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REACTION STRUCTURE OF ETHYLENE HYDROGENATION ON METALLIC CATALYSTS

Part 2. The Reaction on Evaporated Nickel Film

By

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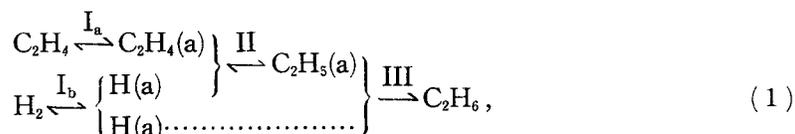
Abstract

Hydrogenation of ethylene over an evaporated nickel film was investigated at temperatures from 0 to 150°C by the use of deuterium as a tracer. It was found that C₂P₆ (P: protium) was predominantly formed at the initial stage of reaction of C₂P₄ with D₂, similarly to the previous case of an evaporated copper film, while the ratio of the evolution rate of P₂ to that of PD was far smaller than that observed with copper.

The rates of elementary steps constituting ethylene hydrogenation over nickel were evaluated according to the method reported previously. The rate-determining step of ethylene hydrogenation was found to change with rise of reaction temperature beyond the so-called optimum temperature from chemisorption of hydrogen to hydrogenation of adsorbed half-hydrogenated ethylene as concluded in the previous works. The difference between nickel and copper catalysts mentioned above was concluded to be due to the difference of a mechanism of hydrogen adsorption.

Introduction

Steady hydrogenation of ethylene catalyzed by nickel and other transition metals has been concluded^{1,2)} to proceed *via* a set of steps as



where step I_b or III is rate-determining at temperatures below or above the so-called optimum temperature, respectively, so far as step I_a is assumed so fast as to be nearly in equilibrium. Ethylene hydrogenation on nickel film freshly evaporated, however, has been found¹⁾ to accompany dissociative

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Reaction Structure of Ethylene Hydrogenation. Part 2, Ni

adsorption of ethylene which results in the so-called self-hydrogenation of ethylene and disturbs the analysis of steady hydrogenation of ethylene according to scheme (1). Methods of observation to eliminate this side reaction and to give a quantitatively reproducible result are investigated in the present work, and the rates of steps of scheme (1) are evaluated according to the reaction structure theory³⁾ applied previously⁴⁾ to the observed results with copper catalyst and devised partly in the present work. In the calculation of rates, the presumption on step I_a mentioned above is excluded. The results derived are discussed with reference to those of copper catalyst⁴⁾.

Experimental

Catalyst used was a nickel film evaporated, similarly as described in previous paper⁵⁾, under a vacuum of 3×10^{-7} mmHg from a nickel wire (0.5 mm in diameter and 99.9% purity) onto the inner surface of a cylindrical reactor made of Pyrex glass. The geometrical area of the film was *ca.* 9 cm². As a reference catalyst, a nickel wire (0.1 mm in diameter, *ca.* 2 m in length and 99.9% purity) was used. The wire was sealed in the reactor and was activated as usual⁶⁾ by electrically red-heating in atmospheric air for 10 min, followed successively by reduction in 30 mmHg hydrogen at 300°C for one day and evacuation for 2 hr at the same temperature.

Quantitative and reproducible observations of the evolution rate of individual deuterio-substituted product are necessary for carrying out the present analyses of the rates of steps of scheme (1). A freshly evaporated film (signified by F) has been found⁵⁾ to give reproducible hydrogenation activity; however, the reaction on film F accompanies considerable dissociative adsorption of ethylene which results in the self-hydrogenation of ethylene¹⁾. Film F once used for hydrogenation and subsequently outgassed *in vacuo* at the reaction temperature (signified by S) is known¹⁾ to preclude practically dissociative adsorption of ethylene, but its catalytic activity is not reproducible. The present work was carried out with film R which was treated before each run of reaction by heating in 34 mmHg hydrogen for one day or more, followed by evacuation for *ca.* 2 hr both at 300°C. Hydrogenation activity of film R was reproducible and about one half of that of film F.

