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— Review —

REACTION STRUCTURE OF ETHYLENE HYDROGENATION ON METALS^{*)}

By

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Abstract

Methods of determining the rates of elementary steps in ethylene hydrogenation traced by deuterium and their applications to the reaction on various metals are reviewed. The activity of metal for steady hydrogenation of ethylene is proposed to depend on two principal factors, *i. e.* the activity of metal for hydrogen chemisorption and the irreversibility of ethylene adsorption during ethylene hydrogenation.

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I. Introduction

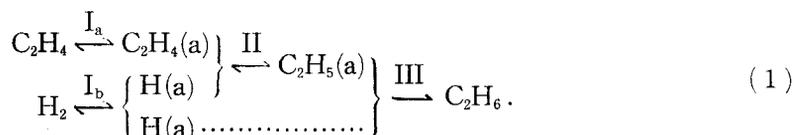
There are many investigations on ethylene hydrogenation catalyzed by

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metal¹⁾ as a fundamental one of catalyzed hydrogenation of olefins and a standard test reaction for hydrogenation catalysts. Some investigations were carried out to obtain theoretical or empirical correlation between catalytic activity and physical property, such as *d*-character, of metal²⁻³⁾, but no firm conclusion has been arrived at. In order to get clue to this subject, it is necessary to determine the rates of elementary steps constituting ethylene hydrogenation on various metals, because they might more directly reflect the properties of catalyst than the overall reaction rate.

Steady hydrogenation of ethylene on most transition metals has been concluded to proceed *via* the following set of elementary steps:¹⁾



Theory for determining the rates of all steps in the above scheme was developed by the present author and applied to the reaction on various metals⁵⁻⁹⁾. On the other hand, KEMBALL¹⁰⁾ proposed a method to explain the deuterium distributions in ethylene and ethane at an early stage of ethylene deuteration by four parameters relating to various probabilities in the reaction. BOND *et al.*¹¹⁻¹⁴⁾ evaluated these parameters with respect to the reaction on various metals supported on alumina. YASUDA and HIROTA¹⁵⁾ also discussed another method to determine the rates of elementary steps in olefin hydrogenation proceeding *via* associative mechanism.

The purpose of this article is to review theories for determination of the rates of steps in ethylene hydrogenation and their applications. On the basis of the results obtained, the mechanism of the hydrogenation and the activity order of metals are discussed.

II. Theories for Evaluation of Unidirectional Rates of Elementary Steps

Unidirectional rate of every step in scheme (1) can be evaluated by using deuterium as a tracer as reviewed in this section. Symbols used are as follows.

- V_s : steady rate of ethylene hydrogenation,
- $v_+(s), v_-(s)$: forward or backward unidirectional rate of step *s*,
- P, D, H: atom of protium, deuterium or hydrogen (irrespective of P or D),

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- $V^{E_l}, V^{P_{2-m}D_m}, V^{A_n}$: evolution rate of d_l -ethylene (E_l), d_m -hydrogen ($P_{2-m}D_m$) or d_n -ethane (A_n),
 X_l, Y_m, Z_n : fraction of E_l in C_2H_4 , $P_{2-m}D_m$ in H_2 or A_n in C_2H_6 ,
 x_l, y_0, y_1 : fraction of $E_l(a)$ in $C_2H_4(a)$, $P(a)$ or $D(a)$ in $H(a)$ ($y_0 + y_1 = 1$),
 X, x : average deuterium fraction in C_2H_4 ($\equiv \sum lX_l/4$) or in $C_2H_4(a)$ ($\equiv \sum lx_l/4$),
 P_F, P_H, P_A : partial pressure of C_2H_4, H_2 or C_2H_6 .

2. 1. Methods of the present author

KEII¹⁶⁾ formulated first the deuterium distributions in ethylene and ethane formed at an initial stage of ethylene deuteration as functions of the relative rates of steps in scheme (1) on the basis of the reaction structure theory of HORIUTI¹⁷⁾. His method was constructive but so complicated as to be not accepted widely. HORIUTI¹⁸⁾ and MIYAHARA and YATSURUGI¹⁹⁾ put forward his method and showed that the rates of steps in scheme (1) are determinable from the evolution rates of the isotopic products in ethylene deuteration. However, the applicability of their methods is limited to a special case of step I_a being in quasi-equilibrium. Their theory was developed by the present author⁶⁻⁹⁾ as a general method for determination of the rates of all steps in scheme (1).

In a steady reaction of ethylene with hydrogen involving deuterium atoms, the evolution rates of d_l -ethylene, d_m -hydrogen and d_n -ethane are given according to scheme (1) as

$$V^{E_l} = x_l v_-(I_a) - X_l v_+(I_a), \quad (l = 0, \dots, 4), \quad (2)$$

$$V^{P_{2-m}D_m} = \frac{2}{(2-m)!m!} y_0^{2-m} y_1^m v_-(I_b) - Y_m v_+(I_b), \quad (m = 0, 1, 2), \quad (3)$$

and

$$V^{A_n} = (y_0^2 x_n + 2y_0 y_1 x_{n-1} + y_1^2 x_{n-2}) v_+(III), \quad (n = 0, \dots, 6), \quad (4)$$

respectively, where isotopic effects are ignored and the term including $v_-(III)$ in Eq. (4) is equated to zero since $v_-(III)$ is negligibly small under usual experimental conditions¹⁾.

On the other hand, steady state conditions for overall hydrogenation, deuterium numbers in adsorbed ethylene, and adsorbed d_l -ethylene^{*)} are expressed, respectively, as

*) Cf. ref. (18), p. 178.

