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Rate Analysis of Elementary Steps in Propene Hydrogenation over Evaporated Rhodium Film

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The hydrogenation of propene over evaporated Rh film was studied at temperatures from −44 to 0°C using deuterium as a tracer. The initial formation rates of all isotopic isomers in hydrogen, propene, and propane were measured with a mass spectrometer and the position of the deuterium atom in propene-d_1 was determined by microwave spectroscopy. On the basis of these experimental results, the rates of elementary steps were determined by a proposed method. The results show that the adsorption of propene and hydrogen is slow but the half-hydrogenation of adsorbed propene is several times faster than the overall hydrogenation, and the *sec.*-propyl intermediate contributes more to the hydrogen exchange between propene and hydrogen than does the *normal*-propyl intermediate.

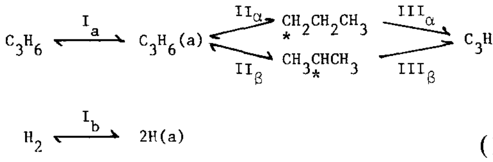
1. INTRODUCTION

There are many studies on the rate analysis of elementary steps in ethylene hydrogenation over metallic catalysts (*1–4*), but few studies have been made for the rate analysis of propene hydrogenation probably due to its complexity. Kemball's method (*3*), which has often been used in the former (*3, 4*), is almost useless in the latter because 80 simultaneous equations must be solved. A method of the analysis more easily applicable to propene hydrogenation was proposed by Yasuda and Hirota (*5*). Hirota *et al.* (*6*) applied it to the reaction over Cu and concluded that propene adsorbs rapidly while hydrogen adsorbs slowly and the adsorbed propene is more rapidly half-hydrogenated to an *n*-propyl intermediate than to a *sec.*-propyl intermediate. Their method is, however, quite complicated in practical use and is not able to determine some elementary step rates. In addition, their analysis of the experimental results (*6*) is partly inexact as will be described later. Our purpose in the present study is to determine the rates of elementary steps in propene hydrogenation over Rh by our own method, which has some advantages when compared to the method of Yasuda and Hirota (*5*).

Rhodium is the most active metal for olefin hydrogenation while Cu shows much less activity (*7*). It is therefore interesting to compare the catalytic properties of these metals for elementary steps in propene hydrogenation. The results of this study will also be discussed with reference to the results obtained for ethylene hydrogenation over Rh in a previous study (*8*).

2. METHOD OF ANALYSIS

An associative mechanism is adopted in the present rate analysis and each constituent step is denoted as shown in Scheme (1),



(1)

where (a) signifies an adsorbed state and an asterisk (*) denotes the adsorption bond of adsorbed propyls. The forward and backward rates of these steps may be determined by using deuterium as a tracer. We discuss first methods of the rate analysis

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and then apply them to experimental results.

The symbols used are as follows:

V	overall rate of propene hydrogenation,
$v_+(s)$, $v_-(s)$	forward or backward rate of step s
V^{E_l}	formation rate of propene-d_l,
V^{A_n}	formation rate of propane-d_n,
V^{H_2}, V^{HD}	formation rate of H_2 or HD,
x_l	fraction of propene-d_l in adsorbed propene,
y_H, y_D	fraction of H(a) or D(a) in adsorbed hydrogen ($y_H + y_D = 1$).

Other symbols are defined in the text as they appear. "Hydrogen" is a term for all hydrogen isomers (H_2, HD, and D_2).

Any isotopic effects are ignored in order to simplify the analysis.

2.1. *Relations between Elementary Step Rates*

The steady rate of propenene hydrogenation is given in terms of the forward and backward rates of steps in Scheme (1) as

$$V = v_+(s) - v_-(s) \qquad (s = \mathrm{I_a}, \mathrm{I_b}, \mathrm{II}, \text{ or } \mathrm{III}), \quad (2)$$

where

$$v_+(\mathrm{II}) = v_+(\mathrm{II}_\alpha) + v_+(\mathrm{II}_\beta), \quad (3)$$

$$v_-(\mathrm{II}) = v_-(\mathrm{II}_\alpha) + v_-(\mathrm{II}_\beta), \quad (4)$$

$$v_+(\mathrm{III}) = v_+(\mathrm{III}_\alpha) + v_+(\mathrm{III}_\beta), \quad (5)$$

and

$$v_-(\mathrm{III}) = v_-(\mathrm{III}_\alpha) + v_-(\mathrm{III}_\beta). \quad (6)$$

Steps III_α and III_β are practically irreversible under usual experimental conditions so that we have

$$V = v_+(\mathrm{III}_\alpha) + v_+(\mathrm{III}_\beta). \quad (7)$$

From these equations, it follows that

$$v_+(\mathrm{III}_\alpha) = v_+(\mathrm{II}_\alpha) - v_-(\mathrm{II}_\alpha) \quad (8)$$

and

$$v_+(\mathrm{III}_\beta) = v_+(\mathrm{II}_\beta) - v_-(\mathrm{II}_\beta). \quad (9)$$

When propene reacts with deuterium, the formation rates of isotopic isomers of propene, hydrogen, and propane are given as functions of the rates of elementary steps. Therefore, the rates of respective steps may be determined from the observed formation rates of these isomers.

Though the analysis is possible throughout the reaction course, the present paper deals with the initial stage of reaction in order to simplify its procedure.