Apparatus, materials and experimental procedures were the same as described in the previous papers^{4,5)}.

Calculation of Unidirectional Rates of Elementary Steps

The rates of steps of scheme (1) can be evaluated by applying the previous method⁴⁾ to experimental results obtained by the use of deuterium as a tracer. The method is summarized as follows.

Evolution rates V^{E_l} , $V^{P_{2-m}D_m}$ (P: protium) and V^{A_n} respectively of E_l , $P_{2-m}D_m$ and A_n , *i. e.* l -, m - and n -fold deuterio-substituted ethylene, hydrogen and ethane, are given according to scheme (1) as

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

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

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

where $v_+(s)$ or $v_-(s)$ ($s = I_a, I_b, II$ or III) is the forward or backward unidirectional rate of step s , x_l or X_l the fraction of $E_l(a)$ or E_l in $C_2H_4(a)$ or gaseous C_2H_4 , y_0 or y_1 the fraction of P(a) or D(a) in H(a) and Y_m the fraction of $P_{2-m}D_m$ in gaseous H_2 , respectively, and the isotopic effect on reaction rate is ignored. H represents hydrogen atom irrespective of P or D. In Eq. (3) the rate $v_-(III)$ is neglected because of the practically irreversible process of step III^2 .

The steady rate, V_s , of ethylene hydrogenation is given as

$$V_s = v_+(s) - v_-(s), \quad (s = I_a, I_b, II \text{ or } III). \quad (5)$$

On the other hand, a steady state condition with respect to the deuterium content of $C_2H_4(a)$ is expressed as

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

where $X \equiv \sum l X_l / 4$ or $x \equiv \sum l x_l / 4$ is the atomic fraction of deuterium in C_2H_4 or $C_2H_4(a)$, respectively. At the initial stage of reaction of C_2P_4 with D_2 , the fractions X_l 's ($l \geq 1$), X and Y_0 are practically zero, and hence the rates $v_-(I_a)$ and $v_-(I_b)$ are given according to Eqs. (2) and (3) as

$$v_-(I_a) = \sum l V^{E_l} / 4x = V^{E_l} / x_l, \quad (l \geq 1), \quad (7)$$

and

$$v_-(I_b) = V^{P_2} / y_0^2 = V^{P_2} / (1-y_1)^2, \quad (8)$$

respectively, and the rate $v_-(II)$ is given according to Eqs. (5) and (6) as

Reaction Structure of Ethylene Hydrogenation. Part 2, Ni

$$v_-(\text{II}) = 6x(V_s + v_-(\text{I}_a))/(y_1 - x). \quad (9)$$

In Eqs. (7), (8) and (9) V^{E_1} 's, V^{E_2} and V_s are observable, and hence the unidirectional rates of steps of scheme (1) are given as functions of y_1 and x , which can be evaluated from observation of the initial evolution rates of P_2 , PD and A_0 as described previously⁴).

The above method of evaluating y_1 and x , however, was found to be unsuitable for the present case because of the formation of PD, presumably due to some side reaction other than step I_b of scheme (1) as described later. In the present work another method is devised as follows.

Following equations are derived from evolution rates of A_0 , A_1 and A_2 given by Eq. (4).

$$\frac{V^{A_1}}{V^{A_0}} = 2\phi + \frac{x_1}{x_0}, \quad (10)$$

$$\frac{V^{A_2}}{V^{A_0}} = \phi^2 + \left(2\phi + \frac{x_2}{x_1}\right) \frac{x_1}{x_0}, \quad (11)$$

where $\phi \equiv y_1/y_0$. Taking account of the initial condition, $X_l=0$ ($l \geq 1$), of the reaction, we have

$$\frac{x_2}{x_1} = \frac{V^{E_2}}{V^{E_1}}, \quad (12)$$

from Eq. (2). Substituting x_1/x_0 of Eq. (10) and x_2/x_1 of Eq. (12) into Eq. (11), we have