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$$V_s = -dP_E/dt = -dP_H/dt = dP_A/dt \quad (5)$$

$$= v_+(s) - v_-(s), \quad (s = I_a, I_b, II \text{ or III}), \quad (6)$$

$$6(X-x)v_+(I_a) - (x-y_1)v_-(II) = 0, \quad (7)$$

and

$$\begin{aligned} X_l v_+(I_a) - x_l v_-(I_a) - x_l v_+(II) + \left\{ \left(1 - \frac{l-1}{4} \right) \frac{2}{3} y_1 x_{l-1} \right. \\ \left. + \left(1 - \frac{l}{6} \right) y_0 x_l + \left(\frac{1}{3} + \frac{l}{6} \right) y_1 x_l + \frac{l+1}{6} y_0 x_{l+1} \right\} v_-(II) = 0. \quad (8) \end{aligned}$$

The rates of evolution and the fractions of gaseous isotopic isomers are measurable and hence the unidirectional rates of respective steps are given as functions of y_1 and x_i 's according to Eqs. (2)~(8). Practical methods of the rate evaluation are described in what follows.

(A) *Analysis with ethylene deuteration (Method A)*

At an initial stage of the reaction of C_2P_4 with D_2 , $X_l (l \geq 1)$, X , Y_0 , and Y_1 are substantially zero and hence the backward rates of steps I_a , I_b and II are given according to Eqs. (2), (3) and (7) as

$$v_-(I_a) = V^{E_l}/x_l = \sum l V^{E_l}/4x, \quad (l \geq 1), \quad (9)$$

$$v_-(I_b) = (V^{P_2} + V^{PD})/y_0, \quad (10)$$

$$v_-(II) = 6xv_+(I_a)/(y_1 - x). \quad (11)$$

Accordingly, the forward rates of these steps are given by Eq. (6). The value of y_1 (or y_0) in the above equations is given by the equation^{6,7)},

$$Y_1 \left(\frac{y_1}{y_0} \right)^2 - 2Y_2 \frac{y_1}{y_0} + \frac{V^{PD}}{V^{P_2}} Y_2 - \frac{V^{D_2}}{V^{P_2}} Y_1 = 0, \quad (12)$$

or

$$3 \left(\frac{y_1}{y_0} \right)^2 + 2 \left(\frac{V^{E_2}}{V^{E_1}} - \frac{V^{A_1}}{V^{A_0}} \right) \frac{y_1}{y_0} + \frac{V^{A_2}}{V^{A_0}} - \frac{V^{A_1}}{V^{A_0}} \frac{V^{E_2}}{V^{E_1}} = 0. \quad (13)$$

The values of x_i 's, and hence x , can be calculated by the simultaneous equations,

$$\left. \begin{aligned} \sum x_i &= 1, \\ x_1 &= (V^{A_1}/V^{A_0} - 2y_1/y_0) x_0, \\ x_l &= V^{E_l} x_l / V^{E_1}, \quad (l = 2, 3, 4). \end{aligned} \right\} \quad (14)$$

Thus, the unidirectional rates of respective steps can be evaluated from the

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observed evolution rates of isotopic isomers at an initial stage of ethylene deuteration.

(B) *Analysis with the reaction of equimolar C₂P₄ and C₂D₄ with equimolar P₂ and D₂ (Method B)*

Equation (8) is rewritten in matrix representation as

$$\begin{bmatrix} b_0 & c_0 & 0 & 0 & 0 \\ a_1 & b_1 & c_1 & 0 & 0 \\ 0 & a_2 & b_2 & c_2 & 0 \\ 0 & 0 & a_3 & b_3 & c_3 \\ 0 & 0 & 0 & a_4 & b_4 \end{bmatrix} \begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} X_0 \\ X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix}, \quad (15)$$

where

$$\begin{aligned} a_i &= (l-5) y_1 v_-(\text{II})/6v_+(\text{I}_a), \\ b_i &= 1 + (4y_1 - ly_1 + ly_0) v_-(\text{II})/6v_+(\text{I}_a), \\ c_i &= -(l+1) y_0 v_-(\text{II})/6v_+(\text{I}_a). \end{aligned} \quad (16)$$

Taking account of $V^{E_l} = dX_l P_E/dt$, Eqs. (5) and (6), Eq. (2) is rewritten as

$$dX_l/dt = -(X_l - x_l) v_-(\text{I}_a)/P_E \quad (17)$$

and further as

$$\frac{dX_l}{dt} = - \left(X_l - \sum_{i=1}^5 \frac{M_{i,l+1}}{M} X_{i-1} \right) \frac{v_-(\text{I}_a)}{P_E} \quad (18)$$

by substitution of x_l from Eq. (15). In Eq. (18) M is the coefficient matrix of x_l in the left side of Eq. (15) and $M_{i,l+1}$ is the cofactor of $(i, l+1)$ element of M . Thus, X_l 's are given as the solutions of five differential equations with three parameters, y_1 , $v_+(\text{I}_a)$ and $v_-(\text{II})$.

When reaction is carried out with equimolar C₂P₄ and C₂D₄ and equimolar P₂ and D₂, the following relations hold throughout the reaction:

$$y_1 = y_0 = 0.5 \quad (19)$$

and

$$X_l = X_{4-l}, \quad x_l = x_{4-l}. \quad (20)$$

Taking account of the experimental condition and the initial condition of reaction, Eq. (18) is simplified, and finally we have⁹⁾

$$v_+(\text{I}_a)/v_-(\text{II}) = (2(dX_1/dX_2)_0 - 1)/3 \quad (21)$$

and

$$v_-(I_a) = 2V^{E_1} (3v_+(I_a)/v_-(II) + 2). \quad (22)$$

The unidirectional rates of steps I_a and II can be evaluated according to Eqs. (6), (21) and (22) by measuring V_s , V^{E_1} and V^{E_2} at an initial stage of the reaction.

The backward rate of step I_b is given by Eqs. (3), (19) and the initial condition $Y_1=0$ as

$$v_-(I_b) = V^{PD}/2y_0y_1 = 2V^{PD}, \quad (23)$$

and, accordingly, the forward rate $v_+(I_b)$ is given by Eq. (6). Thus, the unidirectional rates of the steps are evaluated without less accurate measurement of the deuterium distribution in ethane.