2.2. *Rates of Steps I_a and I_b*

Since the amounts of deuteropropene, H_2, and HD are practically zero at the beginning of propene deuteration, the backward rates of steps $\mathrm{I_a}$ and $\mathrm{I_b}$ are given by equations

$$v_-(\mathrm{I_a}) = V^{E_l}/x_l \qquad (l \geq 1) \qquad (10)$$

and

$$v_-(\mathrm{I_b}) = (V^{H_2} + \tfrac{1}{2} V^{HD})/y_H, \qquad (11)$$

respectively. The rate of propane-d_n formation, on the other hand, is given as

$$V^{A_n} = (y_H z_n{}^\alpha + y_D z_{n-1}{}^\alpha) v_+(\mathrm{III}_\alpha) + (y_H z_n{}^\beta + y_D z_{n-1}{}^\beta) v_+(\mathrm{III}_\beta), \quad (12)$$

where $z_n{}^\alpha$ or $z_n{}^\beta$ is the fraction of adsorbed *n*-propyl-d_n or *sec*.-propyl-d_n in each adsorbed propyl, respectively, and the steady-state conditions for adsorbed *n*-propyl-d_n and *sec*.-propyl-d_n are expressed as

$$(y_H x_n + y_D x_{n-1}) v_+(\mathrm{II}_\alpha) = z_n{}^\alpha (v_-(\mathrm{II}_\alpha) + v_+(\mathrm{III}_\alpha)) \quad (13)$$

and

$$(y_H x_n + y_D x_{n-1}) v_+(\mathrm{II}_\beta) = z_n{}^\beta (v_-(\mathrm{II}_\beta) + v_+(\mathrm{III}_\beta)). \quad (14)$$

From Eqs. (8), (9), (13), and (14), we have

$$z_n{}^\alpha = z_n{}^\beta = y_H x_n + y_D x_{n-1}. \quad (15)$$

Substitution of Eq. (15) into Eq. (12) leads to

$$V^{A_n} = (y_H{}^2 x_n + 2 y_H y_D x_{n-1} + y_D{}^2 x_{n-2}) V \quad (16)$$

since $v_+(\mathrm{III}_\alpha) + v_+(\mathrm{III}_\beta) = V$, and elimination of x_n's and $v_-(\mathrm{I_a})$ from Eqs. (10) and (16) leads to

$$3\left(\frac{y_D}{y_H}\right)^2 + 2\left(\frac{V^{E_2}}{V^{E_1}} - \frac{V^{A_1}}{V^{A_0}}\right)\frac{y_D}{y_H} + \frac{V^{A_2}}{V^{A_0}} - \frac{V^{A_1}}{V^{A_0}}\frac{V^{E_2}}{V^{E_1}} = 0. \quad (17)$$

This equation can be solved for y_D/y_H $(=(1 - y_H)/y_H)$ using the observed values of V^{E_l}'s and V^{A_n}'s. The y_H value calculated by this method gives the fraction of H(a) in the adsorbed hydrogen atoms that react with adsorbed hydrocarbon species (*2*). When step I_b is a single elementary step, y_H is also determined from V^{H_2} and V^{HD} (*2, 9*). In ethylene hydrogenation over Group VIII metals such as Ni, however, the y_H value thus determined is too small to explain the observed deuterium distributions in ethylene and ethane (*10*). This result led us to suppose that step I_b consists of at least two elementary steps in such a hydrogenation reaction and Eq. (17) was derived for the rate analysis in such a case (*2, 10*). In ethylene hydrogenation over Cu, step I_b is thought to be a single elementary step since both the methods give the same value of y_H (*2*).

The value of x_l can be determined by solving the following equations which are derived from Eqs. (10) and (16):

$$\Sigma x_l = 1,$$
$$x_1 = (V^{A_1}/V^{A_0} - 2y_D/y_H)x_0,$$
$$x_l = x_1 V^{E_l}/V^{E_1} \quad (l = 2, 3, \ldots, 6). \quad (18)$$

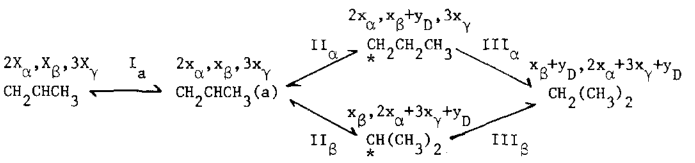
Using the values of x_l and y_H, we can calculate $v_-(I_a)$ and $v_-(I_b)$ according to Eqs. (10) and (11), respectively, and $v_+(I_a)$ and $v_+(I_b)$ by Eq. (2). It is noteworthy that the present method to determine $v_-(I_a)$ and $v_-(I_b)$ is still effective even when the reaction involves the dissociative adsorption of propene.

Although the method of Yasuda and Hirota (*5*) is useful to determine $v_-(I_a)$ throughout the reaction course, their actual rate analysis of propene deuteration over Cu (*6*) is inexact, because they set y_D (denoted by *d* in their analysis) constant. The value of y_D should increase with the progress of propane deuteration due to increase in the deuterium content in propene and, in fact, they have shown that the y_D value determined from V^{H_2}, V^{HD}, and V^{D_2} increases with the progress of the reaction (*6*).

2.3. *Rates of Steps II_α and II_β*

The rate analysis of steps II_α and II_β requires a measurement of the D atom location in propene or propane because hydrogen atoms in the methyl (CH_3) and methylene (CH_2) groups in propene exchange with deuterium via step II_β during propene deuteration while the hydrogen atom in the methenyl (CH) group exchanges via step II_α. The D atom location can be observed by microwave spectroscopy or by proton NMR together with mass spectrometry.

In the following discussion, average deuterium fractions in the methylene, methenyl, and methyl groups in gaseous propene are denoted by X_α, X_β, and X_γ and those in adsorbed propene by x_α, x_β, and x_γ, respectively. The mean deuterium numbers in the respective groups in hydrocarbon species are shown in Scheme (19).



