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The Mechanism of the Catalytic Hydrogenation of Propene on Nickel, Palladium, and Platinum (The Application of Microwave Spectroscopy to Isotopic Analysis)[1]

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The catalytic hydrogenation of propene with deuterium gas and its isotopic exchange reaction with deuterium oxide have been carried out at room temperature, and the remaining propene has been subjected to microwave spectroscopic analysis so as to determine the isotopic isomer-distribution of propene-d_1 and -d_2. From the results, the following conclusions have been drawn: (1) the rate-determining step in the hydrogenation on platinum as well as nickel and palladium catalysts is the addition of hydrogen to the half-hydrogenated species; (2) the kinds of chemisorbed species and their distribution prior to the rate-determining step are not always the same, but depend on the metals, and (3) the life-time of the chemisorbed propene is shorter than the successive time interval of its exchange process on nickel, but this is not the case on platinum nor, probably, on palladium.

In previous reports,[3,4] the chemisorbed states of propene on nickel and palladium catalysts were investigated on the basis of the subspecies-distributions[5] of propene-d_1 in the products of the exchange and hydrogenation reaction with deuterium gas and deuterium oxide:

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[3] J. Hirota and Y. Hironaka, *J. Catalysis*, **4**, 602 (1965); K. Hirota, Y. Hironaka and E. Hirota, *Tetrahedron Letters*, **1964**, 1645.

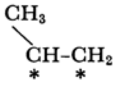
[4] Y. Hironaka and K. Hirota, This Bulletin, **38**, 1558 (1965).

[5] Subspecies may be called "isotopic isomers."

$$C_3H_6 + nD_2 \rightarrow C_3H_{8-y}D_y, \text{ and } C_3H_{6-x}D_x, \quad (1a)$$

$$C_3H_6 + nD_2O \rightarrow C_3H_{6-x}D_x. \quad (1b)$$

It has been proposed that the main chemisorbed states of propene are the associative-type I on nickel and the π-allyl-type II on palladium. In addition, both reactions were found to occur with the half-hydrogenated state, C_3H_7, as an intermediate.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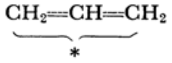

II

Since these findings are very important to a discussion of the mechanism of catalytic hydrogenation, a similar investigation was made of platinum, using the mass spectrometric and microwave-spectroscopic methods in the analysis, as adopted in previous reports. The object of the present paper is not only to report the new knowledge obtained and to discuss it from the standpoint of the mechanism of catalytic hydrogenation in general, but also to report the superiority of microwave spectroscopy for isotopic analysis.

Experimental

The platinum catalyst was prepared from chloroplatinum acid by reduction with formaldehyde.

The other materials and procedures were the same as those in the cases of nickel and palladium.[3,4] The subspecies distribution of propene-d_2 in the product was determined, as was that of propene-d_1, by applying the microwave spectroscopic method to the samples, without any separating procedure.

The reaction times in both reactions were selected in such a way that the parameter, $\psi = \frac{1}{6}\sum_x x d_x$, an indication of the exchange degree, took a value similar to that of nickel and palladium (about 10%). (Cf. Table I (A))

Results

Table I (B) shows the isotopic distribution of the deuteropropenes remaining after the reactions. Deuteropropenes with higher x values can be observed, because d_5 and d_6 were negligibly small in the cases of most nickel and palladium catalysts.

The distribution of deuterium in the propene-D_2 system was slightly wider than that in the propene-D_2O system when Ni and Pd were used as catalysts, but, according to the present research, the deuterium-distribution of the proepene-D_2O system is, on the contrary, wider than that of the propene-D_2 system.

In the subspecies distrubtion of propene-d_1, shown in Table II, the characteristic differences of the three catalysts are obvious. There is a tendency for the methylene group to be most exchangeable on platinum, though only the methine group was easily exchanged in the case of nickel; there is also a difference in the case of palladium, by which all the three groups were exchanged with nearly equal probabilities. However, it is

TABLE I. EXPERIMENTAL CONDITIONS AND DEUTERIUM-DISTRIBUTION OF REACTION PRODUCTS

(A) Experimental condition

No.	Catalyst	g.	Sample (mole × 10^{-3})				Reaction	
			C_3H_6	D_2O	D_2	C_3H_6/D_2	Temp.	Time
5505	Pt-black	0.50	2.18	—	1.09	2.0	20°C	20 min.
41017	Pt-black	0.30	2.18	9.9	—	—	25°C	100 hr.

