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Selective Formation of *trans*-2-Butene-1,4-d_2 and (E)-2-Methyl-2-Butene-1,4-d_2 in Deuteration of 1,3-Butadiene Derivatives over Thorium Oxide Catalyst

YUZO IMIZU, KOZO TANABE, AND HIDESHI HATTORI

Departmeni of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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Stereoselective hydrogenations of 1,3-butadiene and 2-methyl-1,3-butadiene over thorium oxide catalyst were investigated to elucidate the intermediates of the reactions. Hydrogenation of 1,3-butadiene produced predominantly *trans*-2-butene. Deuterium tracer studies provided direct evidence that 1,4-addition was a dominant mechanism. Deuteration of 1,3-butadiene yielded exclusively monoenes-d_2, while no deuterium was exchanged with hydrogen in 1,3-butadiene. Deuteration of 2-methyl-2-butene gave mainly (E)-2-methyl-2-butene-1,4-d_2. For both reactants, most stable conformations of starting diens (*s-trans* form) were reflected on the structure of the products. The geometrical structures as well as molecular identity of a hydrogen molecule were maintained during hydrogenation. Reaction of a mixture containing 1-butene and 1,3-butadiene-d_6 in the presence of hydrogen revealed that 1-butene and 1,3-butadiene independently underwent isomerization and hydrogenation, respectively. The nature of their active sites is discussed. Key intermediate of the hydrogenation of conjugated diene is postulated to be the *syn* form of methyl- or dimethyl-π-allyl carbanion which is hydrogenated before interconverting to their isomeric *anti* form of the π-allyl carbanion.

INTRODUCTION

The catalytic characteristics which distinguish a certain nonmetallic catalyst from a metallic one have recently been reported for ZnO (*1*), MoS_2 (*2*), MgO (*3*), and ZrO_2 (*4*) in the hydrogenation of 1,3-butadiene. The features in common with these catalysts are: (i) a partial hydrogenation takes place to produce only butenes, (ii) dideuterio species are mainly formed in the deuteration, and (iii) the molecular identity of hydrogen atoms is maintained during the reaction. However, these catalysts exhibit their own characteristics in the relative amounts of three butenes.

The hydrogenation of conjugated dienes can proceed either by 1,2- or by 1,4-addition. The occurrence of one or the other type of hydrogenation helps to elucidate the nature of the reaction intermediates. Zinc oxide (*1*) and MoS_2 (*2*) give 1,2-addition of the hydrogen molecule to 1,3-butadiene selectively to yield 1-butene. On the other hand, 1,4-addition is the predominant process over MgO (*3, 5*) and ZrO_2 (*4*). By 1,4-addition, *cis*-2-butene is selectively formed over MgO, while *trans*-2-butene is formed over ZrO_2.

Some uncertainty exists as to whether the *cis/trans* selectivity in the 1,4-addition process is affected by the thermodynamic stability of the products. Thus, *cis*-2-butene present in lesser quantity at equilibrium might undergo isomerization before desorption. Using 2-methyl-1,3-butadiene as a reactant and analyzing the resulting

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dideuterio-2-methyl-2-butene by the ^{13}C NMR provided further information regarding the 1,4-addition process.

If isomerization of *n*-butenes is initiated by the abstraction of hydrogen (*6*), the same type of intermediates could be operating both for isomerization of *n*-butenes and for hydrogenation of 1,3-butadiene. Therefore, it is necessary to make clear the relation between the isomerization and the hydrogenation from the viewpoints of both reaction mechanisms and nature of active sites.

In this paper, we present thorium oxide as a third nonmetallic hydrogenation catalyst for the 1,4-addition. We have run experiments to provide answers to the following three questions: (i) Does thorium oxide possess properties in common with the other nonmetallic hydrogenation catalysts? (ii) Can isomerization and hydrogenation proceed independently? (iii) What governs the selectivity in the 1,4-addition process for the hydrogenations of 1,3-butadiene and 2-methyl-1,3-butadiene?

EXPERIMENTAL METHODS

Catalysts and pretreatment. Thorium oxide was prepared by heating thorium oxalate (Wako Pure Chemical Industries Ltd.) in air at 500°C for 8 hr. The catalyst had a surface area of 62.3 m^2/g, and was ground and sieved to 35 $\sim$ 42 mesh. Prior to a reaction, the catalyst was pretreated with oxygen at 500°C for several 10-min periods before being outgassed at the same temperature to below 10^{-5} Torr (1 Torr $= 133.3\ Nm^{-2}$). Usually 50 $\sim$ 200 mg of fresh catalyst was used. In some series of runs, the catalyst was regenerated by the treatment with oxygen at 500°C and its activity and selectivity were consistently reproducible.

