JOURNAL OF CATALYSIS **76**, 65–74 (1982)

A Mechanistic Study of Hydrogenation of Conjugated Dienes over a Lanthanum Oxide Catalyst

YUZO IMIZU,[1] KENJI SATO, AND HIDESHI HATTORI

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

Received September 21, 1981; revised February 17, 1982

Mechanisms of hydrogenation of 1,3-butadiene and 2-methyl-1,3-butadiene(isoprene) over lanthanum oxide were studied by a tracer technique employing deuterium. The activity of lanthanum oxide for the hydrogenation of 1,3-butadiene varied with a pretreatment temperature and attained a maximum following outgassing at 650°C. In the deuteration of 1,3-butadiene, the products consisted mainly of *trans*-2-butene-1,4-d_2 which resulted from 1,4 addition of D atoms to the reactant molecule. It was suggested that the reaction intermediate was a *trans*-π-allylic carbanion and that the interconversion of the *trans*-π-allylic carbanion to the *cis*-π-allylic carbanion was slow. The characteristic feature was a retention of the geometrical structure of the 1,3-butadiene molecule during the reaction. In the deuteration of 2-methyl-1,3-butadiene, the main product was 2-methyl-2-butene-1,4-d_2 which was produced by 1,4 addition of D atoms. The 2-methyl-2-butene-1,4-d_2 consisted of 64% (E)-form and 36% (Z)-form.

INTRODUCTION

The catalytic properties of lanthanum oxide have been investigated by several workers in recent years. Minachev *et al.* (*1*) found that lanthanum oxide is highly active for hydrogenation of ethylene when pretreated at a high temperature. Rosynek *et al.* (*2–4*) studied the characterization of the surface by ir spectroscopy and catalytic behavior for butene isomerization. They found that active sites are generated by removal of surface CO_2 strongly held on the surface. For both hydrogenation of ethylene and butene isomerization, it was suggested that the active sites were of basic property. Fukuda *et al.* (*5*) measured the surface properties and found the existence of basic sites by the indicator method. They carried out coisomerization of *cis*-2-butene-d_0/d_8 and reported that the isomerization involved an intramolecular H transfer. It was suggested that a π-allylic carbanion mechanism was operating in butene isomerization. This allylic mechanism in butene isomerization has also been suggested by Goldwasser and Hall (*6*) and Rosynek *et al.* (*7*).

We previously reported preliminary results of study of the catalytic behaviors of lanthanum oxide for hydrogenation of 1,3-butadiene and of 2-methyl-1,3-butadiene (*8*). Hydrogenation occurred by the process of 1,4 addition of H atoms to conjugated dienes. This 1,4 addition of H atoms in the hydrogenation of 1,3-butadiene was also observed for ZrO_2 (*9*), MgO (*10, 11*), and ThO_2 (*12*). For these catalysts, secondary hydrogenation to produce butane was entirely negligible, this being due to a great difference in hydrogenation rate between conjugated dienes and monoenes; a conjugated diene undergoes hydrogenation much faster than a monoene. On the basis of the above, we proposed that hydrogenation of conjugated dienes over ThO_2 and MgO proceeds via π-allylic carbanion intermediates. The catalytic properties of La_2O_3 have much in common with those of ThO_2 and MgO not only for hydrogenation but also for other reactions such as double bond isomerizations of olefins (*5*) and of unsatu-

---

[1] Present address: Department of Environmental Engineering, Kitami Institute of Technology, Kitami 090, Japan.

0021-9517/82/070065-10$02.00/0

rated compounds containing nitrogen (*13*) or oxygen (*14*).

The present work was undertaken to learn more about the mechanisms of the hydrogenation of 1,3-butadiene and 2-methyl-1,3-butadiene over La_2O_3. The results suggest that the reactions involve π-allylic carbanion intermediates.

EXPERIMENTAL METHODS

Catalyst. Lanthanum trihydroxide, the starting material of the catalyst, was prepared by precipitation from an aqueous solution of $La(NO_3)_3$ by addition of aqueous ammonia. The precipitate was washed with deionized water and dried at 100°C. The $La(OH)_3$ was ground to 24–42 mesh and decomposed to La_2O_3 in a reactor under a vacuum at various high temperatures for 3 hr. The final vacuum was less than 10^{-5} Torr (1 Torr = 133.3 N m^{-2}). Magnesium oxide was prepared by decomposition of $Mg(OH)_2$ (Kanto Chemical Co. Ltd) at 1100°C in a vacuum (*11*). Thorium oxide was prepared from thorium oxalate by decomposition at 500°C in air and was outgassed at 500°C before use (*12*). For preparation of ZrO_2, $Zr(OH)_4$ was precipitated from an aqueous solution of $ZrOCl_2$, washed, and calcined at 500°C in air. Prior to a reaction, ZrO_2 was outgassed at 500°C (*15*).

