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Intermediates of Hydrogenation of Conjugated Dienes and of the Isomerization of *n*-Butenes on CdO Catalyst

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The deuteration of butadiene on CdO gives 55% but-1-ene and 45% *cis*-but-2-ene with maintenance of deuterium molecular identity in either the 1,2- or the 1,4-addition. The isomerization of *cis*-but-2-ene to but-1-ene or vice versa occurred easily on CdO but the *cis–trans* interconversion was very slow. The hydrogenation of butadiene proceeds through the π-allyl anion, and the double-bond migration of butenes also occurs through a common intermediate, the π-allyl anion. It was clearly shown that the π-allyl anion formed on CdO is reactive for both 1,2- and 1,4-addition in the hydrogenation of butadiene. Accordingly, it is concluded that the selective 1,4-addition cannot be a sign of π-allyl anion intermediates but the *cis/trans* ratio in the 1,4-addition may be a good sign of π-allyl anion intermediates.

INTRODUCTION

Since Burwell and his co-workers (*1*) found a unique nature of chromium oxide for the catalytic hydrogenation of ene and/or yne compounds, similar characteristics, maintenance of hydrogen molecular identity in the hydrogenated products, have been found on Co_3O_4 (*2*) and on ZnO (*3*). The hydrogenation of butadiene on ZnO catalyst gives more than 90% but-1-ene and several percent *cis*-but-2-ene. A careful study of the deuteration of butadiene on ZnO proved that the 1,2-addition giving but-1-ene as well as the 1,4-addition giving *cis*-but-2-ene retain the deuterium molecular identity in the products (*4*). More recently, the hydrogenation of butadiene has been performed on various oxides, but no general trend exists in selectivity for 1,2- and/or 1,4-additions. For example, Co_3O_4 and MgO prefer the 1,4-addition but the 1,2-addition prevails on Cr_2O_3 and on ZnO. Accordingly, it may be a wrong idea that the 1,4-addition is a characteristic of basic oxides on which hydrogenation proceeds through π-allyl anion intermediates (*5*). This paper provides evidence that the π-allyl anion formed on CdO is reactive for both the 1,2- and the 1,4-additions.

The interesting question why CdO and MgO are active for the hydrogenation of conjugated dienes but not for the hydrogenation of olefins and for the H_2–D_2 equilibration reaction will be discussed from the viewpoint of ionic and nonionic intermediates, and a new general concept about this problem will be presented in a future paper.

EXPERIMENTAL

The reaction was performed in a conventional closed circulation system of about 340 ml of total volume. The analysis of the component gases was carried out by on-line gas chromatography. The mass spectroscopic analysis of deutero compounds was carried out at 12-eV ionization voltage, and the deuterium distribution was calculated by using the parent peaks. The analysis of H_2, HD, and D_2 was performed with 70-eV ionization voltage. Cadmium oxide (Kishida Chemicals Co.) was activated by evacuating at about 450°C for 4–5 hr. Samples which had been pretreated with oxygen

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or with carbon monoxide at 450°C gave the same results when the samples were activated by the same procedure. The purification of gases, butadiene, butene, H_2, and D_2 was described in the previous paper (*6*).

RESULTS AND DISCUSSION

Cadmium oxide evacuated at 450°C has no catalytic activity for the H_2–D_2 equilibration reaction at room temperature as shown in Table 1, where the values in parentheses are the results of a different run with renewed catalyst. It has been accepted that catalysts active for the hydrogenation reaction of olefins are also active for the H_2–D_2 equilibration reaction. This rule holds for CdO catalyst too, that is, CdO shows no catalytic activity for the hydrogenation of olefins; 25 mm Hg but-1-ene with 90 mm Hg H_2 gave 0.2% butane in 120 min at room temperature.