Materials. All nondeuterio hydrocarbons were purchased from commercial source: 1,3-butadiene, butenes, and propene from Takachiho Chemicals Co.; 2-methyl-1,3-butadiene and 2-methyl-propene from Tokyo Kasei Co. 1,3-Butadiene-d_6 was obtained from Merck Sharp and Dohme of Canada, Ltd. *cis*-2-Butene-d_8 was prepared by repeated exchange of butenes with D_2 over MgO and separated from the other butenes by glc (*7*). All were shown by glc to be more than 99.8% pure. The perdeuterio compounds were distilled and outgassed. The other gases were purified by passage through 4A molecular sieves kept at $-78°$ or 0°C.

Cylinder hydrogen was purified by permeation through a Pd–Ag thimble. Deuterium, obtained by the decomposition of D_2O with a magnesium ribbon at 500°C, was purified by passage through 13X molecular sieves at -196°C. Mass spectrometric analysis showed 98.6% D_2 and 1.4% HD.

Reaction procedures. The hydrogenation reactions were carried out in a closed recirculation reactor with a volume of about 400 cc, and in the temperature range of 0 $\sim$ 110°C. For NMR studies, a reactor of large volume, about 1.4 liters, was employed. Reactants (the ratio of hydrogen to hydrocarbon was 2:1) were premixed by circulating them in a reaction loop with the catalyst bypassed. Products were withdrawn periodically for gas chromatographic analysis over a 5-m VZ-7 (Gaschro Industry Ltd.) column, operating at 0°C.

Mass and NMR spectrometric analyses. The hydrocarbons were separated chromatographically and collected at -196°C for subsequent mass and NMR spectrometric analyses to determine the amounts and location of deuterium in the products. All mass spectrometric analyses were made on a Hitachi RMU-2 mass spectrometer using ionizing voltage of 9 eV for hydrocarbons and 70 eV for the isotopes of hydrogen. As the fragmentation was very low (less than 1% of the parent peak), analysis of hydrocarbons was based on parent peak heights after correction of ^{13}C isotopic impurity. The correction factors for H_2, HD, and D_2 were those obtained for standard samples

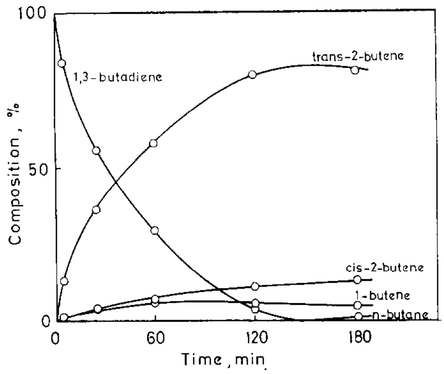


FIG. 1. The time course of hydrogenation of 1,3-butadiene over thorium oxide at 80°C.

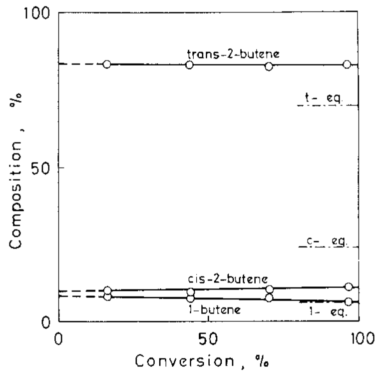


FIG. 2. Percentage of each butene produced in 1,3-butadiene hydrogenation over thorium oxide at 80°C.

and background correction were made on every analysis. The ^1H NMR spectra were taken at 100 MHz using a JEOL JNM-PS 100 spectrometer in CCl_4 with tetramethysilane as an internal reference.

The ^{13}C NMR spectrum was taken at 25.00 MHz (JNM-FX 100 PFT) using proton noise decoupling in $CDCl_3$ with tetramethylsilane as an internal reference. The precision of the chemical shift data is at least ±0.06 ppm (8K data points in the time domain for a 6000-Hz spectral width). Assignments of carbon-13 resonance peaks were made by comparing the spectra with reported chemical shifts (*8*).

RESULTS

1. *Hydrogenation of 1,3-Butadiene*

A typical time course of the hydrogenation at 80°C is given in Fig. 1. The products were the three *n*-butenes. Butane was not formed until most of the 1,3-butadiene disappeared. Fig. 2 shows the percentage of each butene as a function of hydrogenation conversion. *trans*-2-Butene was predominantly formed. Even though the butenes were not formed in thermodynamic equilibrium with each other, their percentages, 1-butene (7.8%), *trans*-2-butene (83.3%), and *cis*-2-butene (9.1%) did not change significantly with the conversion. Previous work showed that the isomerization of *n*-butenes can easily occur at 80°C over thorium oxide (*9*). In sections 2 and 4 the possibility that the product butene undergoes fast isomerization before desorption and the relationship between hydrogenation and isomerization are examined. The compositions of the products at various reaction temperatures are given in Table 1.

