of the hydrogen exchange reaction of it. A new method to elucidate the intermediate of the hydrogenation reaction was proposed to the hydrogenation of butadiene over the MoS_2 catalyst.[3)] According to this method, the reaction of butadiene with HD will give the two geometrical isomers, 3-d_1-1-butene and 4-d_1-1-butene, and if the reaction occurs with stepwise addition of H and D, the reaction schemes can be described depending on the intermediates either the iso-butenyl (σ-allyl) or the n-butenyl as follows;

(1)



(2)



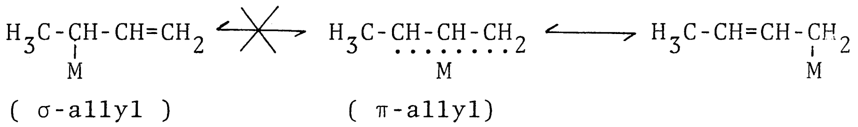
The selectivity to either of the two geometrical isomers is obviously decided by the firstly added H or D atom, because the remaining half of the HD should react successively over the MoS_2 catalyst to maintain the molecular identity of HD in the d_1-1-butene. Accordingly, if the reaction proceeds via the iso-butenyl intermediate, the 3-d_1-1-butene formation may prevail the 4-d_1-1-butene formation in accordance with the isotope effect of the iso-butenyl formation reaction. On the other hand, if the n-butenyl would be the intermediate of the hydrogenation of butadiene, an opposit selectivity, 4-d_1-1-butene > 3-d_1-1-butene, is expected.

As shown in Table 1 (A), the d_1-1-butene formed from the reaction between butadiene and HD is apparently enriched D-atom on the carbon-3 of 1-butene giving 3-d_1-1-butene. Consequently, one may conclude that the hydrogenation of butadiene over the MoS_2

catalyst proceeds via the iso-butenyl intermediate, and this may be the first example confirmed that the intermediate of the hydrogenation is identical with that of the exchange reaction. Furthermore, this result may confirm the reliability of the new method to determine the intermediate of the hydrogenation on the MoS_2 catalyst.

In contrast with butadiene, both n-alkyl and iso-alkyl intermediates on the MoS_2 catalyst have been recognized for the olefins such as propylene and 1-butene during the hydrogenation reaction.4) Taking account of this contrast between butadiene and 1-butene or propylene, the allyl structure in the butenyl species may stabilize the iso-butenyl form rather than the n-butenyl form on the active sites of the MoS_2 catalyst. Furthermore, nearly 100 % selectivity to 1-butene in the hydrogenation of butadiene over the MoS_2 catalyst evidently indicates no possibility of the isomerization of σ-allyl to π-allyl on the active sites;

(3)



$$H_3C\text{-}\underset{M}{\underset{|}{C}}H\text{-}CH{=}CH_2 \;\cancel{\longleftrightarrow}\; H_3C\text{-}\underset{M}{\underset{\cdots\cdots\cdots}{CH\text{-}CH\text{-}CH_2}} \longleftrightarrow H_3C\text{-}CH{=}CH\text{-}\underset{M}{\underset{|}{C}}H_2$$

An interesting similarity has been found over Cu catalyst, on which butadiene is hydrogenated selectively to 1-butene and the iso-butenyl intermediate has been proposed.5) However, in the reaction of butadiene with D_2 on the Cu catalyst, d_o-1-butene was mainly obtained instead of d_2-1-butene as has been observed on the MoS_2 catalyst.

In conformity with the orbital symmetry rule, the molecular addition of hydrogen to the π-bond of olefins or of butadiene seems to be unfavorable. The conservation of hydrogen molecular identity in the hydrogenation reaction has been reported on oxide catalysts such as Cr_2O_3,6) Co_3O_4,7) and ZnO,8) and in the present experiment, the authors have succeeded to demonstrate the stepwise hydrogen addition in keeping hydrogen molecular identity in the hydrogenated products.
Such the maintenance of hydrogen molecular identity may be explained by assuming the isolated active sites, on which hydrogenation is performed.

In this respect, the active sites on the MoS_2 and the oxides require the certain degrees of coordinative unsaturation as has been demonstrated in the homogeneous catalysis. Accordingly, the active sites for the hydrogenation reaction may have three degrees of coordinative unsaturation as was pointed out by Siegel,9) and experimentally shown on the catalysis of sulfured nickel.10)

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