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

which is solved as

$$\phi \equiv \frac{y_1}{y_0} = \frac{1}{3} \left(\frac{V^{A_1}}{V^{A_0}} - \frac{V^{E_2}}{V^{E_1}} \pm \sqrt{D} \right), \quad (14)$$

where

$$D \equiv \left(\frac{V^{A_1}}{V^{A_0}} \right)^2 - 3 \frac{V^{A_2}}{V^{A_0}} + \frac{V^{A_1}}{V^{A_0}} \frac{V^{E_2}}{V^{E_1}} + \left(\frac{V^{E_2}}{V^{E_1}} \right)^2. \quad (15)$$

In Eq. (14) the evolution rates V^{A_n} 's and V^{E_l} 's are observable and hence we can evaluate y_1 ($\equiv \phi/(\phi+1)$). Substituting the value of ϕ thus evaluated into Eq. (10), we obtain the value of x_1/x_0 and hence that of x ($\equiv \sum l x_l / 4$) according to the previous method⁴).

S. SATO and K. MIYAHARA

Results and Discussion

Reaction of C₂P₄ with D₂. Reaction was carried out at temperatures from 79 to 150°C with an equimolar mixture of C₂P₄ and D₂ at 40 mmHg of the initial total pressure. A small amount of reacting gas was sampled at times for mass spectrometric analyses. Hydrocarbon products other than ethylene and ethane were not detected. Amounts of respective deuterio-ethylenes and ethanes increased linearly with the progress of hydrogenation up to *ca.* 20% conversion of ethylene.

Table 1 shows observed results of the initial rates of hydrogenation and evolutions of deuterio-substituted hydrogen, ethylene and ethane. We see that light ethane, A₀, is predominantly formed and P₂ is evolved slower than PD except at the lowest temperature, 79°C. In the case of copper catalyst⁴), P₂ was evolved by several times faster than PD.

From the results y_1 was evaluated as given in Table 2, where $y_1(H)$ is the value of y_1 calculated according to the previous method⁴) from the evolution rates of P₂ and PD and $y_1(A)$ is that calculated according to Eq.

TABLE 1. Rates of hydrogenation and evolutions of deuterio-substituted hydrogen, ethylene and ethane at the initial stage of reaction of C₂P₄ with equimolar D₂ on Ni film R.

Temp. (°C)	Hydrogenation, V _s (mmHg/min)	Hydrogen (%/min)		Ethylene (%/min)			Ethane*) (%)		
		P ₂	PD	E ₁	E ₂	E ₃	A ₀	A ₁	A ₂
79	0.68	0.13	0.11	1.1	0.03	0	78	14	7
100	1.28	0.61	0.83	5.6	0.6	0	59	23	13
120	1.56	1.37	1.53	7.1	0.8	0	57	27	13
150	2.36	4.5	5.3	15.0	1.9	0.2	50	28	16

*) Value of V_{A_n}/V_s .

TABLE 2. Values of y_1 , x_i and x calculated from the results in Table 1.

Temp. (°C)	$y_1(H)$	$y_1(A)$	x_0	x_1	x_2	x_3	x
79	0.30	0.05	0.92	0.07	0	0	0.02
100	0.41	0.09	0.82	0.16	0.02	0	0.05
120	0.36	0.11	0.80	0.18	0.02	0	0.06
150	0.40	0.13	0.76	0.21	0.03	0	0.07