Materials. 1,3-Butadiene and *cis*-2-butene were purchased from Takachiho Chemicals Co., and 2-methyl-1,3-butadiene from Tokyo Kasei Co. These were purified by passage through 4A molecular sieves kept at dry ice acetone temperature. Cylinder hydrogen was purified by permeation through a Pd–Ag thimble. Deuterium was obtained by decomposition of D_2O with a magnesium ribbon at 500°C and was purified by passage through 13X molecular sieves at liquid nitrogen temperature. The isotopic purity of deuterium was 98.6%.

Reaction procedures. Hydrogenation was normally carried out at 0°C in a recirculation reactor with a volume of ca. 300 ml. Reactants consisted of 30 Torr of hydrogen (or deuterium) and 12 Torr of hydrocarbon. For a tracer study, a 1.5- or 2.8-liter reactor was employed. Products were withdrawn periodically from the system for gas chromatographic analysis, a 5-m column packed with VZ-7 (Gaschro Industry Ltd.) being operated at 0°C. The isomerization of *cis*-2-butene was carried out in the recirculation reactor with a volume of ca. 400 ml at 0°C with 100 Torr of *cis*-2-butene.

Mass and NMR analyses. Chromatographically separated hydrocarbons were collected in a liquid nitrogen trap for subsequent mass and NMR analyses. All mass spectrometric analyses were made on a Hitachi M-52 mass spectrometer. An ionization voltage of 9 eV was used for hydrocarbons and 20 eV for the isotopes of hydrogen. As the fragmentations were less than 1% of the parent peaks for hydrocarbons, the analysis was based on the parent peak heights after correction for naturally occurring ^{13}C isotopes. The correction factors for H_2, HD, and D_2 were those obtained for standard samples. The ^1H NMR spectrum was taken in CCl_4 with tetramethyl silane as an internal standard. A JEOL JNM-PS 100 spectrometer was used. The ^{13}C NMR spectrum was taken at 25.00 MHz (JNM-Fx 100 PET) using proton noise decoupling in $CDCl_3$ with tetramethyl silane as an internal reference. Assignments of carbon-13 resonance peaks were made by comparing the spectra with reported chemical shifts (*16*).

RESULTS

Hydrogenation of 1,3-Butadiene

The time dependence of hydrogenation of 1,3-butadiene over the La_2O_3 catalyst outgassed at 550°C is shown in Fig. 1. Products consisted mainly of *trans*-2-butene. Butane was not appreciable even after all 1,3-butadiene was converted to butenes. Product distribution did not change much with the pretreatment temperature of the catalyst.

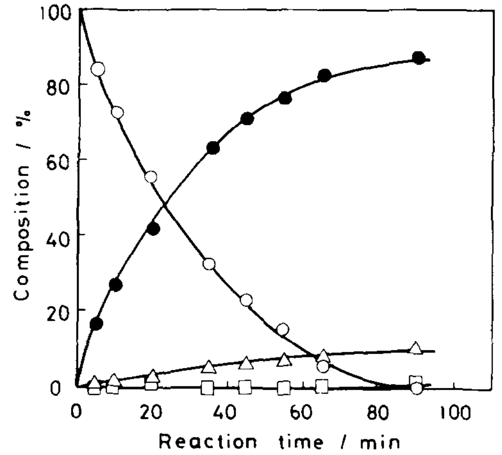


FIG. 1. Time dependence of hydrogenation of 1,3-butadiene at 0°C over 20 mg of the La_2O_3 catalyst outgassed at 550°C. Reactor volume was 300 ml. ○, 1,3-Butadiene; ●, *trans*-2-butene; △, *cis*-2-butene; □, 1-butene.

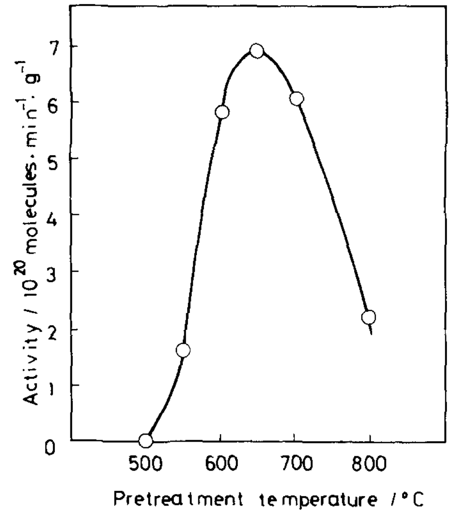


FIG. 2. Variation in activity of La_2O_3 for hydrogenation of 1,3-butadiene as a function of pretreatment temperature.