(B) Distribution of deuterium in remaining propene (%)

No.	d_0	d_1	d_2	d_3	d_4	d_5	d_6	$\psi=\frac{1}{6}\sum x d_x$
5505	60.6	21.9	9.5	4.7	2.6	0.7	—	11.5
41017	53.5	26.9	8.9	4.9	2.7	1.9	1.1	14.7

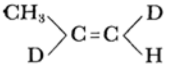
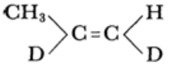
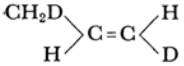
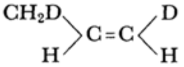
TABLE II. DISTRIBUTION OF SUBSPECIES (%) OF PROPENE-d_1*

No. of run subspecies	5505 Pt, D_2O	41017 Pt, D_2O	3513** Ni, D_2O	3515** Pd, D_2O
CH_2D-CH=CH_2	21.1±1.7	19.5±2.1	22.5±2.7	59.2±2.2
	(7.0)	(6.5)	(7.5)	(19.7)
t-CH_3-CH=CHD	39.1±3.3	47.4±4.8	9.5±2.1	13.1±1.3
c-CH_3-CH=CHD	13.1±2.5	5.8±1.4	9.9±2.2	13.7±1.5
CH_3-CD=CH_2	26.7±3.6	27.3±4.5	58.1±5.1	14.1±1.3

* Trans- and cis-form denotes the position of deuterium against the CH_3 group.

** These two runs, reported already, were shown for the sake of comparison.

TABLE III THE SUBSPECIES DISTRIBUTION OF PROPENE-d_2 IN THE PRODUCTS OF THE METAL/D_2O SYSTEMS

Subspecies		Ni		Pd		Pt	
		Obs.	(Calcd.)	Obs.	(Calcd.)	Obs.	(Calcd.)
CHD_2-CH=CH_2	3,3-d_2	10.0	(11.3)	25.4	(43.6)	25.5	(6.4)
CH_2D-CD=CH_2	2,3-d_2	38.7	(39.6)	19.0	(14.8)	12.1	(24.3)
	*trans*-1,2-d_2	15.8	(17.1)	5.4	(3.5)	8.7	(4.0)
	*cis*-1,2-d_2	17.1	(17.1)	5.6	(3.5)	18.4	(32.4)
CH_3-CH=CD_2	1,1-d_2	4.9	(2.8)	7.5	(3.4)	15.8	(6.8)
	*trans*-1,3-d_2	6.9	(6.8)	18.7	(15.6)	15.9	(23.1)
	*cis*-1,3-d_2	7.1	(6.8)	18.4	(15.6)	3.7	(2.8)

important in the case of platinum that the exchange degree of CH_3CH=CHD is not the same as between its cis- and trans-forms, irrespective of which is used, deuterium gas (No. 5505) or deuterium oxide (No. 41017). Considering this, the same tendency may exist in the case of the Pd/D_2O system,[3] though it is at present difficult to derive such a conclusion because the difference lies within the limits of experimental error.

The above findings can also be confirmed qualitatively by the clear difference in the infrared spectra of the products obtained by the use of the the three catalysts.

In Table III, the subspecies distribution of propene-d_2 is shown in addition to the data on Ni and Pd, which have already been mentioned.[3] The discrepancies among the distributions of the three catalysts and the calculated values shown in brackets will be discussed below.

Discussion

The Half-hydrogenated State. — In view of the similarity between the two reactions, 1a and 1b, in the substancies distribution of C_3H_6-d_1 (Table II), it can be said that the catalytic hydrogenation proceeds on platinum via the half-hydrogenated state, C_3H_7, in the same scheme as on nickel and palladium, making the step A rate-determining at room temperature. In other words, the exchange reaction occurs by the back ward process of the step B

$$\underset{*}{C_3H_6}\ \underset{(B)}{\underset{-H}{\overset{H}{\rightleftarrows}}}\ \underset{*}{C_3H_7}\ \underset{(A)}{\xrightarrow{H}}\ C_3H_8 \qquad (2)$$

$$\underset{*\,*}{C_3H_6} + \underset{*}{D} \rightarrow \underset{*}{C_3H_6D} \rightarrow \underset{*\,*}{C_3H_5D} + \underset{*}{H} \qquad (3)$$

because the coincidence of No. 5505 and No. 41017 in the subspecies distribution of propene-d_1 is too close for the other reaction schemes to be possible.