Reaction Structure of Ethylene Hydrogenation. Part 2, Ni

(14). Substituting the value of V^A , etc. from Table 1 into Eq. (14), we have slightly negative value for D of Eq. (15). Such a negative value of D is considered to be caused mainly by large errors of the observation of V^A 's, and $y_1(A)$ was calculated by assuming the value of D to be zero. Table 2 shows that $y_1(H)$ is several times larger than $y_1(A)$. So far as scheme (1) is concerned, hydrogenation of ethylene is caused by additions of adsorbed hydrogen atoms formed by step I_b and, consequently, $y_1(H)$ should be equal to $y_1(A)$ as observed with copper catalyst⁴. The isotopic effect on rates may give rise to some difference between $y_1(H)$ and $y_1(A)$; however, the isotopic effect on hydrogenation rate observed with nickel catalyst was nearly equal, as shown later (Table 5), to that with copper catalyst on which $y_1(H)$ was equal to $y_1(A)$. Accordingly, the difference between $y_1(H)$ and $y_1(A)$ might be caused by the self-hydrogenation of ethylene, which may not be eliminated completely in spite of the use of film R.

To solve this problem, $y_1(H)$ and $y_1(A)$ were observed with nickel wire catalyst pretreated variously. Results are given in Table 3, where RNW is nickel wire once used for hydrogenation and heated in hydrogen and outgassed *in vacuo* at 300°C, NW-CO₂ is RNW exposed to *ca.* 6 mmHg CO₂ followed by evacuation for a minute at the reaction temperature and NW-C is RNW heated in 40 mmHg ethylene followed by evacuation at 200°C to make its surface carbided⁷. According to the previous results¹⁾ that the self-hydrogenation of ethylene during ethylene hydrogenation is practically precluded by the use of film S or "carbided" film, it may be expected that the reaction over NW-CO₂ or NW-C accompanies no dissociative adsorption of ethylene and, in consequence, $y_1(H)$ agrees with $y_1(A)$. As seen from Table 3, however, $y_1(H)$ is larger than $y_1(A)$ in every case.

TABLE 3. $y_1(H)$ and $y_1(A)$ estimated with variously pretreated Ni wire catalysts:
RNW, reduced Ni wire; NW-CO₂, CO₂ poisoned Ni wire; NW-C, "carbided" Ni wire.

Catalyst	Temp. (°C)	$y_1(H)$	$y_1(A)$
RNW	72	0.44	0.12
	53	0.44	0.13
NW-CO ₂	80	0.49	0.13
	50	0.50	0.14
NW-C	100	0.50	0.16

This result suggests that the disagreement between $y_1(\text{H})$ and $y_1(\text{A})$ is not due to the self-hydrogenation of ethylene but due to some side reaction resulting in PD formation. This problem will be discussed later.

Irrespective of deuterium distribution in gaseous hydrogen, the deuterium fraction of adsorbed hydrogen atoms reacting with ethylene should be given by $y_1(\text{A})$, from which x_i 's and x can be evaluated as given in Table 2. The unidirectional rates of steps other than I_b are evaluated according to Eqs. (5), (7) and (9). In the previous paper⁴⁾ the rate $v_-(\text{I}_b)$ was evaluated from $y_1(\text{H})$ according to Eq. (8), but in the present case Eq. (8) gives an apparent backward unidirectional rate of step I_b because of the presence of side reaction mentioned above. A true rate of step I_b can be evaluated as follows. Irrespective of the presence of the side reaction of step I_b , gaseous protium evolved during deuteration of light ethylene is supplied by adsorbed protium atoms released from adsorbed ethylene *via* step II of scheme (1). Hence desorption rate of these hydrogen atoms is given by

$$\left(\frac{1}{2} V^{\text{PD}} + V^{\text{P}_2}\right) = (1 - y_1(\text{A})) v_-(\text{I}_b) \quad (16)$$

and the rate $v_+(\text{I}_b)$ is evaluated according to Eqs. (16) and (5). Table 4 shows the unidirectional rates of steps evaluated from the results of Tables 1 and 2. Arrhenium plots of these rates are given in Fig. 1. We see from the figure that $v_-(\text{I}_b)$ is far smaller than $v_+(\text{I}_b)$ which is the smallest among the forward unidirectional rates of reversible steps, that is, step I_b is rate-determining. Step II is evaluated to be far faster than hydrogenation rate, V_s , similarly to the case of copper catalyst⁴⁾, while the rate of step I_a is relatively small, as compared with the case of copper catalyst. *Reaction with a mixture of C_2P_4 , C_2D_4 , P_2 and D_2 .* In order to make sure the above conclusion on the rates of respective steps, the reaction with equimolar C_2P_4 , C_2D_4 , P_2 and D_2 was carried out and the results are given