However, if a mixture of hydrogen and butadiene was added onto this catalyst, the hydrogenation of butadiene occurred at room temperature. The results of the reaction between butadiene (25.1 Torr) and D_2 (109.0 Torr) at room temperature are shown in Table 2, where the main products are but-1-ene-d_2 and *cis*-but-2-ene-d_2. The NMR spectroscopic analysis of these products proved that deuterium's molecular identity is maintained in both the 1,2- and 1,4-additions which gave 1,2-d_2-but-1-ene and 1,4-d_2-*cis*-but-2-ene. Conservation of deuterium molecular identity in the two types of hydrogen addition was reported on ZnO catalyst (*4*). In the case of ZnO, the hydrogenation of butadiene yields more than 90% but-1-ene and several percent *cis*-but-2-ene, but deuterium atoms are retained on the 1,2- and 1,4-positions, respectively. The relative contribution of the 1,4-addition of hydrogen to butadiene on CdO was about 45% at lower conversion as shown in Fig. 1. This value is apparently smaller than that on MgO (*7*), but is larger than that on ZnO. This fact may indicate that selectivity for the 1,4-addition of hydrogen to butadiene is not a unique characteristic being reflected in π-allyl anion intermediates. In fact, the hydrogenation of butadiene on Co_3O_4 gives about 80% but-2-ene although a π-allyl anion intermediate is improbable. It is worth mentioning that the 1,4-addition on basic oxides such as CdO, MgO, and ZnO favors the formation of *cis*-

TABLE 2

Deuteration of Butadiene at Room Temperature on 1.0 g CdO[a]

(a) Product Distribution

Time (min)	Conversion (%)	But-1-ene (%)	*trans*-But-2-ene (%)	*cis*-But-2-ene (%)
30	5.3	37.9	5.7	56.4
100	10.6	29.4	8.5	62.1
205	15.9	24.3	10.1	65.6

(b) Deuterium Distribution

Time (min)	Butadiene (%)	But-1-ene (%)	*trans*-But-2-ene (%)	*cis*-But-2-ene (%)
30				
d_0	99.2	0	—	7.4
d_1	0.8	16.6	—	20.2
d_2	0	81.8	—	71.5
d_3	0	1.5	—	0.7
100				
d_0	97.5	0	0	3.9
3d$_1$	2.5	14.8	19.3	20.2
d_2	0	80.1	80.3	73.9
d_3	0	5.1	0.4	2.0
205				
d_0	95.5	2.2	7.1	3.7
d_1	4.5	13.2	18.0	19.6
d_2	0	76.3	72.6	73.3
d_3	0	8.2	2.3	3.4

[a] Butadiene, 25.1 mm Hg; D_2, 109.0 mm Hg.

TABLE 1

H_2–D_2 Equilibration on 1.0 g CdO at Room Temperature

Time (min)	H_2 (%)	HD (%)	D_2 (%)	Total pressure (mm Hg)
0	51.0 (55.7)	0.4 (1.0)	48.6 (43.4)	25.0 (35.0)
150	52.5 (55.7)	0.4 (1.7)	47.1 (42.5)	

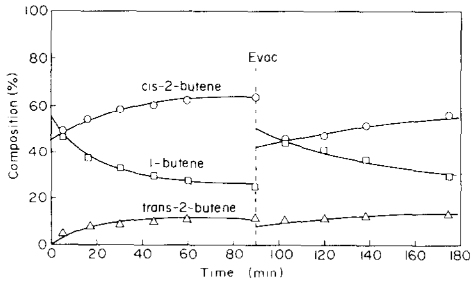


FIG. 1. Hydrogenation of butadiene on CdO at room temperature. Reactant gas was renewed at broken line.

but-2-ene over that of trans-but-2-ene. In contrast, the 1,4-addition on transition metal oxides gives a value for the *cis*/*trans* ratio smaller than unity. Such a significant difference between the basic oxide and transition metal oxide may be explained by the properties of the intermediates, either ionic or nonionic, as will be discussed later in this paper and in more detail in a future paper.

Another interesting feature of CdO is that the composition of *n*-butenes changes during hydrogenation of butadiene as shown in Fig. 1. Two reasons may be considered for this phenomenon: one is a gradual variation of the CdO surface which results in a change in selectivity of the 1,2- and 1,4-additions in the hydrogenation reactions, and the other is simultaneous isomerization of but-1-ene during hydrogenation of butadiene. To clarify this problem, the ambient gas was removed quickly in the process of the hydrogenation of butadiene and the hydrogenation of butadiene was repeated on the same catalyst as shown in Fig. 1.