(19)

The two methyl groups in

$$\underset{*}{\mathrm{C}}\mathrm{H(CH_3)_2}$$

are equivalent so that x_α should be equal to x_γ throughout the reaction so far as X_α is equal to X_γ at the beginning of the reaction.

Taking this into account, the steady-state condition for the average deuterium number in the methylene and methyl groups in adsorbed propene is expressed as

$$5X_\alpha v_+(\mathrm{I_a}) - 5x_\alpha(v_-(\mathrm{I_a}) + v_+(\mathrm{II}_\alpha) + v_+(\mathrm{II}_\beta) - v_-(\mathrm{II}_\alpha)) + 5(5x_\alpha + y_\mathrm{D})v_-(\mathrm{II}_\beta)/6 = 0, \quad (20)$$

and the steady-state condition for the deuterium number in the methenyl group is

$$X_\beta v_+(\mathrm{I_a}) - x_\beta(v_-(\mathrm{I_a}) + v_+(\mathrm{II}_\alpha) + v_+(\mathrm{II}_\beta) - v_-(\mathrm{II}_\beta)) + (x_\beta + y_\mathrm{D})v_-(\mathrm{II}_\alpha)/2 = 0. \quad (21)$$

Since Eqs. (2)–(4) give the equation,

$$v_-(\mathrm{I_a}) + v_+(\mathrm{II}_\alpha) + v_+(\mathrm{II}_\beta) = v_+(\mathrm{I_a}) + v_-(\mathrm{II}_\alpha) + v_-(\mathrm{II}_\beta), \quad (22)$$

we have

$$6v_+(\mathrm{I_a})\,(X_\alpha - x_\alpha) = v_-(\mathrm{II}_\beta)\,(x_\alpha - y_\mathrm{D}) \quad (23)$$

and

$$2v_+(\mathrm{I_a})\,(X_\beta - x_\beta) = v_-(\mathrm{II}_\alpha)\,(x_\beta - y_\mathrm{D}), \quad (24)$$

substituting Eq. (22) into Eqs. (20) and (21). At the beginning of propene deuteration, X_α and X_β are practically zero so that these equations are simplified as

$$v_-(\mathrm{II}_\beta) = 6v_+(\mathrm{I_a})x_\alpha/(y_\mathrm{D} - x_\alpha), \quad (25)$$

$$v_-(\mathrm{II}_\alpha) = 2v_+(\mathrm{I_a})x_\beta/(y_\mathrm{D} - x_\beta). \quad (26)$$

Now x_α and x_β are determined as follows.

The initial increasing rates of X_α, X_β, and X_γ are proportional to x_α, x_β, and x_γ, respectively, i.e.,

$$x_\alpha \Big/ \frac{dX_\alpha}{dt} = x_\beta \Big/ \frac{dX_\beta}{dt} = x_\gamma \Big/ \frac{dX_\gamma}{dt}. \quad (27)$$

The mean deuterium number in adsorbed propene, $\Sigma l x_l$, on the other hand, is given as

$$\Sigma l x_l = 2x_\alpha + x_\beta + 3x_\gamma. \quad (28)$$

Since x_l's are determined as described in Section 2.1., we can solve Eqs. (27) and (28) for x_a, x_β, x_γ, by using the observed values of X_α, X_β, and X_γ.

The values of x_α and x_β are also determined from the D atom location in propane. The deuterium numbers in the methyl (N_α) and methylene (N_β) in propane are given as

$$N_\alpha = 2x_\alpha + 3x_\gamma + y_\mathrm{D} \quad (29)$$

and

$$N_\beta = x_\beta + y_\mathrm{D}. \quad (30)$$

A proton NMR measurement of propane gives $(6 - N_\alpha)/(2 - N_\beta)$ while a mass-spectrometric analysis gives $(N_\alpha + N_\beta)$. Since x_α should be equal to x_γ in the associative mechanism, we can evaluate x_α and x_β by using Eqs. (17), (29), and (30).

When propene adsorbs dissociatively, $v_-(\mathrm{II}_\alpha)$ and $v_-(\mathrm{II}_\beta)$ cannot be determined, because the dissociative adsorption of propene gives rise to additional hydrogen exchange between propene and hydrogen.

Although $v_-(\mathrm{II}_\alpha)$ and $v_-(\mathrm{II}_\beta)$ are experimentally determined, $v_+(\mathrm{II}_\alpha)$ and $v_+(\mathrm{II}_\beta)$ are not, unless $v_+(\mathrm{III}_\alpha)$ and $v_+(\mathrm{III}_\beta)$ are given. It would be impossible, however, to determine $v_+(\mathrm{III}_\alpha)$ or $v_+(\mathrm{III}_\beta)$ experimentally, because there is no method to discriminate the propane molecules produced via step III_α from those produced via step III_β. Therefore, $v_+(\mathrm{II}_\alpha)$ and $v_+(\mathrm{II}_\beta)$ could not be determined experimentally, but their sum, $v_+(\mathrm{II})$, is definitely determined by Eqs. (2)–(4) as

$$v_+(\mathrm{II}) = V + v_-(\mathrm{II}_\alpha) + v_-(\mathrm{II}_\beta). \quad (31)$$

Furthermore, the values of $v_+(\mathrm{II}_\alpha)$ and $v_+(\mathrm{II_b})$ should lie in the following ranges:

$$V + v_-(\mathrm{II}_\alpha) \geq v_+(\mathrm{II}_\alpha) \geq v_-(\mathrm{II}_\alpha), \quad (32)$$

$$V + v_-(\mathrm{II}_\beta) \geq v_+(\mathrm{II}_\beta) \geq v_-(\mathrm{II}_\beta). \quad (33)$$

Yasuda and Hirota (5) derived an equation to give the ratio of $v_-(\mathrm{II}_\alpha)$ to $v_-(\mathrm{II}_\beta)$, which is written in terms of our symbols as

$$v_-(\mathrm{II}_\alpha)/v_-(\mathrm{II}_\beta) = x_\beta/3x_\alpha. \quad (34)$$

This equation is derived from Eqs. (25) and (26) under the assumption that both x_α and x_β are far smaller than y_D. This assumption will be realized only when step $\mathrm{I_a}$ is far faster than both steps II_α and II_β. When x_α is equal to x_β, however, $v_-(\mathrm{II}_\alpha)/v_-(\mathrm{II}_\beta)$

equals $\frac{1}{3}$ irrespective of the value of y_D.