TABLE 4. Unidirectional rates of the elementary steps (mmHg/min).

Temp. (°C)	$v_+(\text{I}_b)$	$v_-(\text{I}_b)$	$v_+(\text{I}_a)$	$v_+(\text{II})$	$v_+(\text{III})(=V_s)$
79	0.72	0.04	4.4	18.1	0.68
100	1.51	0.23	8.3	63.7	1.28
120	2.04	0.48	9.5	71.1	1.56
150	4.01	1.65	16.8	119.7	2.36

Reaction Structure of Ethylene Hydrogenation. Part 2, Ni

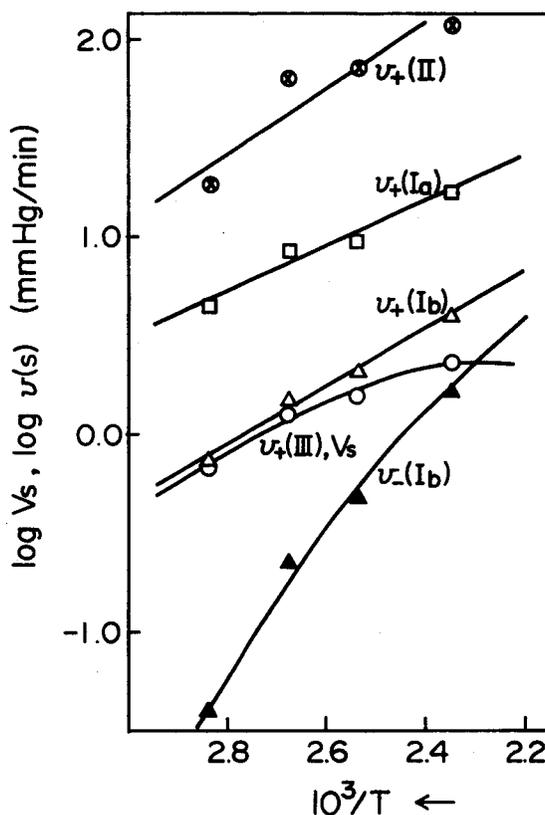


Fig. 1. Arrhenius plots of the rates of hydrogenation and elementary steps at 20 mmHg of initial partial pressures of ethylene and deuterium.

in Table 5. During the reaction at 0 and 45°C P_2 - D_2 equilibration was far slower than hydrogen exchange between C_2P_4 and C_2D_4 and the latter did not attain its equilibrium. In the case of copper catalyst⁴ the hydrogen exchange between C_2P_4 and C_2D_4 was nearly in equilibrium even at the initial stage of their hydrogenation. These results with nickel catalyst show, in conformity with the above conclusion, that the apparent rate of step I_b inclusive of the side reaction of PD formation is the smallest and either or both of steps I_a and II are relatively slow as compared with the case of copper catalyst.

The deuterium fraction of adsorbed hydrogen atoms is *ca.* 0.5 during this reaction, and hence the apparent backward unidirectional rate of step I_b is approximated to $2V^{PD}$ at the initial stage of reaction according to

TABLE 5. Hydrogen exchanges during the reaction with equimolar mixture of C_2P_4 , C_2D_4 , P_2 and D_2 of 40 mmHg initial total pressure over Ni film R.