Activity Dependence on Pretreatment Temperature of Catalyst

The variation of hydrogenation activity is plotted against outgassing temperature of the catalyst in Fig. 2. The activity appeared at an outgassing temperature of 500°C and reached a maximum at 650°C. The surface areas of the La_2O_3 catalyst outgassed at different temperatures were 43 m^2/g (500°C), 39 m^2/g (600°C), 31 m^2/g (650°C), 27 m^2/g (700°C), 21 m^2/g (800°C), and 15 m^2/g (900°C).

Deuteration of 1,3-Butadiene

The isotopic distributions of butenes in the deuteration of 1,3-butadiene over the La_2O_3 outgassed at 600°C are given in Table 1. The butenes consisted mainly of dideuterio isotopic species (90.7%). In 1-butene and *cis*-2-butene, the percentages of the isotopic species other than dideuterio one were relatively large, though the absolute amounts were small. The ^1H NMR spectrum of the *trans*-2-butene indicated that the intensity ratio of methyl hydrogen

TABLE 1

Isotopic Distribution of Products in the Deuteration of 1,3-Butadiene over La_2O_3[a]

Product	Percentage each product	Percentage each isotopic species							
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7,d_8
1,3-Butadiene	60.3	99.7	0.3	0	0	0	0	0	0
1-Butene	0.9	5.4	9.8	75.2	5.7	2.5	1.1	0.3	0
trans-2-Butene	33.2	0.6	3.1	93.7	2.0	0.6	0	0	0
cis-2-Butene	5.5	5.7	8.5	76.5	6.5	2.0	0.6	0.2	0
Butane	0.1[b]	—	—	—	—	—	—	—	—

[a] Reaction temperature, 0°C; catalyst, 0.30 g outgassed at 600°C; reaction time, 240 min; reactor 1.5 × 10^3 ml; reactants, 100 Torr 1,3-butadiene, 148 Torr D_2.

[b] The amount was too small to determine isotopic distribution.

TABLE 2

Isotopic Distribution of the Products in the Reaction of 1,3-Butadiene with a Mixture of H_2 + D_2 over La_2O_3

Product	Percentage each product	Percentage each isotopic species					
		d_0	d_1	d_2	d_3	d_4	d_5–d_8
Hydrogen	—	49.0	1.1	49.9	—	—	—
1,3-Butadiene	51.1	99.7	0.3	0	0	0	0
1-Butene	1.0	51.6	10.6	35.1	2.3	0.4	0
trans-2-Butene	40.1	45.0	5.4	48.7	0.8	0.1	0
cis-2-Butene	7.5	50.7	10.3	37.1	1.7	0.2	0
Butane	0.3[b]	—	—	—	—	—	—
Hydrogen (reactant)		52.1	0.5	47.4	—	—	—

[a] Reaction temperature, 0°C; catalyst, 0.35 g outgassed at 600°C; reaction time, 70 min; reactor 2.8×10^3 ml; reactants, 49 Torr 1,3-butadiene, 112 Torr (H_2 + D_2).

[b] The amount was too small to determine isotopic distribution.

(—CH_3) to olefinic hydrogen (=CH—) was 2.06, and that the peaks of olefinic hydrogen exhibited a 1:2:1 triplet. These results indicate that the two D atoms were located at carbon atoms 1 and 4. Thus, the dideuterio *trans*-2-butene was identified as 1,4-dideuterio-*trans*-2-butene.

The isotopic distributions of the products in the reaction of 1,3-butadiene with a mixture of H_2 and D_2 are given in Table 2. H_2–D_2 equilibration did not practically occur in the presence of 1,3-butadiene. The *trans*-2-butene consisted substantially of nondeuterio (d_0) and dideuterio (d_2) isotopic species.

Reaction of a Mixture of 1,3-Butadiene, cis-2-Butene-d_8, and D_2

A mixture of 1,3-butadiene, *cis*-2-butene-d_8, and D_2 at a ratio of 8:1:20 was allowed to react over the La_2O_3 catalyst outgassed at 600°C. The isotopic distributions of the products are given in Table 3. The isotopic species in the products gave two groups. One group consisted mainly of d_2 isotopic species and included small fraction of d_0, d_1, and d_3 isotopic species. The other group consisted mainly of d_8 isotopic species and small fraction of d_6 and d_7 isotopic species. Apparently, the former resulted from the deuteration of 1,3-butadiene and the latter from the isomerization of *cis*-2-butene-d_8. Among three butenes, *trans*-2-butene consisted mostly of dideuterio isotopic species, which were produced by deuteration of 1,3-butadiene.