2.4. *Rates of Steps* III_α *and* III_β

As described before, $v_+(III_a)$ and $v_+(III_\beta)$ could not be determined experimentally, but if the ratio of the rate constants of both steps were given they could be estimated from $v_-(II_\alpha)$ and $v_-(II_\beta)$ as follows.

The forward rate of an elementary step is proportional to the activities of reactant species. Accordingly, $v_+(III_a)$ may be proportional to the activities of n-C_3H_7(a) and H(a) while $v_+(III_\beta)$ may be proportional to those of *sec.*-C_3H_7(a) and H(a). The activity of H(a) may be the same in both steps since H(a) would migrate easily on the surface of metal catalysts. Therefore, it follows that

$$v_+(III_\alpha)/v_+(III_\beta) = S\gamma(n\text{-}C_3H_7)/\gamma(s\text{-}C_3H_7), \quad (35)$$

where $\gamma(n\text{-}C_3H_7)$ or $\gamma(s\text{-}C_3H_7)$ is the activity of relevant species and S is a special value of $v_+(III_\alpha)/v_+(III_\beta)$ when $\gamma(n\text{-}C_3H_7) = \gamma(s\text{-}C_3H_7)$, i.e., S is the ratio of the rate constants of steps III_α and III_β. So far as steps II_α and II_β are reversible, the activities of *n*- and *sec.*-C_3H_7(a) are given as

$$\gamma(n\text{-}C_3H_7) = \gamma(C_3H_6)\gamma(H)v_-(II_\alpha)/v_+(II_\alpha), \quad (36)$$

and

$$\gamma(s\text{-}C_3H_7) = \gamma(C_3H_6)\gamma(H)v_-(II_\beta)/v_+(II_\beta), \quad (37)$$

where $\gamma(C_3H_6)$ or $\gamma(H)$ is the activity of adsorbed propene or hydrogen atom, respectively. Substitution of the above equations into Eq. (35) leads to

$$v_+(III_\alpha)/v_+(III_\beta) = Sv_-(II_\alpha)v_+(II_\beta)/v_+(II_\alpha)v_-(II_\beta). \quad (38)$$

and eliminating $v_+(II_\alpha)$, $v_+(II_\beta)$, and $v_+(III_\beta)$ from Eqs. (7)–(9) and (38), we have

$$(v_-(II_\beta) - v_-(II_\alpha)S)v_+(III_\alpha)^2 + v_-(II_\alpha)\{v_-(II_\beta)(1 + S) + 2SV\}v_+(III_\alpha) - v_-(II_\alpha)(v_-(II_\beta) + V)SV = 0. \quad (39)$$

If S is given, this equation can be solved for $v_+(III_\alpha)$ since $v_-(II_\alpha)$, $v_-(II_\beta)$, and V are experimentally determined.

Although Hirota *et al.* (*6*) have equated $v_+(III_\alpha)/v_+(III_\beta)$ to $v_-(II_\alpha)/v_-(II_\beta)$, we could not find any reason to justify their equation.

3. EXPERIMENTAL

The reaction apparatus used was a closed circulation system (~1000 ml volume) equipped with a dry-ice trap to prevent mercury vapor contamination. The base pressure of the whole apparatus was 1×10^{-7} Torr (1 Torr = 133.3 N m^{-2}).

The evaporated film of Rh was prepared in the same way as described previously (*8*) and its geometrical area was about 45 cm^2. After each run of the reaction the film was treated with hydrogen at 300°C for 10 hr or more and outgassed at 300°C until the pressure fell to the mid-10^{-7}-Torr range. Heavy propene (99 at.% D) was supplied by Merk & Dohme Ltd., Canada. Hydrogen (H_2 and D_2) and propene (C_3H_6 and C_3D_6) were purified by a conventional method as described previously (*8*–*10*).

The reaction was commenced by admitting an equimolar mixture of propene and hydrogen into the reaction system at 40 Torr of total pressure, and the reaction rate was followed by a Hg manometer. A small amount of gas mixture was sampled at adequate intervals for analysis of isotopic isomers. No product other than propane was found throughout the reaction.

Deuterium distributions in hydrogen, propene, and propane was mass-spectrometrically determined. Mass spectra of hydrocarbons were corrected for the natural abundance of ^{13}C but not for isotopic effects in the fragmentation of propane during ionization at 70 eV. The position of the D atom in propene-d_1 was determined with microwave spectroscopy; the procedure of measurement and the analysis of spectrum were the same as reported by Kondo *et al.* (*11*).