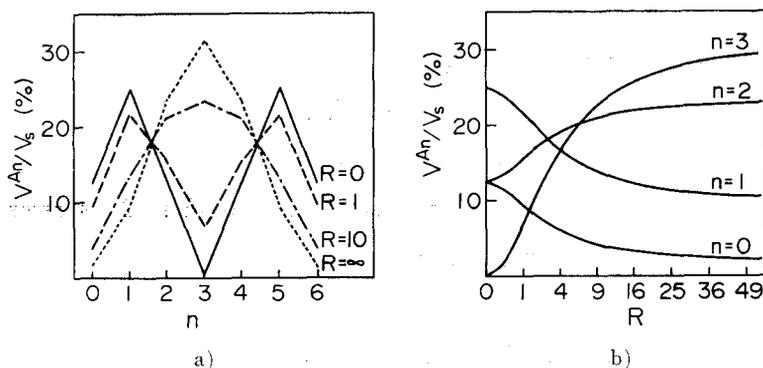


Fig. 1. Calculated evolution rates of d_n -ethanes at an initial stage of the reaction of equimolar C_2P_4 and C_2D_4 with equimolar P_2 and D_2 . ($R \equiv v_-(II)/v_+(I_a)$).

The relative evolution rates of d_n -ethanes, V^{An}/V_s 's, at an initial stage of this reaction can be calculated by Eqs. (4) and (15) as functions of $R (\equiv v_-(II)/v_+(I_a))$ as shown in Figs. 1 a) and b)⁹⁾. With reference to these figures, the value of $v_+(I_a)/v_-(II)$ can be estimated by measuring V^{An}/V_s 's.

2.2. Method of KEMBALL

KEMBALL¹⁰⁾ interpreted the deuterium distributions in ethylene and ethane at an initial stage of ethylene deuteration in terms of the parameters p , q , r and s defined as follows:

$$p = \frac{\text{chance of adsorbed ethylene becoming ethyl}}{\text{chance of adsorbed ethylene desorbing}},$$

$$q = \frac{\text{chance of ethylene acquiring a D atom}}{\text{chance of ethylene acquiring a P atom}},$$

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$$r = \frac{\text{chance of ethyl reverting to ethylene}}{\text{chance of ethyl becoming ethane}},$$

$$s = \frac{\text{chance of ethyl acquiring a D atom}}{\text{chance of ethyl acquiring a P atom}}.$$

According to his treatment, the initial distributions of deuterioethylenes and deuterioethanes are given as the solutions of 18 simultaneous equations involving these parameters, and the set of values of these parameters reproducing the observed distributions is found by trial and error calculation with a computer. This method may be characterized by that the origin of hydrogen atoms is not specified, *i. e.* it may be adsorbed ethyl or gaseous hydrogen other than adsorbed hydrogen atoms. However, this treatment gives no information on the rate of a step in which gaseous hydrogen participates. In order to determine the rate-determining step in ethylene hydrogenation, it is necessary to evaluate the forward and backward rates of hydrogen supply to catalyst surface during ethylene hydrogenation.

In a case of the reaction proceeding *via* scheme (1), the parameters p and r are given in terms of the unidirectional rates of steps I_a and II as

$$p = v_+(II)/v_-(I_a),$$

$$r = v_-(II)/v_+(III) = v_-(II)/V_s.$$

Accordingly, the unidirectional rates of steps I_a and II can be calculated from these parameters; for example, $V_s(r+1)/p$ is the backward rate of step I_a , *i. e.* $v_-(I_a)$. The deuterium fraction of adsorbed hydrogen atoms reacting with adsorbed ethylene or ethyl is, on the other hand, given by $q/(q+1)$ or $s/(s+1)$, respectively, with neglect of isotopic effects. According to the results obtained by KEMBALL¹⁰, BOND *et al.*¹¹⁻¹³ and WELLS *et al.*¹⁴, the value of $q/(q+1)$ is fairly close to that of $s/(s+1)$ with most of the metals used. This suggests that the origin of hydrogen atoms reacting with adsorbed ethylene and ethyl is common.

2.3. Method of YASUDA and HIROTA

YASUDA and HIROTA^{15,20} proposed a method of determining the rates of elementary steps in propylene hydrogenation proceeding by associative mechanism¹¹. Their method is applicable to ethylene deuteration and the procedure is summarized as follows in terms of the present author's symbols.

Elimination of x_n 's from Eqs. (4) and (17) leads to the equation,

$$V^A_n/V_s = (y_0^2 dX_n/dt + 2y_0 y_1 dX_{n-1}/dt + y_1^2 dX_{n-2}/dt) P_E/v_-(I_a) + y_0^2 X_n + 2y_0 y_1 X_{n-1} + y_1^2 X_{n-2}, \quad (n=0, \dots, 6). \quad (24)$$

Since X_n , dX_n/dt and P_E are measurable, V^{A_n}/V_s is given as functions of $y_1 (= 1 - y_0)^*$ and $v_-(I_a)$. The values of y_1 and $v_-(I_a)$ are estimated by simulating the observed evolution rates of deuterioethanes according to Eq. (24). The rate of step I_b is, on the other hand, calculated from the evolution rates of P_2 , PD and D_2 according to Eq. (3).

YASUDA and HIROTA¹⁵⁾ emphasized that their method is possible to evaluate $v_-(I_a)$ not only at an initial stage but throughout the reaction. However the rate of step II is not determinable by their method.

III. Rate-Determining Step and Reaction Structure

The methods mentioned above enable us to evaluate the rates of elementary steps in ethylene hydrogenation and in consequence to determine the rate-determining step. Rate-determining step is usually defined as an extremely slow one among elementary steps. However, this definition is not adequate for a reaction involving an irreversible step such as step III of scheme (1), because the irreversible step is usually far slower than the other steps but not necessarily rate-determining. Including such a case, a general definition of rate-determining step in a single route reaction²¹⁾ is given by HORIUTI's reaction structure theory^{17,18)}. The theory introduces a new function, an imaginary rate $k(s)$, which is the forward unidirectional rate of step s under a special condition of step s being rate-determining, *i.e.* any step other than s is in quasi-equilibrium. When $k(r)$ of step r is far smaller than any other $k(s)$'s, step r is defined as the rate-determining step.