However, in deriving this conclusion, it must be remembered that the water molecule is, as usual, assumed to exist dissociatively on the metal surface.

$$H_2O \longrightarrow \underset{*}{HO} + \underset{*}{H} \qquad (4)$$

Though the non-dissociative adsorption of water molecule is also possible on some parts of metal surfaces,[6] the state seems to be indifferent to the present exchange reaction in view of the above results.

Such being the situation, the scheme of Eq. 3 may be justified, and the so-called Rideal mechanism, Eq. 5, seems to be implausible; i. e., the possibility that the half-hydrogenated state is formed only by the reaction of the hydrogen molecule and chemisorbed propene in one step[7] is of less importance.

$$\underset{*\,*}{C_3H_6} + H_2 \longrightarrow \underset{*}{C_3H_7} + \underset{*}{H} \qquad (5)$$

However, the scheme of the exchange reaction, Eq. 1b, proposed on nickel may not necessarily be derived. The scheme of the reaction may be different on palladium and on other metals. The chemisorbed states[8] of propene are not always the same; rather, they may differ according to the metals as well as according to the reaction conditions. These points will be investigated below.

The Distribution of the d_1 Subspecies.— The characteristic features of the activity of platinum, clarified by the subspecies distribution of propene-d_1, suggest that some new chemisorbed species is produced from propene on platinum simultaneously with the associative state which is

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[6] G. C. Bond, "Catalysis by Metals," Academic Press, New York (1962), p. 219.

[7] G. H. Twigg, *Discussions Faraday Soc.*, **8**, 152 (1950).

[8] Besides, there is a possibility that the associative state, $\underset{*\,*}{C_3H_6}$, is π-bonded rather than σ-bonded to the surface on some metals.

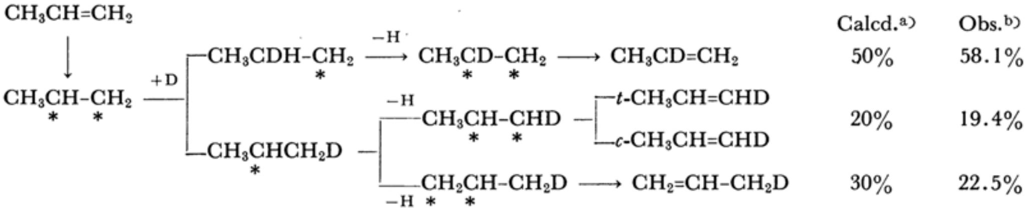
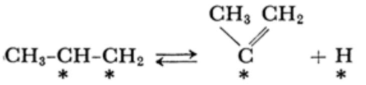


Fig. 1. Scheme of the associative mechanism of the exchange reaction.

a) Percentage of the products on the right side are calculated by neglecting the isotopic effect during hydrogenation and dehydrogenation.

b) The result of Ni/D_2O system (No. 3513) is shown for the sake of the comparison.

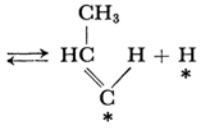
predominant on nickel. In explanation of this, the existence of a dissociative state may be suggested; such a state would especially explain the predominance of the trans-form over the cis-form of $CH_3\text{–}CH{=}CHD$ in the product. Such a suggestion is not new, because the state has already been mentioned on platinum by Farkas[9] and has been proposed by Burwell,[10] who expressed the states as follows:



$$\underset{*}{CH_3\text{-}CH}\text{-}\underset{*}{CH_2} \rightleftarrows \underset{*}{\overset{CH_3\ CH_2}{C}} + \underset{*}{H} \tag{6a}$$

(IIIa)

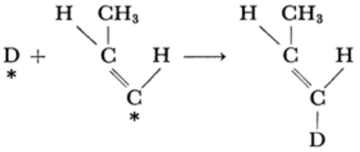
or



$$\rightleftarrows HC(CH_3){=}\underset{*}{C}H + \underset{*}{H} \tag{6b}$$

(IIIb)

Both dissociative states, IIIa and IIIb, are convenient in explaining the broad distribution of deuterated propenes. Of the two dissociative states, however, the state IIIb, $CH_3\text{-}CH{=}\underset{*}{CH}$, would be more abundant, because less CH_3CDCH_2 is produced than the sum of *trans*- and *cis*-CH_3-CHCHD. The chemisorbed species may lie on the metal plane perpendicularly because of the steric hindrance of the methyl group. Therefore, the exchange occurs as follows:



$$\underset{*}{D} + HC(CH_3){=}\underset{*}{C}H \longrightarrow HC(CH_3){=}C(D)H \tag{7}$$

On the other hand, an alternative explanation on the basis of the associative chemisorbed state is possible; i. e., because of the presence of the methyl group, the propene may not be chemisorbed parallel to the metal plane, but may take an inclined state. However, the production of the trans-form from such a state is hard to explain without introducing another assumption into the exchange process.