4. RESULTS AND DISCUSSION

4.1. *Reproducible Condition of Reaction*

The catalytic activity of evaporated Rh

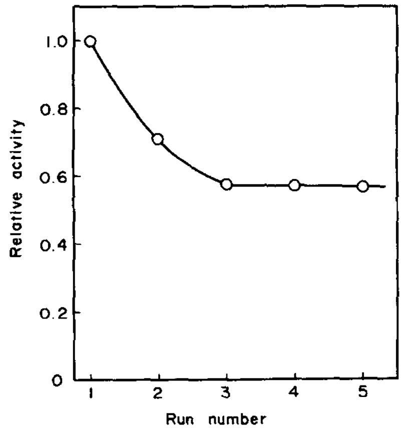


FIG. 1. Activity change of evaporated Rh film for the reaction of C_3H_6 with D_2 at 0°C.

film for propene hydrogenation decreased after the first and second runs of the reaction and then became constant as shown in Fig. 1. This decrease in the activity is probably not due to sintering of the film, since the film was prepared at high temperature (300°C), but due mainly to accumulation of a carbonaceous residue or a surface compound such as an acetylenic complex (*12*) formed by the decomposition of propene. A similar phenomenon has been observed in ethylene hydrogenation over evaporated metal films (*13*).

In order to check the dissociative adsorption of propene, a hydrogen exchange reaction between C_3H_6 and C_3D_6 was carried out over the film used for a few runs of the hydrogenation. The mass-spectrometric analysis of propene showed that the exchange did not occur in the absence of hydrogen at 0 and −45°C. This result suggests that the dissociation of propene hardly takes place on the used film. On this basis, all the reactions in this study were carried out using the film used three or more times for the hydrogenation in order to obtain a reproducible hydrogenation activity and to avoid the dissociation of propene.

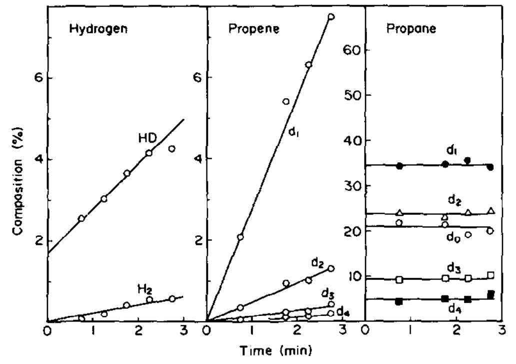


FIG. 2. Time evolution of the isotopic isomers during Reaction A at −8°C.

4.2. *Rate Analysis of Steps I_a and I_b*

C_3H_6 + D_2 (Reaction A). The reaction of C_3H_6 with D_2 was carried out in the temperature range from −44 to 0°C, and the deuterium distributions in propene, hydrogen, and propane were observed at ade-

TABLE 1

Rates of Hydrogenation and Formation of Isotopic Isomers at the Beginning of Reaction A on Evaporated Rh Film

Temp. (°C)	V (Torr/min)	Hydrogen[a] (%/min)		Propene[b] (%/min)					Propane[c] (%)		
		$\dot{Y}_0$	$\dot{Y}_1$	$\dot{X}_1$	$\dot{X}_2$	$\dot{X}_3$	$\dot{X}_4$	$\dot{X}_5$	Z_0	Z_1	Z_2
0	2.4	0.78	2.4	4.9	0.68	0.19	0.09	0	21.5	34.5	22.6
−8	2.0	0.23	1.1	2.8	0.44	0.13	0.06	0	21.1	34.6	23.3
−22	1.1	0.07	0.44	2.0	0.28	0.08	0.04	0	21.2	35.7	22.9
−32	0.92	0.05	0.27	1.7	0.21	0.07	0.03	0	20.1	35.5	24.0
−44	0.52	0.02	0.16	0.82	0.092	0.025	0	0	20.2	35.4	24.6

[a] $\dot{Y}_0 = V^{H_2}/P_H$; $Y_1 = V^{HD}/P_H$ (P_H, partial pressure of hydrogen).

[b] $\dot{X}_l = V^{E_l}/P_E$ (P_E, partial pressure of propene).

[c] $Z_n = V^{A_n}/V$.

quate intervals during 40% conversion of the hydrogenation. Figure 2 shows typical time courses of the isotopic isomers evolution. Deuteropropenes as well as H_2 and HD were formed slowly and the deuterium distribution in propane remained fairly unchanged within the observed range of conversion. The initial formation rates of respective isomers are listed in Table 1.

From the results of Table 1, x_l's and y_H were calculated as listed in Table 2 according to Eqs. (17) and (18). This result shows that about 65% of adsorbed hydrogen is light hydrogen though D_2 was used as a reactant. The dilution of deuterium with light hydrogen on the catalyst surface results from the hydrogen exchange between adsorbed propene and adsorbed hydrogen. The value of y_H slightly decreases with decreasing reaction temperature while the value of x_l remains almost unchanged.

The forward and backward rates of steps I_a and I_b were determined from the results of Tables 1 and 2 as shown in Fig. 3. This figure shows that step I_b is considerably slow, $v_+(I_a)$ is about twice the hydrogenation rate, and $v_-(I_b)$ approaches $v_+(I_b)$ with a rise of reaction temperature. These results are quite similar to those obtained for ethylene hydrogenation over evaporated Rh film (*8*). The activation energy of hydrogenation was 4.3 kcal $mole^{-1}$, which is considerably smaller than 13.0 kcal $mole^{-1}$ obtained by Mann and Lien (*14*) using Rh supported on pumice.

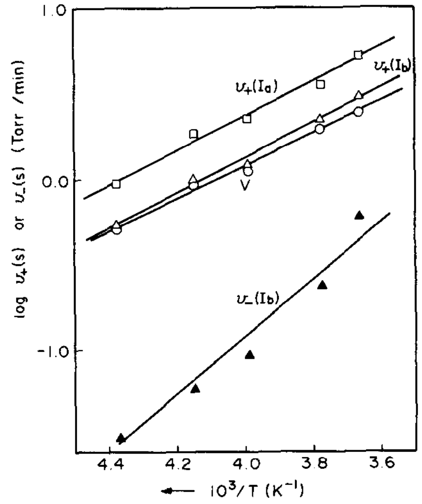


FIG. 3. Arrhenius plots of the rates of hydrogenation, steps I_a and I_b determined from the results of Reaction A. Plots of $v_-(I_a)$ is omitted since most of the plots overlap on plots of *V*.