TABLE 1

Distribution of Butenes Produced in the Hydrogenation of 1,3-Butadiene over ThO_2 at Different Reaction Temperatures

Reaction temperature (°C)	Conversion (%)	Percentage of each butene			Ratio of *trans*- to *cis*-2-butene
		1-Butene	*trans*-2-Butene	*cis*-2-Butene	
0	5.4	8.7	84.7	6.6	12.8
80	16.3	7.8	82.8	9.4	8.8
102	7.9	11.3	71.2	17.5	4.1

TABLE 2

Deuterium Distribution of *trans*-2-Butene in the Deuteration of 1,3-Butadiene over ThO_2 at the Different Reaction Conversions

Conversion (%)	Percentage of each isotopic species				
	d_0	d_1	d_2	d_3	d_4–d_8
5.3	8.9	7.7	82.9	0.5	0.0
(8.0)[a]	(1.0)	(5.4)	(92.6)	(1.0)	(0.0)
13.8	0.9	6.0	92.2	0.9	0.0
24.4	0.8	5.8	92.3	1.1	0.0
32.6	0.7	5.5	92.5	1.3	0.0

[a] Reaction was carried out over deuterated catalyst which had repeatedly been exposed to D_2O vapor followed by evacuation.

The products consisted primarily of *trans*-2-butene and its percentage increased as the reaction temperature became low.

2. Deuteration of 1,3-Butadiene

Table 2 gives the isotopic distribution of the *trans*-2-butene in the deuteration of 1,3-butadiene. Dideuterio-butenes were yielded as the main product, and the number of D atoms exchanged into 1,3-butadiene was almost entirely negligible. The ^1H NMR spectra of the 2-butenes showed that the intensity ratios of methyl hydrogen ($-CH_3$) to olefinic hydrogen ($=CH-$) were 2.0 for *trans*-2-butene and 2.2 for *cis*-2-butene and that the peaks of olefinic hydrogens exhibited a 1:2:1 triplet. The spectrum of 1-butene showed that the relative intensities of H atoms attached to the carbon atoms 1, 2, 3, and 4 were 2.0:1.1:1.0:2.2 and that the peaks of hydrogens at carbon atom 4 exhibited a doublet. These indicate that the two D atoms in a molecule were located at carbon atoms 1 and 4 in 2-butenes, and carbon atoms 3 and 4 in 1-butene. Each dideuterio-butene was identified as 3,4-dideuterio-1-butene, 1,4-dideuterio-*trans*-2-butene, and 1,4-dideuterio-*cis*-2-butene. If *trans*-2-butene were formed by 1,2-addition followed by isomerization, the two D atoms in *trans*-2-butene would have been smeared on all carbon atoms. Therefore, the main path of the formation of *trans*-2-butene involves the direct process of 1,4-addition of hydrogen to 1,3-butadiene and not via 1-butene. This conclusion is further supported by the reaction of a mixture of perdeuterio-1,3-butadiene and 1-butene in the presence of H_2 reported in section 4.

Table 3 includes the results of the reaction of 1,3-butadiene with a mixture of H_2 and D_2. The produced butenes

TABLE 3

Isotopic Distribution of Products in the Reaction of 1,3-Butadiene (52 Torr) with a Mixture of $H_2 + D_2$ (100 Torr) over ThO_2 (500 mg) at 0°C

Reaction time (min)	Product	Percentage of each product	Percentage of each isotopic species				
			d_0 or H_2	d_1 or HD	d_2 or D_2	d_3	d_4–d_8
0	H_2, HD, D_2		51.5	1.0	47.5		
75	H_2, HD, D_2		47.1	7.4	45.5		
	1,3-Butadiene	66.5	100	0	0	0	0
	1-Butene	2.0	63.4	13.8	22.8	0	0
	trans-2-Butene	29.8	55.4	6.3	38.2	0	0
	cis-2-Butene	1.6	59.2	11.0	29.8	0	0
150	H_2, HD, D_2		42.8	11.9	45.3		
	1,3-Butadiene	42.7	99.9	0.1	0	0	0
	1-Butene	3.1	60.0	15.7	24.3	0	0
	trans-2-Butene	51.4	52.4	8.9	38.6	0.1	0
	cis-2-Butene	2.8	55.8	13.5	30.7	0	0

TABLE 4

Isotopic Distribution of Products in the Deuteration of 2-Methyl-1,3-Butadiene over ThO_2[a]

Product	Percentage of each product	Percentage of each isotopic species				
		d_0	d_1	d_2	d_3	d_4–d_{10}
3-Methyl-1-butene	0.4	22.0	4.3	73.0	0.7	0.0
2-Methyl-1-butene	4.8	1.7	2.6	94.5	1.1	0.0
2-Methyl-2-butene	31.8	1.0	2.0	95.0	2.0	0.0
2-Methyl-1,3-butadiene	63.4	98.7	1.3	0.0	0.0	0.0