It is obvious that the catalyst surface does not change during the hydrogenation reaction because the restarted hydrogenation gives the same selectivity as obtained in the preceding run. Accordingly, it is concluded that but-1-ene formed by the 1,2-addition of hydrogen to butadiene is subsequently isomerized during hydrogenation of butadiene.

The hydrogenation of other conjugated dienes such as isoprene and 1,3-pentadiene was also performed on CdO catalyst, and the results are summarized in Table 3, where the 1,4-addition of isoprene gives 2-methyl but-2-ene and the 1,2-addition gives 3-methyl but-1-ene and 2-methyl but-1-ene, respectively.

The relative contribution of the 1,2- and 1,4-additions seems to differ little for different dienes. An empirical rule shows that the hydrogenation of isoprene on heterogeneous catalysts favors the formation of 2-methyl but-1-ene over the formation of 3-methyl but-1-ene, but the hydrogenation in homogeneous catalyst gives the reverse selectivity (*6*). This selectivity for 1,2- or 3,4-addition of hydrogen to isoprene was explained by a steric interaction of the methyl group.

As shown in Table 2, CdO undoubtedly has a selectivity quite different from most heterogeneous catalysts. In general, active sites for the hydrogenation reaction on the transition metal oxide require a specific structure such as three degrees of coordinative unsaturation (*8*). In contrast, the hydrogenation reaction through ionic intermediates such as the π-allyl anion or the carbonium

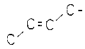
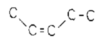
TABLE 3

Hydrogenation of Isoprene and 1,3-Pentadiene on 4.0 g CdO at Room Temperature

(a) Isoprene (16.2 mm Hg) + D_2 (38.8 mm Hg)

Time (min)	Conversion (%)	$C-\overset{C}{C}-C=C$ (%)	$C=\overset{C}{C}-C-C$ (%)	$C-\overset{C}{C}=C-C$ (%)
55	2.2	24.9	12.7	62.4
130	3.8	27.8	12.5	59.7
1200	13.1	23.6	8.7	67.8

(b) 1,3-Pentadiene (16.8 mm Hg) + D_2 (47.2 mm Hg)

Time (min)	Conversion (%)	$C=C-C-C-C$ (%)	 (%)	 (%)
30	13.9	23.2	22.9	53.9
50	19.7	19.8	28.0	52.0
110	22.8	17.6	28.0	54.5
180	27.0	16.7	28.6	54.7

cation would require no such specific structures for active sites because the formation of intermediates in this type of reaction is controlled by the basic or acidic strength of the surface. The different selectivity on CdO is perhaps due to less structure sensitivity of the hydrogenation reaction on CdO.

As shown in Fig. 1, the isomerization of but-1-ene can proceed on CdO in the presence of butadiene. If but-1-ene (15 Torr) is added alone to CdO catalyst, but-1-ene is selectively isomerized to *cis*-but-2-ene as shown in Fig. 2. On the other hand, if *cis*-but-2-ene (20 torr) is added to CdO catalyst, the isomerization to but-1-ene prevails over the *cis–trans* interconversion as shown in Fig. 3. Preferential but-1-ene formation from *cis*-but-2-ene is a rather unique characteristic, because the ratio but-1-ene/*trans*-but-2-ene is usually smaller than unity on almost all catalysts, even ZnO (*9*) and CaO (*10*).

One exception is known, the La_2O_3 catalyst, on which double-bond migration is preferential to the *cis–trans* interconversion (*11*). It is known that the *anti*-π-allyl anion is more stable thermodynamically than the *syn*-π-allyl anion, so that the *anti*-π-allyl anion formation is favored in the isomerization of but-1-ene, which results in giving *cis*-but-2-ene selectively, and the reverse isomerization gives but-1-ene. However, it is known that a direct interconversion between the *syn*- and *anti*-allyl conformations occurs on ZnO (*12*), and the barrier of this interconversion may depend on oxides.