Deuteration of 2-Methyl-1,3-Butadiene

The isotopic distributions of the products

TABLE 3

Isotopic Distribution of the Products in the Reaction of a Mixture of 1,3-Butadiene, *cis*-2-Butene-d_8, and D_2[a]

Product	Percentage each product	Percentage each isotopic species								
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1,3-Butadiene	37.1	97.7	0.3	0	0	0	0	0	0	0
1-Butene	1.1	4.7	5.8	61.9	0.4	0	0	0.6	2.7	24.0
trans-2-Butene	45.2	0.5	2.6	96.7	0.1	0	0	0	0	0.1
cis-2-Butene	16.5	1.3	1.3	36.8	0.3	0	0	0.7	4.4	55.2

[a] Reaction temperature, 0°C; catalyst, 0.060 g outgassed at 600°C; reaction time, 180 min; reactor, 977 ml; reactant, 90 Torr 1,3-butadiene, 11 Torr *cis*-2-butene-d_8, 215 Torr D_2.

TABLE 4

Isotopic Distribution of the Products in the Deuteration of 2-Methyl-1,3-butadiene over La_2O_3[a]

Product	Percentage each product	Percentage each isotopic species					
		d_0	d_1	d_2	d_3	d_4	d_5–d_{10}
2-Methyl-1,3-butadiene	77.9	99.4	0.6	0	0	0	0
2-Methyl-2-butene	20.3	2.6	4.5	90.5	2.1	0.3	0
2-Methyl-1-butene	1.7	7.8	5.1	84.1	2.4	0.6	0
3-Methyl-1-butene	0.1	64.2	4.3	28.8	2.2	0.5	0

[a] Reaction temperature, 0°C; catalyst, 0.60 g outgassed at 600°C; reaction time, 360 min; reactor, 2.8×10^3 ml; reactant, 100 Torr 2-methyl-1,3-butadiene, 189 Torr D_2.

in the deuteration of 2-methyl-1,3-butadiene over the La_2O_3 catalyst outgassed at 600°C are given in Table 4. The main product was dideuterio 2-methyl-2-butene. The ^1H NMR spectrum of the 2-methyl-2-butene exhibited a triplet at 5.2 ppm (olefinic 1H), and unsymmetrical doublet at 2.4 ppm (methyl 2H, splitting due to adjacent olefinic H on carbon atom 3). The intensity ratio of the hydrogens of three methyl groups to the olefinic hydrogens was 7.01, which was close to the value of 7 expected if two deuteriums are located on the three methyl groups. Therefore, it was concluded that the main product in the deuteration of 2-methyl-1,3-butadiene over the La_2O_3 catalyst was 2-methyl-2-butene-1,4-d_2.

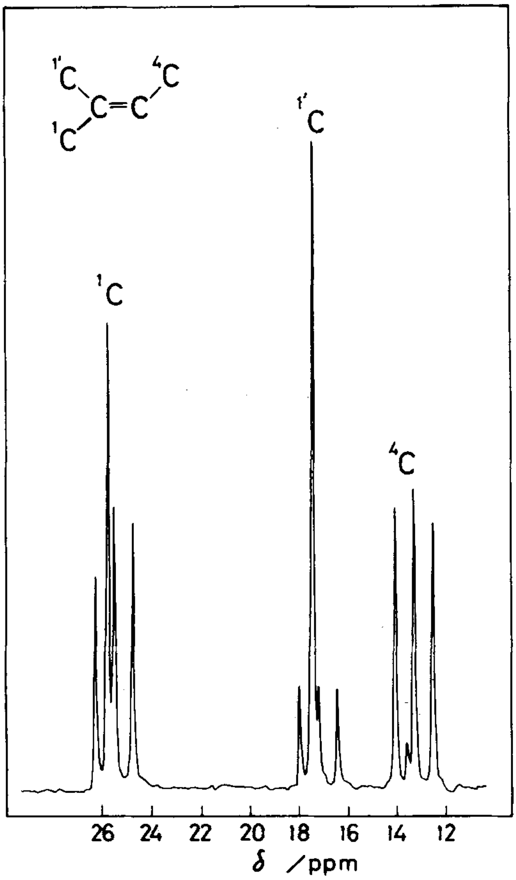


FIG. 3. Carbon-13 NMR spectrum for 2-methyl-2-butene produced in the deuteration of 2-methyl-1,3-butadiene over La_2O_3.

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(4) atom appeared as a triplet, and the signals for the C(1) and C(1′) atoms were singlets superposed with triplets. Integration of the spectrum indicated that the percentages of monodeuterio carbon (CH_2D) in C(4), C(1), and C(1′) were 100, 64, and 36%, respectively. Therefore, the 2-methyl-2-butene-1,4-d_2 consisted of 64% (E)-form and 36% (Z)-form.