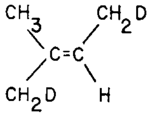
[a] A mixture of 206 Torr of D_2 and 100 Torr of 2-methyl-1,3-butadiene was reacted for 22 hr over 500 mg of ThO_2 at 22°C.

consisted substantially of the d_0 and d_2 species. Percentages of the d_1 isotopic species were relatively small and corresponded to that of HD presented in the gas phase. Therefore, H_2 (or D_2 or HD) maintains its molecular identity during the hydrogenation, though the H_2–D_2 equilibration reaction was not completely inhibited in the presence of 1,3-butadiene.

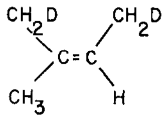
3. Deuteration of 2-Methyl-1,3-butadiene

The deuteration of 2-methyl-1,3-butadiene yielded dideuterio-methyl-butenes as the main isotopic species (Table 4). Product distribution was quite similar to that observed in deuteration of 1,3-butadiene in the sense that the main product, 2-methyl-2-butene, resulted from 1,4-addition. A large percentage of 3-methyl-1-butene-d_0 (22%) corresponded to only 0.08% total reaction mixture and most of it seemed to be impurity of the reactant. The 2-methyl-2-butene from reaction of 2-methyl-1,3-butadiene with D_2 showed the following ^1H NMR in $CDCl_3$: triplet at 5.2 ppm (olefinic, 1H, splitting due to adjacent CH_2D group on carbon atom 3), unsymmetrical doublet at 2.4 ppm (methyl, 2H, splitting due to adjacent olefinic hydrogen on carbon atom 3). The last two were too poorly resolved to integrate the peak intensities. The ^1H NMR of this species showed that the ratio of intensities of the hydrogens of three methyl groups to the olefinic hydrogen was 7.2 and that the signal of the olefinic hydrogen was split into a triplet due to CH_2D group on carbon atom 3. The observed value 7.2 is very close to 7.0 which is expected when the two D atoms are located on the three methyl groups. This observation indicates that the two D atoms in 2-methyl-2-butene are located at carbon atoms 1 and 4.

There exist two 2-methyl-2-butene-1,4-d_2 isomers **1** and **2** created by the substitution of deuterium:



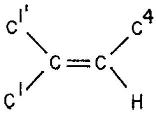
1



2

(E)-2-Methyl-2-butene-1,4-d_2 **1**, and (Z)-2-methyl-2-butene-1,4-d_2 **2** are similar to geometrical isomers of 2-butene. Stothers *et al.* reported that ^{13}C NMR provides the direct assay of deuterium content of methyl and/or methylene carbons (*10*). This method was applied to distinguish an isomeric pair **1** and **2**.

The ^{13}C NMR spectrum of the 2-methyl-2-butene produced in the reaction is shown in Fig. 3. The signal for the C^1 and C^4 atoms appears as a triplet, while the signal of the $C^{1'}$ atom is a singlet from the following nomenclature:



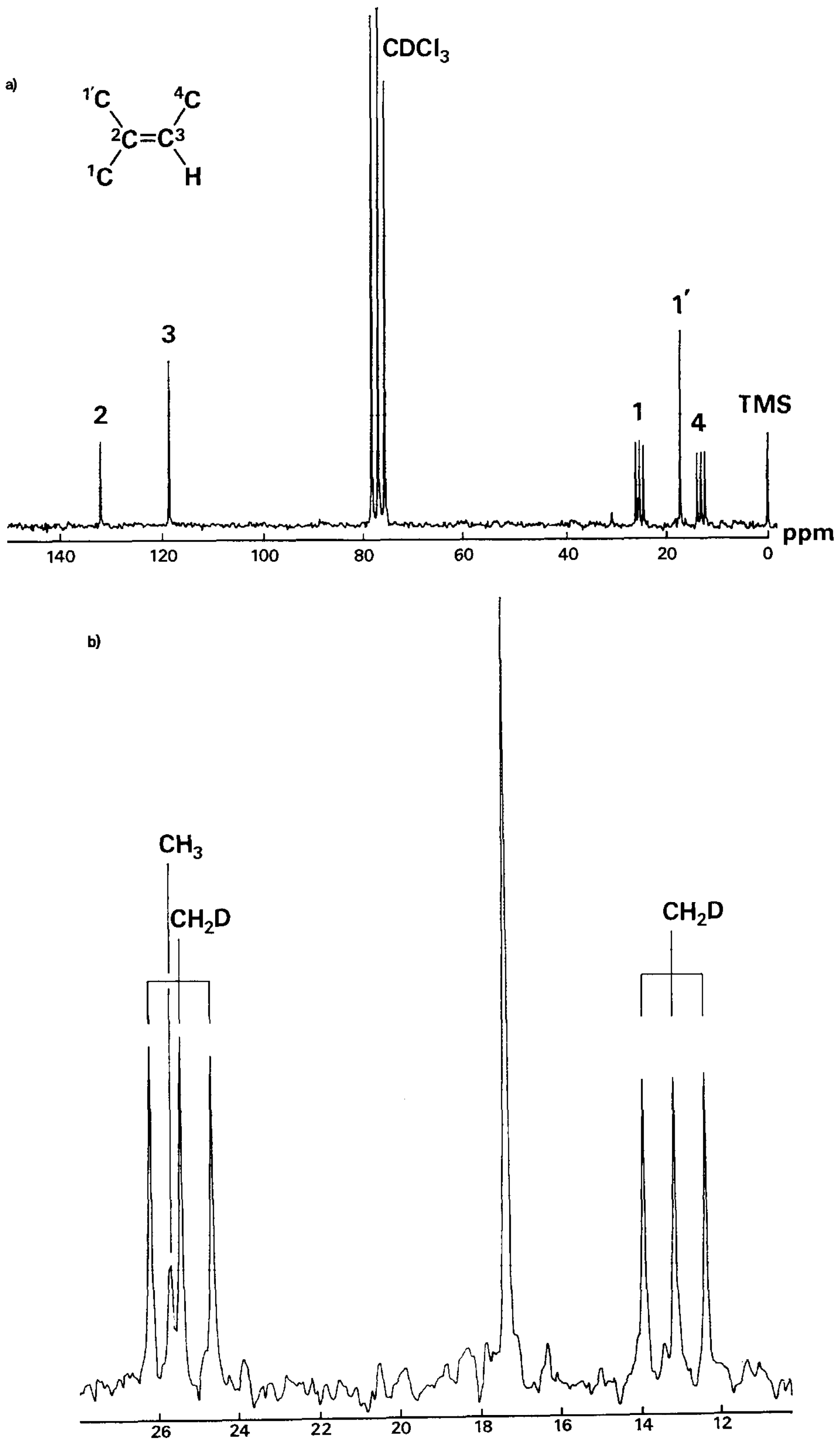

a)
1′C
4C
2C=C3
1C
H
CDCl3
3
2
1′
1
4
TMS
ppm
140
120
100
80
60
40
20
0
b)
CH3
CH2D
CH2D
26
24
22
20
18
16
14
12

TABLE 5

Isotopic Distribution of Products in the Reaction of Equal Amounts of 1-Butene and Perdeuterio-1,3-butadiene (30 Torr) and Twice the Amount of Hydrogen (60 Torr) at 70°C

Product	Percentage of each product	Percentage of each isotopic species						
		d_0	d_1	d_2	d_3	d_4	d_5	d_6
1-Butene	50.1	99.9	0.1	0	0	0	0	0
trans-2-Butene	2.6	15.9	0.2	0	0	1.4	9.6	72.9
cis-2-Butene	2.2	82.9	2.2	0	0	0.3	1.8	12.8
1,3-butadiene	45.1	0	0	0	0.2	1.7	11.6	86.4
1,3-butadiene	(0 min)	0	0	0	0.3	1.7	11.7	86.3

Integration of the spectrum indicates that the percentages of mono-deuterated carbon (CH_2D) in C^1 and C^4 are 89 and 100%, respectively. The signal of CH_2D at $C^{1'}$ was too small to be integrated. Therefore, the 2-methyl-2-butene-1,4-d_2 consists of 89% (E)-form **1** and 11% (at most) (Z)-form **2**.

4. 1-Butene Isomerization and Hydrogenation of 1,3-Butadiene

Equal amounts of 1-butene and perdeuterio-1,3-butadiene and twice the amount of H_2 were reacted over thorium oxide to elucidate the relationship between hydrogenation and isomerization. 1-Butene and 1,3-butadiene underwent isomerization and hydrogenation, respectively, at a rate of the same order. Table 5 and Fig. 4 summarize the isotopic distribution of the products in the reaction of 1-butene, perdeuterio-1,3-butadiene, and H_2. It is considered that the isotopic isomers, $d_0 \sim d_3$, were produced by the isomerization and the isotopic isomers, $d_4 \sim d_6$, were produced by the hydrogenation. Thus, the ratios of *cis* to *trans* isomers were calculated to be 4.7 for the isomerization and 0.1 for the hydrogenation. These values were close to the values, 3.4 and 0.1, which were obtained for the separated experiments of 1-butene isomerization (*9*) and the hydrogenation of 1,3-butadiene, respectively. This conformity shows that the isomerization and the hydrogenation proceed independently.