In the case of ethylene hydrogenation, $k(s)$'s ($s = I_a, I_b, II$ and III) are evaluated from the unidirectional rates of respective steps, $v_+(s)$ and $v_-(s)$, as follows:

$$\begin{aligned} k(I_a) &= v_+(I_a), \\ k(I_b) &= v_+(I_b), \\ k(II) &= v_+(II) \frac{v_+(I_a)}{v_-(I_a)} \sqrt{\frac{v_+(I_b)}{v_-(I_b)}}, \\ k(III) &= v_+(III) \frac{v_+(I_a)}{v_-(I_a)} \frac{v_+(I_b)}{v_-(I_b)} \frac{v_+(II)}{v_-(II)}, \end{aligned} \quad (25)$$

where each step other than III is assumed reversible.

*) In their treatment, y_1 is defined as a possibility of adsorbed hydrocarbon species acquiring D(a).

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The relative magnitude of $k(s)$'s and their temperature-dependencies are named reaction structure.

IV. Reaction Structure Analysis of Ethylene Hydrogenation on Various Metals

Complete reaction structure of ethylene hydrogenation on various metals was experimentally determined by the present author⁶⁻⁹⁾: the results are reproduced in this section.

Evaporated film of metal was used as catalyst, which was pretreated with hydrogen at 200 or 300°C after each run of the reaction in order to reproduce its catalytic activity and to suppress side reactions, especially the self-hydrogenation of ethylene caused by its dissociative adsorption, which might strongly affect the deuterium distributions in the products of ethylene deuteration. Reaction was carried out with an equimolar mixture of ethylene and hydrogen at total pressure of 40 mmHg.

Copper

With Cu film, y_1 , x_1 and x were evaluated from the evolution rates of isotopic isomers of ethylene, hydrogen and ethane at the initial stage of ethylene deuteration (called Reaction A in what follows) as shown in Table 1. In this case Eqs. (12) and (13) gave the same value of y_1 . The unidirectional rates of elementary steps evaluated by Method A are shown in Fig. 2. Steps I_a and II are far faster than steps I_b and III in the observed temperature range and $v_-(I_b)$ approaches to $v_+(I_b)$ with rise of temperature.

The rates of steps were also evaluated by Method B. Plots in Figs. 3 a) and b) show the time courses of hydrogen isotopic mixing between d₀- and d₄-ethylene during the reaction of equimolar d₀- and d₄-ethylene with equimolar P₂ and D₂ (called Reaction B in what follows). The P₂-D₂ equilibration during this reaction was much slow in agreement with the above

TABLE 1. Values of y_1 , x_1 and x (Cu)

Temp. (°C)	y_1	x_0	x_1	x_2	x
78	0.144	0.97	0.03	0	0.008
91	0.115	0.90	0.09	0.01	0.028
103	0.100	0.88	0.11	0.01	0.033
135	0.088	0.67	0.31	0.02	0.088

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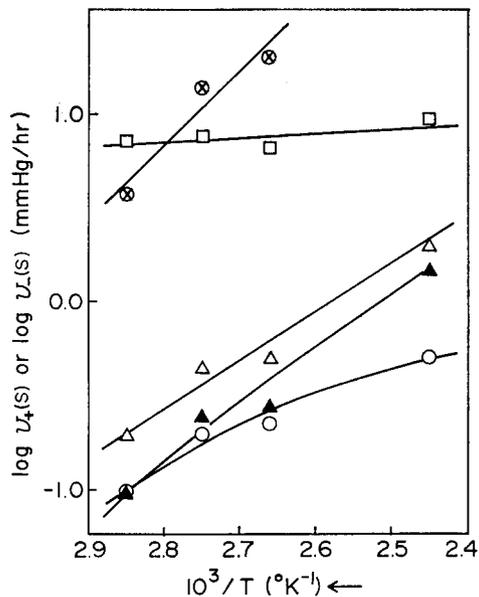


Fig. 2. Arrhenius plots of the rates of steps in ethylene hydrogenation on Cu.

□, $v_+(Ia)$ and $v_-(Ia)$; \triangle , $v_+(Ib)$; \blacktriangle , $v_-(Ib)$; \otimes , $v_+(II)$ and $v_-(II)$; \circ , $v_+(III)$ ($=V_s$).

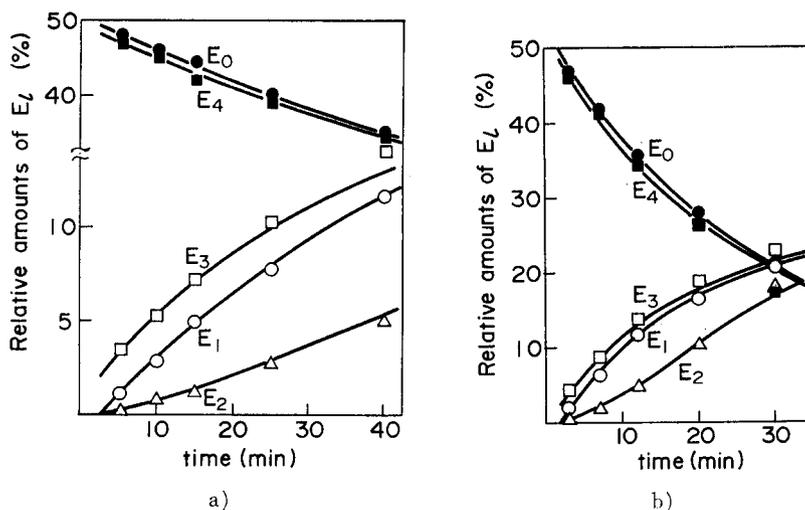


Fig. 3. Hydrogen exchange between C_2P_4 and C_2D_4 during Reaction B on Cu at 101°C a) and 137°C b).