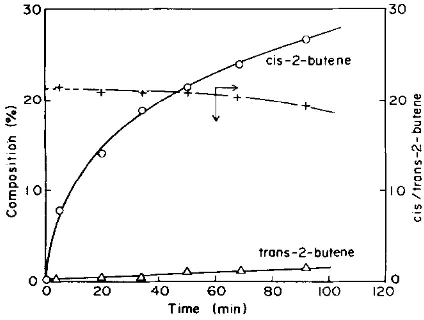


FIG. 2. Isomerization of but-1-ene on CdO at room temperature.

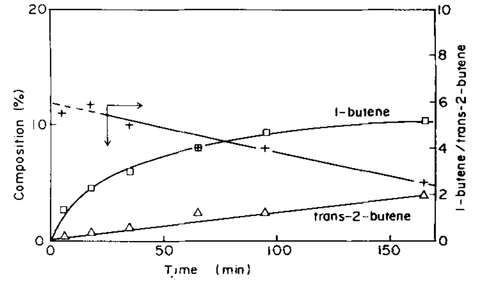
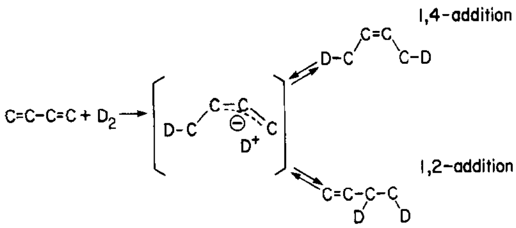


FIG. 3. Isomerization of *cis*-but-2-ene on CdO at room temperature.

Thus far the isomerization of *n*-butene and the hydrogenation reaction of butadiene have been studied from different viewpoints. However, the isomerization of *n*-butenes via allylic intermediates should closely relate to the hydrogenation of butadiene, because both reactions may proceed through a common intermediate. The results obtained on CdO seem to provide a typical example where the hydrogenation of butadiene and the isomerization of *n*-butenes proceed through a common intermediate, the π-allyl anion. This is described in Scheme 1.



Scheme I

The isomerization of *n*-butenes taking place on transition metal oxides may occur by either a hydrogen addition mechanism or a hydrogen abstraction mechanism. The former proceeds through a *sec*-butyl intermediate and the latter occurs via σ- or π-allyl intermediates. Isomerization via the *sec*-butyl intermediate usually needs the presence of hydrogen, but isomerization through allyl intermediates can proceed without hydrogen and sometimes hydrogen retards the reaction as was observed on Cr_2O_3 (*13*).

The isomerization reaction via *sec*-butyl intermediates is usually inhibited strongly by a small amount of butadiene. In contrast, the isomerization reaction on CdO proceeds in the presence of butadiene as shown in Fig. 1, and this phenomenon is well explained by the above scheme through a common intermediate.

The fact that *cis*-but-2-ene is converted to but-1-ene via a π-allyl anion intermediate may prove that a π-allyl anion may react not only in the 1,4-addition but also in the 1,2-addition. Accordingly, it is an incorrect hypothesis that the hydrogenation of butadiene through π-allyl anion would give 1,4-addition selectively (*5*). In contrast to the π-allyl anion, nonionic π-allyl intermediates formed on transition metal oxides may favor the *syn* conformation because of steric interactions. Accordingly, the *cis*/*trans* ratio in the 1,4-addition of butadiene may be adopted as a good indicator of anionic or nonionic allyl intermediates. In fact, the 1,4-addition on such basic oxides as CdO, MgO, and ZnO gives a high *cis*/*trans* ratio, but the *cis*/*trans* ratio in the 1,4-addition on transition metal oxides is usually smaller than unity. The hydrogenation of olefins may not occur on CdO and on MgO because of the difficulty of anionic intermediate formation compared with conjugated dienes. On the other hand, the hydrogenation of dienes on transition metal oxides occurs on specific sites on which olefins can be hydrogenated.

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