Comparison of ThO_2, ZrO_2, MgO with La_2O_3 for cis-2-Butene Isomerization

The ratios of 1-butene to *trans*-2-butene in the *cis*-2-butene isomerization over ThO_2, ZrO_2, MgO, and La_2O_3 are summarized in Table 5. Over ThO_2, ZrO_2, and La_2O_3, double bond migration to 1-butene was much faster than geometrical isomerization to *trans*-2-butene. Over the MgO catalyst, these rates were comparable.

TABLE 5

The Ratio of 1-Butene to *trans*-2-Butene Produced in *cis*-2-Butene Isomerization[a]

Catalyst	Pretreatment temperature (°C)	1-butene/*trans*-2-butene[b]
MgO	1100	1.0
ThO_2	500	3.0
ZrO_2	500	7.3
La_2O_3	600	2.5

[a] Reaction temperature, 0°C; initial pressure, ca. 100 Torr.

[b] Initial value.

DISCUSSION

The variation of the activity of La_2O_3 for the hydrogenation of 1,3-butadiene as a function of outgassing temperature is similar to those for butene isomerization (*4*, *5*) and for the exchange of CH_4 with D_2 (*17*). The activities appeared on outgassing above 500°C and exhibited maxima at about outgassing of 650°C. Both butene isomerization and the exchange of CH_4 with D_2 were suggested to proceed by carbanion mechanisms in which the basic sites on the catalyst were involved (*4*–*6*, *17*).

Rosynek *et al.* (*7*) reported that the ir band intensity of the OH groups on La_2O_3 decreased as the outgassing temperature was raised, and complete disappearance of the band occurred following outgassing at 600 ~ 650°C. They suggested that the active sites for butene isomerization are produced by the removal of surface hydroxyl groups, and involve the presense of both disordered surface anions and exposed underlaying La^{3+} cations in acid–base pair-site configurations. The similarity in the variation of the activity for the hydrogenation to those for the isomerization and the exchange suggests that the hydrogenation of 1,3-butadiene also occurs on such pair-sites.

The formation of *trans*-2-butene-1,4-d_2 as the main product in the deuteration of 1,3-butadiene indicates that the *trans*-2-butene was formed by a direct process of 1,4 addition of deuterium atoms to 1,3-butadiene and not by the secondary process of isomerization of 1-butene or *cis*-2-butene. The formation of *trans*-2-butene-d_2 in the reaction of 1,3-butadiene-d_0, *cis*-2-butene-d_8, and D_2 as a main product supports this conclusion.

Although 1-butene and *cis*-2-butene were minor products in the hydrogenation of 1,3-butadiene, the percentages of non-d_2 species in 1-butene and *cis*-2-butene produced in the deuteration of 1,3-butadiene were greater (~25%) than that in *trans*-2-butene (~6%). The H scrambling was also observed in the hydrogenation with a mixture of H_2 and D_2 (Table 2), and in the deuteration in the presence of *cis*-2-butene-d_8 (Table 3). Taking account of a large amount of *trans*-2-butene as compared with 1-butene and *cis*-2-butene, however, the absolute amounts of the non-d_2 species of *trans*-2-butene produced in the deuteration of 1,3-butadiene were larger than those of 1-butene and *cis*-2-butene. The total amount of non-d_2 species in all butene products was only 9% at the conversion level of 40%. These H scrambling may result either from successive isomerization which partly involves H exchange or from the minor hydrogenation process which involves H exchange and nonselective production of three butenes.

Considering the occurrence of the H scrambling to a small extent, the results of the reaction of 1,3-butadiene and a mixture of H_2 and D_2 given in Table 3 suggest that the molecular identity of hydrogen is retained during the main hydrogenation.

The characteristic features in the hydrogenation of 1,3-butadiene over La_2O_3 are summarized as follows.

(i) The hydrogenation rate for 1,3-butadiene is much greater than that for butenes.

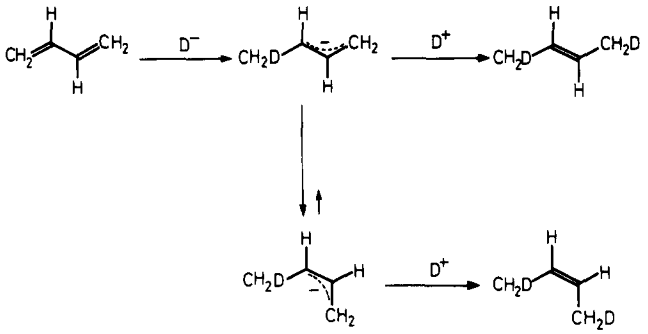
(ii) The hydrogenation of 1,3-butadiene involves the direct 1,4 addition of hydrogen atoms to give primarily *trans*-2-butene.