In the hydrogenation of 1,3-butadiene, a small amount of *cis*-2-butene-d_8 (8.5% of 1,3-butadiene) was added as a tracer to the reactant mixture. The fractions of d_8 isotopic species in 1-butene and *trans*-2-butene were entirely negligible. Most of the *trans*-2-butene was produced directly from 1,3-butadiene and not via *cis*-2-butene. The results of poisoning experiments for the reaction of a mixture of 1,3-butadiene, 1-butene, and hydrogen are summarized in Table 6. The time courses of the reactions are shown in Figs 5 and 6 for NH_3 poisoning and CO_2 poisoning, respectively. The hydrogenation was retarded by all poisons. The *cis/trans* ratio was not changed by poisoning with H_2O and CO_2, while the ratio was increased by poisoning with NH_3 and CO.

DISCUSSION

In the hydrogenation of 1,3-butadiene over the thorium oxide catalyst, a high selectivity for the *trans*-2-butene formation was observed under all the conditions employed. Deuterium tracer experiments showed that *trans*-2-butene is exclusively

Fig. 3. Proton noise decoupled ^{13}C NMR spectrum of 2-methyl-2-butene in $CDCl_3$ from reaction of 2-methyl-1,3-butadiene with D_2 at 22°C. Shielding scale in ppm from TMS. (a) Whole range; (b) expanded in the region of methyl carbons.

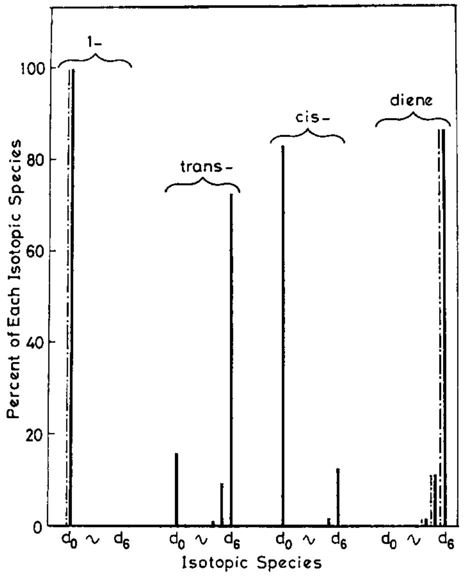


FIG. 4. Isotopic composition of products in the reaction of 1-C_4H_8, 1,3-C_4D_6, and H_2 over thorium oxide at 70°C. The one point broken line is the isotopic composition of starting 1-C_4H_8 and 1,3-C_4D_8.

TABLE 6

Poisoning Effects in the Reaction[a] of 1,3-Butadiene, 1-Butene, and Hydrogen

Poison[b]	k^c	*cis-/trans-* 2-Butene
None	1.00	0.7
H_2O	0.70	0.7
CO_2	0.30	0.7
O_2	0.75	0.8
NH_3	0.17	1.7
CO	0.39	1.5

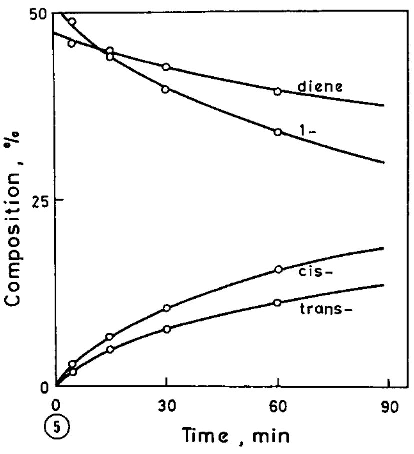
[a] A mixture of 30 Torr of 1,3-butadiene and 1-butene and 60 Torr of hydrogen was reacted at 70°C.

[b] Catalyst was poisoned by adsorption of several Torr of poisons at 70°C followed by evacuation for 5 min.

[c] Relative rate of total conversion.

formed by 1,4-addition. However, 1-butene in the presence of an equal amount of 1,3-butadiene undergoes isomerization. These facts do not conflict, since the amount of 1-butene produced from 1,3-butadiene is small, and the occurrence of 1-butene isomerization does not significantly influence the selectivity data in the hydrogenation.

The three characteristic features in common with certain nonmetallic catalysts were observed over thorium oxide. On the metallic catalyst, it is well known that the deuteration of ethylene accompanies the hydrogen exchange between D_2 and ethylene, and, so far, the deuterio-ethylene formation has been explained by the reverse



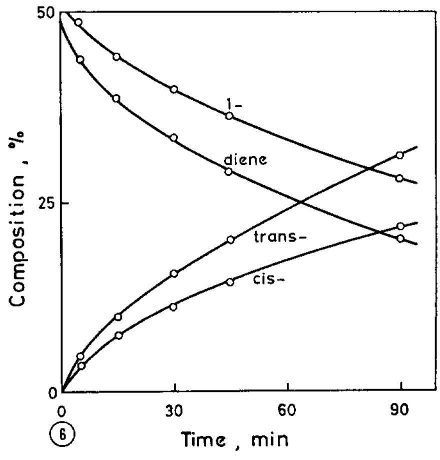


FIG. 5. The time course of reaction of 1-C_4H_8, 1,3-C_4H_6, and H_2 over thorium oxide poisoned by NH_3. Reaction temperature, 70°C.