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TABLE 2. Evolution rates of d_1 - and d_2 -ethylene and relative rates of steps I_a and II at the initial stage of Reaction B on Cu

Temp. (°C)	\dot{X}_1 (%/min)	\dot{X}_2 (%/min)	$v_+(I_a)/V_s$	$v_+(II)/V_s$
101	0.43	0.10	610	250
137	1.6	0.39	740	310

$$\dot{X}_i = dX_i/dt.$$

results of slow step I_b . The relative forward rates of steps I_a and II, $v_+(I_a)/V_s$ and $v_+(II)/V_s$, were evaluated as given in Table 2 according to Eqs. (21) and (22) from the initial evolution rates of d_1 - and d_2 -ethylene. Both the relative forward rates thus obtained are considerably larger than those evaluated by Method A. In order to elucidate this discrepancy, the time courses in Figs. 3 a) and b) were simulated by a computer calculation. The simulation was carried out by Runge-Kutta-Gill method²²⁾ according to Eqs. (5) and (18), into which the rates of steps I_a and II were introduced from Table 2. The results given by the full lines in Figs. 3 a) and b) are in good agreement with the observed time courses, showing satisfactory

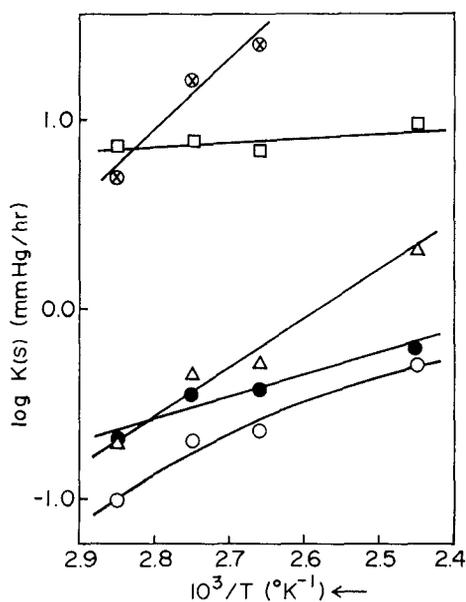


Fig. 4. Reaction structure of ethylene hydrogenation on Cu.
 \square , $k(I_a)$; \triangle , $k(I_b)$; \otimes , $k(II)$; \bullet , $k(III)$; \circ , V_s .

accuracy of Method B. The discrepancy between the results of Methods A and B is consequently attributed to the errors of the mass-spectrometric analysis of deuterioethane in Method A. The rates of steps I_a and II are underestimated by Method A when these steps are far faster than ethylene hydrogenation⁹.

The reaction structure of ethylene hydrogenation on Cu film is shown in Fig. 4. At temperatures below or above *ca.* 80°C, $k(I_b)$ or $k(III)$ is the smallest among $k(s)$'s, respectively, *i.e.* the rate-determining step switches from step I_b to III with rise of temperature beyond *ca.* 80°C.

Nickel

Table 3 shows the values of y_1 calculated by Eqs. (12) and (13) (denoted by $y_1(H)$ and $y_1(A)$, respectively) at the initial stage of Reaction A on Ni film. The cause of considerable difference between $y_1(H)$ and $y_1(A)$ is discussed later. For the present calculation, $y_1(A)$ should be used for the value of y_1 , because $y_1(A)$ is the deuterium fraction of adsorbed hydrogen atoms actually reacting with the adsorbed hydrocarbon species. The unidirectional rates of respective steps evaluated by Method A are shown in Fig. 5. This result is similar to that obtained with Cu; however, the relative rate, $v_+(I_a)/V_s$, of step I_a is small as compared with that obtained with Cu. The result of Reaction B (Table 4) proves the above conclusion, that is, hydrogen exchange between d₀- and d₄-ethylene was not equilibrated at the

TABLE 3. Values of y_1 (Ni)

Temp. (°C)	$y_1(H)$	$y_1(A)$
79	0.30	0.05
100	0.41	0.09
120	0.36	0.11
150	0.40	0.13

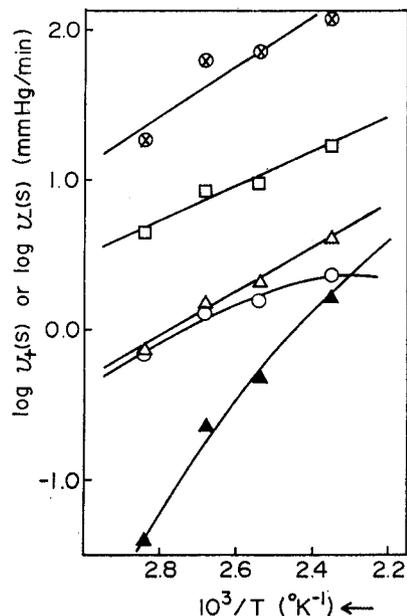


Fig. 5. Arrhenius plots of the rates of steps in ethylene hydrogenation on Ni.

□, $v_+(I_a)$ and $v_-(I_a)$; △, $v_+(I_b)$;
 ▲, $v_-(I_b)$; ⊗, $v_+(II)$ and $v_-(II)$;
 ○, $v_+(III)$ ($=V_s$).

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TABLE 4. Hydrogen exchanges during Reaction B on Ni

Temp. (°C)	Time (min)	Conversion (%)	Hydrogens (%)			Ethylenes (%)				
			P ₂	PD	D ₂	E ₀	E ₁	E ₂	E ₃	E ₄
45	2.5	7	47.4	2.0	50.6	30.0	15.3	10.0	17.6	26.1
	5	14	46.8	2.4	50.8	24.7	19.7	15.7	20.1	19.8
	10	29	42.6	3.5	53.9	15.7	24.4	26.2	22.6	12.0
	15	40	38.8	4.7	56.5	10.4	25.0	32.7	23.6	8.3
	25	57	32.2	6.8	61.0	7.5	25.0	35.8	24.8	7.0
0	30	6	46.4	1.9	50.7	32.1	14.4	9.4	16.1	27.9
	60	12	46.1	2.2	51.7	17.8	22.2	23.4	23.3	12.3
	100	18	44.4	2.6	53.0	11.7	25.1	30.1	24.6	8.5
	300	28	42.5	3.0	54.5	7.4	26.1	36.6	24.0	6.0

early stage of hydrogenation reaction. Step I_a on Ni is thus concluded to be not in quasi-equilibrium against the presumption used in the theories of HORIUTI^{17,18)} and others^{16,19)}.