(iii) Molecular identity of hydrogen is retained during the reaction.

These features are essentially the same as those for ThO_2 (12). Feature (iii) distinguishes certain nonmetallic hydrogenation catalysts from metallic ones, and was observed for Cr_2O_3 (18), Co_3O_4 (19), and ZnO (20) in the hydrogenation of ethylene and for ZnO (21), MoS (22), MgO (10), ZrO_2 (1), and ThO_2 (12) in the hydrogenation of 1,3-butadiene. This feature suggests that two hydrogen atoms formed by dissociative adsorption of one hydrogen molecule on one site do not migrate to other sites, probably because each active site is isolated from others.

As discussed in our previous papers (11, 23), features (i) and (ii) seem to be characteristic of hydrogenation in which anionic intermediates are involved. As for feature (i), since the formation of a π-allylic carbanion from a conjugated diene is much easier than the formation of an alkyl carbanion from an alkene, 1,3-butadiene undergoes much faster hydrogenation than butenes do. As for the preferential occurrence of the 1,4 addition over the 1,2 addition in feature (ii), the electron density of a π-allylic carbanion is the highest at the terminal carbon atom and, therefore, the addition of the second H atom as an H^+ to the terminal carbon atom would selectively occur.

Therefore, the mechanism for the deuteration of 1,3-butadiene could be schematically drawn in Scheme I.



SCHEME I. Deuteration of 1,3-butadiene.

In Scheme I, contribution of the s-*cis* form of 1,3-butadiene was neglected since 1,3-butadiene consisted of 93% s-*trans* conformer and 7% s-*cis* in gas phase at 0°C (12, 24–27). The deuterium molecule is adsorbed by heterolytic splitting to form a D^+ and a D^-. At first, a D^- ion attacks a terminal carbon atom of 1,3-butadiene to form a *trans*-π-allylic carbanion. The *trans*-π-allylic carbanion undergoes either interconversion to a more stable *cis*-π-allylic carbanion or addition of an H^+ to produce *trans*-2-butene. If the interconversion is slow compared with the addition of an H^+ to *trans*-π-allylic carbanion, *trans*-2-butene-1,4-d_2 would be selectively yielded. This was the observed result. The reaction scheme for La_2O_3 is essentially the same as that for ThO_2, but different from that for MgO. Over MgO, *cis*-2-butene was selectively produced in the hydrogenation of 1,3-butadiene (10). The difference in selectivity is interpreted by the difference in the relative rates between *cis–trans* interconversion within π-allylic carbanion and the addition of an H^+ to a *trans*-π-allylic carbanion. The addition is faster for La_2O_3 and ThO_2 while the interconversion is faster for MgO.

Provided that the butene isomerization sites are the same as the 1,3-butadiene hydrogenation sites, the ratio of 1-butene to *trans*-2-butene in *cis*-2-butene isomerization would reflect the easiness of the interconversion between *trans*-π-allylic carbanion and *cis*-π-allylic carbanion. The high values of 1-butene/*trans*-2-butene ratio for

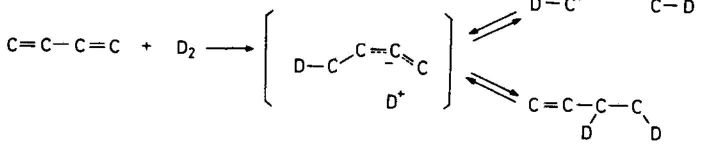
La_2O_3 and ThO_2 and the low value for MgO support the above interpretation.

Recently, Goldwasser and Hall (*6b*) has reported that the interconversion over La_2O_3 needs a high activation energy, 20 kcal/mol. This also supports our view.