FIG. 6. The time course of reaction of 1-C_4H_8, 1,3-C_4H_6, and H_2 over thorium oxide poisoned by CO_2. Reaction temperature, 70°C.

process from the ethyl intermediate (*11*). Over thorium oxide, exclusive formation of dideuterio monoene species and no H–D exchange into reactant dienes with D_2 indicate that the reverse process from the butenyl intermediate is not a significant component.

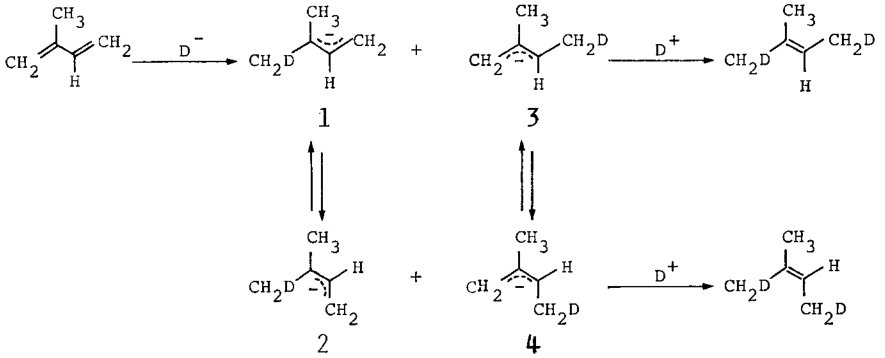
The molecular identity of hydrogen (or deuterium) atoms was maintained during the reaction. This phenomenon was also reported for ZnO (*1, 12*), Cr_2O_3 (*13*), Co_3O_4 (*14*), MgO (*3*), ZrO_2 (*4*), and MoS_2 (*2*). The maintenance of the molecular identity of hydrogen suggests that two hydrogen atoms formed by dissociative adsorption from one molecule on an active site do not migrate to other sites in the presence of conjugated diene, and that each active site is isolated from others.

The details of active sites for hydrogenation were not well investigated in this study. However, some outlines are figured out by comparing hydrogenation with 1-butene isomerization. Previous work showed that 1-butene isomerization was initiated by the abstraction of proton, and was not promoted by hydrogen, and that the reaction was presumed to occur via carbanion intermediates (*9*). Carbanion intermediates are also postulated in the case of 1,3-butadiene hydrogenation as discussed later. A labeling study of the system containing 1-butene, 1,3-butadiene, and H_2 revealed that the hydrogenation and isomerization occurred independently and suggested that two kinds of active sites existed. The poisoning experiments for the same system showed that CO_2 and H_2O retarded the two reactions at the same proportion, while CO and NH_3 retarded hydrogenation more strongly than they did isomerization. It is assumed that there are two types of active sites, one of which is active only for isomerization and the other of which is active for both isomerization and hydrogenation.

One possible explanation for those may be as follows. The active sites for both reactions are very similar because of the formation of the same carbanion intermediate and the same proportion of retardation with CO_2 and H_2O for both reactions. The difference between two active sites is assumed to be in a number of coordinative unsaturation, since the hydrogenation reaction requires the active site on which the hydrogen molecule is able to be dissociated into two atoms in addition to those which serve sites for hydrocarbons to be hydrogenated (*15*), and NH_3 and CO prefer the more unsaturated metal ion (*16*). Perhaps, the hydrogenation sites are less coordinatively saturated, and adsorb NH_3 and CO more strongly than do the isomerization sites.