TABLE 2

Values of y_H and x_l's Determined from the Results of Table 1

Temp. (°C)	y_H	x_0	x_1	x_2	x_3	x_4	x_5
0	0.67	0.57	0.36	0.05	0.014	0.007	0
−8	0.67	0.56	0.36	0.06	0.017	0.008	0
−22	0.66	0.56	0.37	0.05	0.015	0.007	0
−32	0.65	0.56	0.38	0.05	0.016	0.007	0
−44	0.65	0.57	0.38	0.04	0.011	0	0

C_3D_6 + H_2 (Reaction B). The rates of steps I_a and I_b in the reaction of C_3D_6 with H_2 were determined similar to Reaction A. The formation rates of isotopic isomers in propene, hydrogen, and propane were observed at the beginning of the reaction (Table 3) and then x_l's and y_D were determined as given in Table 4. In Reaction B, y_D should correspond to y_H in Reaction A, but the values of y_D in Table 4 are smaller than the values of y_H in Table 2. This discrepancy is probably due to the isotopic effect of hydrogen on the hydrogenation rate; H(a) reacts more rapidly with adsorbed hydrocarbon species than D(a). Since our analysis determines y_D (or y_H) from the deuterium distributions in propene and propane, y_D may be underestimated while y_H may be overestimated. We believe, therefore, that there is no essential difference between these results.

Figure 4 shows Arrhenius plots of the rates of hydrogenation, steps I_a and I_b in Reaction B. It is found from Figs. 3 and 4 that Reaction B is about 1.7 times faster than Reaction A over the temperature range observed. This difference in the hydrogenation rate is due to the isotopic effect of hydrogen. The backward rate of step I_a, however, is not very different in both reac-

TABLE 3

Rates of Hydrogenation and Formation of Isotopic Isomers at the Beginning of Reaction B on Evaporated Rh Film

Temp. (°C)	V (Torr/min)	Hydrogen (%/min)		Propene (%/min)				Propane (%)		
		$\dot{Y}_2{}^a$	$\dot{Y}_1$	$\dot{X}_5$	$\dot{X}_4$	$\dot{X}_3$	$\dot{X}_2$	$\dot{Z}_8$	$\dot{Z}_7$	$\dot{Z}_6$
0	4.5	0.26	2.8	4.4	1.5	0.32	0	7.1	29.4	40.6
−10	3.1	0.10	1.3	2.9	0.94	0.10	0	6.3	27.8	42.0
−22	2.1	0.042	0.60	2.1	0.85	0.08	0	5.7	27.9	41.8
−43	0.86	0.004	0.076	0.57	0.31	0.05	0	4.6	25.2	42.3

[a] $\dot{Y}_2 = V^{D_2}/P_H$. The other symbols are the same as those in Table 1.

tions, suggesting little isotopic effect on the desorption rate of propene. The backward rate of step I_b in Reaction B is slightly greater than in Reaction A probably due to the underestimation of y_D in the former and the overestimation of y_H in the latter.

The activation energy of hydrogenation in Reaction B was 4.7 kcal mole^{-1}, which is somewhat greater than in Reaction A. This difference in activation energy is unusual because the deuteration of an olefin usually shows higher activation energy than the ordinary hydrogenation in a low-temperature range (*13*). The relatively higher activation energy in Reaction B might be due to a little change in the catalytic activity of Rh film.

4.3. *Rate Analysis of Steps II_α and II_β*

Position of the D atom in propene-d_1. Since our rate analysis of these steps requires a measurement of the D fractions in the methyl, methenyl, and methylene groups in propene as described before, the present analysis estimated these D fractions from the position of the D atom in propene-d_1 or -d_5, which was measured by microwave spectroscopy. The relative amounts of geometrical isomers in propene-d_1 formed from Reaction A are shown in Table 5. When propene hydrogenation involves the associative mechanism alone, propene-1-d_1 (*cis* + *trans*) should be equal to two-thirds of 3-d_1, and *cis*-1-d_1 should be equal to *trans*-1-d_1 throughout the reaction course (*1*, *11*). The results of Table 5 satisfy fairly well these necessary conditions for the associative mechanism. These results, however, differ from the result obtained by

TABLE 4

Values of y_D and x_i's Determined from the Results of Table 3

Temp. (°C)	y_D	x_6	x_5	x_4	x_3	x_2
0	0.37	0.48	0.36	0.13	0.033	0
−10	0.40	0.38	0.46	0.15	0.021	0
−22	0.32	0.55	0.31	0.13	0.020	0
−43	0.30	0.50	0.30	0.16	0.032	0

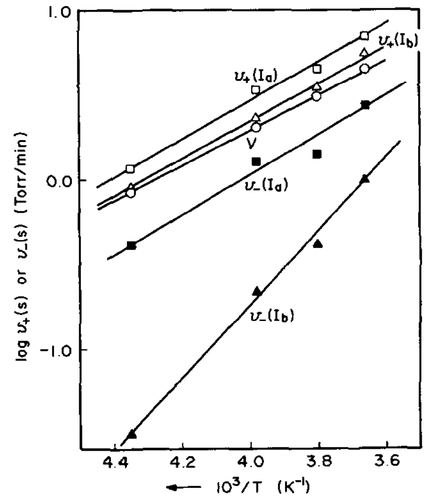
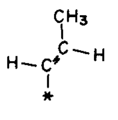


FIG. 4. Arrhenius plots of the rates of hydrogenation, steps I_a and I_b determined from the results of Reaction B.