Parallel with the dissociative process, the exchange reaction on platinum may be realized by the associative process proposed for on nickel; it is shown diagramatically in Fig. 1. According to this scheme, the production of 3-d_1, 2-d_1 and, *t*- and *c*-1-d_1 can be explained quantitatively, because the isotopic effect can be neglected, and the subspecies distribution of propene-d_1 can be given by Eq. 8 on the assumption that the addition of D to $\underset{*}{CH_3CH}\text{–}\underset{*}{CH_2}$ occurs at an equal rate:

$$3\text{-}d_1 : 2\text{-}d_1 : (t+c)\text{-}1\text{-}d_1 = 3 : 5 : 2 \tag{8}$$

The application of Eq. 8 to the data of nickel gives a semi-quantitative coincidence between theory and experiment. However, the Pt/D_2O system (No. 41017) gives a different result. By assuming the associative mechanism on platinum, the amounts of *c*-1-d_1 and *t*-1-d_1 are made equal to be 5.8% and the percentages of other subspecies are calculated (cf. Table IV). It is evident from the table that, except for *t*-1-d_1, the amounts agree well with the calculated values.

TABLE IV. THE ISOTOPIC DISTRIBUTION OF THE PROPENE-d_1 PRODUCED ON PLATINUM CATALYSTS (%)
(Run: No. 41017)

	c-1-d_1	*t*-1-d_1	3-d_1	2-d_1
Obs.	5.8	47.8	19.5	27.3
Calcd.	(5.8)	(5.8)	19.4	29.0

This indicates that the difference between 47.8 and 5.8% (i. e., 42.0%) in *t*-1-d_1 results from the occurrence of the dissociative mechanism, while the residual 5.8% results from that of the associative mechanism.

Finally, it must be mentioned that, by the associative mechanism, the d_1-distribution of Pd/D_2O cannot be explained at all. Judging from the above reasoning, the dissociative mechanism may possibly play some role in the exchange reaction in the case of palladium as well as in those of platinum.

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[9] A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **60**, 22 (1938).

[10] R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

Distribution of Propene-d$_2$.—In Table III, the calculated subspecies distribution of propene-d$_2$ is shown in parentheses. Those values have been obtained on the assumption that the second exchange occurs independently and in the same way as that of the first. In the case of nickel, the values coincide well, indicating that the second exchange occurs independently of the first exchange. This finding, already reported by Morino and Hirota,[11] can be explained by the fact that the desorption of the propene-d$_1$ produced occurs at a faster rate than the second exchange process at the same chemisorbed state. However, since no such tendency is indicated in the case of platinum, the chemisorbed state on this metal may have a life-time sufficient to allow both processes to have some correlation. Of course, it cannot be said, from the results shown in Table III alone, that the lifetime of chemisorbed propene on platinum is longer than that on nickel.

As for palladium, an intermediate property of nickel and platinum is suggested in the present distribution, as it is in the propene-d$_1$ distrubtion. Such a result may be brought about from the adsorbed state on palladium, which is of the π-allyl type, as has been suggested in a previous paper.

Conclusion

As far as the reaction conditions in the present paper are concerned, the following conclusions are obtained: (i) the rate-determining step in the catalytic hydrogenation on nickel, palladium and platinum is the addition of hydrogen to the half-hydrogenated species, C_3H_7; (ii) the kinds of chemisorbed species and their distribution prior to the rate-determining step, however, vary with the metal, and (iii) the life-time of the chemisorbed propene is shorter than the successive interval of its exchange process so far as nickel is concerned, while this may not be true in the case of platinum and probably in that of palladium as well.

It must be mentioned, however, that further investigations are now going on in order to investigate if the above conculsions, especially Eq. 2, are applicable to these metals irrespectively of their methods of preparation and the presence of carriers.

We wish to express our sincere thanks to Professor Yonezo Morino and Dr. Eizi Hirota, the University of Tokyo, for their discussions and help in performing the present research.

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[11] Y. Morino and E. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **85**, 535 (1964).