The rate of step I_b, evaluated according to Eq. (23) from the rate of PD formation in Reaction B is somewhat larger than that obtained by Method A. This arises, as mentioned later, from the same cause of the discrepancy between $y_1(H)$ and $y_1(A)$ in Reaction A.

The reaction structure given in Fig. 6 shows that the rate-determining step is I_b or III at temperatures far below or above *ca.* 170°C, respectively. The activation heat of step III is negative as already discussed in the previous works^{17,23)}.

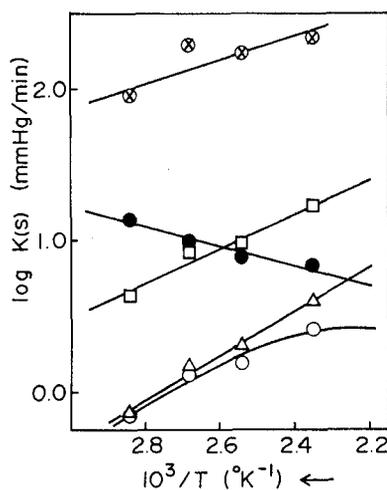


Fig. 6. Reaction structure of ethylene hydrogenation on Ni.

□, $k(I_a)$; △, $k(I_b)$; ⊗, $k(II)$;
●, $k(III)$; ○, V_s .

Platinum

Similarly to the case of Ni, $y_1(H)$ and $y_1(A)$ in Reaction A on Pt were different, and the rates of steps were evaluated with $y_1(A)$ as shown in Fig. 7. Step II is fast but step I_a is as slow as step I_b in contrast with the cases of Cu and Ni. Hydrogen mixing in ethylene during Reaction B

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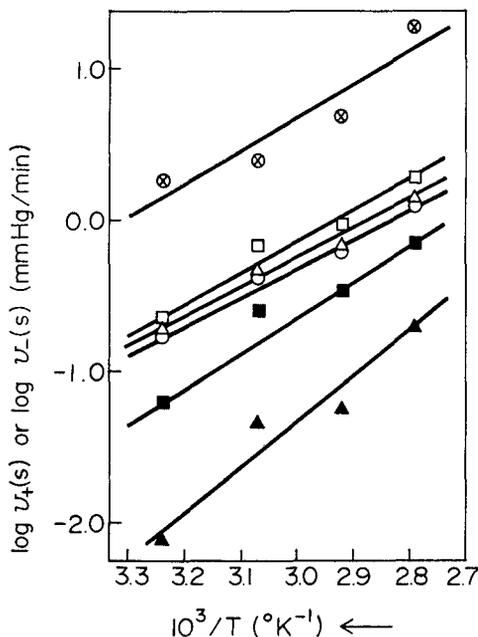


Fig. 7. Arrhenius plots of the rates of steps in ethylene hydrogenation on Pt.

□, $v_+(I_a)$; ■, $v_-(I_a)$; △, $v_+(I_b)$; ▲, $v_-(I_b)$; ⊗, $v_+(II)$ and $v_-(II)$; ○, $v_+(III)$ ($=V_s$).

TABLE 5. Rates of hydrogen exchanges in hydrogen and ethylene at the initial stage of Reaction B on Pt

Temp. (°C)	\dot{Y}_0	\dot{Y}_1	\dot{Y}_2	\dot{X}_1	\dot{X}_2
		(%/min)		(%/min)	
33	-0.4	0.3	0	0.05	0.02
53	-0.7	0.6	0	0.12	0.06
69	-1.4	1.7	0	0.37	0.16
82	-1.9	2.8	0	0.62	0.27

\dot{Y}_m or \dot{X}_l is the time derivative of Y_m or X_l , respectively.

was much slower than ethylene hydrogenation (Table 5), also indicating slow step I_a . Step I_a , however, should not rate-control ethylene hydrogenation on Pt as discussed below. The rate-law of ethylene hydrogenation on Pt has been found¹⁾ the same as those obtained with Cu and Ni, *i.e.* the rate is proportional to $P_E^0 P_H^1$ in the temperature range of the present work.

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This indicates that step I_b is rate-determining similarly to the cases of Cu and Ni. Furthermore, ethylene adsorption on Pt has been found^{24,25} strong and nearly irreversible at room temperatures. On the basis of these facts, it may be concluded that adsorbed ethylene is irreversibly held on Pt surface during the hydrogenation and hydrogen chemisorption retarded by strongly adsorbed ethylene rate-determines the hydrogenation. The reversibility of step I_a expressed as $v_-(I_a)/v_+(I_a)$ increases with rise of temperature as seen from Fig. 7.

A complete reaction structure as derived with Cu and Ni is not obtained in this case since step I_a is not reversible. However, step III is expected to be rate-determining at higher temperature similarly to the cases of Cu and Ni, because $v_-(I_b)$ approaches to $v_+(I_b)$ with rise of temperature.

Rhodium

The results obtained with Reactions A and B on Rh were very similar to those obtained with Pt. The rates of steps on Rh evaluated by Method A is given in Table 6. The rate-law on Rh¹⁾ is the same as on Pt, indicating step I_b being rate-determining.

TABLE 6. Unidirectional rates of respective steps
in ethylene hydrogenation on Rh (mmHg/min)

Temp. (°C)	$v_+(I_b)$	$v_-(I_b)$	$v_+(I_a)$	$v_-(I_a)$	$v_+(II)$	$v_+(III) (= V_s)$
0	1.61	0.21	1.95	0.55	9.8	1.4
-45	0.16	0.01	0.17	0.02	0.95	0.15

V. Mechanism of Hydrogen Chemisorption

The difference between $y_1(H)$ and $y_1(A)$ in Method A was observed with Ni, Pt and Rh of group VIII metal but not with Cu of group Ib metal. This difference may arise from the following causes :

- (i) isotopic effect ;
- (ii) light ethane formation by self-hydrogenation of ethylene ;
- (iii) P_2-D_2 equilibration proceeding *via* a side step in parallel with step I_b ;
- (iv) step I_b , consisting of two elementary steps, at least.