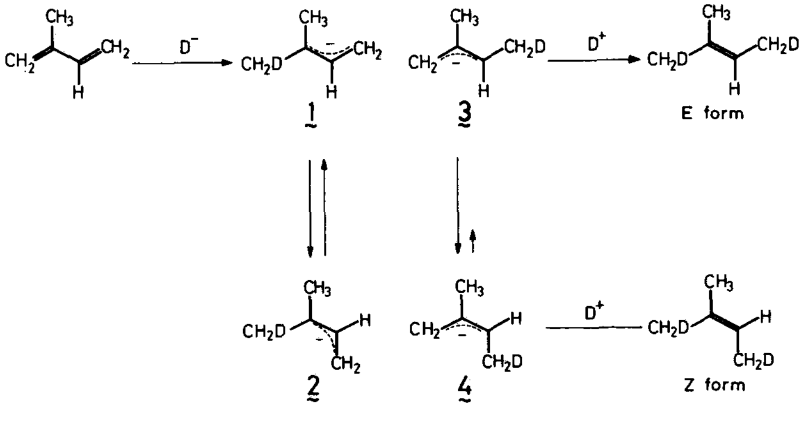
The catalytic behavior of ZrO_2 for hydrogenation studied by Yamaguchi and Hightower (*9*) is similar to those of La_2O_3 and ThO_4. Hydrogenation of 1,3-butadiene yielded mainly *trans*-2-butene by the process in which 1,4 addition of H atoms was involved. The hydrogenation of *cis*-2-butene was much slower than that of 1,3-butadiene. The ratio of 1-butene to *trans*-2-butene was high in *cis*-2-butene isomerization. Although Yamaguchi and Hightower did not consider the ionic character of the intermediate of 1,3-butadiene hydrogenation over ZrO_2, it seems probable that hydrogenation proceeds via the π-allylic carbanion mechanism in which the interconversion between *trans* and *cis*-π-allylic carbanions is slow.

Goldwasser and Hall (*6b*) have discussed the easiness of the interconversion between *trans* and *cis*-π-allylic carbanion in terms of softness of the countercations. As softness increases, the interconversion becomes more difficult if compared in the same group in the periodic table. A fast interconversion on MgO and slow interconversion on La_2O_3 and ThO_2 are consistent with their view, though the cations of these catalysts are not in the same group in the periodic table. To generalize such relation, however, further experimental data are needed.

Tanaka and Okuhara (*28*) proposed the following scheme for the deuteration of 1,3-butadiene over CdO.



They claimed that if the reaction involves an anionic intermediate, the *cis*/*trans* ratio in the 2-butenes should be high because of a greater stability of *cis*-π-allylic carbanion compared with a *trans*-π-allylic carbanion. In this scheme, however, they did not take into account the facts that the 1,3-butadiene molecule exists mostly in the s-*trans* conformation and that the energy barrier for the rotation of the s-*trans* to s-*cis* conformer is as high as about 7 kcal/mol (*24, 25, 29*). They assumed that *cis*-π-al-

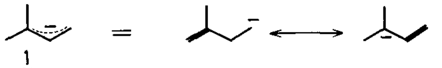


SCHEME II. Deuteration of 2-methyl-1,3-butadiene.

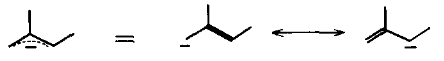
lylic carbanion could be primarily formed directly from 1,3-butadiene.

The dynamic nature of the intermediates in the hydrogenation of 2-methyl-1,3-butadiene over La_2O_3 is different from that for the hydrogenation of 1,3-butadiene. Since 2-methyl-1,3-butadiene consists of 97.8% s-*trans* conformer and 2.2% s-*cis* conformer in gas phase at 0°C (*23*), the reaction scheme for the deuteration of 2-methyl-1,3-butadiene could be drawn in Scheme II.

As shown in Scheme II, two possible D^- additions might occur. The 1,1-dimethyl allyl anion **1** and the 1,2-dimethyl allyl anion **3** are to be formed by addition of D^- to carbon atoms 1 and 4 of the reactant, respectively. The anions **1** and **3** can be considered to have two extreme forms (*30*).



1



3

The extreme forms of the anion **1** are a primary anion and a tertiary anion, while the extreme forms of the anion **3** are a primary anion and a secondary anion. This seems to show the lower stability of the anion **1** as compared to the anion **3**. If the position of D^- addition is determined primarily by the energy level of a resulting anion, the addition of a D^- to the carbon atom 4 to form the anion **3** would be more favorable than the addition to the carbon atom 1 of the 2-methyl-1,3-butadiene molecule. Some uncertainties, however, still remain as to whether the anion **1** or the anion **3** is the reaction intermediate. In our previous paper (*11*), it was supposed that the intermediate might be the anion **1**. The reason was as follows. Since MgO catalyst gave primarily *cis*-2-butene in the hydrogenation of 1,3-butadiene, it was considered that the interconversion between *trans*-π-allylic carbanion and *cis*-π-allylic carbanion was fast on MgO. If, in the hydrogenation of 2-methyl-1,3-butadiene, the intermediate was the anion **3** and the interconversion of the anion **3** to the anion **4** was fast, predominant formation of the Z-form would be expected. The experimental result showed that MgO catalyst gave 60% (E)-forms and 40% (Z)-form. Further studies are required to clarify the real intermediate in the hydrogenation of 2-methyl-1,3-butadiene.