Temp. (°C)	Time (min)	Conver- sion (%)	Hydrogen (%)			Ethylene (%)					$2V^{PD}/V_s$
			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	16.3	10.0	17.6	26.1	0.16
	5	14	46.8	2.4	50.8	34.7	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	0.11
	60	12	46.1	2.2	51.7	17.8	22.2	23.4	23.3	13.3	
	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	

Eq. (3). The value of $2V^{PD}$ is as small as 10~20% of V_s as given in Table 5. A marked decrease of P_2/D_2 ratio with time shown in Table 5 may be due to the isotopic difference between P_2 and D_2 in hydrogenation rate. The isotopic effect, $\alpha \equiv V^P/V^D$, *i.e.* the ratio of decreasing rate, V^P , of protium atoms to that, V^D , of deuterium atoms in H_2 at the initial stage of reaction, is evaluated from the results of Table 5 as 2.3 at 45°C and 1.9 at 0°C, which are close to *ca.* 1.8, of the case of copper catalyst⁴⁾ at 92°C. *Mechanism.* As mentioned before, the difference between $y_1(H)$ and $y_1(A)$ suggests that scheme (1) of ethylene hydrogenation over nickel catalyst accompanies a side reaction giving rise to PD formation, and the side reaction was concluded to be not the self-hydrogenation of ethylene. P_2 and PD were hardly produced in the course of deuteration of ethylene at 0°C but, as seen from Table 5, PD was produced in the course of ethylene hydrogenation with a mixture of P_2 and D_2 . These results show that the true backward unidirectional rate, $v_{-}(I_b)$, of step I_b , is very small, and the P_2 - D_2 equilibration during the reaction with a mixture of P_2 and D_2 at 0°C proceeds by the side reaction alone. Accordingly, the value of $2V^{PD}$ in Table 5 gives the backward unidirectional rate of this side reaction.

KEMBALL⁵⁾ has observed that the rate of ethylene hydrogenation over evaporated nickel film at $-120 \sim -100^\circ\text{C}$ is independent of ethylene partial pressure, P_E , and proportional to 0.5th power of hydrogen partial pressure, P_H . According to MASUDA⁶⁾ the rate of ethylene hydrogenation over nickel

Reaction Structure of Ethylene Hydrogenation. Part 2, Ni

wire at $-45\sim 0^\circ\text{C}$ is independent of P_E and proportional to 0.7th power of P_H . These experimental results are consistently interpreted by assuming that step I_b of scheme (1) consists of two steps as



where $\text{H}(a)_1$ and $\text{H}(a)_2$ denote hydrogen atoms in two different states of adsorption; $\text{H}(a)_2$ reacts with $\text{C}_2\text{H}_4(a)$ and $\text{C}_2\text{H}_5(a)$, but $\text{H}(a)_1$ does not. Step I_{b2} of scheme (17) is a process of the change of adsorbed state, *e.g.*, surface diffusion of hydrogen atoms between two different crystal surfaces as concluded for ethylene hydrogenation over tungsten catalyst⁹. With such a discrimination of the adsorbed state of hydrogen atoms, $y_1(\text{H})$ or $y_1(\text{A})$ gives the deuterium fraction of $\text{H}(a)_1$ or $\text{H}(a)_2$ during deuteration of ethylene, respectively, and $y_1(\text{H})$ is larger than $y_1(\text{A})$ so far as step I_{b2} is not in equilibrium. The rates $v_+(I_b)$ and $v_-(I_b)$ are now the forward and backward unidirectional rates of combined steps I_{b1} and I_{b2} of scheme (17) and are given as

$$v_+(I_b) = \frac{v_+(I_{b1}) \cdot \frac{1}{2} v_+(I_{b2})}{v_+(I_{b1}) + \frac{1}{2} v_-(I_{b2})}, \quad (18)$$

$$v_-(I_b) = \frac{v_-(I_{b1}) \cdot \frac{1}{2} v_-(I_{b2})}{v_+(I_{b1}) + \frac{1}{2} v_-(I_{b2})}, \quad (19)$$