With respect to the isotopic effect on the rate of ethylene hydrogenation,

it has been found nearly equal with every metal used⁶⁻⁸), while no significant difference between $y_1(\text{H})$ and $y_1(\text{A})$ was observed on Cu. Accordingly, the isotopic effect might be not a main cause of the difference so far as the reaction mechanism is common for Cu and transition metals.

Self-hydrogenation of ethylene during ethylene deuteration resulting in light ethane formation was observed with freshly evaporated metal films²⁶. Such a formation of light ethane may give rise to an apparent decrease of $y_1(\text{A})$. The self-hydrogenation on metals, however, has been found^{7,26} suppressed by repeating ethylene hydrogenation on the same catalyst pretreated with hydrogen after each run, and completely eliminated by the use of the catalyst pretreated with ethylene at higher temperature. The discrepancy of y_1 value was still observed with these catalysts⁷, and hence the self-hydrogenation is concluded to be not the cause.

If $\text{P}_2\text{-D}_2$ equilibration takes place rapidly *via* a side step of step I_b , *e. g.*



where $\text{H}(\text{a})_c$ does not take part in ethylene hydrogenation, P_2 evolved *via* step I_b during Reaction A should readily react with D_2 to form PD by this side step and results in excess $y_1(\text{H})$ over $y_1(\text{A})$. Reality of this mechanism is examined as follows. As step I_c is assumed to contribute only to $\text{P}_2\text{-D}_2$ equilibration, $v_+(\text{I}_c)$ must be equal to $v_-(\text{I}_c)$. The rate of PD formation at an initial stage of Reaction B is given as

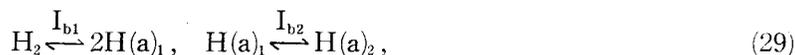
$$V^{\text{PD}} = (v_-(\text{I}_b) + v_-(\text{I}_c))/2, \quad (27)$$

from which $v_-(\text{I}_c)$ is evaluated by introducing $v_-(\text{I}_b)$ from Eq. (10). The rate of P_2 formation at an initial stage of Reaction A is given as

$$V^{\text{P}_2} = (1 - y_1(\text{A}))^2 v_-(\text{I}_b) - Y_0 v_+(\text{I}_b) - Y_0 v_+(\text{I}_c), \quad (28)$$

where the formation of P_2 *via* step I_c is neglected since the protium fraction in $\text{H}(\text{a})_c$ might be negligibly small. As Y_0 is very small at the initial stage, $v_+(\text{I}_c)$ evaluated by Eq. (27) should be much larger than $v_-(\text{I}_c)$ by Eq. (27). This result contradicts with the assumption that step I_c does not contribute to ethylene hydrogenation, and hence this mechanism is ruled out.

Step I_b is now considered to consist of two steps as



where $\text{H}(\text{a})_1$ or $\text{H}(\text{a})_2$ is an adsorbed hydrogen atom inactive or active, respectively, for hydrogenation of the adsorbed hydrocarbon species. Ac-

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ording to scheme (29), the deuterium fraction of $H(a)_1$ or $H(a)_2$ in Reaction A is given by $y_1(H)$ or $y_1(A)$, respectively, and the former is larger than the latter so far as step I_{b2} is not in equilibrium. This model of step I_b is also consistent with other experimental evidence, *i.e.* the change of the rate-law of ethylene hydrogenation on Ni with temperature. It has been found at temperatures below optimum that the reaction order in ethylene pressure is constantly about zero¹⁾ while the order in hydrogen pressure changes from unity to 0.7²⁷⁾ with fall of temperature to $0 \sim -45^\circ\text{C}$ and, further, to 0.5¹⁰⁾ at $-100 \sim -120^\circ\text{C}$. As already discussed in the preceding section, step I_b is the rate-determining step of ethylene hydrogenation on Ni at low temperature. The observed change of the reaction order in hydrogen pressure is, however, not simply interpretable by a single elementary step I_b being rate-determining. If the rate-determining step changes from step I_{b1} to I_{b2} with fall of temperature, the order in hydrogen pressure should gradually change from unity to one-half as observed. Furthermore, the fact that P_2 - D_2 equilibration during Reaction B on Ni fairly took place even at 0°C while P_2 and PD hardly appeared in the gas phase of Reaction A at the same temperature, is interpretable by two steps model of step I_b . A mechanism of ethylene hydrogenation similar to scheme (29) has been proposed by CARTIER and RYE²⁸⁾ in their study of the flash filament desorption of ethylene and deuterium from W surface. Two or more states of adsorbed hydrogen atoms have been found on Ni^{29,30)}, Pt³¹⁻³⁵⁾ and Rh³⁶⁾ by IR, flash desorption or temperature programmed desorption method. Though a reactivity of each adsorbed hydrogen for ethylene hydrogenation has not yet been made clear, it may be reasonably expected that one of these adsorbed species is a precursor of the hydrogen atoms active for hydrogenation and hydrogen exchange of ethylene.

The rates of steps I_{b1} and I_{b2} in scheme (29) can be evaluated from the results of Reactions A and B. The backward rate of step I_{b1} is given at an initial stage of Reaction B as

$$v_-(I_{b1}) = 2V^{PD}, \quad (30)$$

and then its forward rate, $v_+(I_{b1})$, is evaluated by the following steady state condition :

$$V_s = v_+(I_{b1}) - v_-(I_{b1}) = (v_+(I_{b2}) - v_-(I_{b2}))/2. \quad (31)$$

On the other hand, the forward overall rate of step I_b is expressed in terms of $v_+(I_{b1})$, $v_+(I_{b2})$ and $v_-(I_{b2})$ as

$$v_+(I_b) = v_+(I_{b1}) + v_+(I_{b2})/2 - (v_-(I_{b2})/2). \quad (32)$$

Since $v_+(I_b)$ is known as described in Section IV, $v_+(I_{b2})$ can be evaluated according to Eqs. (30), (31) and (32). For example, with Pt at 53°C, $v_+(I_{b2})$ is estimated to be about twice of $v_+(I_{b1})$.