In any case, the formation of 64% (E)-2-methyl-2-butene-1,4-d_2 and 36% (Z)-2-methyl-2-butene-1,4-d_2 suggests that the geometrical structure was retained to some extent during the reaction. The retention of the geometrical structure, however, was not so extensive as in the case of the hydrogenation of 1,3-butadiene. The interconversion between two isomeric π-allylic carbanions occurred at a considerable rate. Considering the case of ThO_2 where the interconversion was slow and 89% (E)-form and 11% (Z)-form were formed, the dynamic nature of the π-allylic carbanion on La_2O_3 is of an intermediate nature between that for MgO and that for ThO_2.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research, No. 454113, of the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. Minachev, K. M., Khodakov, Y. S., and Nakhshunov, V. S., *J. Catal.* **49,** 207 (1977).
2. Rosynek, M. P., and Magnuson, D. T., *J. Catal.* **46,** 402 (1977).
3. Rosynek, M. P., and Magnuson, D. T., *J. Catal.* **48,** 417 (1977).
4. Rosynek, M. P., and Fox, J. S., *J. Catal.* **49,** 285 (1977).
5. Fukuda, Y., Hattori, H., and Tanabe, K., *Bull. Chem. Soc. Japan* **51,** 3150 (1978).
6. (a). Goldwasser, J., and Hall, W. K., *J. Catal.* **63,** 520 (1980). (b). Goldwasser, J., and Hall, W. K., *J. Catal.* **71,** 53 (1981).
7. Rosynek, M. P., Fox, J. S., and Jensen, J. L., *J. Catal.* **71,** 64 (1981).
8. Imizu, Y., Hattori, H., and Tanabe, K., *J. Chem. Soc. Chem. Commun.* 1092 (1978).
9. Yamaguchi, T., and Hightower, J. W., *J. Amer. Chem. Soc.* **99,** 4201 (1977).

10. Hattori, H., Tanaka, Y., and Tanabe, K., *J. Amer. Chem. Soc.* **98,** 4652 (1976).

11. Tanaka, Y., Imizu, Y., Hattori, H., and Tanabe, K., *Proc. 7th Intern. Congr. Catalysis, 1980 Tokyo* **II,** 1254 (1981).

12. Imizu, Y., Tanabe, K., and Hattori, H., *J. Catal.* **56,** 303 (1979).

13. Hattori, A., Hattori, H., and Tanabe, K., *J. Catal.* **65,** 245 (1980).

14. Matsuhashi, H., Hattori, H., and Tanabe, K., *Chem. Lett.* 341 (1981).

15. Nakano, Y., Iizuka, T., Hattori, H., and Tanabe, K., *J. Catal.* **57,** 1 (1979).

16. Abruscato, G. J., Ellis, P. D., and Tidwell, T. T., *J. Chem. Soc. Chem. Commun.* 988 (1972).

17. Utiyama, M., Hattori, H., and Tanabe, K., *J. Catal.* **53,** 237 (1978).

18. Burwell, R. L., Jr., Littlewood, A. B., Cardew, M., Pass, G., and Stoddart, C. T. H., *J. Amer. Chem. Soc.* **82,** 6272 (1960).

19. Tanaka, K., Nihira, H., and Ozaki, A., *J. Phys. Chem.* **74,** 4510 (1970).

20. Conner, W. C., and Kokes, R. J., *J. Phys. Chem.* **73,** 2436 (1969).

21. Naito, S., Sakurai, Y., Shimizu, H., Ohnishi, T., and Tamaru, K., *Trans. Faraday Soc.* **67,** 1529 (1971).

22. Okuhara, T., Tanaka, K., and Miyahara, K., *J. Chem. Soc. Chem. Commun.* 42 (1976).

23. Tanaka, Y., Hattori, H., and Tanabe, K., *Chem. Lett.* 37 (1976).

24. Tai, J. C., and Allinger, N. L., *J. Amer. Chem. Soc.* **98,** 7928 (1976).

25. Carreira, L. A., *J. Chem. Phys.* **62,** 3851 (1975).

26. Lipnick, R. L., and Garbisch, E. W., Jr., *J. Amer. Chem. Soc.* **95,** 6370 (1973).

27. Smith, W. B., and Massingil, J. L., *J. Amer. Chem. Soc.* **83,** 4301 (1961).

28. Tanaka, K., and Okuhara, T., *J. Catal.* **61,** 135 (1980).

29. Radom, L., and Pople, J. A., *J. Amer. Chem. Soc.* **92,** 4786 (1970).

30. Pines, H., and Stalick, W. M., *in* "Base Catalyzed Reactions of Hydrocarbons and Related Compounds." Academic Press, New York, 1977.