The mechanism of hydrogenation of conjugated diene will now be discussed. Magnesium oxide catalyzes selectively the hydrogenation of 1,3-butadiene by 1,4-addition to give predominantly *cis*-2-butene (*5*). The selective hydrogenation was explained by the π-allylic carbanion mechanism (*3*), since 1-methyl-π-allylic carbanion is most stable in the *anti* form (*17*). On the contrary, the experimental evidence on thorium oxide catalyst indicates that the preferred conformation of 1-methyl-π-allylic species is the *syn* form. Nevertheless, a carbenium ion mechanism would choose 1,2-addition rather than 1,4-addition (*18*), and does not account well for the following order of the relative rates for hydrogenation of several olefins: 1,3-$C_4H_6 \geqq$ 2-methyl-1,3-$C_4H_6 >$ 1-$C_4H_8 >$ iso-$C_4H_8 \geqq C_3H_6 >$ *cis*-2-C_4H_8. Thus, the carbenium ion mechanism is rejected and the mechanism is suggested to be as follows. Hydrogen is adsorbed heterolytically to form H^+ and H^-. At first, H^- attacks 1,3-butadiene at a terminal carbon atom to form 1-methyl-π-allylic carbanion which is primarily in the *syn* form reflecting the most stable *s-trans* conformation of 1,3-butadiene in the gas phase (*19, 20*). Second, since the electron density in a 1-methyl-π-allylic carbanion is the highest at the other terminal carbon atom, H^+ selectively attacks the carbon atom before the *syn* species interconverts to the more stable *anti* species to form *trans*-2-butene. The decreasing yield of *trans*-2-butene as the reaction temperature is increased suggests that the *syn* and the *anti*-π-allylic species can interconvert more readily at higher temperature. Since the *syn* form is different from the *anti* form not only in the structure but also in the thermodynamic stability, some uncertainty is left that the *cis/trans* selectivity might be determined by the thermodynamic factor or the structural one, even though the interconversion between the *syn* and *anti* forms was fast. Using 2-methyl-1,3-butadiene makes clear what governs the selectivity.

In the case of the deuteration of 2-methyl-1,3-butadiene, there exist four kinds of dimethyl-π-allylic species. Two of them are *syn* form and the rest of them are *anti* form. Their structures are shown in Scheme 1. The *anti*-1,2-dimethyl-π-allylic carbanion **4** is more stable than the *syn* form **3** by analogy with 1-methyl-π-allylic carbanion. Two isomers of 1,1-dimethyl-π-allylic species **1**, **2** created by the substitution of deuterium have practically the same stability. Second, D atom attacking a π-allylic species results in the formations of (E)-1,4-d_2 from the *syn* species **1** and **3**, and (Z)-1,4-d_2 from the *anti* species **2** and **4**. Over thorium oxide, the substantial formation of (E)-1,4-d_2 species shows that the interconversion between the *syn* and *anti* species is slower than the second hydrogen attacking process, and gives further evidence that the main path of the hydrogenation of conjugated dienes involves the direct process of 1,4-addition. The intermediate should be *syn*-1,1-dimethyl-π-allylic carbanion **1** or *syn*-1,2-dimethyl-π-allylic carbanion **3**.



SCHEME 1. Deuteration of 2-methyl-1,3-butadiene over thorium oxide.

The factor determining the relative stabilities of an isomeric pair **1** and **3** is not clear as to whether it is steric or electronic. The addition of fluoroboric acid to 2-methyl-1,3-butadiene-iron tricarbonyl generates the 1,1-dimethyl-allyl-Fe$(CO)_3$ cation and not the isomeric *anti*-1,2-dimethyl-π-allyl-Fe$(CO)_3$ species (*21*). In this case, steric factors have been reported to be responsible to a very large extent for the rather marked difference in chemical properties displayed by π-allyl-Fe$(CO)_3$ cation (*22*). Over MgO, produced 2-methyl-2-butene-1,4-d_2 from this reaction consisted of 60% (E)-1,4-d_2 and 40% (Z)-1,4-d_2 (*23*). Since *cis*-2-butene was selectively produced in the hydrogenation of 1,3-butadiene over MgO, the interconversion between the *syn* and *anti* species is considered to be fast over MgO. If the hydrogenation of 2-methyl-

1,3-butadiene proceeds via 1,2-dimethyl species **3** or **4** over MgO, (Z)-1,4-d_2 would mainly be produced. This was not the observed result. If the reaction proceeds via 1,1-dimethyl species **1** or **2**, almost equal quantities of (E)- and (Z)-1,4-d_2 would be produced. This was the observed result. Therefore, 1,1-dimethyl species are more plausible than 1,2-dimethyl species in the carbanionic hydrogenation of 2-methyl-1,3-butadiene. Consequently, the hydrogenation over thorium oxide is considered as follows. 2-Methyl-1, 3-butadiene is adsorbed in the *s-trans* form and a D^- produced by dissociative adsorption of D_2 attacks at the carbon atom 1 to form *syn*-1,1-dimethyl-π-allylic arbanion **1**. This species is attacked by a D^+ at the carbon atom 3 before interconversion to the *syn* form 2 to produce (E)-2-methyl-2-butene-1,4-d_2.

Thorium oxide is known to be a basic catalyst (*10*, *24*) and its basicity is weaker than that of MgO (*25*). The less strong basicity may bring about the *syn* species as a half hydrogenated state being hydrogenated before interconversion to the *anti* species. Because of the slow interconversion between the *syn* and *anti* species over thorium oxide, the conformational stability of the starting dienes are reflected on the resulting hydrogenated molecule. In other words, the geometrical structure of a hydrocarbon is maintained during hydrogenation.

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