VI. Adsorption Strength of Ethylene on Metal and Activity of Metal for Ethylene Hydrogenation

Table 7 shows the catalytic activity of Cu, Ni, Pt and Rh at 0°C and the relative backward rates of step I_a , $v_-(I_a)/V_s$, evaluated at *ca.* 80°C by the present method. The value of $v_-(I_a)/V_s$ is considered to show a degree of the reversibility of ethylene adsorption during ethylene hydrogenation, and appears to decrease with increase of the activity of metal. This was further checked by the experimental data of BOND *et al.*¹¹⁻¹³⁾ on the deuterium distributions in ethylene and ethane at the initial stage of ethylene deuteration over various metals supported on alumina. Table 8 shows the values of $v_-(I_a)/V_s$ evaluated from their results on the reaction carried out at

TABLE 7. Relative activities of Rh, Pt, Ni and Cu films for Reaction A and relative backward rates of step I_a

Metal	log activity*)	Temp. (°C)	$v_-(I_a)/V_s$
Rh	0	0	0.4
		80	0.8**)
Pt	-1.74**)	85	0.6
Ni	-1.61	79	5.4
Cu	-5.52**)	78	73.7

*) Relative rate of Reaction A at 0°C per unit geometrical area of metal film ($V_s(\text{Rh}) \equiv 1.0$).

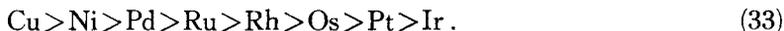
**) Value estimated by extrapolation.

TABLE 8. Relative backward rates of step I_a evaluated from the results of BOND *et al.*¹¹⁻¹³⁾

Metal	Temp. (°C)	P_E	P_{H_2}	$v_-(I_a)/V_s$
		(mmHg)		
Pt	54	99	98	0.3
Ir	86	100	100	0.2
Ru	80	75	76	2.5
Os	36	50	50	0.6
Pd	67	100	100	3.9

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ca. 80°C with equimolar ethylene and deuterium. The following sequence of metals for the value of $v_-(I_a)/V_s$ is assembled from Tables 7 and 8 :



The order of the catalytic activities of metals for $\text{P}_2\text{-D}_2$ equilibration^{37,38} is, on the other hand, as follows :



This order is just the reverse of the order (33), indicating that a metal much active for hydrogen chemisorption adsorbs ethylene more strongly during ethylene hydrogenation. These results give the understanding of the activity order of metals for ethylene hydrogenation.

Logarithmic activity of metal relative to that of Rh is plotted against logarithmic $v_-(I_a)/V_s$ in Fig. 8, where the activities of metals used by BOND *et al.* are referred to those observed by SCHUIT and VAN REIJEN³⁷. The activity order of the metals plotted around the full line in Fig. 8 is the same as that for $\text{P}_2\text{-D}_2$ equilibration³⁷ or *para*-hydrogen conversion³⁹ as expected from the reaction structure of ethylene hydrogenation (*i.e.* its rate-determining step at low temperature is hydrogen chemisorption). Platinum is, however, less active than Rh contrary to the expectation from their activity order for $\text{P}_2\text{-D}_2$ equilibration³⁸. The rate of hydrogen chemisorption evaluated from the rate of $\text{P}_2\text{-D}_2$ equilibration in the absence of ethylene

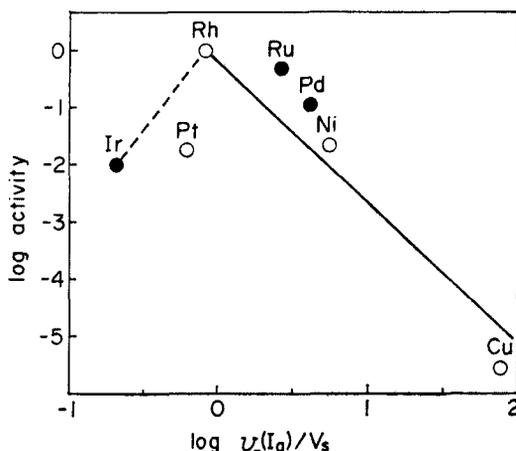


Fig. 8. Correlation between the catalytic activity of metal for ethylene hydrogenation and the relative backward rate of step I_a ($v_-(I_a)/V_s$): \circ , present author's results; \bullet , $v_-(I_a)/V_s$ was evaluated from the data of BOND *et al.*¹¹⁻¹³) and the activities of the metals were referred to SCHUIT and VAN REIJEN³⁷).

is larger than the rate of ethylene hydrogenation by a factor of *ca.* 2 with Cu⁶⁾, *ca.* 10 with Ni⁴⁰⁾ and *ca.* 300 with Pt⁸⁾. This result indicates that hydrogen chemisorption during ethylene hydrogenation is more intensively inhibited by more irreversibly adsorbed ethylene. Accordingly, a volcano-type correlation shown in Fig. 8 is understandable as follows: (i) hydrogen chemisorption rate-determines ethylene hydrogenation and is more intensively retarded by more irreversibly adsorbed ethylene; (ii) a metal more active for hydrogen chemisorption adsorbs ethylene more irreversibly during ethylene hydrogenation; (iii) in consequence, the hydrogenation-activity of metal increases with decrease of $v_-(I_a)/V_s$ from that on Cu to Rh and decreases with further decrease of $v_-(I_a)/V_s$ owing to the strong inhibition of hydrogen chemisorption by irreversibly adsorbed ethylene. Thus, Rh might be the most active metal for ethylene hydrogenation among transition metals.

HORIUTI and MIYAHARA⁴⁾ discussed the activity order of metals for ethylene hydrogenation as a function of the initial heat of hydrogen adsorption on metal assuming reversible adsorption of ethylene over every metal and predicted that some metal having lower initial heat of hydrogen adsorption than Rh is more active than Rh for ethylene hydrogenation. Ethylene adsorption is, however, not necessarily reversible and its reversibility during ethylene hydrogenation decreases with decrease of the initial heat of hydrogen adsorption on metal as found in the present work. Accordingly, hydrogen adsorption on such a metal will be intensively retarded by irreversibly adsorbed ethylene similarly to the cases of Pt and Ir and its activity for ethylene hydrogenation will never exceed that of Rh.

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