Ueda *et al.* (*15*), who observed the excess of 1-d_1 over 3-d_1 in propene deuteration over Rh powder at 30°C.

Table 6 shows the distribution of propene-$d_5(h_1)$ subspecies formed from Reaction B. The H atom location in this reaction should correspond to the D atom location in Reaction A, but the results of Table 6 considerably differ from those of Table 5; not only 1-h_1 exceeds 3-h_1 but *trans*-1-h_1 exceeds *cis*-1-h_1 over the whole temperature range. This discrepancy could not be explained by kinetic isotope effects. A remarkable excess of *trans*-1-d_1 over *cis*-1-d_1 has been observed by Hirota and Hironaka (*16*) for propene deuteration over Pt powder at 20°C. They ascribed their result to the formation of adsorbed *trans*-propenyl,



concurrent with the associative adsorption of propene. Their explanation seems reasonable since the adsorbed propenyl would favor the *trans*-propenyl form due to a steric hindrance of the methyl group in the propene molecule. The adsorbed *trans*-propenyl may also be responsible for the fact that *trans*-1-h_1 exceeds *cis*-1-h_1 during Reaction B. The dissociative adsorption of olefins, however, is generally suppressed by lowering reaction temperature (*13*), whereas the increase of *trans*-1-h_1 with decrease in the reaction temperature indicates that the dissociative adsorption occurs rather intensively at low temperature. This unexpected result remains unexplained. It is also not clear why only Reaction B involves the dissociative adsorption of propene in spite of the same pretreatment of the catalyst as in the series of Reaction A. This difference may indicate that C_3D_6 undergoes dissociation more easily than C_3H_6.

Estimation of $v_-(II_\alpha)$ and v_- (II_β). The rate analysis of steps II_α and II_β is impossible when the reaction involves the dissociative adsorption of propene, because the hydrogen exchange between propene and hydrogen via these steps can not be discriminated from the exchange caused by the dissociation of propene. The present rate analysis is, therefore, carried out using the results of Reaction A, in which the dissociative adsorption is eliminated.

Since the methylene group of propene has two hydrogen atoms while the methenyl group has one hydrogen atom, x_α/x_β would approximate to $\frac{1}{2}$[propene-1-d_1]/[propene-2-d_1] at the beginning of reaction. The total D number in adsorbed propene, $\Sigma l x_l$, on the other hand, is equal to $(5x_\alpha + x_\beta)$ and x_l's are given in Table 2. We can therefore calculate x_α and x_β and then $v_-(II_\alpha)$ and $v_-(II_\beta)$ according to Eqs. (25) and (26).

The results (Table 7) show that $v_-(II_\alpha)$ is fairly smaller than $v_-(II_\beta)$ both at −9 and

TABLE 5

Distributions of Deuteropropenes and Propene-d_1 Subspecies in Reaction A on Evaporated Rh Film

Temp. (°C)	Conv. (%)	Distribution of deuteropropenes (%)					Distribution of propene-d_1 subspecies[a] (%)			
		d_0	d_1	d_2	d_3	$d_{4\sim}$	*cis*-1-d_1	*trans*-1-d_1	2-d_1	3-d_1
−9	51	76.0	21.3	2.6	2.4	0	16.4 ± 1.8	17.4 ± 3.0	7.8 ± 0.8	(19.5 ± 1.1) × 3
−30	55	72.7	23.5	3.4	0.4	0	15.7 ± 3.1	17.3 ± 2.2	3.3 ± 0.5	(21.1 ± 2.1) × 3
−30	60	69.6	25.5	4.4	0.5	0	17.0 ± 2.8	16.1 ± 1.5	5.3 ± 0.7	(20.5 ± 1.6) × 3

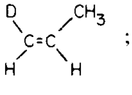
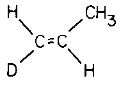
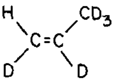
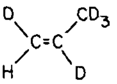
[a] *cis*-1-d_1,  ; *trans*-1-d_1,  ; 2-d_1, CH_2CDCH_3; 3-d_1, CH_2CHCH_2D.

TABLE 6

Distributions of Deuteropropenes and Propene-d_5 ($-h_1$) Subspecies in Reaction B on Evaporated Rh Film

Temp. (°C)	Conv. (%)	Distribution of deuteropropenes (%)					Distribution of propene-d_5 subspecies[a] (%)			
		d_6	d_5	d_4	d_3	$d_{2\sim}$	*cis*-1-h_1	*trans*-1-h_1	2-h_1	3-h_1
0	43	78.5	18.1	3.2	0.1	0	19.4 ± 2.6	27.0 ± 4.0	22.7 ± 4.8	(10.3 ± 1.6) × 3
−10	53	70.1	24.4	4.6	0.7	0.2	20.8 ± 2.2	31.8 ± 3.7	13.2 ± 1.4	(11.4 ± 1.1) × 3
−22	44	78.7	18.3	2.6	0.4	0	16.6 ± 1.4	40.5 ± 4.3	11.7 ± 1.4	(10.4 ± 1.0) × 3
−43	45	80.8	17.1	2.0	0.2	0	14.1 ± 1.3	50.1 ± 5.6	9.9 ± 0.9	(8.7 ± 0.8) × 3

[a] *cis*-1-h_1,  ; *trans*-1-h_1,  ; 2-h_1, CD_2CHCD_3; 3-h_1, CD_2CDCHD_2.