where the stoichiometric number¹⁰, 2, of step I_{b2} is taken into account. On reference to temperature dependences of the true unidirectional rates of step I_b , $v_+(I_b)$ and $v_-(I_b)$, given in Fig. 1 and the rate of $\text{P}_2\text{-D}_2$ equilibration during ethylene hydrogenation given in Table 5, step I_{b2} should be much slower than step I_{b1} at temperatures as low as -100°C , and hence $v_-(I_{b2})$ in Eq. (18) is negligible as compared with $v_+(I_{b1})$. Consequently, hydrogenation rate is proportional to 0.5th power of P_H as observed by KEMBALL⁸. With rise of reaction temperature from -100 to $-45\sim 0^\circ\text{C}$, $v_-(I_{b2})$ becomes not negligible as compared with $v_+(I_{b1})$, and hence the reaction order with respect to P_H is larger than 0.5 and smaller than unity as observed by MASUDA⁶. In the temperature range, $79\sim 150^\circ\text{C}$, of the present observation, hydrogenation rate is concluded to be proportional to P_H as reported in many papers², because $v_-(I_{b2})$ estimated from the difference between $y_1(\text{H})$ and $y_1(\text{A})$ is several times larger than $v_+(I_{b1})$.

S. SATO and K. MIYAHARA

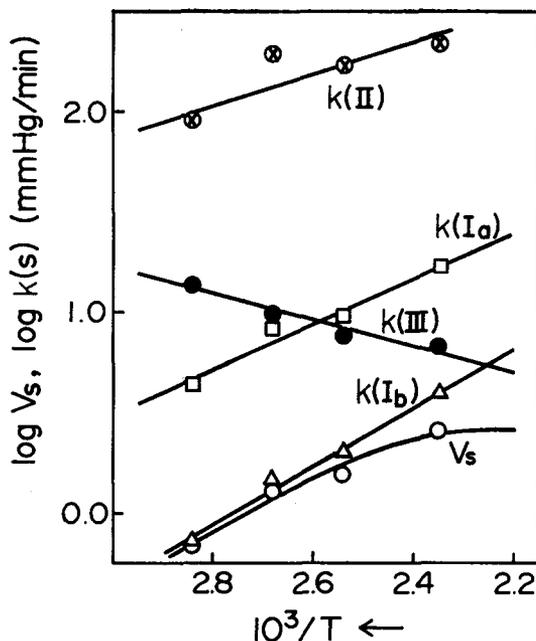


Fig. 2. Reaction structure of ethylene hydrogenation on Ni.
 $P_E = P_H = 20$ mmHg.

The reaction structure³⁾ was derived from the results of Table 4 as shown in Fig. 2, where $k(s)$ ($s = I_a, I_b, II$ or III) is the forward unidirectional rate of step s in a special case where steps of scheme (1) other than s are in equilibria and is expressed in terms of $v_+(s)$ and $v_-(s)$ as

$$\left. \begin{aligned} k(I_a) &= v_+(I_a), \\ k(I_b) &= v_+(I_b), \\ k(II) &= v_+(II) \frac{v_+(I_a)}{v_-(I_a)} \sqrt{\frac{v_+(I_b)}{v_-(I_b)}}, \\ k(III) &= v_+(III) \frac{v_+(I_a)}{v_-(I_a)} \frac{v_+(I_b)}{v_-(I_b)} \frac{v_+(II)}{v_-(II)}. \end{aligned} \right\} \quad (20)$$

The smallest one among $k(s)$'s gives the upper bound of steady hydrogenation rate, V_s . Figure 2 shows that activation heat of step III is negative and, in consequence, the slowest step should change from step I_b to III with rise of temperature beyond *ca.* 170°C. These results are in agreement with the conclusions of previous work^{1,2)}.

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Reaction Structure of Ethylene Hydrogenation. Part 2, Ni

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