-30°C, indicating that *sec.*-C_3H_7(a) contributes less to the D_2–C_3H_6 hydrogen exchange than *n*-C_3H_7(a). Although each $v_+(II_\alpha)$ and $v_+(II_\beta)$ could not be definitely determined, their sum, $v_+(II)$, is definitely determined according to Eq. (31). Table 7 shows that $v_+(II)$ is several times greater than the overall hydrogenation rate.

4.4. *Rate-Determining Step of Propene Hydrogenation*

The present study revealed that step I_a, as well as step I_b, is slower than step II in propene hydrogenation over Rh, but step I_a would not control the hydrogenation rate. If step I_a is rate determining, then the reaction order in propene pressure should be positive, but the observed one over Rh is -0.05 in propene pressure and 0.75 in hydrogen pressure at 67°C (*14*). This reaction order indicates that only step I_b is rate determining as concluded for ethylene hydrogenation over Rh (*8*). It has been concluded in the previous study (*8*) that ethylene adsorption on Rh is so strong that adsorbed ethylene hardly desorbs during ethylene hydrogenation over Rh. Propene may also adsorb strongly on Rh, covering the surface sufficiently to retard the adsorption of hydrogen. We believe that hydrogen adsorption under the retardation of adsorbed propene rate-determines propene hydrogenation over Rh.

TABLE 7

Relative Backward Rates of Steps II_α and II_β Calculated from the Results of Tables 1, 2, and 5

Temp. (°C)	$v_-(II_\alpha)/V$	$v_-(II_\beta)/V$	$v_-(II)/V$	$v_+(II)/V$
−9	0.61	4.9	5.5	6.5
−30	0.41	5.1	5.5	6.5

The final step of olefin hydrogenation (step III) is always the slowest among the constituent steps since the step is practically irreversible under usual experimental conditions, but the step is not rate determining for the hydrogenation at temperatures below an optimum temperature (*2*, *17*). The details of this problem have been discussed previously (*2*, *8*, *9*, *13*, *18*).

4.5. *Catalytic Properties of Rh and Other Metals in Propene Hydrogenation*

The relative rates of steps in propene hydrogenation over Rh are quite similar to those in ethylene hydrogenation over Rh (*8*), in which steps I_a and I_b are slow and step II is several times faster than the overall hydrogenation. The relative rate of propene adsorption ($v_+(I_a)/V$), however, was found to be about 1.5 times greater than that of ethylene adsorption. The rate of olefin hydrogenation on a metal catalyst generally decreases with increasing substitution of alkyl groups about the double bond of olefin (*7*). In agreement with this, we found in our study that ethylene hydro-

TABLE 8

Relative Rates of Steps[a] in the Hydrogenation of Propene on Cu[b]

$v_+(\mathrm{I_a})/V$	$v_+(\mathrm{I_b})/V$	$v_-(\mathrm{II}_\alpha)/V$	$v_-(\mathrm{II}_\beta)/V$
27.6	1.24	400	3.7

[a] These rates were calculated from the result of Hirota *et al.* (*6*) by the present author's method.

[b] Propene pressure, 100 Torr; deuterium pressure, 50 Torr; room temperature.

genation is two or more times faster than propene hydrogenation over evaporated Rh film and about four times faster over evaporated Pd film (*19*) both at 0°C. Such a difference in hydrogenation rate may be related to the adsorption heat of olefin and the number of surface sites occupied by one molecule of adsorbed olefin, both of which may affect the number of vacant sites available for hydrogen adsorption.

Hirota *et al.* (*6*) applied the method of Yasuda and Hirota (*5*) to their results of propene deuteration over Cu at room temperature, but could not determine $v_-(\mathrm{II}_\alpha)$ and $v_-(\mathrm{II}_\beta)$. Their experimental data were also analyzed by our method and the result (Table 8) shows that the order of step rates over Cu is $\mathrm{II}_\alpha > \mathrm{I_a} > \mathrm{II}_\beta > \mathrm{I_b}$. Propene adsorption is thus reversible during propene hydrogenation over Cu unlike over Rh. A similar result has been obtained for ethylene adsorption during ethylene hydrogenation over these metals (*8, 9*).

It is interesting, furthermore, that the ratio, $v_-(\mathrm{II}_\alpha)/v_-(\mathrm{II}_\beta)$, is remarkably smaller in the reaction over Rh than in the reaction over Cu. This ratio is also estimated from the results of Hirota and Hironaka (*20*), who observed the distributions of propene-d_1 subspecies formed from propene deuteration over Ni and Pd. As their data lack the deuterium distribution in propane, $v_-(\mathrm{II}_\alpha)/v_-(\mathrm{II}_\beta)$ (= S_{II}) is approximated by Eq. (34). It should be remembered that the equation gives a correct value of S_{II} when $x_\alpha = x_\beta$ or both x_α and x_β are much smaller than y_{D}. If $x_\alpha < x_\beta$ or $x_\alpha > x_\beta$, Eq. (34) will overestimate or underestimate S_{II}, respectively. By taking account of this limitation of Eq. (34), S_{II} is estimated to be unity or more (probably less than 10) with Ni and about 0.3 with Pd (in this case x_α is nearly equal to x_β).

It is found from Tables 7 and 8 and the above results that S_{II} decreases in the following sequence of metals;

$$\mathrm{Cu} > \mathrm{Ni} > \mathrm{Pd} > \mathrm{Rh}.$$

This sequence is quite the reverse of the activity order of these metals for olefin hydrogenation (*7, 14*). In addition, the adsorption strengths of olefin and hydrogen on these metals increase with an increase in the hydrogenation activity of metal (*2*). It seems reasonable, therefore, to suppose that S_{II} depends on the adsorption strengths of reaction intermediates or their coverages on the catalyst surface. At the present stage of study, however, the data are too scanty to discuss this problem any further.

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